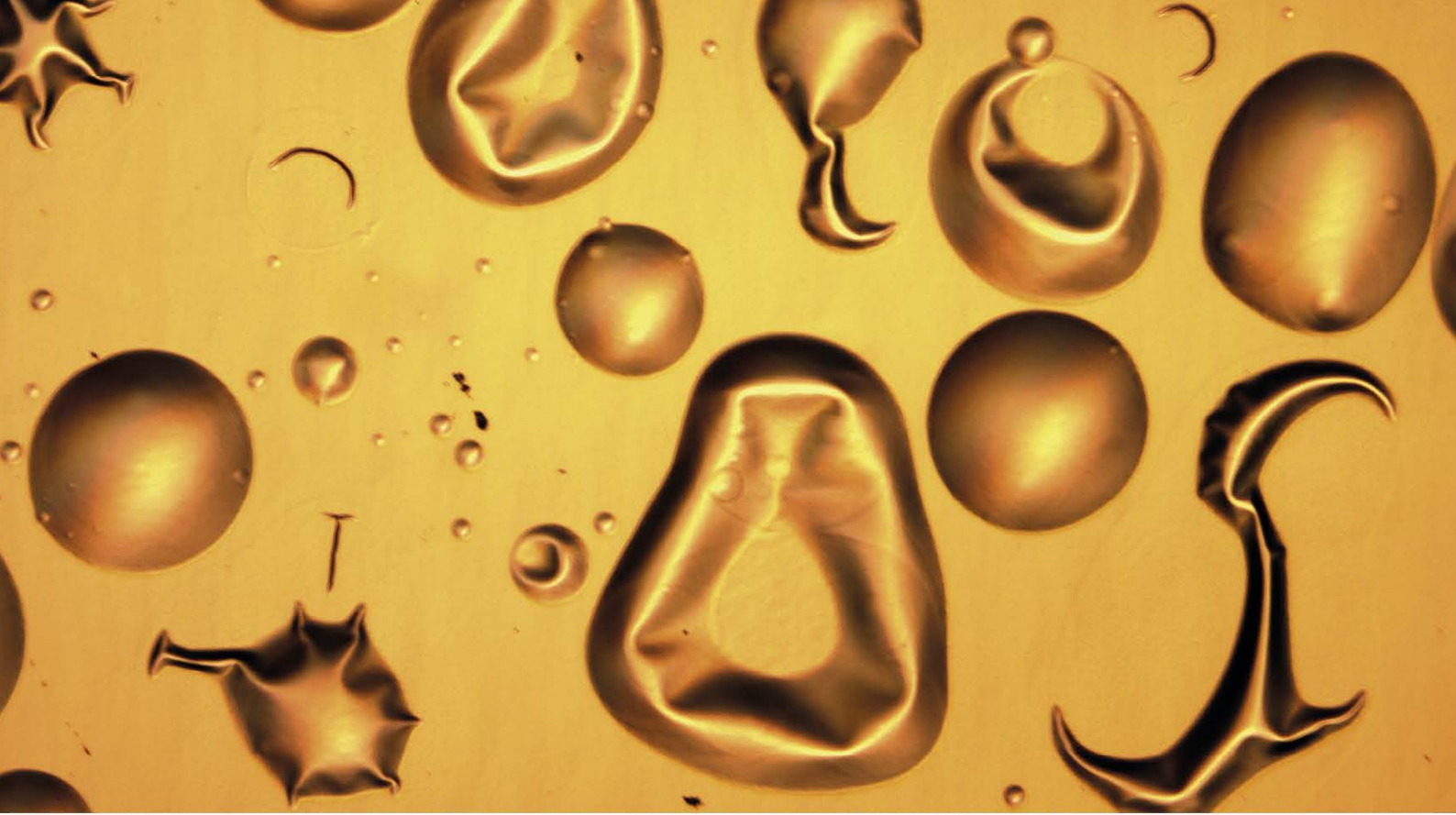




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Carina Ehrig

Characterization of Inorganic Semiconductors for Solar Energy Conversion and their Stability in Aqueous Media

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**Charakterisierung
von anorganischen Halbleitern
für die Solarenergieumwandlung
und ihre Stabilität in wässrigen Medien**

Der Technischen Fakultät
der
Friedrich-Alexander Universität
Erlangen-Nürnberg

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vorgelegt von
Carina Ehrig
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Abstract

Gallium nitride (GaN) is a well-established semiconductor in optoelectronic applications. It has a wide band gap of 3.4 eV and is thus excitable in the near-UV range. A promising application of GaN is its use as a photoelectrode driving photocatalytic reactions such as water splitting for generation of H_2 without consumption of fossil fuel or emission of CO_2 . For such applications the corrosion resistance of the photoelectrodes in aqueous media is one of the main factors determining their lifetimes and thus plays an important role for their applicability for highly efficient solar energy conversion. It has been demonstrated in photocatalytic experiments that under UV-illumination n-type GaN acts as oxygen-evolving photoanode and p-type GaN as hydrogen-evolving photocathode. In the present work, the degradation of GaN under various conditions is investigated. Specifically, the corrosion resistance of pure and metal-coated GaN photoelectrodes in aqueous media is studied by electrochemical measurements. Furthermore, the influence of an externally applied potential under light excitation as well as the effect of long-term photoinduced stress are investigated. It is observed that without illumination the GaN surfaces and GaN-metal interfaces are rather stable for a broad potential range, whereas they undergo degradation when exposed to UV light.

Parallel to the III-V semiconductor GaN, semiconducting magnesium silicide (Mg_2Si) presents an alternative material type which is not as well characterized as GaN in its use as photoelectrode. It is a promising candidate for low-cost and efficient absorber layers

for solar energy conversion. Its main application so far is as a high-performance thermoelectric material. Little is known, however, about its applicability as a photo-active material. Semiconducting Mg_2Si is the only stable phase in the Mg_2Si system. It has a narrow indirect band gap of 0.78 eV. Its high absorption coefficient furthermore makes it an interesting material for the production of thin solar cells. In the present work, Mg_2Si thin films were produced by thermal evaporation of Mg on Si substrates and by sputtering from a Mg_2Si sputter target on silicon wafers or glass substrates with subsequent annealing. This results in the formation of smooth Mg_2Si layers, which can be adjusted in thickness by varying the annealing temperature, time as well as the amount of deposited magnesium. The Mg_2Si films are characterized in terms of morphological, electrical and optical properties. Furthermore, measurements on the photo-activity of Mg_2Si as well as its stability in aqueous media are discussed.

Kurzdarstellung

Galliumnitrid (GaN) ist ein etablierter Halbleiter in optoelektronischen Anwendungen. Mit einer Bandlücke von 3.4 eV ist es im nahen UV Bereich anregbar. Eine vielversprechende Anwendung von GaN ist seine Verwendung als Photoelektrode um photokatalytische Reaktionen, wie zum Beispiel Wasserspaltung zur H₂ Erzeugung, zu ermöglichen, ohne fossile Brennstoffe zu verbrauchen oder CO₂ auszustoßen. In solchen Anwendungen ist die Korrosionsbeständigkeit der Photoelektroden in wässrigen Medien einer der Hauptfaktoren, der ihre Lebensdauer bestimmt und daher eine wichtige Rolle für ihre Anwendbarkeit in hoch effizient arbeitenden Solarenergieumwandlungen spielt. In photokatalytischen Experimenten wurde gezeigt, dass n-GaN unter UV Beleuchtung als sauerstoffentwickelnde Photoanode und p-GaN als wasserstoffentwickelnde Photokathode fungieren. In der vorliegenden Arbeit wird die Degradation von GaN unter verschiedenen Einflüssen untersucht. In elektrochemischen Messungen wird die Korrosionsbeständigkeit von reinen GaN Photoelektroden sowie von metallbeschichteten GaN Photoelektroden in wässrigen Medien gemessen. Weiterhin werden der Einfluss eines extern angelegten Potentials unter Lichtanregung sowie der Effekt von langzeit-photo-induziertem Stress untersucht. Es wurde festgestellt, dass die GaN Oberflächen ohne Beleuchtung sowohl mit als auch ohne Metallbeschichtung in einem weiten Potentialbereich eher stabil bleiben, wohingegen sie unter UV Licht degradieren.

Parallel zum III-V Halbleiter GaN stellt halbleitendes Magnesiumsilizid (Mg₂Si) einen alternativen Materialtyp dar, welcher bezüglich seiner Verwendbarkeit als Photoelektrode nicht so gut charakterisiert ist

wie GaN. Es ist ein vielversprechender Kandidat für preiswerte und effiziente Absorberschichten für die Solarenergieumwandlung. Seine bisherige Hauptverwendung findet es als hochleistungs-thermoelektrisches Material. Allerdings ist wenig bekannt über seine Eignung als photoaktives Material. Halbleitendes Mg_2Si ist die einzig stabile Phase im Mg_2Si System. Es hat eine niedrige indirekte Bandlücke von 0.78 eV. Sein hoher Absorptionskoeffizient macht es weiterhin zu einem interessanten Material für die Herstellung von dünnen Solarzellen. In der vorliegenden Arbeit werden Mg_2Si Dünnschichten durch thermisches Verdampfen von Mg auf Si Substraten sowie durch Sputtern von einem Mg_2Si Target auf Siliziumwafer oder Glassubstrate mit anschließender Temperung hergestellt. Dies resultiert in der Bildung von glatten Mg_2Si Schichten, deren Dicke durch die Temper-Temperatur sowie die Menge des aufgetragenen Magnesiums variiert werden kann. Die Mg_2Si Filme werden hinsichtlich ihrer morphologischen, elektrischen und optischen Eigenschaften charakterisiert. Außerdem werden Messungen bezüglich der Photoaktivität von Mg_2Si sowie dessen Stabilität in wässrigen Medien diskutiert.

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1 Introduction

Up to date the large majority of consumed energy originates from fossil fuels. The US energy administration, for example, states that in 2013 more than 80 % of the total energy stemmed from petroleum, coal, and neutral gases¹. The fossil fuel consumption and the corresponding greenhouse gas emission have a huge impact on the climate change. Therefore, there is a great need for alternative energy concepts to enable an environmentally friendly production of carbon-neutral green and renewable energy.

Solar energy presents an alternative renewable source to achieve independence from petroleum, coal and gas. The world's total solar energy irradiating on the earth is approx. 120.000 TW per year. Less than 0.02% of the solar energy are necessary to replace the total energy consumption from fossil fuels and nuclear power. The main problems are an efficient solar energy harvest, conversion and storage [1]. For a single band gap absorber system, the conversion efficiency of solar radiation into stored chemical energy can be up to 31 % [2, 3].

Solar energy conversion is a versatilely introduced term and includes the conversion of solar into chemical or electrical energy in solution (e.g., in photoelectrochemical reactions) as well as under dry conditions (e.g., in solar cells).

In general, when discussing photovoltaics, the main focus is on the efficient harvesting and conversion of solar energy. On the other hand, it became more and more obvious in the recent years that due to the unsteady availability of solar energy, another very important question is how to store the converted energy and be able to use it on

¹ http://www.eia.gov/forecasts/aeo/section__energyconsump.cfm

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demand. An alternative approach to photovoltaics is photocatalytic fuel generation by a photoelectrochemical process, where abundant raw materials (e.g., water or carbon dioxide) are transformed into hydrogen, oxygen or energetic organic species that can serve as chemical fuels [4]. Here as well, such a process needs to be economical and have a high efficiency. Currently, there is an increasing interest in the development of an efficient and stable photoelectrochemical system that enables the direct conversion of solar energy, e.g., into chemical energy in the form of storable chemical fuels. It is noticeable that especially Japanese research groups contribute to the research field of solar energy conversion in solution.

There are various approaches to solar energy conversion in solution, such as photocatalysis [1], or photoelectrolysis [5], or photoassisted electrolysis [6], to mention some.

One of the main applications in photoelectrochemistry are photo-reduction of CO_2 , detoxification of organic pollutants, or water splitting. In the latter process, molecular hydrogen, which is an important alternative energy source, is produced by illuminating a semiconductor photoelectrode in an aqueous solution. Photoexcited electrons or holes migrate to the semiconductor surface to drive i.a. the reduction of protons to hydrogen. The aim for these solar energy conversion processes is to drive them without an external potential but just with solar illumination. Photoelectrochemical water splitting was first mentioned in 1972 by Fujishima, where TiO_2 was used as semiconducting photoelectrode [7]. One research focus in photoelectrochemical water splitting reactions nowadays is on investigating the stability of semiconducting electrodes.

The dissolution of semiconductors in photoelectrochemical applications is an undesired process since it reduces the efficiency and stability and thus the reliability and lifetime of photoelectrolysis systems. On the other hand, this etching of semiconductors in solution is important for industrial processes and is an extensively studied process. Wet etched smooth or roughened semiconductor surfaces have different applications, e.g., in GaN-based MOS structures [8].

The ability to split, e.g., water is not provided by many semiconductors. One group of materials, which has been studied for a long time, are oxide semiconductors with band gaps larger than 3 eV [9]. While they behave stably in aqueous solutions, they provide rather low efficiencies [10–12]. Another promising material group are the III-nitride semiconductors like GaAs and GaInP₂ (see, e.g., [13]). They are furthermore well-known for their excellent chemical stability to wet etching [14]. In this work, investigations on gallium nitride (GaN) are performed, which also belongs to the group of III-nitride semiconductors.

GaN is an inorganic, wide-band-gap semiconductor with a direct band gap of approx. 3.4 eV [15]. It is mainly used as optoelectronic material for example in light-emitting diodes [16], short-wavelength photodetectors [17], high-power electronic devices [18, 19], as well as for gas- and biosensing [20]. On the other hand, it can be used as photoelectrode in solution which has the potential of absorbing light in the near UV region to drive photoelectrochemical reactions like water splitting [6, 21–23]. Another application area is the photoelectrochemical CO₂ reduction to produce so-called “valuable” carbons while reducing CO₂ [24–27].

So far, in the literature, GaN was found to have considerable resistance to corrosion in plenty of aqueous electrolytes [14, 28]. On the other hand, GaN is known as a highly defective material which is also caused by a large lattice mismatch between the epilayer of GaN and a foreign substrate (mostly sapphire). It contains dislocations in high concentrations of around 10^7 - 10^{11} cm⁻², thus influencing the electronic properties at the sites where the dislocations terminate at the surface [29, 30]. This also has far-reaching consequences in terms of degradation of GaN surfaces in aqueous solutions and under illumination, which is widely referred to as photo-oxidation [28, 31, 32]. By that the GaN-bound nitrogen evolves from the n-GaN surface, leading to a decomposition of the GaN surface. It is known that in aqueous solutions p-GaN is much more stable than n-GaN [24, 33, 34]. The disadvantage of p-GaN, on the other hand,

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is that lower photocurrents flow and thus p-doped electrodes do not work as efficiently as n-GaN electrodes [22, 35]. The stability of GaN in aqueous media is very important to ensure reliably working photoelectrodes with a long lifetime. For that the understanding and prevention of photocorrosion of GaN plays an important role.

The aim of this work is to study changes of the GaN surface in photoelectrochemical reactions in order to gain knowledge about the stability of GaN samples in aqueous solutions. GaN samples were stressed under different conditions, including variations in the aqueous medium, light illumination, duration of applied stress, externally applied stress as well as in the contact of GaN with metals. Furthermore, the influence of NiO co-catalyst particles deposited on GaN surfaces was studied.

One main technique employed to investigate the stressed GaN surfaces in the present work was EDX. It allows for an analysis of the change in elemental composition of GaN surfaces after treatments in detail, which had not yet been done in previous studies. It is investigated how the processes taking place at the GaN–electrolyte interface vary for n-type and p-type GaN and for different stress conditions. Based on the findings, model systems are suggested for the occurring processes. Additionally, the Tafel plot method was applied on GaN under dark conditions and UV illumination in aqueous solutions to determine corrosion rates.

Besides GaN, which belongs to the III-V nitride semiconductors, the properties of magnesium silicide were studied in this work. Silicides are intermetallic compounds that consist of silicon and at least one other element to form either binary or ternary silicides. They can exist as metal-rich silicides (e.g., Mg_2Si), monosilicides (e.g., PtSi) or disilicides (e.g., FeSi_2). Most of them have metallic properties, but there are also a few semiconducting silicides [36–38]. They can be fabricated either with monocrystalline [39] or polycrystalline [40] morphology.

Contrary to GaN, semiconducting magnesium silicide (Mg_2Si) has an indirect band structure [41–49] and a narrow band gap of around 0.78 eV [36].

This material is investigated since its raw materials, magnesium and silicon, are abundant, inexpensive, and environmentally harmless. Contrary to other silicides, in the Mg–Si phase diagram, there is only one stoichiometric phase – Mg_2Si [50, 51]. Non-doped Mg_2Si exhibits n-type conductivity [36, 49, 52–56] and can be easily doped [57–59]. Due to its high figure of merit, Mg_2Si is an established material for applications in thermoelectrics [57, 60, 61]. Furthermore it is applicable for reinforcement.

In recent years the applicability of Mg_2Si for (near-infrared) optoelectronic devices was studied. Due to its narrow band gap, Mg_2Si is proposed to be a suitable material for the use as infrared detector in the wavelength range of 1.2 - 8 μm [62–66]. Udono *et al.*, for example, fabricated a p-n Mg_2Si junction diode, consisting of n- Mg_2Si and Ag doped p- Mg_2Si [64]. The application of Mg_2Si as energy converting material for light in the visible range is less investigated, although it is reported that Mg_2Si has a high absorption coefficient of $3.5 \cdot 10^5 \text{ cm}^{-1}$ at 2.5 eV (approx. 500 nm), which is about 40 times higher than that of c-Si [67]. By that it should be possible to realize thinner solar cells and thus to reduce the production costs. Kato *et al.* suggested the use of Mg_2Si as bottom layer in tandem solar cells due to the narrow band gap [40]. They observed a change in conductivity of a Mg_2Si layer on a Si substrate under AM 1.5 illumination. Caused by the demand for miniaturization of devices the focus was set more and more on thin film characterization of Mg_2Si [68, 69]. Thin Mg_2Si films are mostly fabricated by growing Mg_2Si on silicon substrates. Mg_2Si film thicknesses ranging from 200 nm to 200 μm were reported [62, 70–73]. Usually these Mg_2Si thin films are non-porous and free of cracks.

One main application of Mg_2Si is particle strengthening in Mg and Al alloys. The addition of little amounts of silicon leads to the

1 Introduction

formation of so-called “Chinese script” or polygonal Mg_2Si [74–77]. The mechanical properties of these alloys are improved by adding Mg_2Si in an appropriate way [78, 79]. Furthermore, in presence of Mg_2Si , Mg-Zn-Mn alloys are protected against corrosion [80]. Ben-Hamu *et al.* reported that Mg_2Si is stable even after 72 hours in a 3.5 % NaCl solution which is saturated with $\text{Mg}(\text{OH})_2$. It thus protects Mg-Zn-Mn alloys from corrosion or strongly reduces corrosion under these extreme conditions. Serikawa *et al.* reported that RF sputtered Mg_2Si is stable under wet conditions and passes the salt spray test without corrosion [81]. However, little is known about the use of Mg_2Si as electrode in photoelectrochemical applications and its stability in aqueous solutions. Song *et al.* reported the use of Mg_2Si thin film electrodes, fabricated by pulsed laser deposition [71]. Mg_2Si is also proposed to be suitable as anode for rechargeable lithium batteries [71, 82].

The focus of the investigations on Mg_2Si in the present work is on the fabrication of thin films of poly- Mg_2Si with thicknesses from 50 nm to 3 μm and their characterization in terms of electrical and optical properties. Thin films are produced either by thermal evaporation of magnesium on silicon substrates or sputtering of Mg_2Si on glass substrates with subsequent annealing. The resistivity and doping, mobility, and carrier concentrations were measured for both types of underlying substrates (silicon and glass). Transmission and reflection measurements for different Mg_2Si thicknesses were carried out. Optoelectronic devices such as p-Si–n- Mg_2Si junctions were fabricated to study Mg_2Si as solar cell device. Furthermore, the application of Mg_2Si as photoelectrode and its stability in aqueous media are shown and discussed. Finally, the Tafel plot method was also applied to Mg_2Si to determine corrosion rates under dark conditions and illumination.

2 Fundamentals of Photo-Electrochemistry

2.1 The semiconductor–electrolyte interface

The investigation of semiconductor-electrolyte interfaces is a highly interdisciplinary field, involving topics from electrochemistry, semiconductor physics, as well as material and surface science. Its realization has fundamental meaning, for example in the application in photoelectrochemical cells for water splitting, microelectronics, energy storage, and solar cells [83].

To understand the mechanisms that drive reactions at the semiconductor–electrolyte interface, the solid state physics of the semiconductor and the electrochemical reactions at the interface are often considered individually and then are observed together with the focus at the interface. Occurring reactions can be explained via interfacial charge transfers, electronic band structures as well as charge transports and optoelectronic effects.

The history of understanding processes at semiconductor–liquid interfaces and so the history of photoelectrochemistry goes back to 1839, when E. Bequerel discovered the photovoltaic effect by illuminating a silver chloride electrode (AgCl) in an electrochemical cell. This phenomena was caused by photoinduced charge separation and generated an electric field at the charged AgCl–liquid interface, implying that silver halides behave as semiconductors. This explanation of the effect was made not until 1954 at Bell laboratories, when researchers

did pioneering work on photochemistry by exposing germanium to light. The basic research on fundamentals of photoelectrochemistry goes back to the 1950s and 1960s, where applications for electronics in general were of note. High effort on the development of first models was taken to understand the processes at semiconductor–liquid interfaces. Fundamental knowledge of energetics and kinetics of electron transfer across the semiconductor–electrolyte junctions was gained [84]. Also, around 1970, first applications of photoelectrochemical systems emerged. Fujishima *et al.* reported direct water splitting reactions with a semiconducting TiO_2 photoelectrode [7]. The 1973 mineral oil embargo followed by a worldwide energy crises intensified the efforts on solar energy conversion research to find alternative energy sources [85]. Around 1975, the influence of metal catalysts was studied in order to reduce surface recombination and degradation processes. From the 1980s and 1990s on more and more applications of semiconductors in electrochemistry arose, but still details of reactions at the semiconductor–electrolyte interface were not fully understand [83]. Today, the analysis techniques are much more better to evaluate in detail on an atomic level, which processes occur at the semiconductor–electrolyte interface and how they can be manipulated to achieve, e.g., higher efficiencies.

When a metal electrode is immersed in an electrolyte, the Fermi level E_F of the metal aligns with the potential of the electrolyte by transferring electric charges at the interface. A double layer, consisting of ions and charges at the metal surface develops. This so-called Helmholtz double layer plays an important role on most electrochemical processes. It involves a narrow region of the electrolyte close to the electrode surface as well as an opposite charged layer in the electrode. At the inner Helmholtz plane, non-solvated ions are specifically adsorbed to the surface. The outer Helmholtz plane corresponds to the plane of closest approach for solvated ions. A discharge of the double layer is not possible due to the formed solvation shell. The Gouy-Chapman layer model extends the Helmholtz double

layer model by considering a diffuse space charge layer extending from the outer rigid Helmholtz plane with an excess of positive or negative ions.

Contrary to metals, semiconductors have a lower charge carrier concentration. When a semiconductor is immersed in an aqueous solution, the excess charge is not only located on the surface but forms a space charge region which reaches into the semiconductor. One problem that arises but is still not sufficiently clarified is the determination of rate constants of occurring redox reactions at the semiconductor–electrolyte interface. By knowing these rate constants, optimal processes and systems could be chosen, e.g., for photo etching of semiconductors in industrial semiconductor production or the development of efficient working photoelectrochemical systems. Already in the 1960s, several model systems were developed. One basic consideration for example was made by Marcus, who developed a model to describe the charge transfer between two different molecules which are located at opposite sides of a boundary layer of two insoluble solutions. This model only considers the distance between the molecules [86, 87]. Another approach for the interpretation of the semiconductor-electrolyte interface was made by Gerischer. It describes the electronic energy states in solutions. Due to electron exchange at the interface, an equilibrium of the Fermi level in the semiconductor and of a redox couple in solution can be achieved. Details can be found, e.g., in [88–90]. Also the reaction kinetics need to be considered. It is distinguished between whether a reaction is activation or diffusion-controlled. In case of diffusion-controlled reactions, the electrode processes are so fast that reactants or products of the reaction can not be sufficiently transported. To minimize the influence of diffusion, highly concentrated solutions, electro-active species with a high mobility, and slow electrode processes are required. In an activation-controlled process, the rate of reaction is controlled only by the rate of the electrochemical charge transfer process, which is also considered in activation-controlled corrosion processes.

When the semiconductor absorbs light, electron-hole pairs are generated. Due to the high concentration of holes as majority carriers in p-type semiconductors and electrons as majority carriers in n-type semiconductors, only the concentration of the appropriate minority carriers changes significant with light absorption. Band bending occurs, depending on the positions of the electrochemical potentials and the doping of the semiconductor. Either a depletion or accumulation region of free charge carriers is formed. Figure 2.1 shows the corresponding schematic band diagrams for n-type and p-type semiconductors in aqueous solutions as photoelectrodes which absorb light. When an n-type semiconductor absorbs photons which energies exceed that of the band gap, electron-hole pairs are generated within the space charge region of the semiconductor. Photogenerated holes as minority carriers contribute to charge transfer reactions at the surface. Due to the built-up electric field, an upward band bending occurs and these photogenerated charge carriers are separated as shown in figure 2.1 (a). The strength of the band bending is dependent on the chemical potential of the electrolyte, the applied external potential, and the surface state concentration [91]. Figure 2.1 (b) shows a p-type semiconductor under light absorption. Due to the downward band bending, photogenerated electrons accumulate at the p-type semiconductor surface, whereas the holes diffuse into the bulk. When no excess charge is present at the interface, no band bending occurs since no space charge region is formed. The corresponding potential is called flat band potential E_{fb} . By knowing E_{fb} , the conduction and valence band edges of the semiconductor can be calculated.

2.2 Basic concepts of (photo-)electrochemistry

Every redox reaction is described by an oxidation and reduction reaction. To investigate the partial reactions, the electrochemical

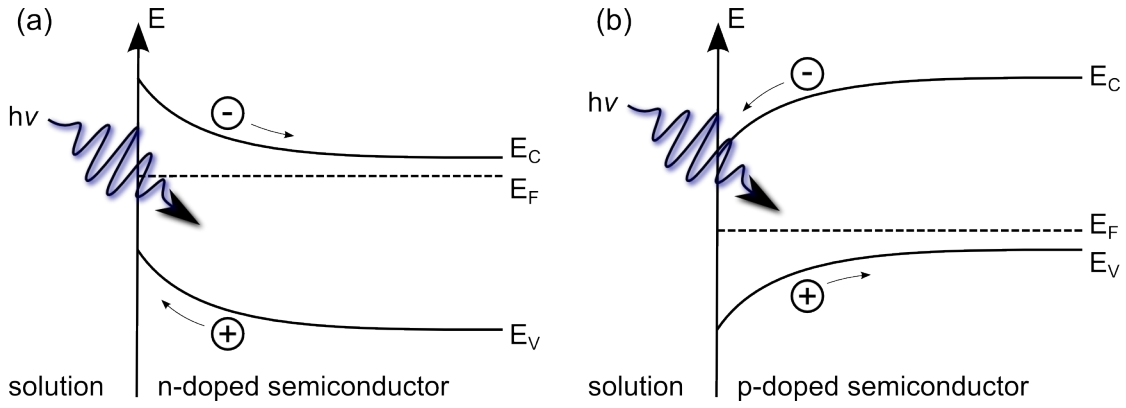


Figure 2.1: Band bending diagram of E_{cb} and E_{vb} at a semiconductor–electrolyte interface for an n-type semiconductor (a) and p-type semiconductor (b) to explain the principle mechanism under light absorption. In case of (a), photogenerated holes accumulate at the surface of the n-type semiconductor whereas in case of (b) photogenerated electrons accumulate at the p-type semiconductor surface.

cell can be divided in two half cells. As long as an electrochemical equilibrium is existent and the occurring reactions are reversible, each half cell can be investigated by the Nernst equation. The Nernst equation describes the concentration dependency of the redox potential. It is written as

$$E = E^0 + \frac{RT}{zF} \log \frac{c_{ox}}{c_{red}}, \quad (2.1)$$

where E is the electrode potential, E^0 is the standard electrode potential, R is the gas constant, T the absolute temperature, z the number of exchanged electrons, F the Faraday constant, c are the concentrations of the corresponding redox species, respectively. The difference of the potentials of the half reactions results in

$$\Delta E = E_{red} - E_{ox}, \quad (2.2)$$

from which it can be determined whether the electrochemical reaction runs spontaneously or not. This is done by determining the Gibbs

energy

$$\Delta G = -z \cdot F \cdot \Delta E. \quad (2.3)$$

In case of $\Delta G < 0$, the electrochemical reaction occurs voluntarily.

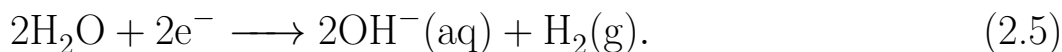
When an external potential E is applied, the electrode potential in the photoelectrochemical cell (PEC) differs from the equilibrium potential and an overpotential is build up. This overpotential presents the difference between the electrode potential and equilibrium potential. The potential dependence of the reaction rate will be discussed in section 2.2.3.

2.2.1 Water splitting

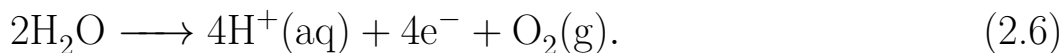
Photoelectrochemical water splitting is picked as an example in this work. The overall water splitting reaction is given as



When light with an energy greater than the band gap energy of the semiconductor hits the surface of a photoelectrode, electron-hole pairs are generated and each of these species can be used for participating in photoelectrochemical reaction. In case of water splitting, there are two half reactions. On the one hand, gaseous hydrogen (H_2) evolves at the so-called cathode, where electrons are released into the electrolyte to reduce protons:



On the other hand, oxygen (O_2) evolves at the anode, where electrons are collected. For small pH values it can be written as:



Occurring recombination of the photogenerated electron-hole pairs as well as a back reaction of the gaseous products needs to be inhibited

although it can not be excluded completely. Furthermore, in presence of chloride-containing electrolytes, such as NaCl, the formation of gaseous chlorine (Cl_2) occurs since it has a lower overpotential than the competing O_2 evolution at the anode (although the O_2 evolution is thermodynamically preferred):



From a thermodynamic perspective the Cl_2 evolution is less likely due to the standard electrode potential of chlorine of $E_{\text{Cl}_2}^0 = +1.36 \text{ V}$, where Cl^- ions are oxidized to gaseous Cl_2 which is slightly higher than the standard electrode potential for O_2 evolution, $E_{\text{O}_2}^0 = +1.23 \text{ V}$.

In literature it is often distinguished between photocatalysis or photoelectrochemistry. In photocatalytic processes, the semiconductor is dispersed in an electrolyte and oxidation and reduction processes happen without an externally applied potential – occurring reactions run voluntarily. In photoelectrochemical measurements, the setup consists of several electrodes, at least a working electrode, which acts as the photoelectrode and a counter electrode, where it is possible to apply an external potential. Often these terms are mixed up and used arbitrarily. In the following, due to simplification, all reactions are referred to as photoelectrochemical processes, but they also include photocatalytic reactions (for example, the photoinduced degradation experiments in section 6.1).

2.2.2 Electronic energy levels

Since photoelectrochemical processes involve both reactions on a semiconducting material as well as in solution, the potentials of both media need to be investigated, including the Fermi levels E_{F} of the semiconductor as well as the redox potentials of the redox systems in the electrolyte. The Fermi level E_{F} regulates the oxidability of the semiconductor. For example, by applying an external potential, E_{F} of the semiconductor changes.

In general, E_F is written on an absolute scale versus the vacuum level. The redox potential ϕ_{redox} on the contrary corresponds to a redox system which is measured versus a standard reference electrode (e.g., normal hydrogen electrode, NHE, or standard calomel electrode, SCE). In general, ϕ_{redox}^0 for the H^+/H_2 redox system was determined arbitrarily as zero for redox potentials in electrochemistry. The energies of the redox system and the vacuum level can be converted by

$$E_F = -E_{\text{ref}} - e\phi_{\text{redox}}, \quad (2.8)$$

where E_{ref} is the energy of the reference electrode vs. the vacuum level. It varies from 4.3 to 4.7 eV [92]. An average value of 4.5 eV vs. NHE is used, which corresponds to 4.7 eV vs. Ag/AgCl. Equation 2.8 also refers to the fact that the Fermi levels E_F of both the semiconductor and the redox system must be equal on both sides at the semiconductor–electrolyte junction. Thus, it can be also written as

$$E_F = -4.5 \text{ eV} - e\phi_{\text{redox}} \text{ vs. NHE.} \quad (2.9)$$

In principle, when no external potential is applied to an electrochemical system, no net current is flowing through the PEC system and thus the electrode potential is identical with the equilibrium potential. These equilibrium potentials for several redox pairs were measured against a reference electrode. All equilibrium potentials are enlisted in a so-called standard electrode potential list. From these data, statements about the redox behavior of the redox pairs can be made, e.g., how easily a redox pair can be oxidized or reduced. The more positive the value, the more noble the species and the less it can be oxidized. For example, the standard electrode potential of the H_2/H^+ redox pair is 0 V and for O_2/OH^- redox pair it is 1.23 V vs. NHE.

2.2.3 Electrochemical techniques

Cyclic voltammetry

Several electrochemical measurement techniques are used in this work, including cyclic voltammetry (CV) measurements. The aim of measuring CV curves is to explain processes that take place on the electrodes and thus, statements about the electrochemical and kinetic behavior of electro-active species can be made.

In this work, a three-electrode setup is used as depicted in Figure 2.2 (a). It consists of a working electrode (WE), a counter electrode (CE), and a highly resistive reference electrode (RE). This allows for referencing the potential between WE and RE which possesses a well-defined, constant electrode potential. In order to adjust the potential between WE and RE, a potentiostat regulates the potential between WE and CE until the desired potential between WE and RE is reached. The current is measured between WE and CE. The open circuit potential (OCP) corresponds to the potential where no net current is flowing. In a CV diagram, the measured current is plotted vs. the adjusted potential and concerns only processes involving the WE.

The potential of the WE is changed linear in time between a potential upper and lower limit at a constant scan rate. Thus, an increasing and afterwards decreasing potential is applied, resulting in a triangular potential characteristics due to this cyclic changes of the potential. The flowing current can have two reasons: on the one hand, charge transfer exists, where charge carriers are exchanged between electrode and electrolyte, also called Faraday current. On the other hand, charging of the double layer exists, resulting in a capacitive current. When positive currents are measured, the WE is driven as anode, whereas in case of negative currents, the WE behaves as cathode.

Beginning from the OCP, first the negative potential in the cathodic region was driven until the polarization changed and measurements

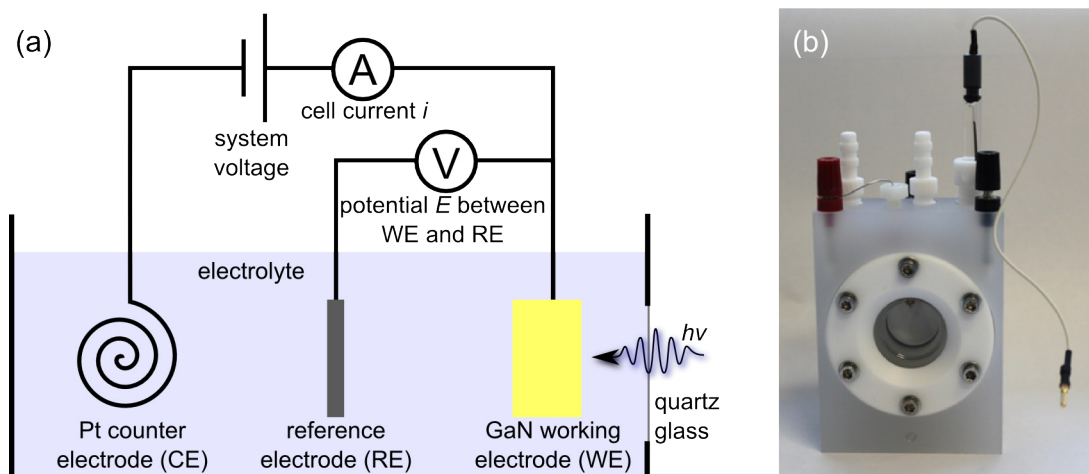


Figure 2.2: (a) Schematic diagram of a three-electrode setup. GaN as photoelectrode is illuminated with UV light through a quartz glass. The potential E is adjusted between GaN and an Ag/AgCl RE and the current i is recorded between the RE and a platinum ring CE-electrode. (b) Photo of the photoelectrochemical cell (PEC) used in this work.

continued to the anodic region and from there again back to the OCP, defining one measurement cycle. After six measurement cycles it stopped again at the OCP. The scan direction of the branches of the CV curves shown in this work are measured always from the reductive to the oxidative region. If not stated otherwise the scan rates used for each measurement in this work was 100 mV/sec and the plotted curves are taken from the second of overall six measurement cycles (the total measurement time for six cycles was approx. 12 minutes). Figure 2.2 (b) shows a photo of the used photoelectrochemical cell in this work.

Chronoamperometry

In chronoamperometry (CA) measurements, the recorded currents are positive when a positive potential is applied and negative, when a

negative potential is applied. The electric current i over the electrolysis time t is described as diffusion-controlled reaction by the Cottrell equation

$$i = \frac{zFAc\sqrt{D}}{\sqrt{\pi t}}, \quad (2.10)$$

where z is the number of electrons needed for the redox reaction, F is the Faraday constant, A the area of the electrode, c the initial concentration, and D the diffusion coefficient.

The generated electric charge Q which passed through the electrode is calculated by integrating the electric current over time:

$$Q = \int i dt, \quad (2.11)$$

where i is the measured current between the WE and CE and t is the total electrolysis time. It needs to be considered that side reactions can consume a part of the generated charge. The fraction of the current used for a specific reaction is indicated by the Faraday efficiency (FE) which is given by the ratio of consumed electric charge to the available total electric charge. The FE depends on many factors such as the redox reaction itself, the electrode material, electrolyte composition, and temperature.

The Tafel extrapolation method

One popular electrochemical method for measuring even very small corrosion rates is realized by electrochemical polarization with the Tafel plot method. This method is well-applied for metal electrodes. Until now, the implementation of this method is not commonly used for semiconductors. Only few groups applied it (for example Ghamarian *et al.* in case of semiconducting CuInSe₂ thin films [93]). The transfer of this technique from a metal to a semiconducting electrode is justified since it makes no difference from a thermodynamic

point of view. However, it needs to be considered that the conducting properties are different, since the concentration of mobile electrons is lower and with electrons and holes there are two types of charge carriers in semiconducting electrodes. Thus, the kinetics of the charge transfer are different. Thermodynamics give statements about the probability of corrosion but not about the velocity of the process which is described by electrochemical reaction kinetics. The theory of the Tafel plot method can be looked up, e.g., in [94–96]. It needs to be considered that the determined corrosion rates refer to the dissolution or etching of the corresponding metal or semiconductor electrodes, but not an oxidation.

The total current i that is plotted in a current-potential curve is the sum of cathodic and anodic partial currents. For very high anodic applied potentials, mainly the anodic currents contribute to the total current and vice versa for very negative cathodic potentials. In case of a flowing Faraday current, the electrode potential deviates from the equilibrium potential and an electrochemical reaction can be enforced. There are several kinds of overpotentials, depending which reactions take place. In case of an inhibited charge transfer, a transfer overpotential emerges, a diffusion overpotential develops in case of mass transport, and for chemical reactions a reaction overpotential appears.

At the OCP, equilibrium potential, or free corrosion potential (E_{corr}) as it is referred to in the field of corrosion research, the absolute values of the anodic partial current and the cathodic partial currents are the same. However, to the outside no net current flows, but still, little exchange of electro-active species takes place. At this potential E_{corr} , the electrode will be freely corroding. A corrosion current density j_{corr} is generated, from which the corrosion rates can be calculated. j_{corr} is also called exchange current density since it presents a direct kinetic measure for the velocity of the dissolution of the electrode at E_{corr} .

Tafel in 1905 found out that the logarithm of the current density in an electrochemical reaction varies linearly with the electrode potential [97]. By plotting the current-potential curve in a semi-logarithmic way, j_{corr} can be determined by the intersection of the linear extrapolation of the partial currents, presenting the Tafel region. The location of the peak of the Tafel plot on the potential axis corresponds to the corrosion potential E_{corr} [98].

The Tafel method is valid when several conditions are fulfilled [99]. At least one of the branches of the polarization curves needs to be activation-controlled. Furthermore, well-defined anodic or cathodic Tafel regions over at least one decade of current must exist. Uniform corrosion must be guaranteed. Additionally, it must be assumed that the anodic and cathodic reactions are the only reactions occurring at E_{corr} . Also, the recorded polarization curves are steady-state.

Tafel measurements are usually conducted in higher concentrated 1 M NaCl to reduce the resistance of the electrolyte which has influence on the reaction kinetics to avoid diffusion-limited reactions. Additionally, a low scan rate of 1 mV/sec was adjusted to avoid diffusion-controlled reactions. It needs to be considered that the corresponding Tafel slopes should not exceed 200 mV/decade to guarantee an activation-controlled process and involving a slow reaction step at the electrode surface. This activation-controlled process is described by the Butler-Volmer equation [100], in which the total current density is dependent from the overpotential for anodic and cathodic reactions that take place at the same electrode:

$$j = j_{\text{corr}} \left[\exp \left(\frac{(1 - \alpha_a)zF\eta}{RT} \right) - \exp \left(\frac{-\alpha_c zF\eta}{RT} \right) \right], \quad (2.12)$$

where $\eta = E - E_{\text{corr}}$ is the overpotential, and α_a and α_c are the anodic and cathodic transfer coefficients which can be determined from the slope of the Tafel plot, respectively. The derivation of this equation is based on the assumption of an overcoming of an activation

barrier. This in turn is linked with a rearrangement of the solvate covering of the ion and is described by the Marcus theory [101].

By using the following equation, based on Faraday's law, the corrosion rate r can be finally calculated:

$$r = \frac{1}{z} \frac{Mj}{\rho N_A e}, \quad (2.13)$$

where z is the number of available electrons (two in case of GaN and Mg₂Si), N_A is the Avogadro constant, $M_{\text{GaN}} = 83.73$ g/mol and $M_{\text{Mg}_2\text{Si}} = 76.7$ g/mol are the molar masses of GaN and Mg₂Si, respectively, and $\rho_{\text{GaN}} = 6.1$ g/cm³ and $\rho_{\text{Mg}_2\text{Si}} = 1.9$ g/cm³ are the densities of GaN and Mg₂Si, respectively. The obtained unit is given in cm/s, which then can be converted in nm/min, or mm/y, as it presents the commonly used unit in the corrosion research field.

3 Motivation: GaN and Mg₂Si

3.1 GaN as wide band gap semiconductor in photoelectrochemistry

3.1.1 Conditions for photoelectrochemical reactions

Photoelectrochemical reactions like, e.g., the generation of H₂ from aqueous solutions by water splitting [9, 102] as well as photoelectrochemical CO₂ reduction have attracted big attention. Several conditions must be fulfilled to trigger these reactions.

For photoelectrochemical water splitting at zero potential as an example, the semiconductor must first have suitable band edge positions. This means that the conduction and valence band edge energies straddle the electrochemical potentials of the two half reactions for H₂ and O₂ generation. The thermodynamic difference between the potentials of these half reactions for water splitting is 1.23 V on an absolute scale. Due to occurring anodic and cathodic polarization losses, as well as a current-resistance drop in the electrolyte and the used electrode material, causing an overpotential, water splitting is only possible by exceeding this potential of 1.23 V. This implies that the conduction band minimum energy level must be positioned at a more negative potential than the potential for reducing the proton H⁺ to H₂. Furthermore, the valence band maximum potential must be located more positively than the oxidation potential of water to

O₂. Additionally, a high photon to electron conversion efficiency with the semiconductors band gap large enough to split water must be guaranteed. Materials with band gaps of at least 1.8 eV are thus required. Also, to gain higher conversion efficiencies, the band gap should additionally allow absorption in the visible region of light up to 1000 nm to drive water splitting reactions. Finally, from the practical point of view, the material durability is important to have stable photoelectrodes working reliable over time without dissolving in solution. Thus, a high corrosion resistance in aqueous media is one of the main factors determining the lifetimes of the semiconducting electrodes.

In literature, several types of semiconductors are applied as photoelectrodes, including metal oxides, oxynitrides, organic semiconductors, or photocatalyst particles [9, 24]. Semiconductors can be used purely as photoelectrodes, as tandem photoelectrochemical cells or as Schottky barriers, forming a semiconductor–metal barrier [24, 90].

GaN has a wide direct band-gap of approx. 3.4 eV [15] (approx. 365 nm). It is excitable in the near-UV range and can straddle both the electrochemical potentials for water splitting and CO₂ reduction. The band edge positions of GaN are suitable for realizing photoelectrochemical reactions, e.g., zero potential H₂ generation [103] or CO₂ reduction to valuable products [25]. On the other hand, the large band gap severely reduces the maximum efficiency under solar illumination.

3.1.2 Choice of electrolytes and influence of metals

The electrolyte plays an important role for the stability of GaN. The conductivity and concentration of electro-active species influence reactions at the GaN–electrolyte interface. In literature, most photoelectrochemical processes are carried out in acids like HCl or H₂SO₄,

3.1 GaN as wide band gap semiconductor in photoelectrochemistry

e.g., [104, 105], or bases like NaOH or KOH [8, 31, 106]. They are amongst others used to achieve higher efficiencies and photocurrents.

In this work, the electrolytes were chosen in order to adjust realistic environmental conditions. Ultrapure water is used as electrolyte with a very low conductivity, and 0.1 M NaCl as a well conducting electrolyte. Both solutions, since they were produced from ultrapure water which becomes acid with time, have a slight acid pH value which is expected to be 5. Furthermore, NaCl is the main content of seawater, which is available and safe. Concerning the worldwide water situation, the usable freshwater supply on earth is less than 1 % of all freshwater resources² as it is amongst others mentioned by Tu *et al.* [23]. From an economic point of view, the supply of fresh water for water splitting processes in aqueous solutions will be limited³. On the other hand, only few studies about photoelectrochemical H₂ generation in seawater exist in literature, see, e.g., [107]. Only during the last few years several groups started to investigate GaN in NaCl solutions, e.g., [23, 108].

Furthermore, the effect of GaN stability under the influence of metals was studied in this work. GaN used in optoelectronic devices such as LEDs is contacted by metals. Silver in practice is used since it represents a mirror for GaN to trap light in LEDs. Under moist conditions, this metal presence could lead to undesired interactions with the GaN surface. Also in photoelectrochemistry, metals and their interaction with GaN have an enormous influence on the GaN–electrolyte interface and could also influence the stability of the GaN photoelectrode. The publication of Tu *et al.* is one of the few works that investigate the influence of metals on an n-GaN surface gold nanoparticle coating, but more from an efficiency point of view [35]. Silver, gold, platinum, and nickel were chosen in this work in reference

² <http://www.unwater.org>

³ <http://www.unesco.org/new/en/natural-sciences/environment/water/wwap/wwdr/wwdr4-2012/>

to their different standard electrode potentials E^0 , which are +0.79 V, +0.58 V, +1.19 V, and -0.25 V vs. NHE, respectively.

3.1.3 Electronic energy levels of GaN in solution

The flat band potential E_{fb} was introduced in section 2.1. By determining its value, the positions of the band edge potentials can be calculated. This is exemplarily done in this work for n-GaN. The most common technique for the estimation of E_{fb} is electrochemical impedance spectroscopy (EIS). It uses the fact that the electric properties of a semiconductor–electrolyte interface can be approximated as a connection of several capacitances such as the space charge capacitance C_{sc}^2 of the semiconductor.

In a so-called Mott-Schottky plot the space charge capacitance is plotted as $1/C_{\text{sc}}^2$ vs. an applied potential E . The Mott-Schottky-Plot is derived from the following equation:

$$\frac{1}{C^2} = \left(\frac{2}{eN_{\text{d}}\epsilon_{\text{GaN}}\epsilon_0} \right) \left[(E - E_{\text{fb}}) - \frac{k_{\text{B}}T}{e} \right], \quad (3.1)$$

where N_{d} is the donor density, ϵ_{GaN} is the dielectric constant of GaN, ϵ_0 is the permittivity of the free space, k_{B} is the Boltzmann constant, T is the temperature, and e is the elementary charge. Information about the derivation of this formula and the choice of the appropriate circuit diagram for the determination of E_{fb} can be obtained from, e.g., [109].

E_{fb} can be determined from the intersection of the linear extrapolation with the x-axis: $1/C_{\text{sc}}^2 = 0$. The values received from EIS measurements in literature are more or less consistent and comparable with each other (despite some small shifts due to the influence of some additional surface layers, which are negligible). Many groups postulated equations which all have a band edge potential variation of approx. 0.059 V in common when the pH value is changed by one unit

[103, 110, 111]. It is assumed that this almost Nernstian dependency is due to the attachment of H^+ ions as potential-determining species on the surface [103]. Thus, the pH value has a strong influence on E_{fb} . Fujii *et al.* applied the Mott-Schottky analysis also to p-type GaN. They found out that the band edge positions are nearly the same for n-type and p-type GaN [33, 105].

The calculation of E_{fb} in this work is based on experimental findings in literature [103, 110, 111]. Referring to the relationship found by Kocha *et al.*, E_{fb} can be calculated by $E_{fb} = -0.75 - 0.055 \cdot \text{pH}$ (in V vs. SCE) [110]. Since a near neutral pH value of 5 for ultrapure water and NaCl is assumed in this work, it results in $E_{fb} = -1.03$ V vs. SCE, which corresponds to a value of -1.06 V vs. Ag/AgCl and -0.86 V vs. NHE. From E_{fb} , a conduction band edge of $E_{cb} = -0.80$ V vs. NHE = -3.70 eV and a valence band edge of $E_{vb} = 2.63$ V vs. NHE = -7.13 eV were determined for n-GaN. The conversion was made according to equation 2.9.

Furthermore, the electrochemical redox potentials from the used electrolytes in this work at pH 5 were calculated. It includes the reduction of H^+ to H_2 as well as the oxidation of OH^- to O_2 and Cl^- to Cl_2 , corresponding to the Nernst equation 2.1. The redox levels were determined as $\phi_{H^+/H_2} = -0.29$ V vs. NHE = -4.21 eV, $\phi_{OH^-/O_2} = 0.94$ V vs. NHE = -5.44 eV, and $\phi_{Cl^-/Cl_2} = 1.06$ V vs. NHE = -5.56 eV. In figure 3.1, the energetic positions of all potentials are plotted in a scheme. It can be clearly seen that the redox potentials of H_2 , O_2 , and Cl_2 evolution are straddled by the valence and conduction band edges of GaN. Thus, GaN as photoelectrode is suitable for the electrolysis of water and photoelectrochemical water splitting should be possible without an externally applied potential.

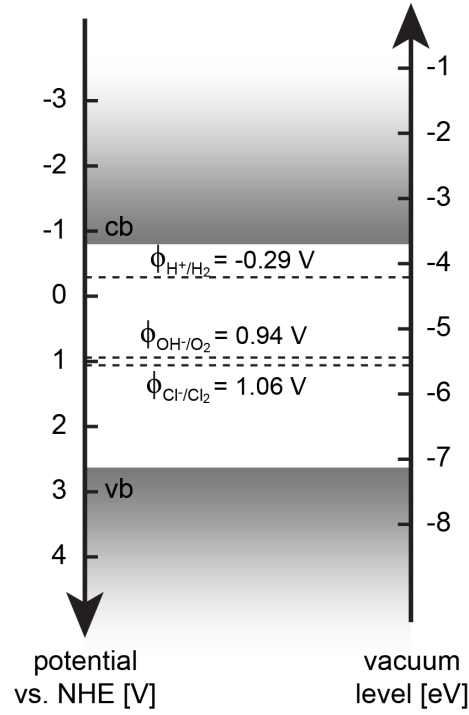


Figure 3.1: Energetic positions of the conduction band (cb) and valence band (vb) of n-GaN at the n-GaN–electrolyte interface to aqueous solution with a near neutral pH value of 5. The potentials of the band edges and the redox systems in the electrolyte are given on the electrochemical scale with respect to NHE (vs. V). Additionally, the absolute scale vs. the vacuum level (in eV) is plotted.

3.1.4 GaN as photoelectrode and its stability

Water splitting

The aim of conducting water splitting experiments is the evolution and storage of H₂. In an ideal case it is only driven by solar radiation without an externally applied potential E . Furthermore it needs to be considered that n-type semiconductors in general work as photoanodes and p-type semiconductors work as photocathodes [112].

3.1 GaN as wide band gap semiconductor in photoelectrochemistry

In general, p-type semiconductors are used as photoelectrodes for water splitting reactions since they are able to generate H_2 under zero potential conditions ($E = 0$ V). For a p-GaInP₂/GaAs device, a H_2 production efficiency of approx. 12.4 % was reported [13]. Kobayashi *et al.* reached an overall quantum efficiency of 4-6 % for p-GaN in Na_2SO_4 under UV excitation and zero potential condition [113]. However, p-type GaN shows low photocurrents which lead to a low efficiency for photoelectrochemical reactions [21]. The weak photocurrents for p-GaN are explained by the doping with Mg leading to a deep Mg acceptor level with an activation energy of approx. 180 eV [114] causing high resistivities. Usually a high acceptor concentration in the range of 10^{19} cm^{-3} is used to achieve p-doping of GaN. This leads to a thin depletion layer and an insufficient charge separation and thus recombination of photogenerated charge carriers.

On the other hand, n-GaN is often used as photoelectrode since it has a better crystallinity and the doping concentration is better adjustable [21]. Since n-GaN works as photoanode, H_2 evolves and is collected from a metal CE. Often acidic or basic solutions are used as electrolytes to increase efficiencies of H_2 production. Besides, an additional applied potential is needed to increase photocurrents [105, 115]. Waki *et al.* for example reported of a solar-to-hydrogen conversion efficiency of 0.3 % for an external potential of 0.5 V in NaOH [115]. In [116], conversion efficiencies of N-polar n-GaN of 0.61 % were achieved in HCl whereas it was 0.55 % for Ga-polar n-GaN.

The drawback of n-GaN in turn is that photo etching simultaneously takes place during water splitting. Photocatalyst particles that are attached to the semiconductor surfaces can enhance the efficiency and furthermore improve the stability of the photoelectrodes (like, e.g., ZnO [117], RuO₂ [118] or NiO [119]). Ohkawa *et al.* achieved an average energy conversion efficiency from light to H_2 of about 1 % for n-GaN with NiO co-catalyst particles in NaOH under zero potential

conditions for 500 h. The FE for H₂ production was about 90 % [119, 120].

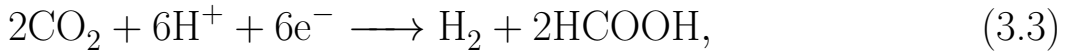
The absorption of GaN and thus the band gap can be furthermore changed by the ability of GaN to form solid solutions with AlN (e.g., [121]) and InN making band gap engineering possible. Indium for example narrows the band gap of GaN making it possible to absorb light also in the visible range and thus increasing the efficiency [14, 22, 122–125].

Reduction of CO₂

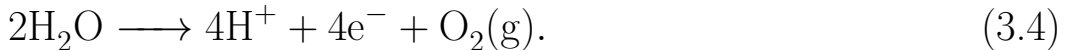
Another application for GaN is photoelectrochemical CO₂ reduction, where worldwide in huge amounts produced CO₂ caused i.a. by industrial processes can be converted to more valuable materials like, e.g., formic acid (HCOOH). The overall CO₂ reduction reaction is described as



and can be split into two half reactions, where the CO₂ reduction itself takes place at the cathode



and water oxidation occurs at the anode of the system



Since higher energies are necessary for CO₂ reduction, this reaction presents a greater challenge than water splitting. The evolution of gaseous H₂ in aqueous solutions is an undesired side reaction and competes with the CO₂ reduction at the cathode. In a press release of Panasonic in 2012, an efficiency of 0.2 % was achieved for the generation of formic acid [126]. Yotsuhashi *et al.* for example reported a FE of approx. 9% for the formation of HCOOH from CO₂ conversion for pure n-GaN [26]. Attempts of photoelectrochemical CO₂ reduction on GaN were also made in this work.

Photoelectrochemical etching of GaN

Several names in the literature describe changes of the semiconductor surfaces. For GaN electrodes, e.g., the terms photo etching [111], photoassisted anodic etching [127], dissolution [105, 128], photodegradation [129], anodic decomposition [111], attack [130], photocorrosion [112] or photo-oxidation [28] can be found.

The high amount of literature studies concerning etching of GaN in acidic or alkaline solutions represents the high importance of GaN etching for industrial processes.

Selective etching of GaN has a great industrial importance, e.g., in the fabrication of GaN-based MOS structures [8]. Furthermore, etching is interesting from a scientific point of view since it gives valuable information for the understanding of GaN material. It therefore is useful to study defect decoration or identify the polarity of GaN [14, 116, 131]. The etching of GaN is furthermore applied to gain knowledge about its defect sides [14, 132]. Dislocations on the GaN surface are often visible as nanometer-scale pits [133]. Also point defects and impurities are probably trapped within the range of these dislocations [30]. Since recombination of the photogenerated holes and electrons takes place at the dislocation sites, an etching and thus dissolution of n-GaN is not observed there [129]. However, etching preferably takes place at non-defect sites of n-GaN, leading to an inhomogeneous etching of the n-GaN surfaces [111].

It is important to know the rate constant of redox reactions at the GaN–electrolyte interface for selecting good-working photocatalytic material systems or improving processes such as photo etching of semiconductors in the semiconductor production. Previous studies showed that it is possible to increase the efficiency of GaN by crystallographic wet etching which increased the surface area [129]. Pankove already reported in 1972 about electrolytic GaN etching in NaOH, but without giving an etching rate [134].

As for photoelectrochemical water splitting, also for studying etching processes, usually strong acidic or basic solutions are used [28, 106, 135]. For example, in [28], a photo etch rate of 400 nm/min in 1:3 diluted KOH and 40 nm/min in 1:10 diluted HCl was determined for n-GaN. An etch rate of 50-300 nm/min was found in 0.04 M KOH [31] whereas in [106] it was 90 nm/min in 2 M KOH. In general, a huge variety of measurement parameters like different concentrations makes it difficult to make consistent conclusions. Etch rates were also determined for NaCl as electrolyte. Tu *et al.* reported an etch rate of 0.016 nm/sec in 1 M NaCl [23].

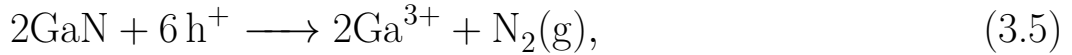
Photo-oxidation of GaN

For photoelectrochemical processes, the stability of GaN in aqueous solutions is important. Thus, the aim is to avoid degradation of GaN surfaces. As mentioned above, especially n-GaN is used as photoelectrode since it has high efficiencies, e.g., in water splitting, but on the other hand it shows poor stability. Photo-oxidation of n-GaN is a well-known mechanism although some details are still not clear. In principal it has the same meaning as photo etching since both terms describe basically the same process but it corresponds to a more scientific point of view.

By above band gap illumination, free electrons and holes are generated at the semiconductor–electrolyte interface. Previous studies showed, that these photogenerated minority charge carriers are all created within the space charge region. Average values of the electron diffusion length of 250-280 nm are given for p-GaN [136], whereas they are around or smaller than 250 nm for holes in n-GaN [30, 137]. It thus can be expected that only a small part of the n-GaN layer contributes to the photocurrent. This can be changed by applying less doped n-GaN samples to increase the space charge region enabling more holes contributing to water splitting reactions. Such studies on the dependency on doping were made, e.g., in [23, 105]. The

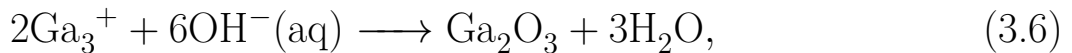
penetration depth of light in GaN, $1/\alpha$, is less than 100 nm below 365 nm [138]. The generated charge carriers are separated by the present electric field in the space charge region and a photocurrent flows which depends on the width of the space charge region.

Photo-oxidation is reported only for n-GaN. It is triggered by the accumulated holes at the n-GaN surface which occurs due to the band bending, see figure 2.1 (a). Photogenerated holes play the major role in photo-oxidation and also degradation of n-GaN. Photo-oxidation of GaN was proposed by Minsky *et al.* [28] by drawing a parallel to the etching of GaAs, which was already well understood by then [130, 139, 140]. Youtsey *et al.* postulated the corresponding reaction equation for the photo-oxidation of n-GaN [31]

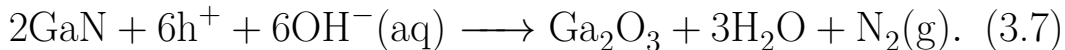


which was confirmed by several other research groups [6, 28, 104, 135]. The accumulated holes at the n-GaN surface present broken bonds and react oxidatively with n-GaN, forming gaseous nitrogen (N_2). By the discharging of holes into the electrolyte, the n-GaN surface is etched. Thus, only holes are involved in photoanodic dissolution of n-GaN [111] and decompose n-GaN as oxidizing agents. Since Ga^{3+} ions are present in solution due to evolving N_2 , most likely oxygen-containing compounds like gallium hydroxide ($\text{Ga}(\text{OH})_3$) or gallium oxide (Ga_2O_3) are formed on the n-GaN surface.

Thus, a two-step-process is proposed, consisting of an oxidation and a subsequent oxide dissolution from an n-GaN surface [106]. This is based on the existing oxygen compound in solution, which is dependent on the pH value since it is limited by the diffusion of OH^- ions to the surface [8]. In literature, the formation of Ga_2O_3 is assumed under basic, acidic as well as near-neutral conditions [31, 111, 127, 141]. Different reaction equations are given for the process. Shiozaki *et al.* for example postulated the following reaction under a near-neutral pH value [141]:

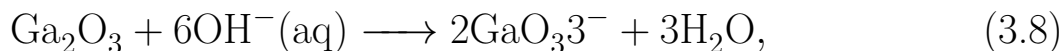


whereas Rotter *et al.* suggested a similar reaction equation which combines the N₂ evolution and oxide formation [8]:



On the other hand it was reported that Ga(OH)₃ formed in NaOH [134, 142].

As Ga₂O₃ is amphoteric, it is soluble both in acids and bases. This would mean that the formed Ga₂O₃ dissolves again after its formation by reacting with further OH[−] ions [106]:



leading to a photo etching of the n-GaN surface as it was shown, e.g., for alkaline solutions like KOH [8]. Therefore, Pourbaix diagrams need to be taken into account since they give an overview of the thermodynamic stability of metals and their aqueous reaction products. It thus can be seen whether a state in aqueous solution at a certain pH value and potential is stable. From the Pourbaix potential–pH equilibrium diagram for the gallium water system it was seen that Ga₂O₃ is stable in the range of pH 4 to 11 and is not dissolving [143].

3.2 Fabrication of Mg₂Si as low band gap semiconductor

Contrary to GaN which is known as photoelectrode material, almost nothing is known about Mg₂Si for these purposes. Mg₂Si is well-known for other applications but less as light absorbing material in photoelectrochemistry, thus making it interesting to investigate its properties in aqueous solutions. The focus of Mg₂Si research in this work is on the fabrication of Mg₂Si thin films to understand and study material properties with respect to its application in photovoltaics and photoelectrochemistry.

3.2 Fabrication of Mg_2Si as low band gap semiconductor

Already in 1858, the Mg_2Si compound was mentioned for the first time by F. Woehler in connection with the fabrication of silane [144]. The preparation of pure Mg_2Si was first successfully achieved in 1908. The focus of research at that time was on the synthesis of Mg_2Si by melting metallurgy, as well as on fundamental electrical and optical properties of Mg_2Si .

Mg_2Si crystallizes at room temperature in the face-centered cubic (fcc) anti-fluorite structure ($Fm\bar{3}m$) [38, 67]. Its lattice constant is reported to be 6.35 Å [36, 62]. Mg_2Si exists either as bulk material or as thin films [38]. The fabrication of thin film Mg_2Si layers can be done by several techniques, as for example atomic deposition methods like molecular-beam epitaxy [62, 145, 146] mechanical alloying [147, 148], ion beam sputtering [70], solid phase crystallization of Mg–Si stacked layers [145, 149], pulsed laser deposition [71], implantation of Mg ions into Si substrates [150], as well as diffusion synthesis methods like sputtering [40, 44, 70, 72, 151–153], electron gun evaporation [154], or thermal evaporation [59, 155, 156].

By evaporating magnesium on silicon with subsequent annealing, Mg_2Si is formed because of the diffusion of magnesium atoms in silicon:



Due to the consumption of silicon from the substrate, volumetric changes during Mg_2Si silicide formation occur, which always results in a shrinkage ($d_{\text{Mg}_2\text{Si}}/(d_{\text{Mg}} + d_{\text{Si}}) < 1$). They are calculated from the atomic density of magnesium and silicon [157] and are given by the following equations [38]:

$$\frac{d_{\text{Si}}}{d_{\text{Mg}}} = 0.43 \quad (3.10)$$

and

$$\frac{d_{\text{Mg}_2\text{Si}}}{d_{\text{Mg}}} = 1.38, \quad (3.11)$$

3 Motivation: GaN and Mg₂Si

where d_{Si} is the thickness of the consumed silicon, d_{Mg} the thickness of the deposited magnesium, and $d_{\text{Mg}_2\text{Si}}$ is the thickness of the generated Mg₂Si layer. From equation 3.10 it becomes clear that more magnesium is consumed than silicon, which appears reasonable since magnesium was found to be the main diffusion species. Chu *et al.* found out with the help of xenon ion markers that mainly magnesium diffuses in to silicon and thus being the predominant diffusion species in Mg₂Si formation [149]. The relations in equations 3.10 and 3.11 show that the final formed Mg₂Si layer appears above the original magnesium–silicon interface, since $d_{\text{Si}}/d_{\text{Mg}} < d_{\text{Mg}_2\text{Si}}/d_{\text{Mg}}$. The grown Mg₂Si film is calculated to be 38 % thicker than the originally deposited magnesium layer.

Hosono *et al.* reported that the thickness of the Mg₂Si layer, d , is proportional to the root of the time of growth, $\sqrt{t}$, meaning that the Mg₂Si growth is diffusion-controlled and the thickness d of the resulting Mg₂Si layer can be expressed as

$$d = \sqrt{4Dt}, \quad (3.12)$$

where D is the diffusion constant which was estimated to be $D = 3.5 \cdot 10^{-10} \text{ cm}^2/\text{s}$ at a growth temperature of 370°C [59].

However, the fabrication of uniform Mg₂Si layers is reported to be rather difficult. The formation of thin films is complicated due to the low condensation coefficients and a high vapor pressure of magnesium, which hinders the formation of epitaxial thin Mg₂Si films [72].

The formation of an ohmic contact on Mg₂Si can be made with various metals. Since Mg₂Si was mainly used as thermoelectric material, it was important that the thermal expansion coefficients of the contact material match to that of Mg₂Si. Furthermore, a low contact resistance of the electrode to Mg₂Si is required as well as no reactions with Mg₂Si at higher temperatures. It was found that nickel was a suitable contact material that is not reactive with Mg₂Si [158, 159]. Nickel can be additionally annealed to improve the adhesion of nickel to Mg₂Si [160, 161]. By that NiSi forms which is a well-known ohmic

3.2 Fabrication of Mg_2Si as low band gap semiconductor

electrode material [157]. Furthermore, also silver forms an ohmic contact on Mg_2Si , whereas gold is known to form a Schottky contact [66]. Ohmic properties were also reported for Mg as electrode material to Mg_2Si [40].

Doping of Mg_2Si is mainly done to lower the resistivity and improve its efficiency as thermoelectric material. It is reported that Mg_2Si can be doped to achieve an increased n-type doping (e.g., with Bi [57, 58, 61], Sb [59, 61, 162], Al [163], or impurities like Co, Sm, Ta [164]), although the solubility of the dopants in Mg_2Si is quite poor. To get a p-type behavior, Mg_2Si is doped with impurities like Ag and Cu that work as acceptors [59, 60].

The indirect band gap of Mg_2Si is in the range of 0.66 to 0.80 eV [36, 52, 53, 62, 165, 166]. The exact band gap energy is still controversially discussed. Most commonly, an indirect band gap value of 0.78 eV is reported [36]. However, also direct band transitions at 0.83 eV and 0.99 eV as well at 0.95 eV and 1.05 eV were determined [62, 167].

4 Materials and Methods for Sample Characterization

4.1 Measurements of morphology, electrical and optical properties

To deposit metals on GaN and Mg_2Si and for the formation of Mg_2Si , the corresponding materials were either thermally evaporated or sputtered. Evaporation of magnesium was carried out at a Kurt J. Lesker thin film deposition system, the other evaporated metals in this work were evaporated in a Leybold Univex 300 evaporation system. Mg_2Si and nickel were DC magnetron sputtered in a Kenotec sputtering chamber and platinum was deposited in a Leybold Z650 sputtering system.

Microscopy and EDX measurements

Light microscopy images were acquired on a reflected-light microscope BX 61 from Olympus. Scanning electron microscopy (SEM) measurements were performed on a Hitachi S 4800 instrument which has a maximum resolution of 1 nm and a variable acceleration voltage of 0.5-30 kV. A secondary electron detector maps the topography, whereas the backscattering electron detector depicts the material contrast of the measured sample surface. Sample surfaces and cross sections were measured. For cross section measurements, the samples were broken in liquid nitrogen.

One main focus in this work was put on energy-dispersive X-ray spectroscopy (EDX) measurements, to gain quantitative data of the stressed GaN samples. EDX measurements were performed on a Lyra 3 Tescan system with an EDX system Quantax 200 XFlash Detector 5010 from Bruker. So far, EDX measurements in that way were not made before for GaN samples in literature. Only Peng *et al.* show an EDX spectrum of an unstressed and stressed n-GaN sample to proof the existence of an oxide phase after experiments [106].

XRD measurements

X-ray diffraction (XRD) is a versatile, non-destructive analytical technique for identification and quantitative determination of the various crystalline forms, known as phases of compounds present in powdered and solid samples. Identification is achieved by comparing the measured diffractograms with an intentionally recognized database (e.g., the international centre for diffraction data, ICDD⁴) containing reference patterns.

An incidence of X-rays on lattice planes in a crystal at an angle θ , causes diffraction, which only occurs when the distance traveled by the rays reflected from successive planes differs by a complete number n of wavelengths. This is described by Bragg's law:

$$n\lambda = 2d \sin(\theta), \quad (4.1)$$

where λ is the wavelength of the incident monochromatic X-ray beam, θ is the angle between the X-ray beam and the lattice plane, and d is the distance of the lattice planes in the material. By varying the angle θ , the Bragg's Laws conditions are satisfied by different d-spacings in polycrystalline materials. Plotting the angular positions and intensities of the resultant diffraction peaks produces a diffraction pattern which is characteristic for the respective sample.

⁴ <http://www.icdd.com>

4.1 Measurements of morphology, electrical and optical properties

Diffraction data were collected at a Siemens D500 diffractometer with Cu-K α radiation ($\lambda = 1.54 \text{ \AA}$), operated at 40 kV and 35 mA with a step of 0.01° .

It is also possible to conduct XRD measurements under a very flat angle of incidence, which is then called grazing incidence X-ray diffraction (GIXRD). GIXRD measurements are very surface sensitive due to the weak penetrating incident light. These measurements were performed on a Philips PANanalytical X'Pert XRD system with Cu-K α radiation at 40 kV and 35 mA with a step of 0.01° .

SIMS measurements

Time-of-Flight Secondary ion mass Spectroscopy (ToF SIMS) is a surface-sensitive method which is based on the mass separation of secondary ions which are generated by a pulsed primary beam on the sample surface. Only negative secondary ions are analyzed, neutral ions are lost. With every pulse a complete mass spectrum is generated. Measurements were performed on a TOF.SIMS 4 instrument (IONTOF). To achieve the measurement of a depth profile, the analyzer is blocked during the time of flight of the secondary ions which is approx. $200 \mu\text{s}$, thus enabling a scanned sputter ion beam from a Cs^+ source on the sample surface.

XPS measurements

In X-ray photoelectron spectroscopy measurements (XPS) the sample is illuminated with focused monochromatic low-energy X-rays from an aluminum source. The spectrum of the generated photoelectrons is recorded by a spectrometer. The intensities of the element-specific photoelectron peaks provide information on the atomic composition in the analyzed volume. A detailed analysis of the photoelectron peaks gives information on the chemical binding states of the detected elements. Although it is a very surface sensitive method, XPS spectra

in sample depths can be recorded by applying sputtering techniques. Measurements were performed on PHI Quantum 2000 instrument from Physical Electronics GmbH with an Al-K α source (1486.7 eV) under an angle of 45°. The analyzed volume has a lateral dimension of approx. 100 μm and is limited in depth by the inelastic path length of the photoelectrons in the analyzed material of some 3 nm.

Van der Pauw measurements

The measurement of the sheet resistance and electrical conductivity was conducted with the help of the van der Pauw method. The measured material is expected to be homogeneous in its thickness and doping and has a plane-parallel form. There are four electric contacts (A, B, C, D) which need to be sufficiently small and located at the border of the sample. A current is impressed between contacts A and B and the falling voltage between contacts C and D is measured. This is done by cyclic permutation for all combinations. By that, a sheet resistance can be calculated, which is independent on the form of the material or the position of the contacts. Knowing the thickness of the measured film, the resistivity can be calculated in Ωcm . Measurements were conducted in a self-rebuild adapter from Ingun (MA 16 starter kit) which is triggered by source measurement units (Keithley 6514 system electrometer and Keithley 237 high voltage source unit).

Hall measurements

Hall measurements were performed in a self-build setup. The sample was contacted with silver epoxy and placed in-between a Helmholtz coil. Before the magnetic field of 0.4 T was applied, the sheet resistance was measured first by the van der Pauw method to determine the resistivity. When a conductor is brought in a magnetic field, the charge carriers are deflected due to the Lorentz force. A Hall voltage U_H is build up perpendicular to the direction of electric current.

4.1 Measurements of morphology, electrical and optical properties

From the Hall coefficient, R_H , and the resistivity, ρ , the charge carrier density n and their mobility μ can be calculated by:

$$U_H = R_H \frac{BI}{d}, \quad \mu = \frac{|R_H|}{\rho}, \quad n = \frac{1}{e|R_H|}. \quad (4.2)$$

A negative sign of R_H indicates an electrical conductivity which is mainly due to electrons, thus n-type behavior can be reasoned.

Transmission and reflection measurements

Transmission and reflection measurements were performed on a Perkin Elmer Lambda 950 UV/Vis Spectrometer. Measurements were performed in the visible and IR range, where a halogen lamp was the light source. The detectors were either a photomultiplier (160 - 900 nm) or an InGaAs photodiode (860 - 2500 nm) which were placed in an integrating sphere coated with spectralon. Solid sample were placed in a sample holder and the measured electrolytes in quartz glass cuvettes. When light hits a sample, dependent on the wavelength it is either absorbed, transmitted, or reflected. It can be written as $A(h\nu) + T(h\nu) + R(h\nu) = 1$. Since the total and diffuse contributions of transmission and reflection can be measured separately, every contribution of $T_{\text{total}} = T_{\text{direct}} + T_{\text{diffuse}}$ and $R_{\text{total}} = R_{\text{specular}} + R_{\text{diffuse}}$ can be measured.

The Beer-Lambert law describes the attenuation of light when passing a medium. It is written as

$$I(d) = I_0 e^{-\alpha(\lambda)d}, \quad (4.3)$$

where I_0 is the light intensity which gets into the material and $I(d)$ is the rest intensity after traversing the distance d . The absorption coefficient α is a parameter which is independent of the thickness of the material and is defined by the penetration depth, at which a photon is absorbed with the probability $1/e$.

The optical band gap E_g of semiconductors can be received from the absorption coefficient α by fitting to Tauc's formula [168]. It is determined as

$$(\alpha h\nu^{1/2}) \propto (h\nu - E) \quad (4.4)$$

for an indirect band gap (like Mg_2Si), and

$$(\alpha h\nu^2) \propto (h\nu - E) \quad (4.5)$$

for a direct band gap (like GaN). From the intersection of the extrapolated linear part with the energy axis, the corresponding values for E_g are determined.

Solar simulator

The solar simulator Sun2000 from ABET-Technologies has a xenon lamp whose radiation intensity is regulated via the power supply. A filter is placed in front of the lamp to simulate an AM 1.5 spectrum of the sun. These are standard test conditions for solar cell measurements. The power of the lamp is adjusted with a reference solar cell to emit light at 1000 W/m^2 . The solar simulator is connected to a Keithley source measurement unit, where the solar cell can be measured dark and under illumination.

4.2 Electrochemical setup

To study the characteristic properties of GaN samples, a standard three-electrode-setup was used. The principle of operation is described in detail in section 2.2.3.

The used photoelectrochemical cell (PEC) in this work was a PECC2 cell from Zahner-Elektrik GmbH as can be seen in figure 2.2 (b). An electrolyte volume of approx. 7 ml is filled into the cell body with a pipette. The solution during experiments is not stirred.

It is a one cell chamber, where a platinum ring CE is placed in front of an optical quartz glass window, which can transmit UV light. The WE (either GaN or Mg_2Si) is placed in a sample holder which is screwed to the cell body. A RE can be placed in a channel in the middle of the top cell body. In this work, a high resistance Ag/AgCl RE with a standard electrode potential of -0.209 V vs. NHE and $+0.035\text{ V vs. SCE}$ was used as reference electrode. It was stored in a 3 M NaCl solution. The positions of the three electrodes were always fixed, allowing no local changes, thus providing reproducible settings. Additionally, the PEC has gas inlet and outlet. The PEC was connected to a potentiostat PGSTAT302N from Metrohm which was driven with the Nova 1.10 software. The potential range is $\pm 10\text{ V}$ with a potential resolution of $0.3\text{ }\mu\text{V}$. The measurable current range is $\pm 2\text{ A}$ with a current resolution of $0.0003\text{ \%}$ of the current range.

The PEC was cleaned before each experiment. For those cleaning purposes, the cell can be totally dismounted. Single parts were put in a beaker and sonicated for 20 minutes in acetone to remove organic leftovers. Afterwards it was rinsed with ultra pure water and was dry blown with compressed air.

The focus on used electrolytes in this work was set on ultrapure water and 0.1 M NaCl solutions. These electrolytes were freshly prepared from analytical grade reagents and deionized water before experiments. The required amount of NaCl was weighted in a volumetric flask and filled up with ultrapure water to the calibration mark. Ultrapure water (ISO 3696) with a resistance of $18.2\text{ M}\Omega$ at 23.0°C was directly tapped from a MilliQ Integral Water Purification System (Merck Millipore). In the following it is referred to as H_2O . Originally, freshly tapped deionized water from the purification system has a pH value of around 6.5 to 7, but it gets acid directly when it is exposed to the ambient atmosphere. As mentioned in section 3.1.2, both electrolytes are expected to have pH values of approx. 5 since they could not be measured directly. This rather acid solutions are caused by the fact that ultrapure water dissolves carbon dioxide from the

ambient atmosphere quite fast after tapping it, leading to a more acid pH value. The specific conductivities of the electrolytes were measured with a conductivity electrode (WTW Cond 330i) and were $0.8 \mu\text{S}/\text{cm}$ at 22.9°C for ultrapure water and $11.18 \text{ mS}/\text{cm}$ at 23.8°C for 0.1 M NaCl . The higher the conductivity, the smaller the electric resistance and the potential drop over the electrolyte. Thus, the chosen solutions present a weak and a well conducting electrolyte. Argon was bubbled through the corresponding electrolyte for at least 20 minutes before each measurement to remove dissolved oxygen.

All experiments were carried out at room temperature either under dark conditions or under illumination (the illumination wavelength was chosen depending on the WE and its excitation ability). During experiments in the PEC it was paid attention that no undesired evolving gas bubbles came to the outlet of the RE to avoid falsification of the measured current. If so, experiment were stopped in order to remove the gas bubbles by gently knocking against the PEC.

Light sources

Samples in the PEC were illuminated with a 200 W Hg(Xe) arc lamp which was mounted in a monochromator setup (Newport, Oriel Apex Monochromator). The monochromator setup can illuminate the samples at a certain wavelength within a wavelength range of 200 nm to 900 nm, tunable in 1 nm steps. Figure 4.1 (a) shows a photo from the setup with the monochromator and PEC.

Samples for the photoinduced degradation experiments were illuminated with high power light-emitting diodes (LED Engin, Inc.). The LEDs had wavelengths of 365 nm, 400 nm, 525 nm, 627 nm, and 940 nm and were mounted on black plastic lids.

GaN samples were placed in crystallizing dishes containing the corresponding electrolytes in volumes of approx. 20 ml as shown in figure 4.1 (b). Figure 4.1 (c) shows a mounted LED which was put over the crystallizing dishes. The black plastic rings are fixed in order

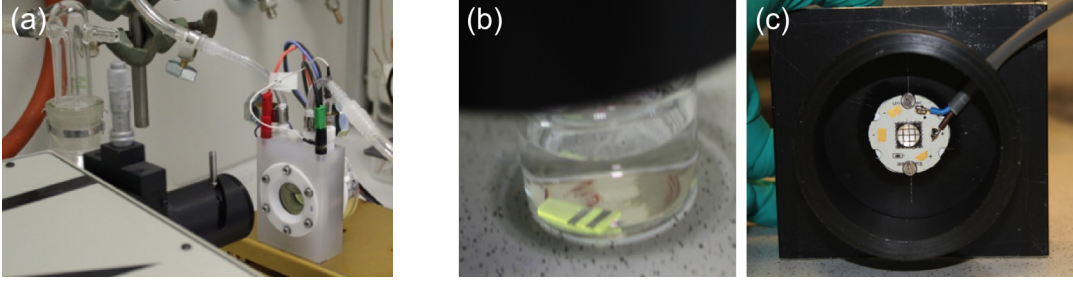


Figure 4.1: Photographs of the illumination setups used in this work. (a) The PEC cell placed in front of a monochromator setup. (b) A GaN sample with evaporated metal stripes is placed in a crystallizing dish in an electrolyte and illuminated from top with a 365 nm LED. The yellow emission of the GaN is clearly visible. Dishes were covered with a quartz glass to avoid evaporation of the electrolyte. (c) The bottom side of an LED used in experiments, attached on a black plastic lid to shield the environment from UV light.

to shield UV radiation from the outside. To avoid evaporation of the electrolyte, the crystallizing dishes were covered with quartz glasses. LEDs were cooled by a fan in order to avoid measuring artifacts due to thermal heating of the LEDs to guarantee an equal treatment of the illuminated GaN samples.

The light intensities at the GaN surfaces were measured with a photometer setup (Newport Power Kit, model PMKIT-UV-0.2W). A photodiode detector was placed in the same distance from the monochromator setup or LED at which also the samples were placed during measurements. This was done by placing the detector at an appropriate distance from the illumination source which corresponds to the distance of the lamp to the sample surface. The intensities at the sample surface were 3.6 mW/cm^2 (365 nm), 6.0 mW/cm^2 (400 nm), 3.6 mW/cm^2 (525 nm), 3.4 mW/cm^2 (660 nm), and 3.2 mW/cm^2 (940 nm). For experiments conducted in the PEC, samples were

4 Materials and Methods for Sample Characterization

positioned 5 cm away from the illumination source. In case of photoinduced degradation experiments, the distance from the samples to the LED was approx. 3 cm.

5 GaN as Electrode for Photo-Catalysis

5.1 GaN sample characterization and preparation

GaN layers with Ga polarity were grown on sapphire substrates (Al_2O_3) by hybrid vapor phase epitaxy (HVPE). For n-type samples a 3–4 μm thick n-GaN buffer was deposited followed by a layer of highly doped n^+ -GaN of approx. 1 μm thickness. n-GaN is doped with silicon at a concentration of 10^{18} cm^{-3} . p-GaN samples have the same composition as n-GaN samples but with an additional p-GaN layer of approx. 200 nm thickness on top. p-GaN is doped with magnesium at a concentration of 10^{19} – 10^{20} cm^{-3} . Figure 5.1 shows SEM images of cross sections of n-type and p-type GaN where the different layers are clearly visible.

Additionally, n-GaN samples with nickel oxide (NiO) co-catalyst particles were investigated which cover the whole n-GaN surface. These n-GaN samples had a thickness of 3.2 μm and a concentration of $1.3 \cdot 10^{17} \text{ cm}^{-3}$. The NiO particles were approx. 200 nm high and had a diameter of about 30 μm [26]. These co-catalysts act as an oxidation center and thus should protect the underlying GaN samples from oxidation and thus degradation.

n-GaN samples were investigated in XRD with Bragg-Brentano geometry as can be seen in figure 5.2 to confirm the existence of a GaN phase. The main peak corresponds to the (002) phase of the hexagonal wurtzite crystal structure of GaN (ICDD Card no.

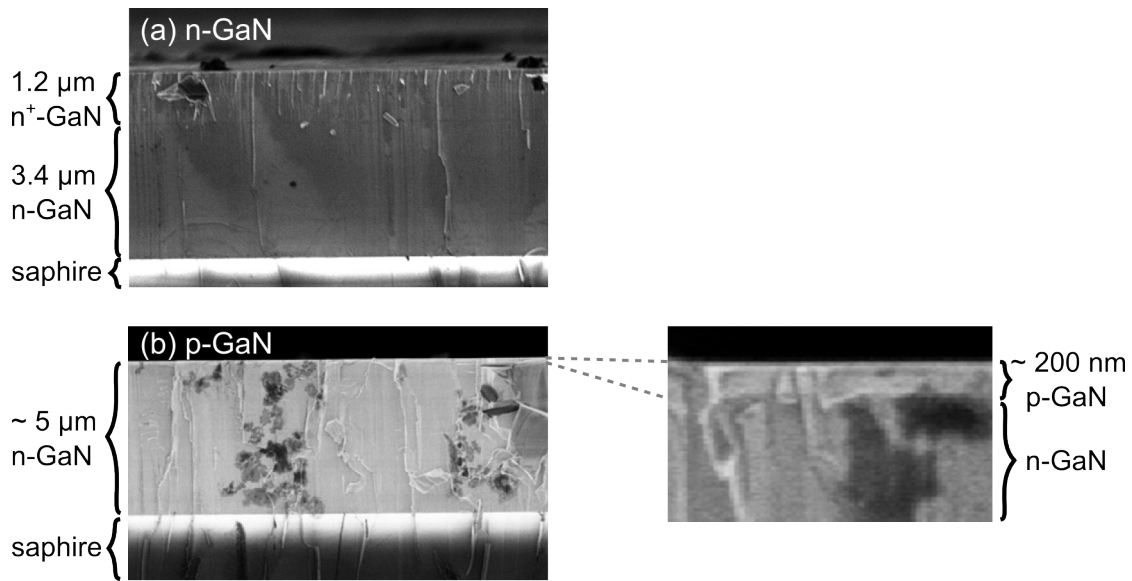


Figure 5.1: SEM images of cross sections of n-GaN (a) and p-GaN (b) samples. The thicknesses of the respective layers are indicated.

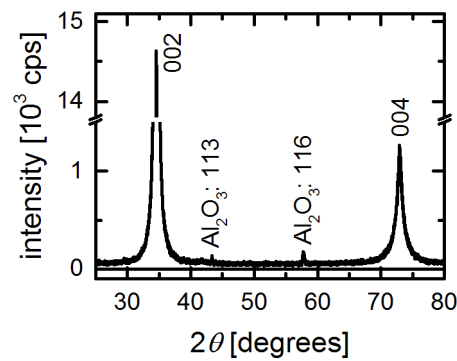


Figure 5.2: XRD diffractograms of an n-GaN sample. The signal from the (002) GaN phase is clearly visible along with weak signals from the underneath Al_2O_3 substrate.

02-1078). Due to the Bragg Brentano geometry, also a weak signal from the underlying Al_2O_3 substrate is detected as well (ICDD Card no. 97-001-0426).

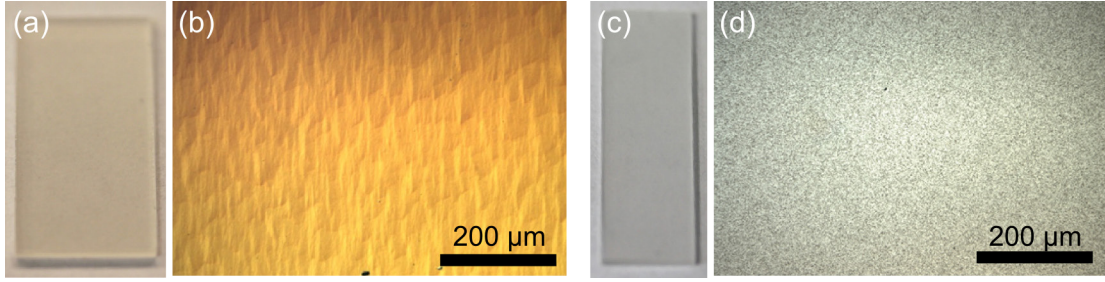


Figure 5.3: Photographs (a, c) and light microscopy images (b, d) of n-GaN (a, b) and p-GaN (c, d) reference sample surfaces before experiments.

In figure 5.3, images and light-microscopy images of the GaN samples that are used in this work are shown. The dimensions of the samples are chosen to fit in the sample holder of the PEC ($1\text{ cm} \times 2.5\text{ cm}$). As will be shown later in this work the surface of the samples changed after various experiments.

Figure 5.4 shows transmission spectra of the used n-GaN and p-GaN samples in this work. In figure 5.4 (a), the transmission of n-GaN and p-GaN samples are plotted whereas in figure 5.4 (b), the transmission spectra of n-GaN samples with and without NiO particles are compared. All samples types show a clear edge in the near-UV area, where the transmission increases up to approx. 70 % – the rest are reflection losses. From the transmission spectrum, the band gap of GaN was determined exemplarily for n-GaN by fitting to Tauc’s formula (cf. section 4.1, equation 4.5). By plotting the square of the determined absorption coefficient product with the energy via the energy, the direct band gap can be received from the intersection of the linear fit with the x-axis. The determined band gap of 3.38 eV is shown in figure 5.4 (c). It is in good accordance with literature (approx. 3.4 eV, [15]) and corresponds to a wavelength of approx. 367 nm.

In figure 5.5 (a), the transmission spectrum of n-GaN is plotted along with emission spectra of 365 nm and LEDs. It can be seen

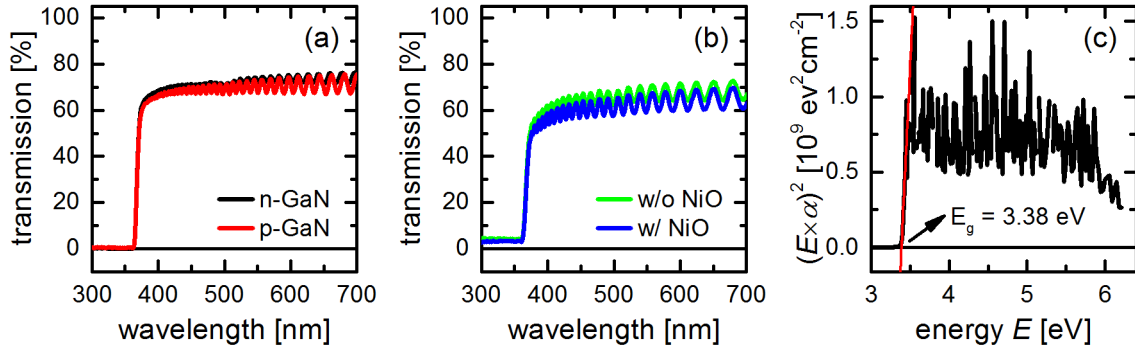


Figure 5.4: Comparison of transmission spectra for n-GaN and p-GaN (a) as well as for n-GaN with and without NiO co-catalyst particles (b). The spectra are nearly the same for every sample. Using equation 4.5 the band gap of n-GaN can be determined from the transmission spectrum (c).

that light from the 365 nm LED (and below that wavelength) can be absorbed by GaN and thus is able to excite GaN. The peak at 400 nm of the corresponding LED cannot excite GaN anymore.

Since light must also cross aqueous solution to reach the sample, also the transmission of H₂O and 0.1 M NaCl solution were measured. Figure 5.5 (b) shows the transmission spectra of H₂O and NaCl. It can be seen that most light is transmitted and nearly all incident light reaches the illuminated samples. Thus, reflection losses at the air–water interface can be neglected. Additionally, the transmission of quartz glass was measured. The spectrum is shown in figure 5.5 (c) together with float glass as comparison. By the use of quartz glass as optical window in the PEC and as cover for the crystallizing dishes for the photoinduced degradation measurements, transmission of UV light to the sample surfaces is guaranteed.

Figure 5.6 (a) shows excitation and emission spectra of an n-GaN reference sample. The excitation spectrum indicates that the n-GaN sample is excitable at least up to 365 nm, thus confirming that the use of a 365 nm LED for illumination guarantees the generation of

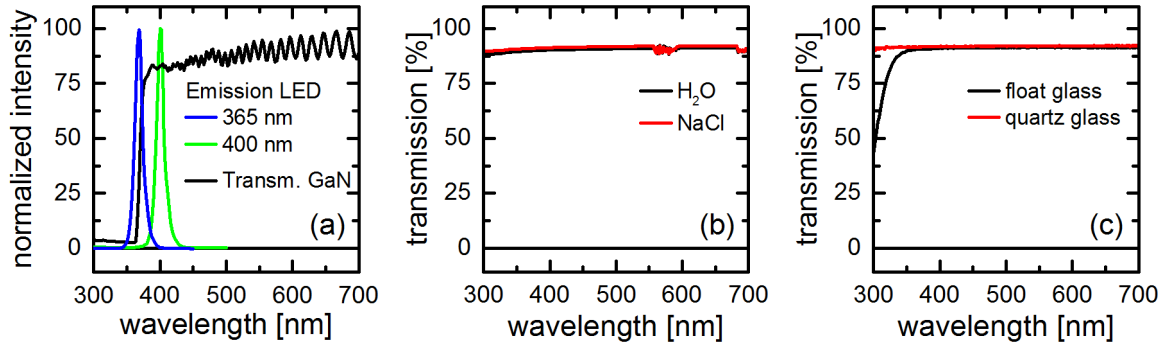


Figure 5.5: Transmission spectra of n-GaN (a, black curve), H₂O (b, black curve) and NaCl (b, red curve), as well as of float glass (c, black curve) and quartz glass (c, red curve). In (a), the emission spectra of the 365 nm and 400 nm LEDs are plotted as a reference.

electron-hole pairs in GaN. The emission spectrum shows a small peak at 362 nm and a large broad peak around 550 nm. The small peak corresponds to an energy of approx. 3.42 eV and originates from band to band emission [169]. The second peak at 550 nm corresponds to an energy of approx. 2.25 eV, causing the emission of light in the yellow range. This yellow luminescence in n-GaN is believed to be emission from the conduction band to a deep acceptor level [170]. Figure 5.6 (b) shows the emission spectra of n-GaN with and without NiO co-catalysts. In case of NiO on the n-GaN surface, the emission is reduced.

Measurements were carried out in the PEC with the monochromator setup used as illumination source. External quantum efficiency (EQE) values were calculated from the corresponding light intensities at the sample surface and the generated photocurrent under OCP conditions. They are enlisted in table 5.1, where an n-GaN sample in NaCl solution was excited with wavelengths from 250 nm to 400 nm in intervals of 25 nm. For 300 nm, a maximum light intensity of approx. 2.8 mW/cm² was measured with fluctuations in the range of 3.0 - 1.8 mW/cm² due

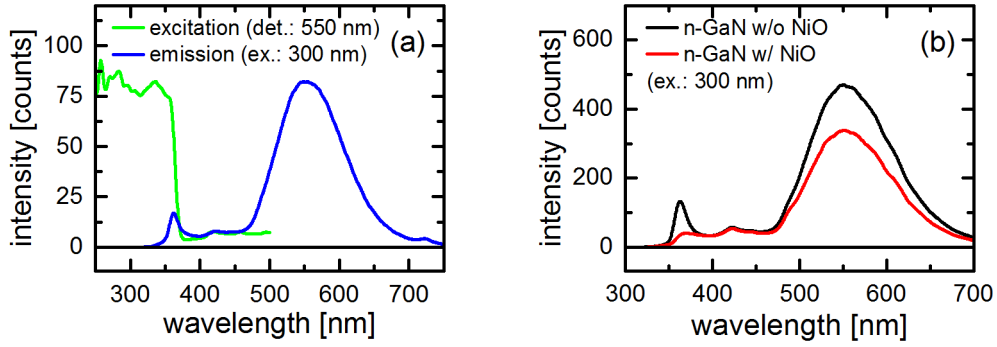


Figure 5.6: (a) Excitation (green line) and emission (blue line) spectra of an unstressed n-GaN reference sample. The excitation spectrum was recorded at an emission wavelength of 550 nm, the emission spectrum was recorded at an excitation wavelength of 300 nm. (b) Emission spectra for n-GaN with (red curve) and without (black curve) NiO co-catalyst particles. Under influence of NiO, the emission of n-GaN is significantly reduced.

to deviations because of small displacements of the monochromator settings. The corresponding EQE for 300 nm is approx. 65 %. Thus, this wavelength is used for the monochromator setup to guarantee a high amount of photogenerated electron-hole pairs.

Before usage as photoelectrodes, GaN samples were cleaned thoroughly by a standard RCA-1 clean procedure in order to remove organic residues from the GaN surface. The RCA clean procedure was carried as follows: a solution of 5:1:1 deionized water, ammonium hydroxide (NH_4OH), and hydrogen peroxide (H_2O_2) was produced by first mixing water and NH_4OH in a beaker and heated up on a hotplate to 70°C . The beaker was then removed from the hotplate and H_2O_2 was added. GaN samples were put in the solution for 15 minutes and afterwards rinsed thoroughly with water. Finally, the GaN samples were blown dry with compressed air.

Afterwards, the samples were provided with a metal at one end in order to guarantee an ohmic contact behavior of the future photo-electrode. Specifically, n-GaN samples were contacted with indium

Table 5.1: Measured surface power densities, determined from the Hg(Xe) arc lamp in the monochromator setup. The corresponding external quantum efficiencies are calculated for n-GaN in NaCl from the corresponding photocurrents under OCP conditions. Maximum values were achieved for a wavelength of 300 nm.

wavelength nm	intensity (mW/cm ²)	photocurrent (A)	EQE (%)
250	0.3	$1.10 \cdot 10^{-5}$	37.9
275	1.7	$9.77 \cdot 10^{-5}$	51.5
300	2.8	$2.19 \cdot 10^{-4}$	65.0
325	1.1	$5.21 \cdot 10^{-5}$	35.8
350	0.9	$4.26 \cdot 10^{-5}$	32.8
375	1.4	$4.43 \cdot 10^{-6}$	2.1
400	1.6	$2.13 \cdot 10^{-7}$	0.1

by pressing a small piece of indium wire onto the n-GaN sample. The p-GaN samples were contacted by a small sputtered platinum stripe and annealed at 500°C for 10 minutes as suggested in literature [171]. Subsequently, a copper wire, which was cleaned before by putting it for one minute in 52°C heated potassium persulfate, was soldered to the metal contacts, which allowed for connecting the GaN photoelectrodes to the electrochemical cell.

In all experiments it needs to be considered that the interaction of the electric contact area of the GaN samples with the electrolyte plays an important role in photoelectrochemical measurements. To avoid undesired interactions of the contact metals with solution, they were not immersed in solution. However, due to partial pressure of the electrolyte, the contact metals could be wetted which would cause an unwanted reaction with the electrolyte. In order to ensure that the contact area is properly insulated, both the metal contacts and the copper wire were isolated with a viscous photo resist (SU-8-2100) and cured over night in a drying oven at 70°C.

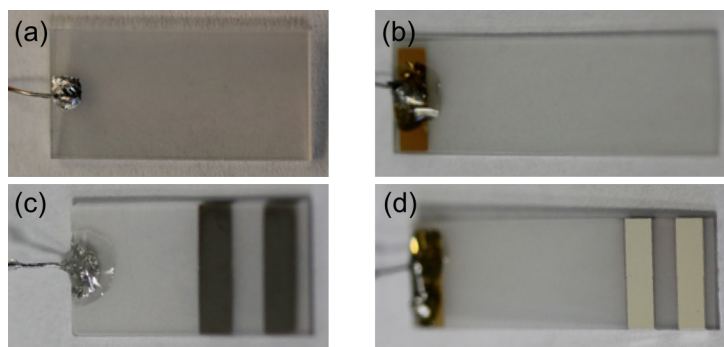


Figure 5.7: Example images of n-GaN (a, c) and p-GaN (b, d) samples without (a, b) and with (c, d) metal stripes deposited onto them as used for the experiments in the PEC.

Additionally, to study the influence of metals on GaN, two metal stripes were either evaporated or sputtered on one side of the GaN surfaces. Silver and gold were evaporated and nickel and platinum were sputtered, resulting in metal coated GaN surfaces. Nickel was sputtered in the DC magnetron mode under argon atmosphere at a pressure of 2 mbar and 400 W with a sputter rate of 54.9 nm/min. Sputtering of platinum was carried out under argon atmosphere, a pressure of 5 mbar and 200 W power with a sputter rate of 5.1 nm/min.

The active area of GaN in the PEC corresponds to the area, which is in contact with the electrolyte and is illuminated with the monochromator setup. If not declared else, it has an area of approx. 0.5 cm^2 .

Figure 5.7 shows images of n-type and p-type GaN samples with and without metal stripes, prepared for the experiments in the PEC.

5.2 GaN as photoactive electrode

The goal was to understand the principle behavior of n-GaN and p-GaN samples driven as photoelectrodes in aqueous solutions with and without UV excitation. A standard three-electrode-setup was used as described in section 2.2.3. GaN was used as working electrode

(WE), Ag/AgCl as reference electrode (RE), and a platinum ring wire as counter electrode (CE). Measurements were carried out by applying cyclic voltammetry (CV) measurements in the PEC in order to characterize the GaN samples. Measurements were carried out under dark conditions (i.e. room light, which does not optically excite GaN) as well as under UV excitation which was realized by the monochromator setup as presented in figure 4.1 (a). GaN samples were studied in ultrapure water and 0.1 M NaCl solution. Due to simplify notation, H₂O is used instead of ultrapure water.

5.2.1 n-GaN as photoanode

CV measurements in ultrapure water

Figure 5.8 (a) shows a section of a CV curve of n-GaN as WE in H₂O, measured in a potential range from -3 V to +3 V vs. Ag/AgCl, i.e. from the reduction to the oxidation region. This extreme measured potential range of 6 V was chosen since water splitting reactions will definitely take place (also including a decomposition of the electrolytes since their potential window is exceeded). Furthermore, the stability of GaN was investigated at these high potentials as will be shown in the next chapter.

n-GaN works as cathode when negative currents flow. This is the case for potentials below -0.2 V (dark conditions) or -0.7 V (300 nm illumination). For the reductive region it obviously makes no difference, whether n-GaN is measured under dark conditions or UV excitation. The current density at -3 V in both cases is approx. -225 $\mu\text{A}/\text{cm}^2$. It thus can be concluded that UV excitation does not effect the cathodic behavior of n-GaN. Reduction reactions take place by an electron transfer from the conduction band into the electrolyte, leading to the evolution of gaseous H₂ from the n-GaN surface according to equation 2.5.

On the other hand, n-GaN is driven as anode, when positive currents flow. As can be seen in figure 5.8 (a), there is a clear difference between dark conditions and 300 nm illumination. The measured current density is in the nA/cm^2 region under dark conditions. Since the potential is driven to a relative extreme anodic potential of +3 V, it can be assumed that gaseous O_2 in small amounts due to the low current density evolved from the n-GaN surface, according to equation 2.6. Under UV excitation with 300 nm, the current in the anodic regime shows a clear shift, indicating that a photocurrent is flowing. The order of magnitude of the photocurrent linearly depends amongst others on the incident light intensity, thus the concentration of photogenerated free charge carriers [28, 31, 91]. At a potential of +3 V, the current density increased from $+3.0 \mu\text{A}/\text{cm}^2$ (dark) to $+143 \mu\text{A}/\text{cm}^2$ (300 nm). The photocurrent is attributed to additional generated electron and hole pairs under UV light illumination. The photogenerated free holes are transferred via surface states either to the O_2/OH^- redox couple in solution to drive the O_2 evolution reaction [110], or to contribute to the photo-oxidation of GaN [8, 172] as described in section 3.1.4. Since the photocurrent for n-GaN as WE occurs only in the anodic region of the measured potential range, it can be concluded that n-type GaN works as photoactive anode.

Since more charge carriers are available, the generated electric charge Q could be increased, also leading to a higher gas evolution rate than under dark conditions. Small gas bubbles on the n-GaN surface could be seen by eye during measurements, probably corresponding to H_2 or O_2 , depending on the applied potential E .

CV measurements in 0.1 M NaCl

Besides H_2O , also NaCl as electrolyte was used to study the behavior of n-GaN. Figure 5.8 (b) shows branches of CV curves of n-GaN as WE in 0.1 M NaCl electrolyte, measured in the range from -3 V to +3 V vs. Ag/AgCl.

For potentials of approx. -0.3 V and lower, negative currents flow and n-GaN works as cathode in NaCl, leading to the evolution of gaseous H_2 from the n-GaN surface. As for H_2O as electrolyte, there is no difference between dark conditions or 300 nm illumination in the current densities in case of NaCl. The current density at -3 V in both cases is approx. -5.68 mA/cm². As for H_2 it was shown that excitation with UV light does not effect the cathodic behavior of n-GaN.

When n-GaN is driven as anode under dark conditions, no features in the CV curve in 5.8 (b) can be seen. As for H_2O , the measured current density is in the nA/cm² region. However, the evolution of O_2 is most likely. Parallel, it is further possible that in case of a chlorine containing electrolyte such as NaCl, gaseous Cl_2 evolves from the n-GaN anode according to equation 2.7. This is possible due to a lower overpotential of chlorine compared to oxygen, although the evolution of oxygen is thermodynamically preferred. The presumable Cl_2 evolution can be verified via subjective smelling (“swimming pool smell”) when the n-GaN sample is driven in the anodic regime. However, a quantitative proof of chlorine with a moistened potassium iodide starch paper which should have turned blue did not work, probably due to the very low amounts of the evolving gas. However, small gas bubbles were observed on the n-GaN surface for both dark conditions and 300 nm illumination.

Under UV excitation a clear photocurrent is flowing in the anodic region which quickly increases and saturates at approx. 1 mA/cm². Compared to dark conditions, it is approx. two orders of magnitudes higher (+11.8 $\mu\text{A}/\text{cm}^2$). Thus, a higher gas rate evolution is likely, which could not be measured in this work. Also for 300 nm, oxidation reactions along with O_2 evolution occur. Depending on the stability of n-GaN it is also possible that the n-GaN surface gets oxidized.

In summary, it was shown that n-GaN works as photoactive anode, generating a photocurrent in the anodic region under UV light excitation. This means that it can be oxidized when driven in the anodic

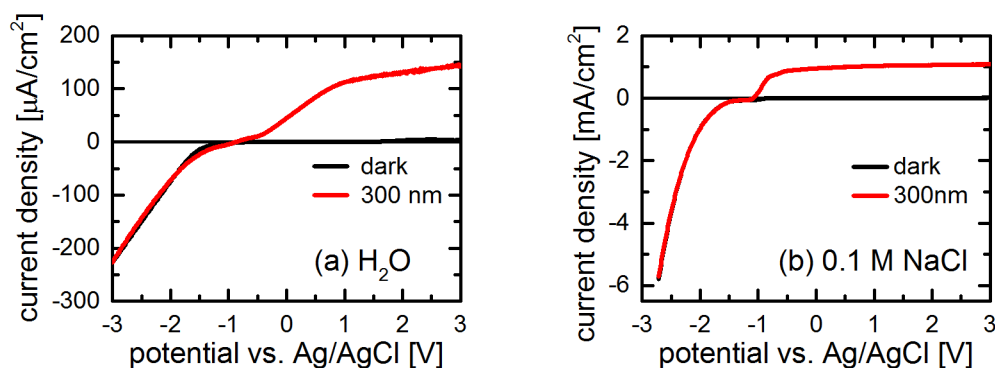


Figure 5.8: CV curves of n-GaN driven as photoelectrode without illumination (black curve) and with 300 nm UV light excitation (red curve) in H₂O (a) and 0.1 M NaCl (b). Note that the current density in the anodic region for NaCl is approx. factor 10 higher than in H₂O.

region. This photo-oxidation of n-GaN will be investigated in detail in the next chapter. Comparing the CV measurements for n-GaN in H₂O and NaCl as seen in figure 5.8, the anodic region and thus the increase of the photocurrent begins at slightly lower potentials for NaCl as electrolyte than for H₂O. This is most likely due to the lower overpotential of chlorine evolution from NaCl. It also needs to be considered that the measured photocurrent densities are approx. one order of magnitude lower for H₂O as electrolyte than for NaCl which is probably due to the better conductivity of NaCl.

Comparison of n-GaN and platinum as working electrodes

The behavior of an n-GaN photoelectrode was compared with a platinum electrode. Both materials were applied as WE to gain knowledge about the behavior of n-GaN in aqueous solution compared to a metal electrode. The platinum ring wire for both materials was the CE. CV measurements were conducted under dark conditions in NaCl. Figure 5.9 shows a comparison of the two measured CV curves.

When both electrodes are driven in the cathodic region, H_2 evolution takes place. The current drops visibly for less negative potentials for Pt than for n-GaN as WE (cf. figure 5.9), meaning that the gas evolution starts earlier for platinum. Thus it can be assumed that the overpotential of H_2 evolution is higher for n-GaN than for Pt. Furthermore it can be assumed that more H_2 evolves in case of Pt since the measured current density at -3 V with -39.5 mA/cm^2 is approx. six times higher than for n-GaN with -5.68 mA/cm^2 .

When both WEs are driven in the anodic regions, it again can be assumed that a higher amount of O_2 is produced for Pt due to higher current densities of three orders of magnitude and thus higher generated electric charges Q (31.7 mA/cm^2 for Pt and $11.8 \mu\text{A/cm}^2$ for n-GaN at +3 V). This is also the same for the evolution of Cl_2 which probably starts earlier, i.e. at lower potentials in the anodic region, due to the lower overpotential. However, since the CV curve for n-GaN in the anodic region runs parallel to the x-axis and does not show any additional features, it can be concluded that the n-GaN surface was not photo-oxidized during measurements and in general showed less activity in gas evolution. One could conclude, that platinum, applied as a catalytic converter on the n-GaN surface, would enhance the oxidation of n-GaN. This will be studied in the next chapter.

CV measurements with NiO co-catalyst particles

Measurements were carried out for n-GaN with and without NiO co-catalyst particles on its surface. Figure 5.10 shows the corresponding CV curves which were recorded in a potential range of -1 V to +1 V vs. Ag/AgCl in NaCl as electrolyte.

In the cathodic region under 300 nm, the current density drops to approx. $-250 \mu\text{A/cm}^2$ for n-GaN without NiO, but remains in the nA/cm^2 region under the presence of NiO.

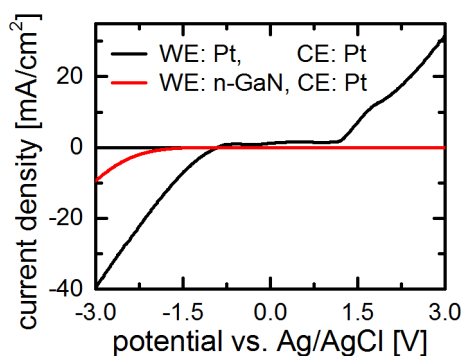


Figure 5.9: Comparison of CV curves with n-GaN (red curve) or Pt (black curve) as WE and Pt as CE in 0.1 M NaCl under dark conditions. H_2 evolution in the cathodic region starts earlier for platinum than for n-GaN. In the anodic region at +3 V O_2 and/or Cl_2 evolution takes place. Here, for platinum the current density is approx. three orders of magnitude higher than for n-GaN. Generally, the conversion of redox-active species is much higher for platinum than for n-GaN.

A clear photocurrent was measured in the anodic region under UV excitation. At +1 V the photocurrent density was approx. 46 % higher for the n-GaN samples with NiO co-catalysts on its surface. The improvement of the photocurrent is due to the protective behavior of NiO. The catalyst particles themselves are oxidized, thus preventing a photo-oxidation of the n-GaN surface. Thus, the photogenerated holes at the interface contribute rather to conversion and gas evolution than to the photo-oxidation and degradation of n-GaN. Details will be discussed in selected experiments in the next chapter.

5.2.2 p-GaN as photocathode

p-GaN was used as WE to study its behavior with and without UV illumination in H_2O and 0.1 M NaCl. As for n-GaN, CV measurements were conducted in a high potential range of -3 V to +3 V vs. Ag/AgCl.

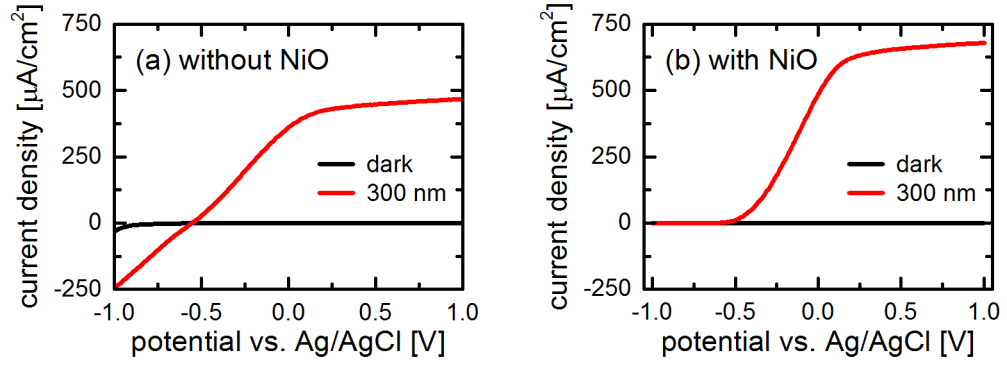


Figure 5.10: Comparison of CV curves of n-GaN driven as photoanode without (a) and with (b) NiO particles under dark conditions (black curve) and 300 nm UV light excitation (red curve) in 0.1 M NaCl. An increase of the photocurrent of approx. 46 % under the influence of NiO is clearly visible.

CV measurements in ultrapure water

Figure 5.11 (a) shows a CV curve for p-type GaN as WE in H₂O.

For p-GaN in the anodic range, the measured current densities are in the same nA/cm² range parallel to the x-axis under dark conditions and 300 nm illumination. At a potential of +3 V, a current density of approx. 0.05 $\mu\text{A}/\text{cm}^2$ was measured both under dark conditions and 300 nm illumination. Due to the low current densities it can be assumed that almost no O₂ evolution takes place from the p-GaN surface. It thus can be concluded that p-GaN driven as anode shows no reaction to UV light.

p-GaN works as cathode for potentials lower than +0.1 V in the dark and lower than +0.6 V under UV excitation. Contrary to n-GaN, where no reaction to UV light in the cathodic regime occurred, a photocurrent is flowing when p-GaN is driven as cathode under 300 nm UV light excitation. At a potential of -3 V vs. Ag/AgCl under dark conditions, the current density is -0.09 $\mu\text{A}/\text{cm}^2$ whereas it is -14.4 $\mu\text{A}/\text{cm}^2$ for 300 nm illumination. It thus is shown that p-GaN

works as photoactive cathode under UV light excitation. Since small bubbles were observed on the p-GaN surface at cathodic potentials it can be assumed that low amounts of H_2 evolved from the p-GaN surface.

CV measurements in 0.1 M NaCl

CV measurements for p-GaN were also carried out in NaCl as better conducting electrolyte. Figure 5.11 (b) shows a CV curve section for p-type GaN as WE in 0.1 M NaCl.

At an anodic potential of +3 V, current densities of approx. $0.05 \mu A/cm^2$ under dark conditions and $+2.6 \mu A/cm^2$ under 300 nm illumination were measured. This presents a noticeable increase of the current density in the anodic region which can be seen in the branches of the CV curves in figure 5.11 (b) for NaCl. Since the p-GaN layers had only a thickness of 200 nm and were grown directly on n-GaN, this response to light in the anodic region is caused most likely by the underlying n-GaN which also reacts to UV light. Due to the relatively small current densities, the evolution of O_2 or Cl_2 is also expected to be small.

As for H_2O , p-GaN reacts to UV light in the cathodic region also in NaCl. At -3 V vs. Ag/AgCl, the current density was approx. $-162 \mu A/cm^2$ under dark conditions and $-184 \mu A/cm^2$ under illumination with 300 nm. The cathodic region starts for potentials of approx. +0.2 V under dark conditions and +0.7 V under UV excitation. H_2 probably evolves from the p-GaN surface under both dark and 300 nm illumination.

Based on the CV measurements it can be concluded that p-GaN rather works as weak photocathode. The photocurrent densities of p-GaN under UV excitation in the cathodic region at -3 V are approx. one order of magnitude lower in H_2O than in NaCl which is most likely due to the better conductivity of NaCl. However, compared to n-GaN, the photocurrent of p-GaN in the cathodic region differs by

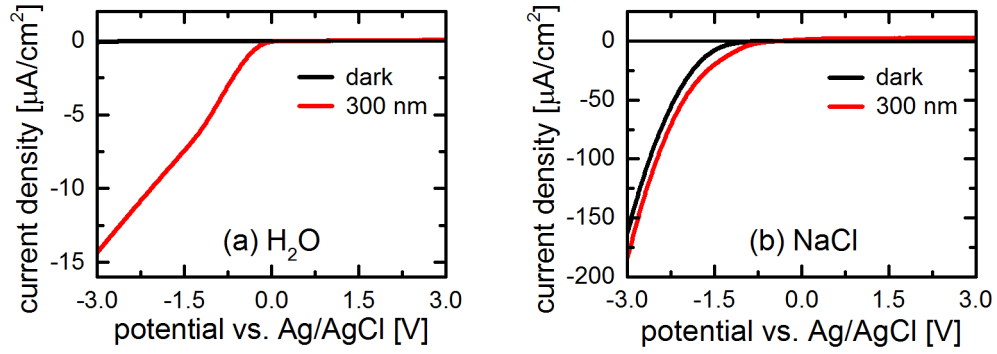


Figure 5.11: Sections of CV curves for p-GaN as WE in H_2O (a) and 0.1 M NaCl (b) under dark conditions (black curve) and under 300 nm illumination (red curve). Under UV excitation, a clear shift of the current in the cathodic regime is visible.

approx. one order of magnitude from the n-GaN photocurrent in the anodic region. One of the reasons that causes smaller currents for p-GaN is, e.g., the more difficult alignment of the magnesium dopants, leading to higher resistances (cf. section 3.1.4). Additionally, fast recombination processes and less driving force between E_{cb} and the H_2 reduction potential also lead to lower photocurrents [113, 125].

OCP values of GaN under dark conditions and UV excitation

The OCP corresponds to an equilibrium potential, where no net current flows. It has different values for n-GaN and p-GaN, H_2O and NaCl , as well as for measurements under dark conditions and 300 nm illumination.

For n-GaN as WE, the OCP changes from approx. -0.2 V (dark, H_2O) or -0.3 V (dark, NaCl) to approx. -0.7 V (300 nm , both H_2O and NaCl). The difference between OCP values recorded under dark conditions and 300 nm illumination for the same samples again illustrates the response of GaN to UV light. Furthermore, the OCP for n-GaN with NiO in NaCl is slightly higher than for n-GaN without NiO. There, it changes from -0.4 V (dark) to -0.9 V (300 nm). This

general shift of the OCP to more negative potentials for n-GaN under UV excitation is due to changes at the GaN–electrolyte interface. These changes can be explained by the band bending as depicted in figure 2.1 (a). Photogenerated holes accumulate at the n-GaN surface, whereas electrons migrate to the bulk of n-GaN where they reach the electrical contacts and contribute to the current flow, resulting in the observed increase of the OCP.

On the other hand, in general the OCPs for p-GaN samples tend to turn to more positive potentials under UV illumination. They shifted from approx. +0.1 V (dark, H₂O) or +0.2 V (dark, NaCl) to approx. +0.6 V (300 nm, H₂O) or +0.7 V (300 nm, NaCl). This shift to more positive potentials under UV excitation for p-GaN can be again explained by the formation of a depletion layer. Photogenerated electrons accumulate at the p-GaN–electrolyte interface and the holes migrate to the bulk as can be seen in the band structure in figure 2.1 (b), finally resulting in lower OCP values.

Independent on the doping of the GaN samples, the differences between the OCP values under dark conditions and 300 nm illumination are slightly higher for NaCl as electrolyte than for H₂O which can be explained with the better conductivity of NaCl.

5.3 Determination of the band edge potentials with the photocurrent method

In section 3.1.3, the flat band potential E_{fb} was calculated for n-GaN based on results from literature [110]. As a result, E_{fb} was determined by the EIS method to be -1.03 V vs. SCE, which corresponds to a value of -1.06 V vs. Ag/AgCl and -0.86 V vs. NHE. From this value, the band edge energies of E_{cb} and E_{vb} can be calculated as already shown in section 3.1.3. Another approach to determine E_{fb}

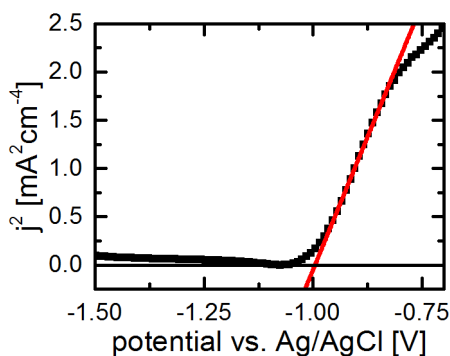


Figure 5.12: Determination of E_{fb} by the photocurrent method for n-GaN measured under 300 nm illumination in NaCl. The square of the photocurrent densities plotted vs. the applied potential. By fitting the linear region of the curve, a value of $E_{fb} = -1.01$ V vs. Ag/AgCl was determined for n-GaN.

besides the EIS technique is the so-called photocurrent method, where the photocurrent j_{ph} is used. In the photocurrent method, a linear dependence of j_{ph}^2 vs. the potential E exists for conditions close to the flat band situation. From this linear region, E_{fb} can be extracted by linear extrapolation from the intercept point with the potential axis [173].

For n-GaN in NaCl solution the corresponding plot is shown in figure 5.12 and the value of E_{fb} can be read from the intercept. It is $E_{fb} = -1.01$ V vs. Ag/AgCl. This value almost matches with $E_{fb} = -1.06$ V vs. Ag/AgCl from the EIS method.

The differing values of E_{fb} from either the EIS or the photocurrent method can be due to slow charge-transfer kinetics at the semiconductor–electrolyte interface, leading to a charge accumulation [103, 174]. This charging effect causes a shift in the E_{fb} values received from photocurrent measurements compared to EIS measurements. It needs to be considered that the EIS technique is usually performed under dark conditions. Under these circumstances, the n-GaN–electrolyte junction is reversed biased, resulting in a low charge

flow of holes to the interface. This is contrary for the photocurrent technique, which provides a higher charge flow with photogenerated minority carriers. Since these holes contribute to the photo-oxidation of n-GaN, E_{fb} can only be calculated correctly as long as the thickness of the thereby generated oxide on the n-GaN layer is small. This was the case with the n-GaN sample used in this work, which showed almost no increase of the EDX measured oxygen content on its surface.

There are several conditions which must be fulfilled for applying the photocurrent method. On the one hand, the photogeneration rate must be constant throughout the depletion region, meaning that the depletion region is much smaller than the absorption length α^{-1} for the irradiated spectrum to ensure the linear relation between the photocurrent and the depletion region. Furthermore, all photogenerated charge carriers in the depletion region need to contribute to the photocurrent. Also, the applied external potential must drop over the depletion region. However, Beach *et al.* found large discrepancies for E_{fb} of n-GaN, depending on the chosen measurement technique, which affected also the band edge potentials. With the EIS method, they set up an equation of $E_{cb} = (-0.816 - 0.047 \cdot \text{pH})$ V vs. SCE, whereas for the photocurrent method an equation of $E_{cb} = (-0.538 - 0.046 \cdot \text{pH})$ V vs. SCE was found. They thus concluded that the EIS technique shows a higher accuracy for E_{fb} [103].

6 Stability of GaN in Aqueous Media

In the previous chapter it was shown that n-GaN and p-GaN under excitation with UV light work as photoactive anode and cathode. In this chapter, the stability of GaN in aqueous media under UV illumination is investigated. GaN samples were investigated purely as well as under influence of deposited metal stripes and NiO co-catalysts on their surfaces. Additionally, the measured period of time was varied. Various measurement methods are applied to the GaN samples, which then are referred to as “stressed” samples. It thereby is distinguished in this chapter between pure optical stress (photoinduced degradation), pure electrical stress without light illumination (electrolysis), as well as a combination of light and an externally applied potential on GaN (photoassisted electrolysis).

6.1 Photoinduced degradation – experiments

With the help of photoinduced degradation experiments, statements about the behavior and stability of GaN samples regarding the type of electrolyte, the presence of metal stripes, and duration of stress can be made.

The measurement setup was already described in section 4.2 and 3.1.2. To make the following descriptions easier, the subsequent notation is used to specify the experimental procedures: (metal/)/electrolyte/illumination/duration of applied stress – thereby

every measurement parameter is separated by slashes. This leads to phrases like, e.g., water/365nm/72h or Ag/water/365nm/72h.

One main analysis technique in this work to study surface changes on GaN were EDX measurements. They were applied in order to to gain knowledge about the elemental compositions and changes of the GaN samples by comparing stressed samples with unstressed (reference) samples. The usage and extent of EDX measurements which were carried out on the stressed GaN samples are unique on this field of degradation research.

6.1.1 EDX analysis

Energy-dispersive X-ray spectroscopy (EDX) measurements were carried on GaN with the help of Eduard Butzen at the Max Planck Institute for the Science of Light in Erlangen.

In principle, little EDX analysis data on stressed GaN samples can be found in literature – at least not in these dimensions and under the varied parameters. For example, Peng *et al.* did EDX analysis on as-grown n-GaN samples as well as on microcrystallites which were a result of n-GaN stressed in H₃PO₄ [106].

All GaN samples were analyzed at an accelerating voltage of 8 kV and an electron current of 10 nA. The measured area had a size of approx. 300 μm^2 in diameter. Measurements were made in the middle of the sample surfaces, or, in case of metal stripes, on the GaN area in-between the two deposited metals.

To get information about the depth in the sample from which the signal is generated, a simulation was carried out with the open source simulation software *Casino*. This software was written by members of the nanofabrication and nanocharacterization research center CRN2 in Quebec, Canada⁵ and calculates electron-matter interactions with the help of Monte Carlo (MC) simulations. As a result, it simulates

⁵ <http://www.gel.usherbrooke.ca/casino/>, <http://www.crn2.ca>

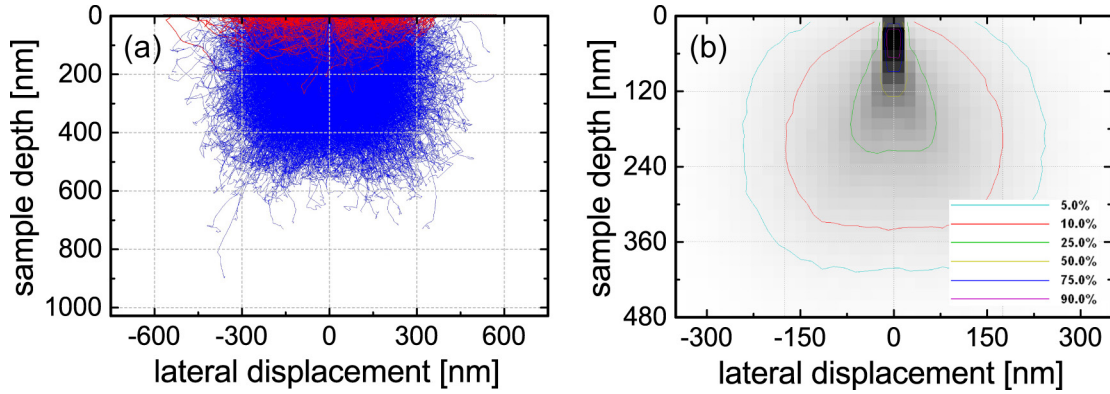


Figure 6.1: (a) Trajectories of emitted X-ray photons contributing to the EDX signal, simulated with 10^5 incident electrons which had an accelerating voltage of 8 kV hitting the GaN surface. The photons originate from surface-near regions in the first hundred nm. Practically no X-ray photons originating from more than 600 nm depth exit the GaN. (b) Distribution of the simulated emitted X-ray photons contributing to the EDX signal, forming a pear-shaped form. The main signal (90%) comes from the first 200 nm of the sample. The last 5% of the signal originates from a GaN sample depth of approx. 400 nm.

the depth from where the X-ray photons are emitted as well as their radial distribution. MC simulations were carried out for 10^5 incident electrons hitting the GaN sample surface with an accelerating voltage of 8 kV. The results of the simulation are shown in figure 6.1. It can be seen that the signal is generated within the first hundred nm of the sample. Thus, changes of the elemental composition of GaN can be detected from the upper surface regions due to the relative accurate surface sensitive analysis method.

Table 6.1 shows EDX values measured on unstressed n-GaN and p-GaN reference samples. Enlisted are the measured fractions of gallium, nitrogen, and oxygen. An almost equal 1:1 distribution of gallium and nitrogen was measured, along with a small fraction of oxygen (1.5 at%). For the p-GaN reference sample, the distribution

Table 6.1: EDX data of the surfaces of unstressed n-GaN and p-GaN reference samples. The ratio of the gallium to nitride content is approx. 1:1.

	n-GaN reference	p-GaN reference
Ga (at%)	47.1	50.1
N (at%)	45.1	43.1
O (at%)	1.5	1.1

of gallium and nitrogen content was quite unbalanced with a gallium content of 50.1 at%, whereas the nitrogen species was measured with 43.1 at%. These variations are probably due to the reproducibility of the GaN sample fabrication. Also for the p-type reference sample, a small amount of oxygen was measured (1.1 at%). In the following measurements on stressed GaN samples, slight deviations can occur due to inhomogeneities in the concentration of the electrolytes or the contacting of the GaN samples. But the measured tendency was always reproducible.

6.1.2 Influence of the electrolyte on GaN stability

One aspect of stability investigations was the influence of weak or well conducting electrolytes.

Both n-type and p-type GaN therefore were immersed completely either in H₂O or NaCl solution with pH values of around 5. Figure 6.2 gives an overview with photos and light microscopy images of reference samples as well as the GaN samples stressed either under the H₂O/365nm/72h or NaCl/365nm/72h method. For the reference samples under the light microscope, the pure GaN surfaces have their characteristic structures.

Compared to the reference, n-GaN stressed in H₂O significantly changed to a grainy and roughened surface, whereas n-GaN samples in

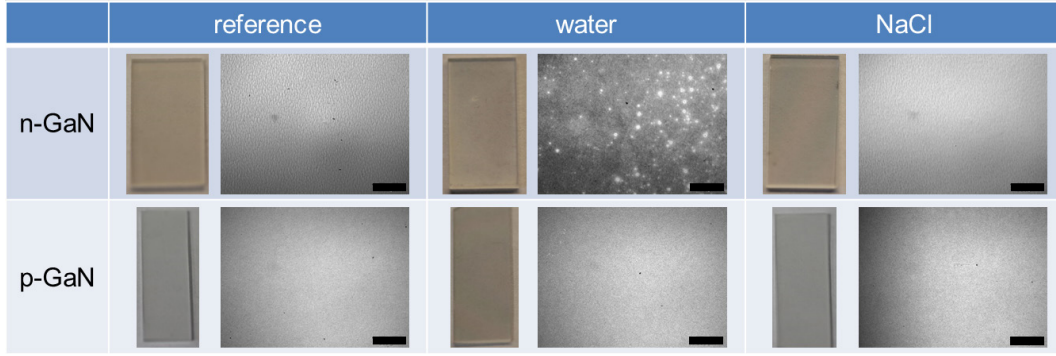


Figure 6.2: Photos and light microscopy images showing the influence of aqueous solutions on GaN surfaces: Overview of n-GaN and p-GaN samples, stressed with the $\text{H}_2\text{O}/365\text{nm}/72\text{h}$ and $\text{NaCl}/365\text{nm}/72\text{h}$ methods. For each sample, photos and light microscope images of the corresponding GaN surfaces are shown. Whereas p-GaN remains unaffected by both electrolytes, the n-GaN surface changed in water, but not in NaCl solution. Scale bars: $500\ \mu\text{m}$.

NaCl showed almost no changes on the n-GaN surface. The stressed p-GaN surfaces did not show any changes and remained unchanged for both types of electrolytes. Table 6.2 shows the EDX measured element contents n-GaN and p-GaN samples stressed with the H_2O and $\text{NaCl}/365\text{nm}/72\text{h}$ method.

Based on the content of the investigated species, the elemental compositions (apart from some small statistical deviations) do not change significantly for the measured samples – except for n-GaN stressed with the $\text{H}_2\text{O}/365\text{nm}/72\text{h}$ method. There, the nitrogen content decreased and on the other hand, the oxygen fraction on the n-GaN surface increased. Consequential, it can be concluded that the n-GaN surface gets oxidized in H_2O and that no oxidation took place in NaCl. n-GaN as photoanode is more stable in chlorine containing solutions since the overpotential of N_2 formation which causes the photo-oxidation is probably higher than for chlorine. Thus, Cl_2 evolution is more likely than n-GaN degradation in NaCl. For

Table 6.2: EDX data of n-GaN and p-GaN surfaces which were stressed with the H₂O/365nm/72h and NaCl/365nm/72h method. The stressed n-GaN samples in H₂O shows a considerable change in the single elemental contents, whereas the other samples did not show any changes in their elemental composition.

	n-GaN			p-GaN		
	reference	H ₂ O	NaCl	reference	H ₂ O	NaCl
Ga (at%)	47.1	43.2	44.2	50.1	50.1	49.9
N (at%)	45.1	33.0	49.2	43.1	43.3	43.0
O (at%)	1.5	19.1	0.8	1.1	1.0	1.2

p-GaN samples, the elemental composition neither changed in H₂O nor in NaCl as electrolytes – the p-GaN surfaces remained unchanged.

Figure 6.3 shows SEM images taken of the surfaces of an n-GaN reference and samples stressed with the H₂O/365nm/72h and NaCl/365nm/72h method. In figure 6.3 (b), changes of the n-GaN surface in H₂O can be seen. Rod-like structures partially cover the n-GaN surface. By EDX measurements it was found out that these rod-like structures contain mostly gallium and oxide, thus it can be concluded that a gallium-oxide compound formed. The formation of rod-like, gallium oxide consisting structures on the n-GaN surface was also reported in [175].

6.1.3 Influence of metal stripes on GaN stability

It was further investigated, whether the presence of metals would have an effect on the GaN surfaces under an illumination with UV light of 365 nm for 72 hours.

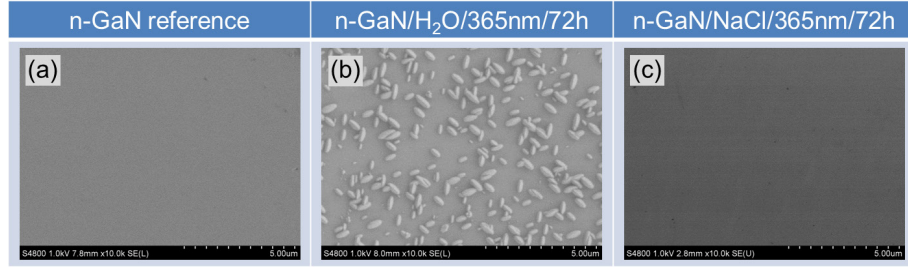


Figure 6.3: SEM images of an n-GaN reference sample (a) and n-GaN stressed with the H₂O/365nm/72h (b), and NaCl/365nm/72h method (c). Whereas the surface in NaCl remained intact, the influence of H₂O on n-GaN causes the formation of rod-like structures that consist of gallium and oxide (see text) and partially cover the whole sample surface.

n-GaN under metal influence in H₂O and NaCl

The behavior of the method n-GaN under metal influence in H₂O is studied. Figure 6.4 shows photos and light microscopy images of n-GaN reference samples and n-GaN samples stressed with the n-GaN/metal/H₂O/365nm/72h method.

The n-GaN surfaces are attacked, visible in a roughened surface. This is independent on the deposited metal types and can be seen already by eye. These surface changes are especially distinct close or in-between the metal stripes. A gradient formed, extinguished from the GaN areas close to the metals. The border areas at the far end from the metal areas on the contrary were not at all or less attacked. Changes on the GaN surfaces can be also proven by placing GaN samples under an UV lamp, emitting at 362 nm. As already seen in the PL spectra of GaN in figure 5.6, GaN sample can be excited with this wavelength and light is emitted at around 550 nm in the yellow spectral range. This emission could be also seen when the samples were put in the electrolyte and excited with the 365 nm LED. Figure 6.5 shows an n-GaN reference sample and exemplarily an n-GaN

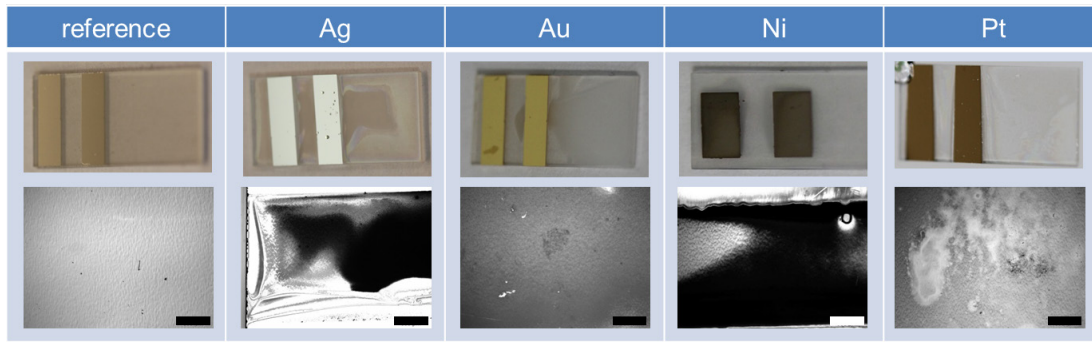


Figure 6.4: Influence of metals on n-GaN stressed with the $\text{H}_2\text{O}/365\text{nm}/72\text{h}$ method. The photos and light microscopy images show both GaN and metal areas from a reference sample and stressed n-GaN samples. All metals adhere well on the n-GaN surfaces, which all undergo significant changes under the applied stress, especially close at the metal stripes. Scale bars: $500\ \mu\text{m}$.

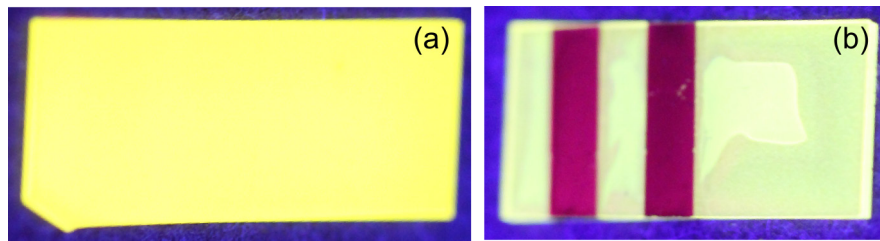


Figure 6.5: Photos taken under an UV lamp from an n-GaN reference (a) and an n-GaN sample stressed with the $100\text{nmAg}/\text{H}_2\text{O}/365\text{nm}/72\text{h}$ (b). The characteristic yellowish emission of n-GaN under UV light excitation can be clearly seen. Emission is uniform at the reference sample and clearly weakened on the areas of the stressed n-GaN sample which were attacked.

sample stressed with the $100\text{nmAg}/\text{H}_2\text{O}/365\text{nm}/72\text{h}$ method. The n-GaN reference sample homogeneously emits yellowish light whereas the emittance of the stressed n-GaN sample in figure 6.5 (b) has significantly lowered on areas where the n-GaN surface was attacked. On the other hand, even after 72 hours, all metals adhered well to

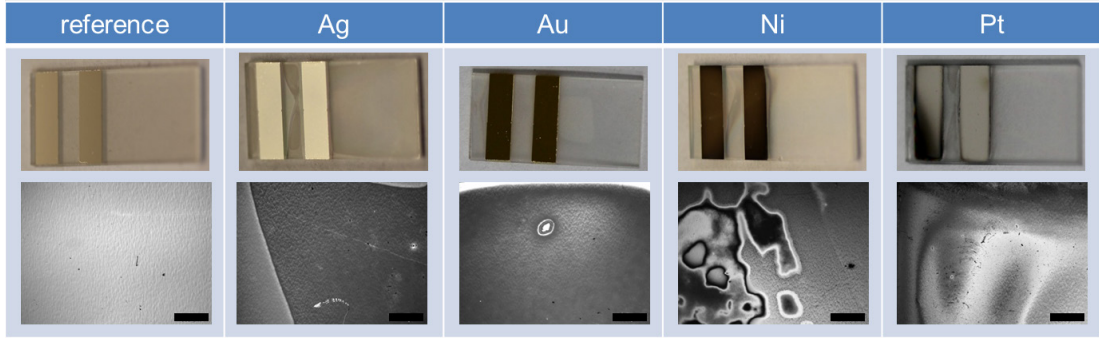


Figure 6.6: Photos and light microscopy images showing the influence of metals on n-GaN surfaces stressed with the NaCl/365nm/72h method. Especially close to the metal regions the n-GaN surfaces are strongly attacked. The metals themselves did not detach from the n-GaN surface. Scale bars: 500 μm .

the n-GaN surface and did not change. They obviously protect the underlying GaN surface from surface changes.

The behavior of n-GaN under metal influence was also studied in 0.1 M NaCl solution instead of H_2O . Figure 6.6 shows the corresponding photos and light microscopy images. The results are qualitatively similar to the ones observed for H_2O . Changes on the stressed n-GaN surface can be clearly seen by a different color reflection from the degraded surface. It can be concluded that the occurring mechanism appears to be the same as in H_2O . Contrary to pure n-GaN, which was not attacked in NaCl (cf. figure 6.2 and 6.3 (c)), the presence of metals clearly leads to an attack of the n-GaN surface. Similar to H_2O , the n-GaN surface close to the metal stripes has changed most. At the far end from the metal covered GaN regions, a change of the n-GaN surface is not present. The metals themselves remained unchanged and adhered well to the n-GaN surface. Analogous to H_2O , as can be seen in figure 6.6, they obviously protect the underlying GaN surface.

Table 6.3: EDX data on n-GaN surfaces coated with different metal types (recorded close to the metals), stressed with the H₂O/365nm/72h and NaCl/365nm/72h method. Compared to n-GaN samples without metal influence the presence of metals leads to an increase of surface changes of n-GaN, meaning a decrease of the gallium and nitrogen content and an increase of the oxygen content.

	reference	Ag		Au		Ni		Pt	
		H ₂ O	NaCl	H ₂ O	NaCl	H ₂ O	NaCl	H ₂ O	NaCl
Ga (at%)	47.1	27.4	33.1	41.3	49.0	28.6	41.6	42.5	30.5
N (at%)	45.1	1.9	7.3	30.2	41.9	0.8	30.4	28.6	2.0
O (at%)	1.5	66.7	53.8	22.4	3.7	67.7	21.5	19.0	62.0

Table 6.3 gives an overview of EDX data, obtained from n-GaN surfaces that were treated with the H₂O/365nm/72h and NaCl/365nm/72h procedure under 100 nm thick metal influence. The tendency in general is a decrease of the gallium and nitrogen species going along with a strong severe increase of oxygen, especially for silver, nickel, and platinum. This trend could be already observed for pure n-GaN stressed with the H₂O/365nm/72h method. Now these changes under metal influence are even more distinct. Additionally, degradation also occurred on n-GaN sample surfaces in NaCl, which before had no effect on pure n-GaN.

The decrease of the nitrogen content was always stronger in H₂O than in NaCl – except for platinum, where 2.0 at% nitrogen was measured in NaCl and 28.6 at% in H₂O. Analogous, the increase of oxygen was stronger in H₂O than in NaCl – except for platinum, where in NaCl 62.0 at% oxygen was measured and 19.0 at% in H₂O. In H₂O, the characteristic changes of the elemental compositions were most distinct for nickel and silver as metal types. For NaCl as electrolyte, platinum and silver had the strongest influence concerning

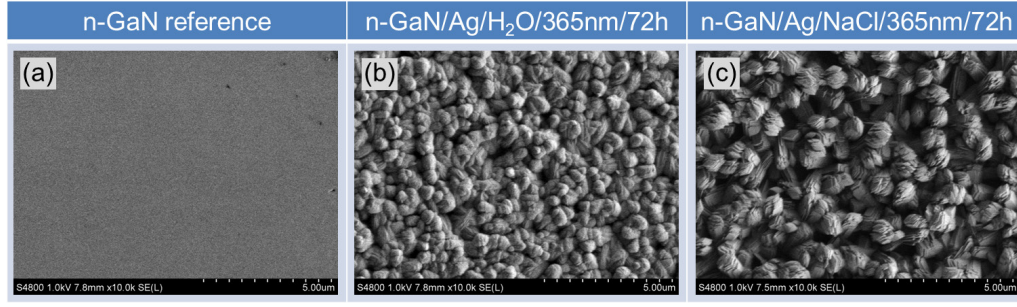


Figure 6.7: SEM images of the surfaces of an n-GaN reference sample (a) and samples treated with the 100nmAg/H₂O/365nm/72h (b) and 100nmAg/NaCl/365nm/72h method (c). In both cases, the stressed surfaces drastically changed and showed roughened coral-like structures containing oxygen (see text), compared to the smooth reference surface of n-GaN.

elemental changes of n-GaN. No traces of the corresponding metal species could be detected on the n-GaN surface by EDX.

Figure 6.7 shows exemplarily SEM images of the n-GaN surfaces, stressed with the 100nmAg/H₂O/365nm/72h and 100nmAg/NaCl/365nm/72h method. Compared to the reference sample, severe changes of the n-GaN surfaces occurred. Since on pure n-GaN samples there was only a change on the surface in H₂O (cf. figure 6.3 (b)), the SEM images also show an attack of the n-GaN surface under silver presence in NaCl, as can be seen in figure 6.7 (c). The gradually developed rod-like structures which formed on pure n-GaN in H₂O (cf. figure 6.3 (b)) under silver influence now cover the complete n-GaN surface close to the silver stripes, forming a coral-like structure. These compartments were measured by EDX and contain a high amount of oxygen and are mainly responsible for the increased oxygen content on the stressed n-GaN surfaces.

It can be concluded that independent on the electrolyte the presence of metal coating accelerates the degradation and oxidation of GaN.

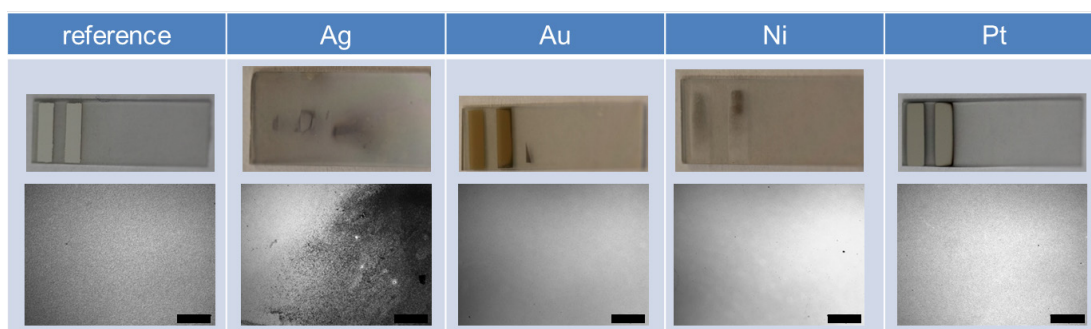


Figure 6.8: Photos and light microscopy images showing the influence of metal stripes on p-GaN surfaces, stressed with the metal/H₂O/365nm/72h method. Silver and nickel partially or almost completely detached from the p-GaN surface. The p-GaN surfaces themselves were not attacked under the influence of the used metals. Scale bars: 500 μ m.

p-GaN under metal influence in H₂O and NaCl

p-GaN samples and their stability in aqueous media under metal presence were also studied. Figure 6.8 shows photos and light microscopy images of reference and stressed p-GaN samples with the metal/H₂O/365nm/72h method. The deposited silver and nickel stripes partially or almost tarnished from the p-GaN surface. Especially silver completely detached, leaving smears on the p-GaN surface which can be seen by eye and under the microscope. Gold and platinum stripes on the other hand did not show big changes at first sight. The microscope images in figure 6.8 show that the p-GaN surfaces themselves remained unchanged for all applied metal types. Only the smears for the case of silver as metal attach on the p-GaN surface but without obviously attacking it.

In case of NaCl as electrolyte, metals also tarnished from the p-GaN surface. Figure 6.9 gives an overview of the stressed p-GaN samples with the metal/NaCl/365nm/72h method. Platinum showed least reaction and nickel had the strongest change – a re-detachment of nickel at the borders of the sample can be seen in figure 6.9 which

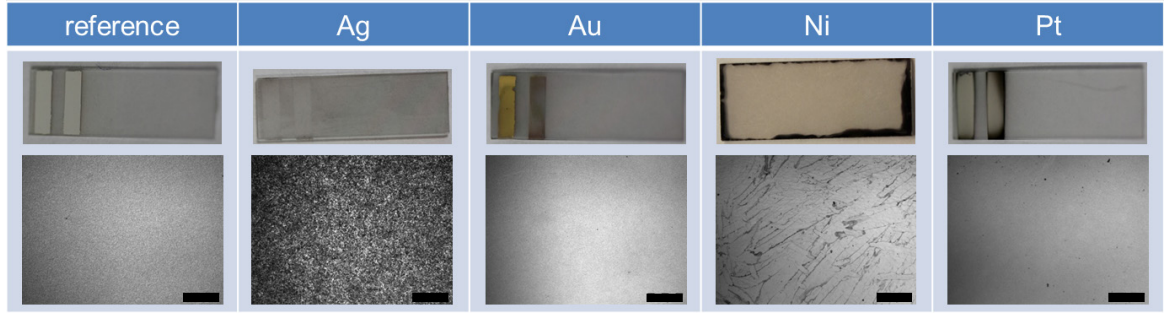


Figure 6.9: Photos and light microscopy images showing the influence of various metals deposited on p-GaN surfaces stressed with the metal/NaCl/365nm/72h method was studied by taking photos and light microscopy images of the metal stripes and the GaN surfaces. For the stressed samples, the metal stripes almost completely detached from the p-GaN surface, whereas the p-GaN surface itself remained unchanged. Scale bars: 500 μm .

probably originated from the tarnished former metal stripes. Judging from the microscopy images in figure 6.9, the p-GaN surfaces themselves remained stable without any changes in both H_2O and NaCl. No attack of the p-GaN surface itself could be determined. Table 6.4 shows the data for p-GaN surfaces stressed with the $\text{H}_2\text{O}/365\text{nm}/72\text{h}$ and NaCl/365nm/72h method.

Slight increases in the oxygen content for some samples lie within the error of measurement. Compared to n-GaN under the same conditions, it can be stated, that the p-GaN surfaces themselves remained stable in their surface composition and did not oxidize, when illuminated with UV light of 365 nm for 72 hours in H_2O or NaCl solution. Also SEM images on stressed p-GaN samples did not show any changes (not shown).

However, what attracted attention for stressed p-GaN samples was that metal traces could partially be detected by EDX on the surfaces. Metal contents were measured in-between the original metal stripe areas, meaning in-between the two metal stripes as well as at the far end side of the sample. In comparison to n-GaN, where

Table 6.4: EDX data for p-GaN samples under influence of various metal types, stressed with the H₂O/365nm/72h and NaCl/365nm/72h method. Except of very small changes the p-GaN surfaces remained practically stable. Traces of some metals were measured on areas which were not originally covered with the metal. These measurements were carried out both in-between the (former) metal stripes and at the far end from them.

	reference	Ag		Au		Ni		Pt	
		H ₂ O	NaCl	H ₂ O	NaCl	H ₂ O	NaCl	H ₂ O	NaCl
Ga (at%)	50.1	50.0	50.7	50.7	51.8	43.8	43.3	47.2	47.7
N (at%)	43.1	42.7	44.1	43.3	39.9	46.1	46.7	42.1	40.1
O (at%)	1.1	1.0	1.4	1.1	1.4	2.9	2.5	3.5	4.2
metal (at%)	–	1.3	0.4	0.0	2.3	0.0	0.7	1.5	0.8
metal far end (at%)	–	1.9	4.0	0.0	1.6	0.0	1.7	1.1	1.0

no traces of metal could be measured on the surfaces, the EDX measurements carried out on p-GaN partially detected the occurrence of metal species, even though the measured amounts were partially at the lower detection limit. These metals probably originate from the primary deposited metal stripes on p-GaN. Especially for nickel in NaCl as shown in figure 6.9, this re-deposition could be already seen by eye. Surprisingly, at the far end sides, the detected species were found in even higher amounts, e.g., 4.0 at% silver in NaCl solution and 1.7 at% nickel in NaCl solution (compared to 0.4 at% and 0.7 at% in-between the metal stripes). In case of nickel in NaCl as shown in figure 6.9, the measured nickel content at the far end from the original nickel stripes does not refer to the re-deposited nickel film, that surrounds the complete borders of the sample, but to the p-GaN surface next to it at the far end side. The nickel content directly surrounding the p-GaN sample was determined with approx. 80-90 at% by EDX. Despite of the clustered re-deposition of nickel at the

edges of the p-GaN sample, a gradient-like homogeneous deposition of the metals across the p-GaN samples could be determined.

The difference in the behavior between n-GaN and p-GaN samples concerning the adhesion of the deposited metals can be seen in figure 6.10. There, the SEM and EDX mapping images of n-GaN and p-GaN are shown, which were treated with the 100nmAg/NaCl/365nm/72h method. In case of n-GaN the silver adhered well and did not spread into the n-GaN region, holding the sharp borderline. This is not the case for p-GaN, where the transition between p-GaN silver became blurry. Silver content was also detected on the former pure p-GaN side.

The detachment and re-deposition of the metals from p-GaN is due to the function of p-GaN as photoelectrode. A detailed discussion and interpretation of these observations will follow later in this chapter. This behavior, as shown in figures 6.10 (d) was also observed for the other used metals in this work. All in all, these re-deposited metal traces probably originate from the more or less intense tarnishing of the metal stripes from the p-GaN surface and will be discussed later in this chapter.

There are obviously two different working mechanism concerning metal interaction with GaN surfaces under UV illumination: the influence of metals has a strong effect on the n-GaN surface under 365 nm illumination in aqueous solution. The presence of metals increased the surface changes and oxidation. The metal stripes on the contrary adhered strongly to the n-GaN surface. Thereby it obviously plays no role, whether a noble or non-noble metal is applied. This effect was also independent on the chosen electrolyte – samples showed the same distinct tendency towards oxidation. For p-GaN on the other hand, regardless of which metal or electrolyte was used, the p-GaN surfaces remained unchanged, but the metals tarnished from the p-GaN surfaces. This detachment showed the same intensity in NaCl and H₂O, and was most intense for silver and nickel.

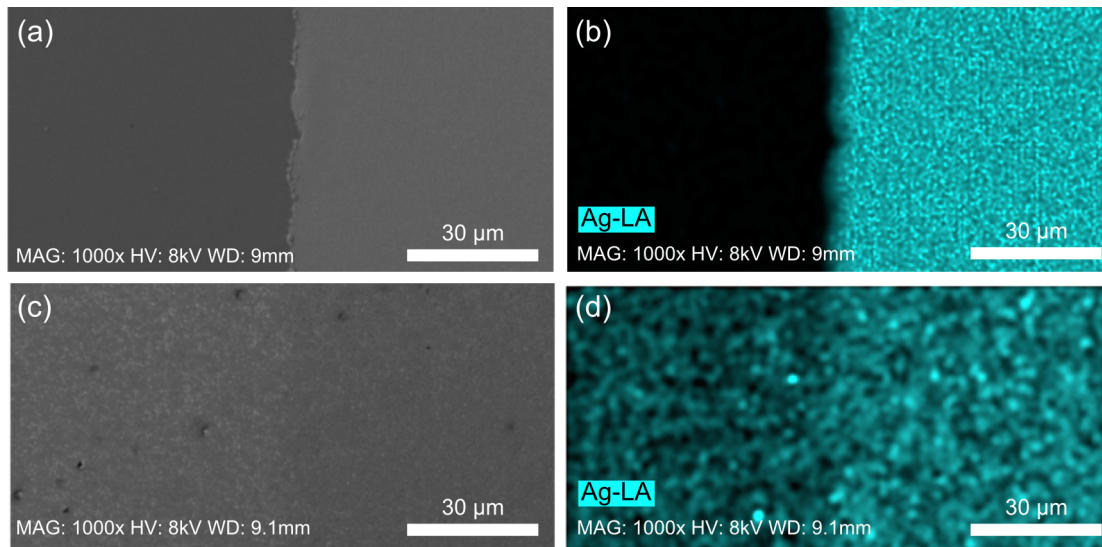


Figure 6.10: SEM images and the corresponding EDX mapping images recorded on stressed n-GaN (a, b) and p-GaN surfaces (c, d) which were treated with the 100nmAg/NaCl/365nm/72h method. The measurements were made in-between the silver stripes at the border of the GaN surface to the deposited silver. (b) In case of n-GaN, there is a well-defined boundary between the n-GaN (black, left) and silver surface (cyan, right). (d) In case of p-GaN, the silver spread over the whole sample surface and a blurry boundary between the p-GaN surface (left) and silver (right) can be determined.

Influence of the metal thickness

All results shown here so far referred to 100 nm thick deposited metal stripes on GaN. However, it was observed that the metal surfaces showed different behavior when their thickness was varied. Thickness variations are shown exemplarily for silver. Besides 100 nm, it was additionally evaporated in 300 nm thickness on both n-GaN and p-GaN samples.

Figure 6.11 shows photos and light microscopy images from the metal stripes on GaN samples which were stressed with the

H₂O/365nm/72h method. In case of n-GaN, a thickness of 100 nm did not cause any features on the silver stripes despite of some small bubbles on the lower silver stripe. The metal adheres strongly to the n-GaN surface and its characteristic structure shows through. Obviously, as already mentioned, the metal layer protects the underlying n-GaN surface. When 300 nm thick silver stripes were deposited, many small bubbles (much more than the few on the 100 nm thick silver stripes) could be seen on the silver stripes of the stressed n-GaN samples. The dimensions of these bubbles were measured with a profilometer and had a height of approx. 4 μm and different diameters between approx. 10 μm and 200 μm . The n-GaN surface itself was attacked in the same way as under the influence of 100 nm silver. The bubbles are probably a result of evolving gases during illumination. As shown in section 5.2.1, n-GaN works as photoanode, thus it is likely that stressed as anode, O₂ or Cl₂ are evolving from the n-GaN surface according to equations 2.6 and 2.7. Furthermore, due to possible photo-oxidation, the evolution of gaseous N₂ from the n-GaN surface according to equation 3.5 is also likely. For 100 nm silver, the metal layer is too thin so that the evolving gas from the n-GaN surface can diffuse easily through the probably permeable metal layer, whereas 300 nm of metal coating present a barrier for the gas. This barrier causes a lifting of the metal from the underlying n-GaN surface during gas formation and after desorption a drop of the expanded metal. This explains the characteristic structure of the bubbles as shown in figure 6.11.

For p-GaN on the other hand, independent of the thickness of the deposited silver stripes, the applied stress to the samples always led to a tarnishing and detachment of silver from the p-GaN surfaces. It turned out that in case of 300 nm, the whole process occurred slower due to the thicker layer, there is more silver that needs to be removed, taking longer time to dissolve. The thinner 100 nm silver layer almost completely detached from the underlying p-GaN, in case of silver causing smears of the metal on the p-GaN surface. These

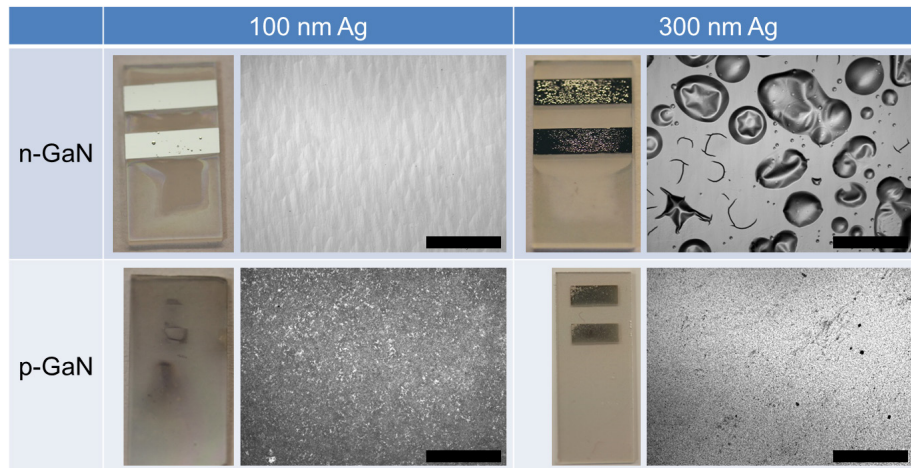


Figure 6.11: Photos and light microscopy images of n-GaN and p-GaN samples which were stressed with the $\text{H}_2\text{O}/365\text{nm}/72\text{h}$ method. Each sample had deposited silver stripes with thicknesses of 100 nm (left column) and 300 nm (right column). In case of n-GaN, no bubbles on the 100 nm silver stripes could be observed whereas bubbles formed for the 300 nm silver coating. The n-GaN surface was attacked in both cases, leading to a roughened structure especially close to the metal area. For p-GaN, the silver stripes detached from the p-GaN surfaces – 100 nm silver almost completely tarnished, whereas for 300 nm the detachment was not as fast due to the thicker metal layer. Scale bars: 200 μm .

observations on silver can be transferred also to the other types of metal stripes in this work which were deposited on the GaN surfaces.

6.1.4 Influence of long-term stress on GaN stability

All samples so far were stressed over a period of 72 hours. GaN samples in this subsection are stressed over a time period of 14 days with and without 100 nm thick silver stripes under 365 nm illumination. This was made in order to see, whether already occurred changes on

n-GaN surfaces might intensify and if the so far stable surfaces of p-GaN might be attacked over a longer time of applied stress. GaN samples exemplarily are investigated in 0.1 M NaCl.

Figure 6.12 gives an overview of photos and light microscopy images of n-GaN and p-GaN samples stressed with the NaCl/365nm/14d method. For every sample, smears can be seen in the light microscopy images. They occur because GaN samples in general were taken out of the electrolyte without rinsing them again with water. Those smears thus correspond to traces of the dried electrolyte – by EDX, traces of NaCl were verified. These smears were not observed for 72 hours but now appear, probably due to the longer period of time. In any cases, no traces of silver were measured on the n-GaN surface. The results of EDX measurements on GaN samples are enlisted in table 6.5.

In case of pure n-GaN stressed with the NaCl/365nm/14d method, nothing changed on the sample surfaces – the same result as for the samples which were stressed for 72 hours as shown in figure 6.2 and table 6.2. On the other hand, applying the 100nmAg/NaCl/365nm/14d method the surface was clearly attacked as it was already the case for 72 hours applied stress (cf. figure 6.6). Surprisingly, the elemental composition after 14 days changed less intense as it did after 72 hours. The nitrogen content of n-GaN in NaCl decreased to 7.3 at% after 72 hours and to 20.0 at% after 14 days. The oxygen content increased to 53.8 at% after 72 hours and 34 at% after 14 days of applied stress. Thus, the oxidation was less distinct for a long-term applied stress.

Pure p-GaN samples were also studied under the same longterm conditions as n-GaN, i.e. by applying the (100nmAg/NaCl/365nm/14d method. The observed results are presented in figure 6.12 and table 6.5. Similar to the results obtained for the 72 hours measurements in tables 6.2 and 6.4, the elemental composition of the p-GaN surfaces did not change. A slight increase of the oxygen content for p-GaN under silver influence up to 3.4 at% was measured but this lies within the error of measurement. No attacks on the surfaces could be noticed. The p-GaN surfaces were all intact but slightly covered with smears

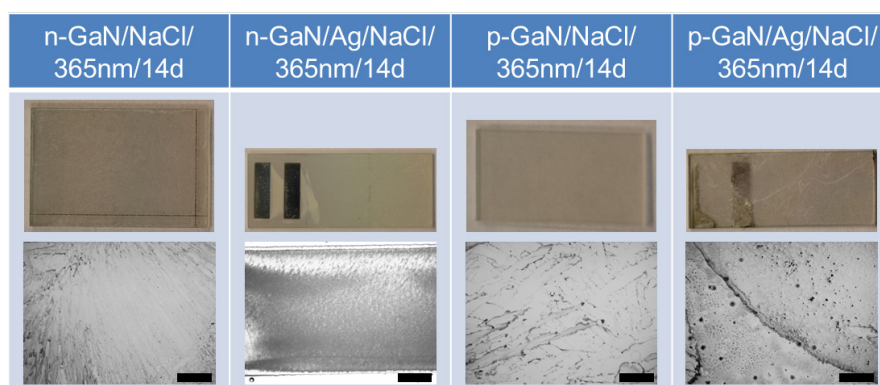


Figure 6.12: Photos and light microscopy images showing the influence of long-term degradation on GaN. n-GaN and p-GaN samples were stressed with the (100nmAg/NaCl/365nm/14d method. Pure n-GaN did not show changes (the smears in the microscopy images are from the electrolyte), whereas the n-GaN surface under silver presence was clearly attacked especially in-between and close to the silver stripes. A whitish layer, probably gallium oxide, has formed. In case of pure p-GaN, no changes on the samples surfaces could be observed – even not under silver influence. The silver stripes themselves partially detached from the p-GaN surface. Scale bars: 500 μm .

of dried NaCl electrolyte. The deposited silver on the other hand partially detached from the p-GaN surface. This was already the case under 72 hours of applied stress, where silver stripes started tarnishing from p-GaN (cf. figure 6.9). Interestingly, over a period of time of 14 days, no traces of re-deposited silver could be measured by EDX. One explanation is that the re-deposited silver is washed away from p-GaN due to the longer time in aqueous solution.

Figure 6.13 shows SEM images for the n-GaN samples stressed with the (100nmAg/NaCl/365nm/14d method. Noticeable are the plenty of small crumbs that are spread everywhere and quite arbitrarily across the n-GaN surface in figure 6.13 (b). EDX data identified them to probably correspond to NaCl. They aligned at the n-GaN surface without attacking it. In figure 6.13 (c), the attack of the n-GaN

Table 6.5: EDX data recorded on GaN surfaces, stressed with and without deposition of 100nm silver under NaCl/365nm/14d conditions. Pure n-GaN under 365 nm excitation remained unchanged, whereas the influence of silver caused an oxidation of the n-GaN surface. The silver stripes as well remained stable on the samples. The p-GaN surfaces themselves showed no changes in their elemental composition. Surprisingly, under these long-term measurements, no traces of silver could be measured under 365 nm illumination. Obviously no re-deposition of the detached silver took place.

	n-GaN			p-GaN		
	reference	365 nm	Ag, 365 nm	reference	365 nm	Ag, 365 nm
Ga (at%)	47.1	51.7	37.3	50.1	51.3	49.2
N (at%)	45.1	42.2	20.0	43.1	42.5	42.0
O (at%)	1.5	0.7	34.0	1.1	0.4	3.4
Ag (at%)	–	–	0.0	–	–	0.0

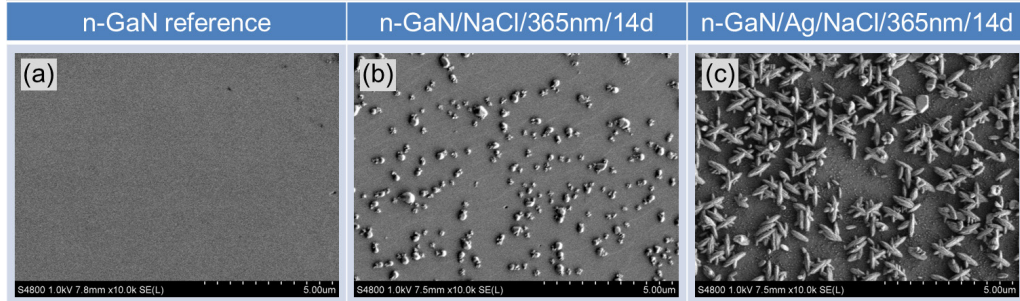


Figure 6.13: SEM images of an n-GaN reference sample (a) and samples stressed with the NaCl/365nm/14d (b) and 100nmAg/NaCl/365nm/14d (c) method. The n-GaN surface in (b) remained unchanged – the grains are dried NaCl crystals. In contrast, the appearance of oxygen-containing rod-like structures in (c) implies a degradation reaction on the n-GaN surface.

surface, stressed with the 100nmAg/NaCl/365nm/14d method, can be clearly seen. Rod-like structures, containing oxygen and gallium as measured by EDX are visible – even if they are just arising and not completely developed to the coral-like structure as seen in figure 6.7 (c) in case of 72 hours stress. They rather correspond to the case of n-GaN stressed with the H₂O/365nm/72h method, shown in figure 6.3 (b).

Figure 6.14 shows SEM images for p-GaN samples stressed with the (100nmAg/NaCl/365nm/14d method. Noticeable are the hexagonal holes, emerging in a high density across the p-GaN reference surface. In literature they are known as V-pits, containing several dislocations and develop during the GaN growth process due to, e.g., stacking mismatch boundaries [176–179]. For the stressed samples, the appearance of NaCl crystals, spread across the p-GaN surfaces, can be noticed on the SEM images, similar to the n-GaN samples. In figure 6.14 (b), the V-Pits seemed to disappeared or rather got plugged with bigger dried NaCl crystals. Also smaller NaCl crystals that are spread across the whole p-GaN surface can be seen. In case of additional silver influence as shown in figure 6.14 (c), the density of NaCl crystals across the surface significantly increased.

6.1.5 Influence of dry conditions and below bang gap illumination

GaN samples that were only illuminated with 365 nm UV light in absence of an aqueous environment (i.e. under dry conditions) did not show any elemental changes of the surfaces after 72 hours or 14 days. Also, 100 nm thick metal stripes under 365 nm excitation and dry conditions had no effect on the GaN surfaces. Changes were neither detected for GaN nor the metals (results not shown). It thus is proven, that an aqueous environment is absolutely essential to drive reactions on the GaN–electrolyte interface.

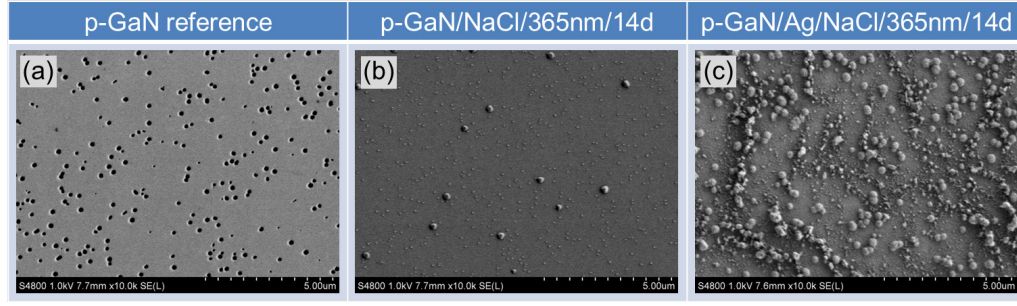


Figure 6.14: SEM images of a p-GaN reference sample (a) and samples stressed with the NaCl/365nm/14d (b) and 100nmAg/NaCl/365nm/14d (c) method. The stressed sample surfaces did not show any compositional changes. The density of the dried NaCl crystals visible in (b) and (c) increases under silver influence.

It was also investigated whether GaN samples in solution show surface changes under dark conditions or 400 nm illumination, i.e. if no additional charge carriers are generated by UV light excitation. Samples were stressed with the (100nmAg/NaCl/dark/72h, and (100nmAg/NaCl/400nm/72h method and afterwards no elemental changes of the GaN surfaces were measured by EDX. Both n-GaN and p-GaN samples remained unchanged, even under the presence of silver (results not shown). The silver stripes adhered stably on both n-GaN and p-GaN surfaces without tarnishing. This was also true for 14 days of applied stress. It obviously needs both the presence of an aqueous solution as well as the excitation with UV light to promote reactions on GaN interfaces.

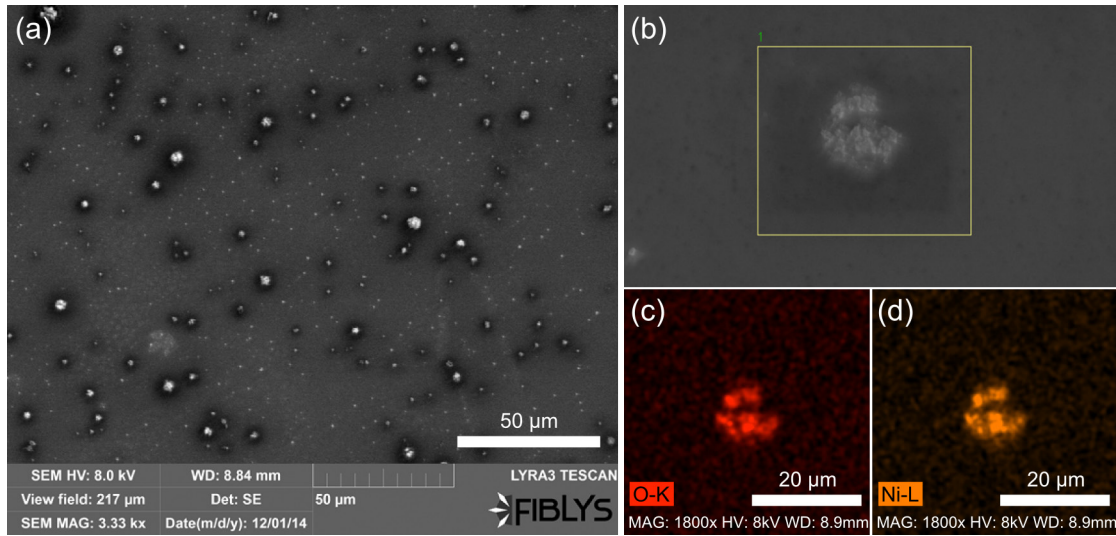


Figure 6.15: SEM image of NiO co-catalyst particles that are distributed across the n-GaN surface (a). From detailed images of single NiO particle with a diameter of approx. $10\ \mu\text{m}$ (b) EDX mapping images were taken to verify that the particles consist of oxygen (c, in red) and nickel (d, in orange).

6.1.6 Influence of NiO co-catalyst particles on GaN stability

n-GaN samples with NiO co-catalyst particles on their surfaces were investigated in terms of stability by photoinduced degradation experiments.

Figure 6.15 shows SEM images of NiO particles, spreading across the whole n-GaN surface. Contrary to [26], where a diameter of $30\ \mu\text{m}$ is stated, the particles investigated on the surfaces are in the range of about $10\ \mu\text{m}$. A detailed SEM image of a particle with a diameter of approx. $10\ \mu\text{m}$ was taken and measured by EDX mapping. There, the single components are analyzed and it can be clearly seen that it is about nickel and oxygen (colored in orange and red, respectively).

Samples from the same load with and without NiO particles were stressed both with and without the influence of 100 nm silver stripes

on their surfaces. Note that n-GaN without NiO in this case has a different charge carrier concentration (cf. section 5.1). Figure 6.16 shows the images for the applied (100nmAg/)/NaCl/365nm/14d methods. Clearly, the presence of NiO particles seems to protect the n-GaN samples as can be seen in the left column and no surface changes could be observed. Surprisingly, the stressed n-GaN sample without NiO catalysts in the column side was clearly attacked in NaCl solution – this effect was not observed for the n-GaN samples which stemmed from another load shown in figure 6.12 under the same measurement conditions. Probably, the differing charge carrier concentration of one order of magnitude (10^{17} cm^{-3} vs. 10^{18} cm^{-3} for the n-GaN samples investigated so far) causes the sensitivity of n-GaN without NiO towards degradation in NaCl.

The lower row in figure 6.16 shows the n-GaN samples in presence of 100 nm thick silver stripes, which well adhered to the surfaces after measurements. Analogous to the pure n-GaN samples, the NiO particles clearly protected the n-GaN surface from changes. The sample on the right without NiO particles was strongly attacked, comparable to the result shown in figure 6.12 under 365 nm illumination.

This protection effect is due to the oxidation of the catalyst particles, thus averting a photo-oxidation of the n-GaN surface since the photogenerated holes at the interface contribute rather to the NiO oxidation. It was already observed in section 5.2.1

Table 6.6 shows the corresponding EDX data. Enlisted are also the values for samples treated with the NaCl/dark/14d method. In that case the elemental composition for both types with and without NiO co-catalyst particles did not change. When applying the NaCl/365nm/14d method to the samples, a clear difference in the presence of NiO co-catalyst particles can be seen, as already observed on the images presented in figure 6.16. Samples without NiO catalysts showed a decrease of the nitrogen content down to 8.8 at% and a strong increase of the oxygen species (47.2 at%). On the other hand, the elemental composition remained constant under the presence of the NiO particles

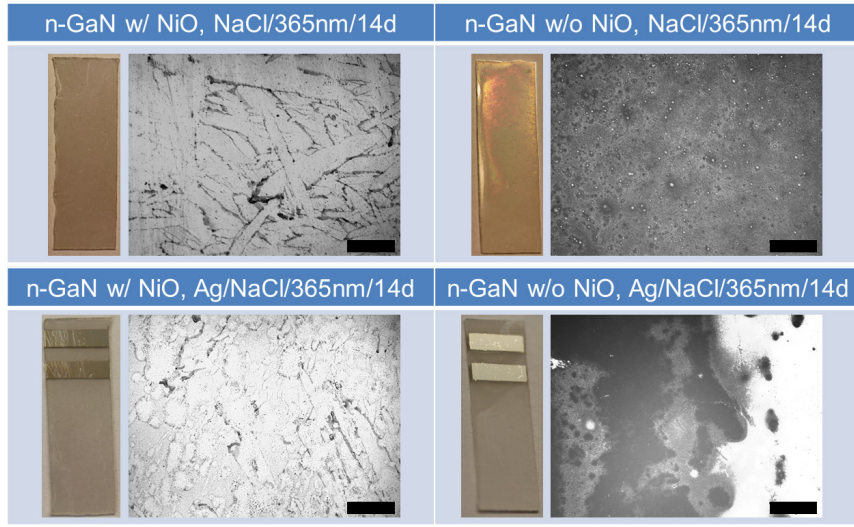


Figure 6.16: Photos and light microscopy images showing the influence of NiO particles on the stability of pure n-GaN (top row) and n-GaN with 100 nm thick silver stressed with the NaCl/365nm/14d method (bottom row) with (left column) and without (right column) NiO co-catalyst particles deposited on their surface. Samples with NiO particles remained unchanged after experiments, whereas the n-GaN surfaces without NiO were clearly attacked. Scale bars: 500 μm .

on the n-GaN surface. As already observed phenomenologically in figure 6.16, the NiO particles protect the underlying n-GaN layer from photo-oxidation. When the n-GaN samples were stressed with the 100nmAg/NaCl/365nm/14d method, samples without NiO coating showed stronger changes under silver influence, resulting in a nitrogen content of 1.5 at%, and a drastically increased oxygen content of 60.3 at%. The sample which had the protecting NiO co-catalysts on its surface was not attacked and the elemental composition did not change, except for a slight increase of the oxygen fraction to 2.2 at% which can be interpreted as statistical deviation.

Additionally, SEM images of the stressed n-GaN samples with the (100nmAg/NaCl/365nm/14d method are shown in figure 6.17.

Table 6.6: EDX data measured on n-GaN surfaces with and without NiO catalyst particles on the surface. Results of EDX measurements on the corresponding reference samples (ref.) as well as samples treated with and without deposition of 100nm silver under NaCl/365nm/14d, or NaCl/dark/14d conditions. The elemental composition of the n-GaN surfaces without NiO changed under UV illumination and even more strongly under the influence of silver. On the other hand, it can be clearly noticed that NiO prevents the n-GaN samples from elemental changes of their surfaces. Under the influence of NiO particles the n-GaN sample surfaces remained unchanged.

	n-GaN w/o NiO				n-GaN with NiO			
	ref.	dark	365 nm	Ag, 365 nm	ref.	dark	365 nm	Ag, 365 nm
Ga (at%)	56.4	52.6	40.9	28.9	55.4	55.7	55.4	46.0
N (at%)	41.5	44.1	8.8	1.5	42.2	42.1	41.2	45.9
O (at%)	0.5	0.1	47.3	60.3	0.5	0.2	0.9	2.2

Whereas the NiO particles obviously protected the n-GaN surface and only dried NaCl crystals can be seen, the surfaces that had no NiO coating were clearly attacked. Coral-like structures formed in both cases (with and without silver influence) as could be already seen in figures 6.7 (c) and 6.13 (c).

It thus was quantitatively proven that those NiO co-catalyst particles indeed protect the underlying n-GaN surface from oxidation.

6.1.7 SIMS measurements on GaN

Data received from EDX measurements can detect changes in the elemental compositions up to 200 nm into the sample (cf. figure 6.1). Another technique to analyze degradation-caused changes and local distributions of the single components in the sample is time-of-flight secondary ion mass spectrometry (ToF SIMS, the following referred

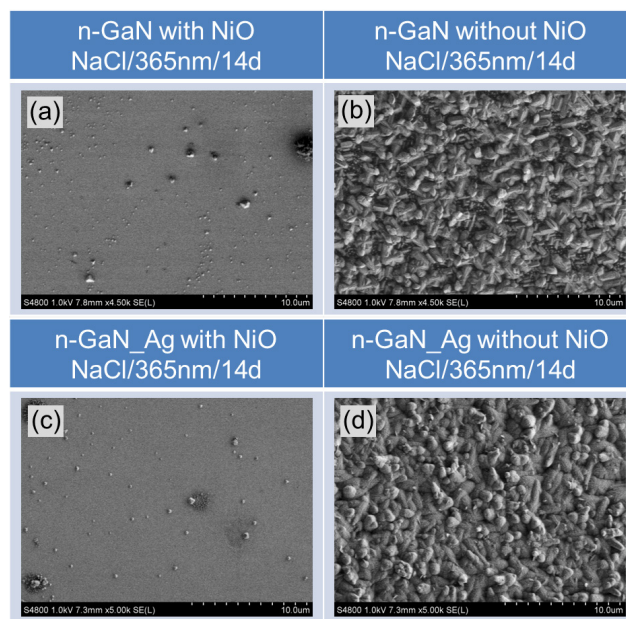


Figure 6.17: SEM images of n-GaN samples with (a, c) and without (b, d) NiO co-catalyst particles, stressed with the NaCl/365nm/14d (a, b) and 100nmAg/NaCl/365nm/14d (c, d) methods. The difference between the situations with and without NiO particles is clearly visible. In the presence of NiO catalysts no changes can be seen, apart from some dried NaCl crystals. The absence of NiO leads to an attack of the n-GaN surfaces, resulting in the formation of rod-like structures.

to as SIMS). SIMS measurements were carried out in cooperation with Dr. Rolf Treichler at Siemens CT RTC MAT ANA Munich. The measured area was approx. 4-5 μm in diameter. SIMS measurements gave information about the distribution of relevant species in the GaN samples.

Since silver had a high impact on n-GaN degradation in both H_2O and NaCl, it was chosen as metal for further investigations and discussions. SIMS measurements were carried out exemplarily for the following samples: an n-GaN and p-GaN reference as well as GaN samples stressed with the 100nmAg/NaCl/365nm/72h method. For

n-GaN under these conditions, the oxygen content was measured to be 53.8 at% as can be seen in table 6.4. The elemental composition of p-GaN stressed by this method on the other hand did not change. As for the EDX analysis, the measurement spot on the stressed GaN sample was on the GaN surface between the two silver stripes. The detected species were O^- , Cl^- , GaN^- , and AlO^- . AlO^- was included in the analysis in order to gain information about possible interactions with the underlying sapphire substrates. AlO^- and GaN^- do not dissociate but leave the sample as compounds and therefore lead to signals that are convolutions of the individual atomic signals. Since neutral nitrogen cannot be detected in SIMS measurements, conclusions about the nitrogen distribution can be drawn from the GaN^- result.

Figure 6.18 shows SIMS measurements on n-GaN samples. In figure 6.18 (a), the profile depth of an n-GaN reference is shown as overview and in magnified spectra. The GaN^- as well as the O^- signal stay at a constant level over the whole depth range. On the other hand, the AlO^- signal displays notable peaks at around 300 nm and 1400 nm depth. These peaks are coincident with a smaller peak in the O^- signal and a small dip in the GaN^- signal. The peaks in the AlO^- signal could be connected to the growth process of the n-GaN samples (e.g., breaks in the growth or change of doping concentration). In a depth of approx. 4500 nm, the sapphire substrate begins, which is visible as a steep increase of the AlO^- and O^- signals and a significant drop of the GaN^- signal.

Figure 6.18 (b) shows SIMS measurement curves of an n-GaN sample, stressed with the 100nmAg/NaCl/365nm/72h method. As for the reference sample, there are two peaks in the AlO^- and O^- signals which are caused by breaks in the n-GaN growth process. Compared to the reference sample, the O^- signal is increased by approx. two orders of magnitude, indicating an oxidation of the n-GaN surface. This is in accordance with the results gained from EDX measurements, where an increase of the oxygen content up to

53.8 at% was measured (cf. table 6.3). The GaN^- signal is constant throughout the sample, except for first 30 nm from the surface where it decreases by up to one order of magnitude, in agreement with the EDX measurements which data showed a significantly decreased nitrogen concentration to 7.3 at% (cf. table 6.3). Finally, the chlorine concentration in the stressed sample is increased by up to four orders of magnitude close to the sample surface. This can be ascribed to the chloride-containing electrolyte.

Concluding, for the 100nmAg/NaCl/365nm/72h stressed n-GaN sample, the increase of the oxygen content could be seen. The signal decreased to its reference level within 500 nm. This can be directly transferred to the oxidation of n-GaN, which then probably occurs within the first 500 nm on the surface.

Further SIMS measurements were carried out on p-GaN for which no changes in the surface were detected in the phenomenological investigations optical as well as for EDX measurements (cf. figure 6.9 and table 6.4). Results of SIMS measurements on reference and 100nmAg/NaCl/365nm/72h stressed p-GaN samples are shown in figure 6.19. The reference levels of the GaN^- and O^- signals measured on the p-GaN reference are comparable to the n-GaN reference sample (cf. figure 6.18).

For the stressed p-GaN the GaN^- signal is constant throughout the sample which indicates that contrary to the stressed n-GaN sample, the nitrogen species did not decrease.

Surprisingly, other than for the n-GaN samples, no AlO^- peaks are visible, although the p-GaN layer was only approx. 200 nm thick, grown on an n-GaN layer. Moreover the fact that for the stressed p-GaN sample the signal of the O^- species increased by one order of magnitude at the surface was also unexpected since in EDX data no increase of the oxygen concentration was detected for stressed p-GaN (cf. table 6.4).

Although the increase is not as high as for n-GaN, it is still considerable and suggests that also stressed p-GaN is oxidized.

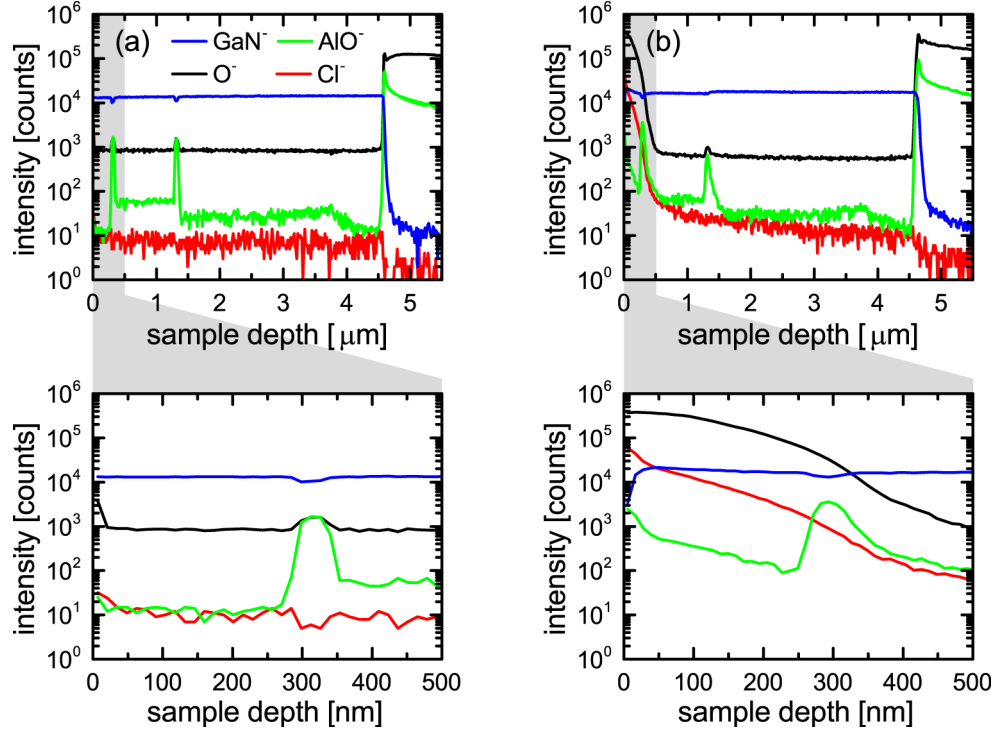


Figure 6.18: Results of SIMS measurements, performed on an n-GaN reference sample (a) and an n-GaN sample stressed with the 100nmAg/NaCl/365nm/72h method (b). In both cases the GaN⁻ signal (blue curve) is constant. For the stressed sample, the oxidation of the n-GaN surface within the first 500 nm can be seen as an increased O⁻ signal (black curve). Furthermore, due to the NaCl electrolyte, the Cl⁻ signal (red curve) increases close to the surface. The two peaks in the AlO⁻ signal (green curve) are caused by short breaks in the growth process during the n-GaN fabrication.

By EDX analysis, a chlorine content on the stressed p-GaN sample was measured at 0.3 at%, which agrees with the increase of the chlorine species in the SIMS spectrum at the p-GaN surface. This increase was even higher than for the stressed n-GaN sample. The sapphire substrate, which was measured for n-GaN at approx. 4500 nm, was not detected within the presented measurement range. It began in

a depth of approx. 5500 nm for the p-GaN samples. Thus, based on the SIMS depth profile, since the p-GaN layer itself was around 200 nm thick, the underlying n-GaN layers must be up to 800 nm thicker than in case of the n-GaN samples.

The AlO^- signal also showed an increase in the surface-near region. The reason for this is not clear but it may have something to do with the presence of multi-quantum-well structures and barriers in the GaN layer, which work as light emitting zones in a LED. Since the structures of the n-GaN and p-GaN sample layers used in this work were intended to be used in LEDs it might be possible that the AlO^- signal correlates to these quantum-well structures. But it needs to be regarded with suspicion.

6.1.8 XPS measurements on GaN

The SIMS measurements provided information about the location of oxygen, nitrogen, and chloride content in the GaN samples and thus gave a trend of the distribution of the respective species. On the other hand, these measurements do not provide information on the chemical composition of the samples. Thus, it is not possible to conclude whether, e.g., oxygen detected by SIMS measurements stems from an oxidized gallium compound or merely from surface oxidation.

In order to gain knowledge about the chemical modification of the n-GaN samples up to a depth of 10 nm, X-ray photoelectron spectroscopy (XPS) measurements were performed in cooperation with Dr. Michael Bayer at Siemens CT RTC MAT ANA Munich. Measurements were performed directly at the sample surfaces (0 nm) as well as below the surface after removal of a layer of 10 nm by sputtering.

XPS measurements were carried out on n-doped GaN, where, based on previous EDX analysis results, a photo-oxidation occurred. Therefore again, an n-GaN reference sample as well as an n-GaN sample

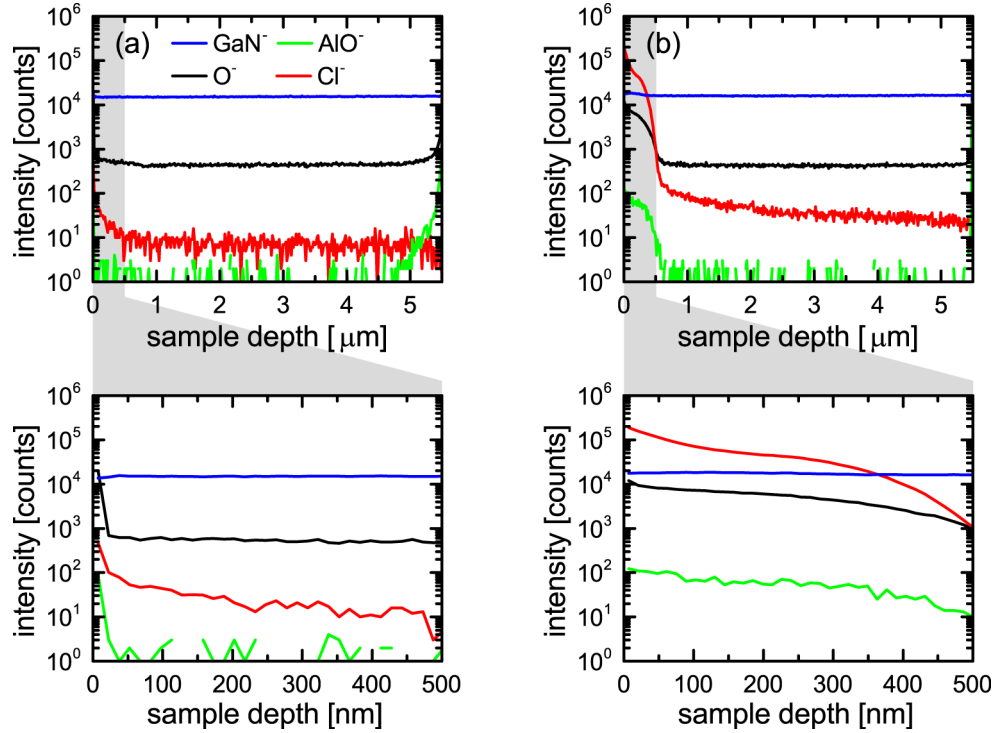


Figure 6.19: Results of SIMS measurements, performed on an p-GaN reference sample (a) and a p-GaN sample stressed with the 100nmAg/NaCl/365nm/72h method (b). While the GaN^- content (blue curve) showed no changes in the stressed sample compared to the reference signal, the O^- (black curve), AlO^- (green curve), and Cl^- (red curve) signals increase close to the surface for the stressed sample.

stressed with the 100nmAg/NaCl/365nm/72h method were measured. The aim was to see which elements exist in the surface-near region of the samples and to which chemical compound they could be referred to. On the stressed n-GaN sample the measurement spot was chosen in-between the two silver stripes.

Figure 6.20 shows survey spectra measured by XPS with all four measured curves of n-GaN reference and stress samples at the direct surface and 10 nm below the surface, respectively.

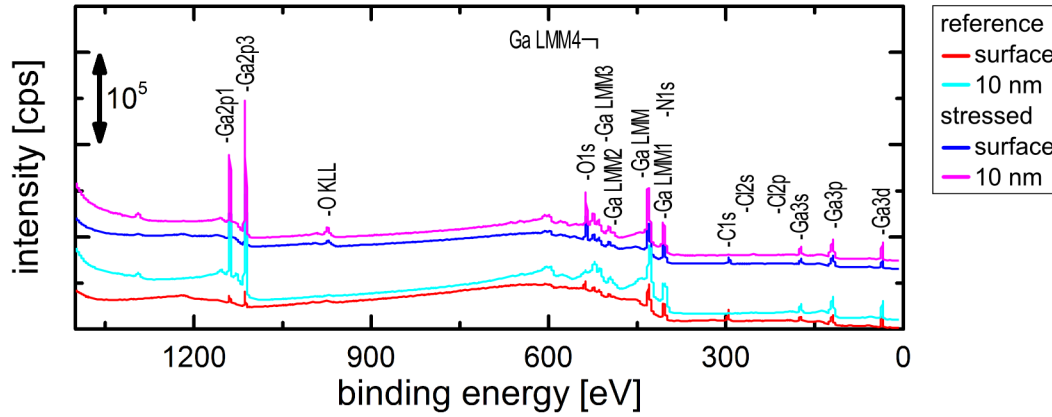


Figure 6.20: XPS survey spectra of a reference n-GaN sample (red and cyan curves) as well as for an n-GaN sample stressed with the 100nmAg/NaCl/365nm/72h method (blue and magenta curves), each measured directly on the surface (red and blue curve) as well as in a depth of 10 nm (cyan and magenta curve). As can clearly be seen from the spectra, the oxygen species in the stressed sample is increased.

Between 400 and 500 eV, Ga auger peaks were measured. At approx. 530 eV a large oxygen peak was measured at the degraded n-GaN sample. This binding energy of the emission line at 530 eV corresponds to the O 1s bond of Ga_2O_3 , implying that a Ga_2O_3 phase is present both at the surface and in 10 nm depth of the stressed n-GaN sample.

For the measurement of the reference sample in 10 nm depth a shoulder structure is indicated at the binding energy of 400 eV. This shoulder is not present for the reference measurement at the surface. The same observation was made for the stressed sample, but here the shoulder is not as distinct.

This shoulder should correspond to nitrogen in the sample (unfortunately, nitrogen could not be measured quantitatively due to an insufficient analysis method as discussed later). It is therefore more pronounced in the reference sample and decreases when the sample is

stressed under illumination, which is due to the photo-oxidation of the sample and therefore a decrease of the nitrogen.

The Cl 2s and Cl 2p peaks of chlorine are present in figure 6.20 in the survey spectra of the stressed n-GaN sample recorded at the surface and in 10 nm depth, indicating a small chlorine content on and in the stressed GaN due to its storage in a NaCl electrolyte. Sodium on the other hand could not be detected.

Carbon is detected on the surfaces of both the reference and the stressed n-GaN sample in the same concentrations and no carbon is detected in 10 nm depth. This is most probably caused by contaminations of the sample surfaces such as C-H chemicals. It needs to be considered that by sputtering, only the relative intensities of surface-near contaminations are removed, since in this work only 10 nm were removed. Usually, surfaces have a macroscopic roughness, which is in the μm region. Thus, often contamination species are still visible after sputtering.

In the following, changes in the composition of the sample as detected by XPS spectra will be discussed for selected regions of the survey spectrum.

Figure 6.21 shows the N 1s spectra of the Ga–N bond at around 397 eV. The reference curve in 10 nm depth shows a peak with a shoulder. This is also the case for the reference sample on the surface (0 nm), even if the emission line shows a decreased intensity and thus it is not as distinct as in 10 nm depth. For the stressed n-GaN samples, these shoulders are clearly not visible anymore, indicating that a part of the nitrogen content decreased. Additionally, gallium Auger LMM1 peaks appear at approx. 420 eV. Therefore, it can be concluded that the Ga-bound nitrogen content decreased in the sample as a result of illumination with UV light.

Figure 6.22 (a) shows a section of the recorded XPS spectra in the binding energy range of 13 to 20 eV. The peak at approx. 19.7 eV corresponds to the Ga 3d core level for a GaN compound. In case of the reference sample for both measurement positions at the surface

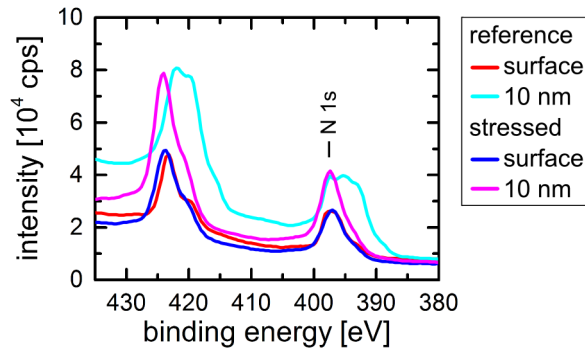


Figure 6.21: XPS spectra for n-GaN reference samples (red and cyan curve) and 100nmAg/NaCl/365nm/72h stressed samples (blue and magenta curve) in the range of 380 to 435 eV, measured on the surface (red and blue curve) and in 10 nm depth (cyan and magenta curve). The N 1s peak at 397 eV, has a shoulder for the reference sample in 10 nm depth, which is not present for the stressed sample, indicating a decrease of the nitrogen species.

and in 10 nm depth a characteristic shoulder at around 16-17 eV can be seen, which vanishes almost completely for the stressed n-GaN sample. This is the binding energy of the gallium-bound nitrogen in GaN. It was related to as N 2s core level at 17 eV in [141, 180]. Since this characteristic edge vanishes for the stressed sample, it can be concluded that the n-GaN sample has a gallium–nitrogen dissociation, meaning that the gallium content has formed other compounds like, e.g., Ga_2O_3 .

Figure 6.22 (b) shows a detail of the XPS spectra in the binding energy range between 520 to 540 eV. For the stressed n-GaN sample the O 1s emission line at 531 eV clearly shows an increase of the intensity on the surface and in 10 nm depth compared to the reference spectra, indicating that an oxidation of the stressed n-GaN surface took place.

Also, the decrease of the N 1s signal at 397 eV (cf. figure 6.21) is a clear indication for the changes at the n-GaN–electrolyte interface.

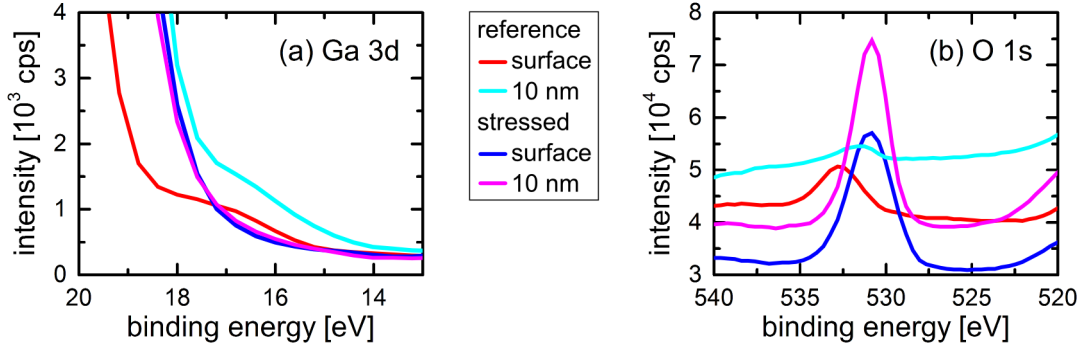


Figure 6.22: XPS spectra in the range of 13 to 20 eV (a) and 520 to 540 eV (b) for n-GaN reference (red and cyan curve) and 100nmAg/NaCl/365nm/72h stressed (blue and magenta curve) samples in 0 nm (red and blue curve) and 10 nm (cyan and magenta curve). The peak at 19.7 eV in (a) corresponds to a Ga 3d core level. The peak at 531 eV in (b) corresponds to the O 1s core level. Since it decreased for the stressed sample, an oxidation of the stressed sample is indicated.

Unfortunately, due to very limited capacities of the CT RTC MAT ANA Munich division, where the XPS measurements were carried out, it was not possible to make quantitative statements about the elemental contents measured by XPS. This also implies that no comparison with the EDX data could be made. The insufficient analysis routine is due to the fact that usually a magnesium source is used for analyzing GaN to distinguish more precisely between the oxygen and nitrogen species [180]. In the present measurements, on the other hand, only an aluminum source was available, leading to a lower accuracy of the recorded spectra. Furthermore, the spectra are not referenced against a C 285 standard, meaning that the measured curves would need to be shifted slightly to more negative energy values to obtain the correct peak positions. Moreover, no detail spectra were recorded (the results presented in figure 6.21, 6.21 and 6.22 are merely magnifications of the survey spectra), which would have provided more detailed information about the individual species.

Although a relative sensitivity factor (RSF) correction was applied, the measured curves were not fitted, meaning that no quantitative statements could be made regarding the exact content of the gallium, nitrogen, and oxygen fractions in the samples. Often the gallium bond peaks have a shoulder, probably corresponding to the presence of either nitrogen or oxygen bound to either GaN or a gallium oxide compound. However, as discussed above, since the curves were not fitted with a corresponding method, no conclusions can be made about the origin of these contents and their amount. Finally, the open source NIST X-ray Photoelectron Spectroscopy data base 20, version 4.1 from the national institute of standards and technology (NIST) was used for the classification of the corresponding XPS peaks⁶. However, it needs to be considered that it does not contain all energy positions from the published literature.

In conclusion, the survey spectra gave valuable information about the stressed n-GaN samples showing evidence of an oxidation of n-GaN on the surface as well as in a sample depth of 10 nm. Other groups also proven the formation of Ga₂O₃ on stressed n-GaN samples in aqueous solutions [23, 128, 141] or by thermal oxidation [141, 180] by XPS measurements. But due to the mentioned insufficiencies a quantitative analysis could not be made in this work and therefore no elemental composition is available. Conclusions about the elemental composition are thus mainly referred to the EDX measurements.

6.2 Discussion of the photoinduced degradation of GaN

In the previous section, GaN samples were stressed in aqueous solutions under 365 nm UV illumination with and without the presence of metal stripes.

⁶ <http://srdata.nist.gov/xps/>

In case of n-GaN it was observed that partially significant changes occurred. Changes in the elemental composition of n-GaN were measured by EDX after a stress period of 72 hours in H₂O as well as in NaCl with and without metal influence. For a long-term stress of 14 days under UV excitation, oxidation of n-GaN samples under metal influence was observed in both H₂O and NaCl. This photo-oxidation was demonstrated by a decreasing nitrogen content as well as a significant increase of the oxygen species, measured by EDX on the stressed n-GaN surface compared to a reference sample. These changes in elemental composition were even more distinct under the presence of metals. XPS and SIMS measurements also confirmed the oxidation on n-GaN samples which were stressed with the 100nmAg/NaCl/365nm/72h method.

On the other hand, the behavior of the p-GaN samples was clearly different to those of n-GaN. The p-GaN surface in H₂O or NaCl under 365 nm excitation showed no changes in their elemental composition – neither under pure conditions nor under the presence of metals. In the latter case, the deposited metals ablated from the sample surfaces going along with a re-deposition of the metals elsewhere on the p-GaN samples. It thus can be concluded that the doping of the GaN samples leads to a different behavior under UV excitation in aqueous media. In the following, these characteristics with regard to the GaN–electrolyte interface, are discussed separately for n-GaN and p-GaN.

6.2.1 n-GaN under UV excitation in aqueous media

An occurring photo-oxidation of stressed n-GaN sample surfaces under UV illumination in aqueous solutions was verified in this work by EDX, SIMS, and XPS measurements. Compared to a reference, stressed n-GaN samples had a partially strong decrease of the nitrogen content as well as a clear increase of the oxygen species.

Some considerations were made to see, whether an attack and thus dissolution of GaN from an energetic point of view can take place at all. The standard enthalpy of formation for GaN amounts approx. $\Delta H_f^0 = -157 \text{ kJ/mol}$ [181]. The negative algebraic sign refers to the energy set free when 1 mol of GaN is generated. By dividing this value by the Avogadro constant, the energy that is necessary for the degradation of one GaN molecule is $2.61 \cdot 10^{-19} \text{ J}$.

According to formula 3.5, six electron-hole pairs are involved in the photo-oxidation of n-GaN. Assuming that each electron-hole pair is generated by one incoming photon, six photons are necessary to drive the reaction. For example, the energy of the incident light at 365 nm, regarding to $E = (h \cdot c)/\lambda$ is $= 5.45 \cdot 10^{-19} \text{ J}$. The necessary photon energy to oxidize n-GaN is determined to be $3.27 \cdot 10^{-18} \text{ J}$. So, the energy of the incident light is $3.27 \cdot 10^{-18} \text{ J}$ and thus approx. one magnitude higher than the determined energy of $2.61 \cdot 10^{-19} \text{ J}$ needed for GaN degradation. This means that the degradation of GaN is thermodynamically possible. Note that also the light intensity contributes to the number of photogenerated charge carriers, enabling etching processes on n-GaN. The etch rate is linear with the incident power and thus depends on the number of photogenerated charge carriers [28, 31]. The higher the light intensity of the GaN excitation, the higher the concentration of photogenerated free holes [91], and the higher the etching rates are [14, 28].

It needs to be considered that the n-GaN photo decomposition described in equation 3.5 competes with the O_2 evolution according to equation 2.6. The enthalpy of formation of water is approx. $\Delta H_f^0 = -286 \text{ kJ/mol}$ [182], implicating that an energy of $4.75 \cdot 10^{-19} \text{ J}$ would be necessary to enable water splitting. This required value is slightly higher than the energy needed for GaN oxidation, which is $2.61 \cdot 10^{-19} \text{ J}$. It thus can be stated that both GaN degradation and O_2 evolution are nearly equiprobable from an energetic point of view.

When n-GaN is in solution, a charge transfer occurs between the semiconductor and the electrolyte. For n-GaN under dark conditions,

according to the Gerischer model, this charge transfer occurs at the E_{cb} of n-GaN, assuming that no surface states are present on the n-GaN surface [89, 90]. It involves electrons as majority carriers. When n-GaN is excited with UV light, electron-hole pairs are generated in the depletion region of the semiconductor, as already mentioned in the previous chapter.

Within the depletion region, the photogenerated electrons diffuse into the n-GaN bulk, and holes, originating from the valence band, accumulate at the n-GaN surface, as already shown in figure 2.1 (a).

While electrons and holes contribute to the charge transport in n-GaN, ionic conduction takes place in the solution. This means that an electrochemical reaction is always involved in the charge transfer across the n-GaN–electrolyte interface, where electrons and holes are emitted or collected by the electrode, including the evolution of gases from the n-GaN surface. Since aqueous solutions are used in this work, water splitting reactions are possible.

In this context it needs to be considered that although n-GaN works as photoanode, driving the formation of gaseous O_2 , the evolution of gaseous H_2 also occurs locally from the n-GaN surface due to the missing CE in solution.

n-GaN under UV excitation in H_2O and the formation of gallium oxide

As already summarized above, local oxidation on the pure n-GaN surfaces under 365 nm excitation occurred only in H_2O .

For the $H_2O/365nm/72h$ method applied to n-GaN, it can be concluded that referring to equations 3.5 and 3.6, due to the accumulation of holes at the n-GaN surface, gaseous N_2 evolves and that a gallium oxide compound subsequently formed on the n-GaN surface, which did not dissolve afterwards due to the pH value of the electrolyte. The photogenerated holes thereby work as oxidizing agents.

Figure 6.23 shows a model sketch of the occurring reactions from the n-GaN–electrolyte interaction under UV excitation in H₂O.

Which gallium oxide compound exactly formed can be determined by quantitative surface analysis methods. Peng *et al.* concluded, that in case of aqueous phosphoric acid, Ga₂O₃ has formed, based on the ratio of the measured gallium and oxygen species [128]. An increased oxygen and decreased nitrogen content were measured by EDX also in this work. Unfortunately, it could not be determined, to which gallium oxide compound it belonged to. Only in case of n-GaN, stressed with the 100nmAg/NaCl/365nm/72h method, a ratio of 33.1 % gallium to 53.8 % oxygen was measured (cf. table 6.3), which approximately corresponds to Ga₂O₃. However, it is very likely that Ga₂O₃ formed on stressed n-GaN, although it could not be determined precisely. In the following, the formed gallium oxide phase is referred to as Ga₂O₃.

The morphology of the generated Ga₂O₃ strongly depends on the pH value of the electrolyte. Ghazali *et al.* reported that for high concentrations of Ga³⁺ and OH[−] ions in solution, the growth of Ga₂O₃ nanorods may be promoted [175]. They found out that in case of those acid solutions, nanorods occurred, whereas nanodots formed for pH values in the alkaline region [175]. Since the pH value of H₂O in this work is assumed to be around 5, the formation of nanorods was not unlikely and in case of H₂O, even a rod-like formation was observed for the 365nm/72h method (cf. figure 6.3 (b)). In EDX measurements it was proven that these rods only consist of gallium and oxide – corresponding to Ga₂O₃. These nanorods only partially covered the n-GaN surface.

Usually, GaN reference sample surfaces appear to be shiny. Peng *et al.* investigated the phenomenological appearance of the formed oxide layers on stressed n-GaN samples in acid solution. They reported that a 100 nm thick Ga₂O₃ film appeared purple-bluish [128]. This color change was also observed by Rotter *et al.*, where the oxides on stressed n-GaN in basic solution showed a soft blue to brown color

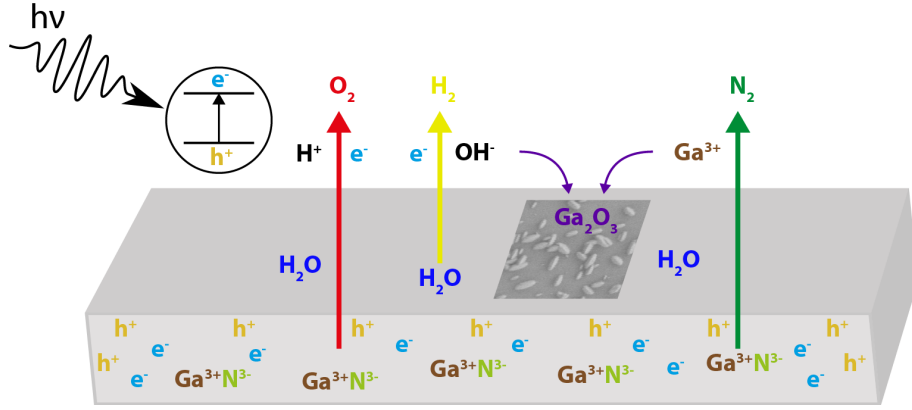


Figure 6.23: Model sketch of an n-GaN sample in H_2O which is excited with UV light. Due to the accumulation of holes at the n-GaN surface, photo-oxidation takes place, leading to the evolution of gaseous N_2 and the formation of an oxide layer on the n-GaN surface. Rod-like structures, containing Ga_2O_3 form on the sample surface. Due to the pH value of H_2O they do not dissolve and thus protect the underlying n-GaN surface. See text for discussion.

[8]. The stressed n-GaN sample surfaces in this work showed also a phenomenological change since the surface appeared in a different color and more dulled than non-degraded n-GaN when moving the sample back and forth under light.

The accumulation of holes at the n-GaN surface is affected by dislocations in GaN. An island-like growth of Ga_2O_3 was reported which took place preferentially at the dislocation sides and thus protected the n-GaN surface from etching by forming coral-like structures or whiskers, depending whether the electrolyte was basic or acidic [14, 32, 129, 132].

In this work, no dislocations on n-GaN reference samples could be noticed by SEM measurements. This observation is also in accordance with Basilio *et al.*, where a pristine n-GaN surface appeared to be smooth [129]. After the photoinduced degradation experiments in this

work, the n-GaN samples in H₂O showed rod-like Ga₂O₃ structures as shown in figure 6.3 (b). This finding suggests that the oxide rods are presumably formed at dislocations.

For strong acids and bases, representing an extreme pH environment, the photoelectrochemically formed Ga₂O₃ layer dissolves again, leading to an exposure of the underlying n-GaN surface which again can be etched [106]. Huygens *et al.* reported that it is possible to photoanodically etch n-GaN in 1 M H₂SO₄ [111]. Also the influence of basic solutions like KOH on n-GaN was studied by several groups [8]. Contrary to the results in literature, no etching of n-GaN in this work took place. This is because Ga₂O₃ did not dissolve from the dislocations due to the pH value of H₂O and NaCl.

Referring to the corresponding gallium-water Pourbaix diagram [143] as mentioned above, the generated Ga₂O₃ on the n-GaN surface should not be dissolved for both H₂O and NaCl as electrolytes. Thus, the importance of the pH value of the electrolyte is again proven for the photoelectrochemical processes. Furthermore, the presence of chloride ions also has a high contribution for the stability of Ga₂O₃ layers and thus the n-GaN surface.

n-GaN under UV excitation in NaCl and the suppression of oxidation

It obviously needs to be distinguished whether the pure n-GaN sample was stressed in H₂O or NaCl, since oxidation reactions of the n-GaN surface occurred for 72 hours in H₂O, but not in NaCl.

NaCl as electrolyte was used in few studies, mainly to study direct water electrolysis with an n-GaN photoelectrode and a Pt CE, e.g., in [23]. The interpretation for reactions in a near-neutral chloride-containing aqueous electrolyte can be also transferred to the photoinduced experiments, where only n-GaN was present as photoelectrode.

However, findings in literature often refer to HCl as acid, chloride-containing acid solution. For example, a difference in the photoelectrochemical behavior of n-GaN in 1 M H₂SO₄ and 1.2 M HCl was observed in [104], which is due to the fact that they both are acidic solutions but with and without the presence of chlorine. It turned out that n-GaN samples in HCl were less attacked than in H₂SO₄, although both solutions were acid. This is because the concentration of holes, causing the photo-oxidation at the n-GaN surface under UV excitation, is much lower in HCl than in H₂SO₄. Huygens *et al.* reported that in HCl the n-GaN surface is stabilized against photoanodic dissolution. Furthermore, the stabilization of n-GaN increased with an increasing Cl⁻ ion concentration [104]. It was additionally found out, that the shift of E_{fb} under illumination is higher in H₂SO₄ than in HCl, meaning that the concentration of holes accumulating at the n-GaN surface is lower in HCl [104]. This is explained by the fact that the photogenerated holes are probably captured by intrinsic surface states and then transferred to the Cl⁻ ions at the n-GaN surface [104]. The involvement of intrinsic surface states is also described in [91]. By this competing reaction of Cl⁻ oxidation, the holes cannot contribute to the dissolution of n-GaN and thus stabilize the n-GaN surface from photo-oxidation and a subsequent anodic decomposition [111]. Thus, the oxidation of Cl⁻ ions occurs more easily than water oxidation [105]. Thereby, the Cl⁻ ions act as hole capturing agents, meaning that the formation of Ga₂O₃ on n-GaN is suppressed. Minsky *et al.* observed etching of n-GaN surfaces in diluted HCl with an etch rate of a few hundred Å min⁻¹, whereas it was a few thousand Å min⁻¹ in KOH [28], indicating the protective function of Cl⁻ ions. Furthermore, they found out that the presence of Cl⁻ ions had no effect on the photocurrent values, confirming that only holes are involved in the photoanodic dissolution of n-GaN [111].

In a study of Tu *et al.* the behavior of n-GaN in HCl and NaCl electrolytes was compared. It was reported that more dissolved amounts of Ga³⁺ ions were detected by the ICP-MS technique in HCl

than in NaCl, indicating that the n-GaN degradation is more severe in HCl [23]. All in all, there are differences in chlorine containing electrolytes – the use of NaCl significantly improves the stability of n-GaN compared to HCl.

In this work, since the photo-oxidation of n-GaN is suppressed in NaCl due to the competing reaction of Cl_2 evolution, almost no N_2 evolution as shown in equation 3.5 takes place, leading barely to a dissolution of Ga^{3+} ions. This in turn caused no distinct formation of a Ga_2O_3 layer on the n-GaN surface and thus, no increased oxygen content could be measured by EDX.

It is obvious that the oxide formation could not be completely suppressed after 72 hours, especially since a relatively low NaCl concentration of 0.1 M was used, but for pure n-GaN in NaCl it was sufficient enough that no increase of the oxide content could be verified, e.g., by EDX measurements (cf. table 6.2). Also in the SEM images for n-GaN in NaCl in figure 6.3 (c), no oxide-like structures (like, e.g., Ga_2O_3 nanorods in H_2O) could be determined.

As also in case of the NaCl/365nm/14d method (cf. figure 6.13 (b)), despite some NaCl sedimentations, no oxide formation was observed on the n-GaN surface – it remained unchanged and was not attacked.

It might also be due to the fact that the solution over 14 days turned to a strong acid pH value, causing the final dissolution. This leads to the assumption that obviously there was still an excess of Cl^- ions in solution, hindering the formation of Ga_2O_3 . The endless supply of Cl^- ions might be due to the relatively high volume of approx. 20 ml solution in the crystallizing dishes.

It needs to be considered that although O_2 evolution is thermodynamically preferred (and thus also takes place on n-GaN in NaCl), the Cl_2 evolution is more likely due to the lower overpotential.

n-GaN under UV excitation in aqueous media under the presence of metals

In case of deposited metals, the n-GaN samples both in H₂O and NaCl degraded under UV light, independent whether they were stressed for 72 hours or 14 days.

In principle, the occurring reaction mechanisms at the n-GaN–electrolyte interface are the same as for pure n-GaN samples, also concerning the role of the electrolyte.

Water splitting reactions occurred. The evolution of gaseous H₂ occurred also before locally from the pure n-GaN sample surfaces. The metal stripes show a tendency towards a cathodic character compared to the n-GaN photoanode surface. The H₂ evolution according to equation 2.5 is now expected to happen from the deposited metal surface.

The evolution of gaseous O₂ (as counter part to the H₂ formation), N₂, or Cl₂ (in case of NaCl) from the n-GaN surface takes place from the n-GaN areas themselves, including the n-GaN areas, that are covered with the deposited metal stripes (see equations 2.6, 2.7, and 3.5). The above lying metal stripes work as barriers, hindering the evolving gases from being released. Metal thicknesses of 100 nm were obviously thin enough so that the evolving gases could diffuse through. When the metals were sufficient thick (e.g., in case of 300 nm), the barrier was too high and the evolving gases could not pass through, but rather were blocked. This explains the formation of small bubbles as they were observed, e.g., on the sample with the silver stripes as shown in figure 6.11. As described before, these bubbles in case of silver had diameters of around 10 μm to 200 μm and were approx. 4 μm high.

Photo-oxidation reactions for n-GaN under metal influence took place more intense than without metal stripes. The changes of the elemental compositions were most distinct for nickel and silver as metals, as determined by EDX measurements, resulting in a decreased

nitrogen content down to 0.8 at% and an increase of the oxygen species up to 66.7 at% in case of nickel (cf. table 6.3).

Figure 6.24 gives an overview of occurring reactions of an n-GaN sample in H₂O, excited with UV light. The presence of nanorod structures containing Ga₂O₃ as observed for pure n-GaN in H₂O was replaced by a layer of coral-like structures which covered the whole n-GaN surface (cf. figure 6.7 (c)). Thus it can be concluded that the complete n-GaN surface was photo-oxidized especially close to the metal stripes. This is probably caused by an increased accumulation of holes at the metal stripes since they are more negatively charged than n-GaN. Thus, a gradient is formed, in which the oxidation of n-GaN is strongest close to the metals and decreases with increasing distance from the metal stripes. In case of H₂O, the formed Ga₂O₃ layer was not dissolved due to the pH value as discussed before in case of pure n-GaN.

Surprisingly, also n-GaN stressed with NaCl under metal influence was photo-oxidized as can be seen in the right SEM image in figure 6.7 (c) – contrary to pure n-GaN in NaCl. By EDX measurements, a significant change of oxygen and nitrogen contents was determined, leading to the assumption that also a Ga₂O₃ compound formed. Especially in case of silver and platinum the changes were severe, resulting in a decreased nitrogen content of 2.0 at% and an increased oxygen species of 62 at% for platinum (cf. table 6.3). Although the changes of the nitrogen and oxygen content in principle were stronger in H₂O than in NaCl, the morphology of the formed Ga₂O₃ layer in NaCl was nearly the same as in H₂O.

The oxide layer on n-GaN stressed with the NaCl/365nm/72h method was also confirmed by XPS measurements in the section before. For example, an increase of the O 1s peak at 530 eV was observed for the stressed sample (cf. figure 6.22 (b)). This peak clearly corresponds to the Ga₂O₃ compound. The phenomenon of n-GaN oxidation in aqueous solutions was also discussed in Tu *et al.*, which performed XPS analysis on a stressed n-GaN sample that was

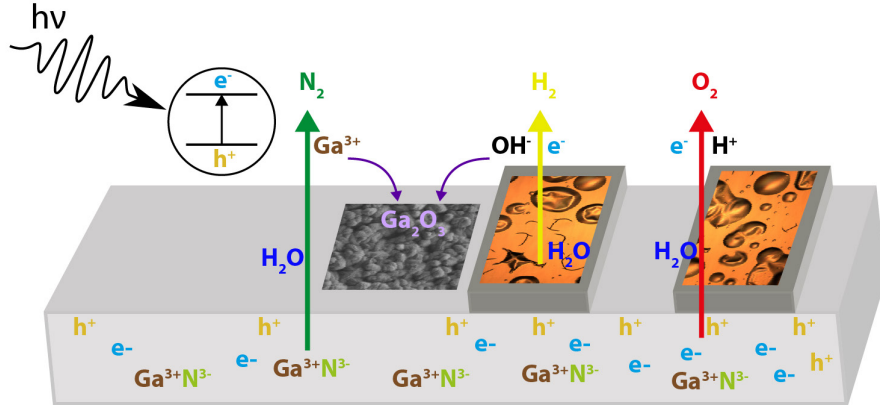


Figure 6.24: Model sketch of an n-GaN sample under metal influence in H_2O which is excited with UV light. The accumulation of holes at the n-GaN surface occurs especially intense close to the metal stripes. Photo-oxidation takes place, leading to the evolution of gaseous N_2 and the formation of a Ga_2O_3 layer on the n-GaN surface. These coral-like structures cover the whole surface especially close to the metal area. Due to the pH value of H_2O they do not dissolve and thus protect the underlying n-GaN surface. When gases evolve from n-GaN under the deposited metal stripes, small bubbles are formed in the metal layer. See text for discussion.

measured in a PEC with a Pt CE at zero potential in a two-electrode system for four hours in 1 M NaCl [23]. They reported that the Ga 2p peak of the stressed sample shifted to a higher binding energy value of approx. 1118.63 eV compared to a reference sample peak at approx. 1118.28 eV, indicating a surface oxidation of n-GaN in NaCl. The peak corresponded to Ga_2O_3 and by performing a depth profile this oxide layer had a thickness of approx. 2 nm [23]. In the present work, a slight shift at around 1118.20 eV was also seen in the XPS spectra (not shown), but due to the insufficient measurement and analysis performance it could not precisely distinguished whether the shift corresponded to such an oxide phase.

The n-GaN sample, stressed with the NaCl/365nm/14d method on the other hand (cf. figure 6.13 (b)) showed nanorod-like structures, consisting of Ga_2O_3 as measured by EDX. Surprisingly, compared to 72 hours, the density of Ga_2O_3 thus decreased after longer exposure time and the underlying n-GaN surface became visible. This was also noticed by EDX data (cf. table 6.3 and 6.5). This dissolution of the oxide might be due to a weak adsorption of Ga_2O_3 to the n-GaN layer, leading to its ablation after 14 days. As already observed for the $\text{H}_2\text{O}/365\text{nm}/14\text{d}$ method, the underlying n-GaN surface was not further attacked.

Contrary to pure n-GaN samples, where the oxidation in H_2O was observed across the whole n-GaN surface, strong, local degradation of n-GaN surfaces under metal influence was observed, which was especially distinct in-between and close to the deposited metal stripes.

It can be concluded that the metals on the n-GaN surface are responsible for this degradation gradient. In any cases, the metal obviously behaves always more noble than the n-GaN surface – thus the standard electrode potential of the metal and its ability to get oxidized or reduced plays a minor role. Additionally, the n-GaN surface as photoanode is charged positively due to the accumulating holes at the surface and the metals in turn show more negative character since they work as cathodic centers. Consequently, the holes will accumulate preferential at the n-GaN surface close to the metal stripes, which explains the strong n-GaN surface attack around the metal areas due to the increased N_2 evolution and following formation of Ga_2O_3 .

The strong degradation can be also explained by a reduction of the band bending close to the metals, which facilitated the accumulation of holes at this area. Tu *et al.* studied the behavior of gold nanoparticles on n-GaN and p-GaN surfaces during photoelectrochemical experiments [35]. They reported that due to the formation of metal induced gap states a strong Fermi level pinning occurs that alters the behavior of the GaN–electrolyte interface. This causes a shift of the

semiconductor band edges and variations of band bending, depending on the semiconductor type. In case of n-GaN, the band bending was decreased by the presence of deposited gold [35]. This reduction of band bending (cf. figure 2.1 (a)) leads to a higher accumulation of photogenerated holes at the interface.

In case of NaCl as electrolyte, the density of holes is much higher close to the metal stripes than the chloride ion density, which is still equally distributed across the n-GaN surface. Thus, the protection by a competing oxidation of chloride ions is not as distinct as it was for pure n-GaN, leading to the evolution of N_2 and O_2 of the n-GaN surface in NaCl.

The polarity of n-GaN is also important in understanding the reactions under UV illumination in aqueous solutions. As mentioned in the beginning, Ga face GaN was used in this work. Zhuang *et al.* reported that based on XPS measurements, there are polarity selective differences in conventional etching. Due to different states of surface bonding, the etching characteristics of Ga and N polar crystals are different [14]. In general, N-face GaN is etched in basic solutions because the OH^- ions can be easily adsorbed on the sample surface due to the negatively charged N-dangling bonds, thus enabling the subsequent photo-oxidation reaction. On the other side, Ga-face GaN remains stable in acids because there is a repulsion between the OH^- ions and the three occupied dangling bonds of N_2 , which prevent OH^- ions from attacking the Ga atoms [14]. To summarize, n-GaN is locally oxidized under UV light in aqueous media under the presence of metals. This behavior was especially distinct close to the metal coatings.

The influence of metals accelerates the photo-oxidation of n-GaN for both H_2O and NaCl solutions. Close to the metal areas, the band bending is decreased, thus attracting the holes at the surface close to the metal areas, where they probably accumulate in high densities and the effect of oxidation is increased. In case of NaCl, Cl_2 evolution is suppressed and with it the formation of Ga_2O_3 is enabled.

n-GaN under UV excitation and the influence of NiO particles in aqueous media

NiO is known as a p-type semiconductor which has a high hole mobility for what it is amongst others applied as a hole transport layer in organic photovoltaics [183]. It has a higher valence band edge energy than GaN [184]. Due to its staggered band alignment with GaN, NiO particles are used as oxidation co-catalysts. The use of NiO for efficiently generated H_2 by solar water splitting is of high interest, since it is a low-cost and easy fabricable material which furthermore is reported to stabilize the n-GaN surface and protects it from etching in NaOH [119, 120, 178]. Already few NiO particles provide an efficient and stable n-GaN photoanode [120]. Ohkawa *et al.* reported of an improvement of efficiency with n-GaN–NiO photoelectrodes [119], since the photo-oxidation took place at the NiO particles, leaving the n-GaN surface unchanged. Additionally, a recombination of electron and holes was suppressed and the photocurrent increased [178].

This was also seen in this work from the CV curves presented in figure 5.10 in the previous chapter. The improvement of the photocurrent at +1 V vs. Ag/AgCl was around 46 % due to the NiO catalyst particles, which collected the accumulated holes from the n-GaN surface. By that, holes were efficiently transferred to the electrolyte, where the redox reactions could take place. Due to the fast separation of the photogenerated charge carriers, the recombination was suppressed and thus the photocurrent increased for the n-GaN sample with NiO particles.

Also, the improvement of stability of n-GaN samples with NiO catalyst particles could be clearly seen in the photoinduced degradation experiments. The elemental composition of n-GaN under NiO influence did not change (cf. 6.6) and only sedimentation of NaCl crystals was spread across the n-GaN surface (cf. figure 6.17 (a, c)). By collecting the accumulated holes from the n-GaN surface which then not further contribute to photo-oxidation reactions, the NiO

particles work as catalytic centers and were oxidized instead of the n-GaN surface.

6.2.2 p-GaN under UV excitation in aqueous media

In general, it is reported that p-type semiconductors in aqueous solutions under UV excitation are stable against photocorrosion [9, 34, 90]. This can be explained by considering the band bending of E_{cb} and E_{vb} of the p-GaN electrode as shown in figure 2.1 (b). The photogenerated holes, driving the evolution of O_2 and N_2 according to equation 2.6 and 3.5, diffuse to the bulk. Since these photogenerated holes are not available anymore at the p-GaN–electrolyte interface, the evolution of N_2 and the subsequent Ga_2O_3 formation on the p-GaN surface are blocked.

p-GaN under UV excitation in H_2O and NaCl

Although H_2 evolution takes place from the p-GaN photocathode, also little O_2 will evolve from its surface as counter reaction due to a missing CE in the photoinduced degradation experiment. As already mentioned for n-GaN, since no external potential was applied, the reaction rate for water splitting was low, but even under OCP conditions as in the photodegradation setup, some small cathodic and anodic partial reactions probably took place.

The whole mechanism of p-GaN under UV excitation in case of H_2O is depicted in figure 6.25.

Contrary to EDX measurements on n-GaN samples, no elemental changes of the p-GaN surfaces were detected (cf. table 6.2). The processes occurring at the p-GaN–electrolyte interface are most likely different ones than for n-GaN. Under all applied stress conditions (aqueous solutions, 365 nm excitation, with or without metal presence), the p-GaN surfaces remained unchanged and were not attacked,

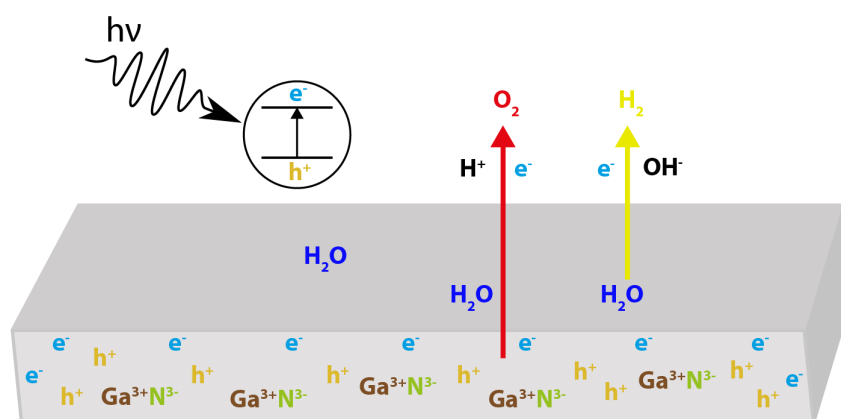


Figure 6.25: Model sketch of a p-GaN sample in H_2O which is excited with UV light. Due to the energetic positions of the redox potentials and band edges in GaN, only little water splitting reactions take place from the p-GaN surface, meaning the evolution of H_2 and O_2 . No photo-oxidation reaction occurs. See text for discussion.

since the photo-oxidation reactions were suppressed, due to the band bending. Even in case of NaCl, Cl_2 evolution can be excluded, since it originates from the oxidation of holes.

This is also true for long-term stress of 14 days. The p-GaN surface remained unchanged (cf. figure 6.14 (b) and the corresponding EDX data in table 6.5). The hexagonal V-pits obviously attracted dried NaCl crystals to locate, but no further impact was recognized.

What also plays an important role is the fact, that the 200 nm thin p-GaN layer due to practical reasons is grown on an n-GaN buffer layer. Since the underlying n-GaN layer is isolated during experiments, the interaction with the electrolyte practically can be excluded. But it is still possible that the underlying n-GaN responds to the incoming UV light due to the transmission of p-GaN for 365 nm, thus it is not certain, which reactions exactly occur at the interfaces.

It needs to be mentioned that the mechanism for the reactions of p-GaN in aqueous solutions under UV light excitation are not as understood as for n-GaN. Less is reported about it in literature.

p-GaN under UV excitation in aqueous media under the presence of metals

As can be seen in figures 6.8 and 6.9, the p-GaN surfaces under metal influence were not attacked and the elemental composition did not change, as found out by EDX measurements. On the other hand, the deposited metals partially tarnished from the p-GaN surface and partially re-deposited somewhere else on the p-GaN surface.

Figure 6.26 shows the depicted principles of reactions occurring on the p-GaN surface in H₂O when excited with UV light. Similar as for n-GaN, by excitation of p-GaN with UV light, electron-hole pairs are generated. Again, as for pure p-GaN, the evolution of gaseous H₂ and O₂ takes place according to equations 2.5 and 2.6. Due to the behavior of p-GaN as photocathode, H₂ evolves from the p-GaN surface, where electrons accumulate due to the band bending as shown in figure 2.1 (b). On the other hand, O₂ evolves from the metal stripes, which are charged more positive compared to the p-GaN surface.

As a side reaction, taking place parallel to the O₂ evolution from the metals, the metals themselves are oxidized, leading to a dissolution of the metal ions Meⁿ⁺. They get reduced by reacting with electrons and re-deposit again on the p-GaN samples surface, which was measured as metal traces by EDX (cf. table 6.4). The corresponding reaction equations are the following:



and



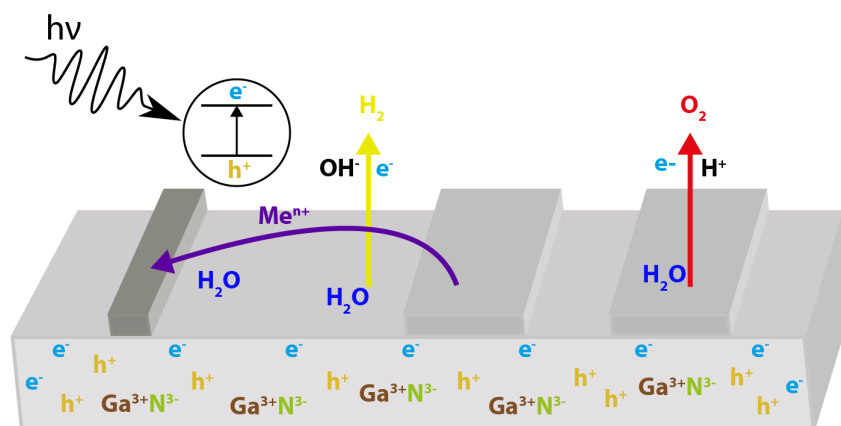


Figure 6.26: Model sketch of a p-GaN sample under metal influence in H_2O which is excited with UV light. The electrons diffuse to the interface whereas the holes migrate to the p-GaN bulk, leading to no attack of the p-GaN surface. H_2 primarily evolves from p-GaN, whereas O_2 evolution takes place from the metal, which simultaneously leads to an oxidation of the metal. The metal detaches from the p-GaN and gets re-deposited somewhere else on the p-GaN samples surface. See text for discussion.

Especially in case of nickel in NaCl, the re-deposition along the border was very distinct (cf. figure 6.9) and clustered. This concentrated re-alignment of dissolved metals was not as strong for the other applied metal types. Based on EDX data it can be assumed that they more or less homogeneously covered the p-GaN surface. In case of NaCl, due to its higher conductivity, the detachment and transport of the diluted metal species is enhanced, which explains the more intense tarnishing and re-deposition, e.g., in case of nickel (cf. figure 6.9).

Tu *et al.* studied the behavior of gold nanoparticles on n-GaN and p-GaN surfaces during photoelectrochemical experiments [35]. In case of p-GaN samples, the band bending of p-GaN was increased under the presence of Au nanoparticles (contrary to n-GaN), thus hindering the transfer of holes to the Cl^- ions in solutions. Additionally, the

H₂ evolution is promoted. They observed that the deposition of gold nanoparticles enhances the photoelectrochemical activity of p-GaN and furthermore improves its stability under illumination [35].

Thus, comparable to NiO, the metals in case of p-GaN also work as kind of co-catalysts since they prevent further attack. The behavior of the deposited metals as sacrificial electrodes prevents the p-GaN surface from photo-oxidation – contrary to n-GaN under metal influence. The photo-oxidation of p-GaN was suppressed. In case of NaCl it can be assumed that no Cl₂ evolution took place. Surprisingly, SIMS measurements on p-GaN stressed with the 100nmAg/NaCl/365nm/72h method showed an increase of the O⁻ signal at the surface (cf. figure 6.19), although the photo-oxidation of the p-GaN surface is expected to be suppressed. The question why this increased O⁻ signal was measured remains unanswered.

The discussion in this section referred to pure GaN material in solution, without the presence of any other electrode. Due to band bending under UV light excitation, different mechanisms occurred. In case of n-GaN on the one hand, the holes accumulated at the interface, causing a photo-oxidation of n-GaN. This included the dissolution of n-GaN due to evolving N₂, and the dissolved Ga³⁺ ions formed Ga₂O₃ on the n-GaN surface. Due to the pH value, the oxide did not dissolve, in fact, leading to an oxidation of n-GaN, but also protected it from further decomposition. This oxide layer was hindered in case of NaCl, where the holes preferentially oxidized the Cl⁻ ions to Cl₂, thus a photo-oxidation took barely place. In case of the presence of metals, the formation of Ga₂O₃ on the n-GaN surface was observed for both electrolyte types, especially close to the metal areas, where an increased hole concentration can be expected. For p-GaN samples on the other hand, no photo-oxidation occurred due to the accumulation of electrons at the interface, which do not cause photo-oxidation. Thus, the p-GaN surfaces themselves remained unchanged. This was also reported by other groups [185, 186]. In case of the presence of

metals, due to the anodic behavior of metals, they oxidized and by reduction re-deposited elsewhere on the p-GaN sample surface.

6.3 Dark conditions – pure electrical stress applied to GaN (electrolysis)

Until now, all observations and discussions concerning the stability of GaN samples are based on the results that were received from the photoinduced degradation experiments in section 6.1. The samples were in aqueous solutions (with or without the presence of metals) and were stressed only by light excitation. Under an UV illumination of 365 nm, a photo-oxidation of the n-GaN surface took place whereas the p-GaN samples remained unchanged.

In this section it is investigated, whether under these dark conditions an externally applied electric potential is able to cause changes on GaN as electrode. In the following, the stability of GaN samples in a PEC with a platinum CE and applied potentials are investigated. In principle, H_2 is evolving from the Pt electrode, whereas from the n-GaN WE O_2 and N_2 evolve, leading to photo-oxidation at the n-GaN surface. In case of p-GaN due to the anodic potential, H_2 as well evolves from the platinum CE. As described in the beginning of this chapter, these dark corrosion and photoassisted electrolysis experiments referred to the photoelectrochemical measurement techniques, were an additional external potential is be applied to the samples.

The selected external potential was chosen as +3 V vs. Ag/AgCl, since it represents an extreme value in the anodic region. For n-GaN samples, which work as photoactive anode as shown in section 5.2.1, this potential is definitely able to trigger an oxidation reaction at the n-GaN surface and is also connected to the decomposition of the

electrolyte, since it exceeds their potential windows. The interesting question is, whether this applied external potential is sufficient enough to drive reactions under dark conditions, i.e. missing UV light excitation. Also for p-GaN on the other hand, which works as weak photoactive cathode as shown in section 5.2.2, it is investigated whether an oxidation of the surface is possible under this applied positive potential, since p-GaN samples surfaces in aqueous media did not show any reaction under pure UV light excitation.

Dark conditions in this section refer to the fact that GaN samples were investigated in the PEC under room light conditions. The PEC could not be covered with a black plastic lid as in the photoinduced experiments due to practical reasons. Still, GaN samples are not excitable under these room light conditions (cf. figure 5.6 (a)).

A duration of 24 hours was chosen as typical measurement time and the corresponding CA curves were recorded. The electric charge Q was calculated according to equation 2.11 and from that the charge density in C/cm^2 could be determined. After measurements it was always checked whether the GaN samples were still properly contacted to ensure the accuracy of the obtained measurement results. This was the case in all results presented in this work.

6.3.1 Influence of the electrolyte under dark conditions

Analogous to the photoinduced degradation experiments, the role of weak and well conductive electrolytes on GaN samples is investigated. Thus, pure GaN samples are stressed with the $H_2O/dark/+3V/24h$ or $NaCl/dark/+3V/24h$ method. Figure 6.27 shows images of the stressed samples, indicating no changes neither on n-GaN nor p-GaN samples. In case of n-GaN, the border line of the immersed and dry area can be seen.

EDX measurements on the sample surfaces are made as quantitative analysis and the data are shown in table 6.7. Compared to the values

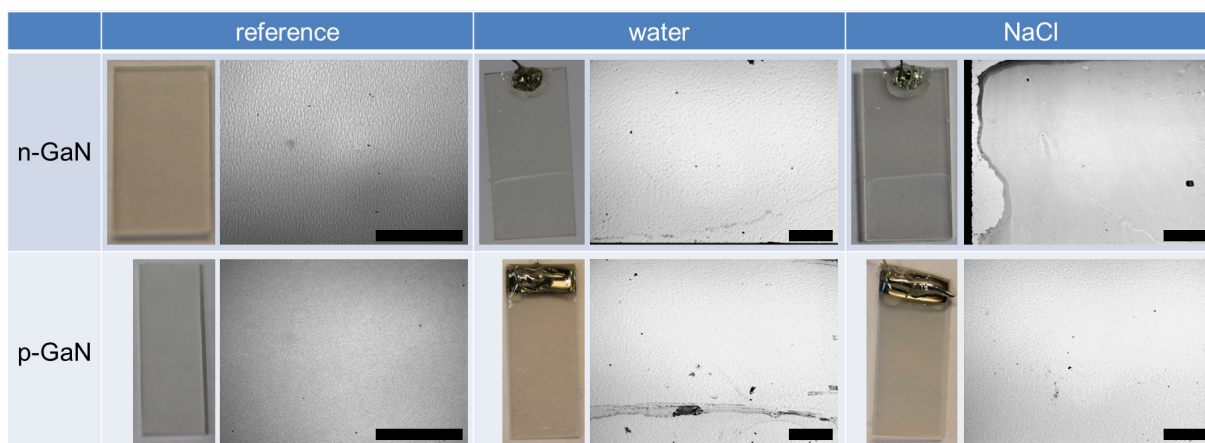


Figure 6.27: Photos and light microscopy images of GaN samples, stressed with the $\text{H}_2\text{O}/\text{dark}/+3\text{V}/24\text{h}$ and $\text{NaCl}/\text{dark}/+3\text{V}/24\text{h}$ method. Scale bars: 1 mm.

of the corresponding reference samples, no changes of the elemental composition of the stressed GaN samples can be found. For each sample, the determined charge densities are in the range of about 10^{-3} C/cm^2 . Thus, without exciting UV illumination, they are nearly in the same range.

Nowak *et al.* reported that an etching of Ga-face n-GaN is possible under dark conditions with an applied external potential [172]. On the other hand it was reported that GaN samples with a Ga polarity are more stable under an anodic applied potential [14]. The higher resistance towards corrosion may be the case also for the Ga-face samples used in this work.

6.3.2 Influence of metal coating under dark conditions

Also, the influence of metal stripe coating and its role in GaN stability behavior was investigated. Exemplarily, 100 nm thick silver stripes were chosen and so the GaN samples were stressed in the PEC with the $100\text{nmAg}/\text{H}_2\text{O}/\text{dark}/24\text{h}$ and $100\text{nmAg}/\text{H}_2\text{O}/\text{dark}/24\text{h}$ method.

6.3 Dark conditions – pure electrical stress applied to GaN (electrolysis)

Table 6.7: EDX data recorded on GaN samples stressed with the H₂O/dark/+3V/24h or NaCl/dark/+3V/24h method. No changes of the elemental composition was measured – all samples remained unchanged under the given conditions. The corresponding electric charge densities are calculated from the CA curve data.

	n-GaN			p-GaN		
	reference	H ₂ O	NaCl	reference	H ₂ O	NaCl
charge density (10 ⁻³ C/cm ²)		14.4	1.28		0.952	7.20
Ga (at%)	47.1	52.3	49.0	50.1	51.5	44.0
N (at%)	45.1	43.5	42.1	43.1	43.1	49.5
O (at%)	1.5	0.1	1.4	1.1	0.2	0.7

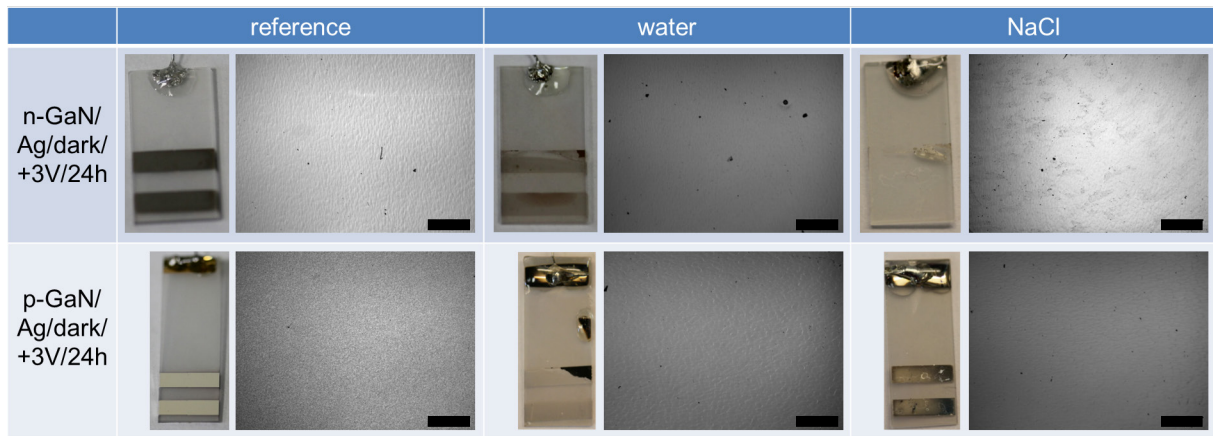


Figure 6.28: Photos and light microscope images of GaN samples stressed with the 100nmAg/water/dark/+3V/24h and 100nmAg/NaCl/dark/+3V/24h method. All GaN surfaces remained unchanged, whereas the metals more or less strongly detached from the samples. Scale bars: 500 μ m.

Those metal stripes were deposited at the lower third of every sample and it was considered that both silver stripes were immersed in the electrolyte.

Figure 6.28 shows GaN samples treated with the 100nmAg/H₂O/dark/+3V/24h and 100nmAg/NaCl/dark/+3V/24h method. Contrary to the silver stripes, which well adhered to the n-GaN surfaces under photoinduced experiments in section 6.1, the silver under an applied anodic potential started detaching in H₂O and finally completely dissolved in NaCl as electrolyte. As shown in the model for n-GaN in figure 6.23, the n-GaN surface, due to its function as photoanode is already positively charged, whereas the deposited silver on its surface has a negative character. Due to the additional applied strong positive potential of +3 V vs. Ag/AgCl, the rather negative charged silver finally blasts away. The almost complete dissipation of silver in NaCl was probably caused due to its better conductivity. As for n-GaN, no changes of the p-GaN surfaces could be determined (cf. figure 6.28). The metals almost completely detached from the p-GaN surface. This detachment was stronger in H₂O than in NaCl solution, which is contrary to n-GaN where an inverted behavior could be observed. The corresponding EDX data are listed in table 6.8. The elemental compositions of all GaN samples did not change, thus it can be stated that both n-GaN and p-GaN surfaces remained not attacked and did not undergo oxidation. No traces of silver were measured. This means that for n-GaN, even though the metals dissolved from the surface they did not re-deposit elsewhere on the sample surface, probably due to the behavior as photoanode.

The generated charge densities in table 6.8 in case of n-GaN in H₂O are comparable with and without silver stripes. In NaCl without silver, an electric charge density of $1.28 \cdot 10^{-3} \text{ C/cm}^2$ was estimated, whereas it was $5.96 \cdot 10^{-3} \text{ C/cm}^2$ under presence of silver. For p-GaN, the calculated charge densities with and without silver in NaCl were in the same range. In H₂O, the generated electric charge density for p-GaN increased due to the presence of silver by factor two.

It can be concluded that even under the application of a high positive anodic potential, no reactions on the GaN surfaces took place under dark conditions. Only a more or less strong detachment of the

6.3 Dark conditions – pure electrical stress applied to GaN (electrolysis)

Table 6.8: EDX data recorded on GaN surfaces that were treated with the 100nmAg/H₂O/dark/+3V/24h and 100nmAg/NaCl/dark/+3V/24h method. No changes in the elemental compositions as well as no traces of silver were measured. The calculated electric charge densities are highest for p-GaN/Ag in NaCl.

	n-GaN			p-GaN		
	reference	Ag, H ₂ O	Ag, NaCl	reference	Ag, H ₂ O	Ag, NaCl
charge density (10 ⁻³ C/cm ²)		47.8	5.96		11.7	6.60
Ga (at%)	47.1	47.0	46.8	50.1	49.6	52.0
N (at%)	45.1	44.6	45.5	43.1	44.0	43.3
O (at%)	1.5	0.7	1.4	1.1	0.7	0.5
Ag (at%)	–	0.0	0.0	–	0.0	0.0

silver stripes occurred, which seems to be quite arbitrary. In case of p-GaN, no re-deposition of silver on the p-GaN surface could be proven. This is another provided evidence that no reactions at the GaN–electrolyte interface are triggered under dark conditions.

Long-term stress under dark conditions

From the 24 hours measurements conclusions can be drawn that pure electrical stress applied on GaN in aqueous media does not lead to changes on the GaN surfaces. GaN electrodes were not attacked. To see whether this might change for a longer period of time, a long-term external potential was applied for 60 hours. It turned out, that even under the NaCl/dark/+3V/60h method, the stability of the GaN samples did not change – both n-type and p-type GaN remained stable. EDX measurements (not shown) confirm that no changes in the elemental composition took place.

It can be concluded that even a long-term applied external potential of +3 V does not lead to any changes on the GaN surfaces under dark conditions. Due to the very low currents in the nA range, no high amounts of electric charge could be generated. Therefore, it is interesting to study both the influence of an external applied positive potential and UV light excitation to investigate the stability of GaN samples in aqueous solutions.

6.4 Photo- and electrical stress on GaN (photoassisted electrolysis)

The photoinduced degradation experiments, where GaN was stressed in solution under pure UV light excitation, showed photo-oxidation of n-GaN which even increased under presence of metals. On the contrary, the p-GaN surface remained unchanged. In the previous section it was shown that dark conditions under an applied positive anodic potential have no effect on the surfaces of GaN samples. In this section, a combination of both light induced stress as well as an externally applied potential are used as stress parameters. Analogous to the dark electrolysis measurements described in section 6.3, GaN samples were stressed at an anodic potential of +3 V vs. Ag/AgCl for 24 hours – but now under UV light excitation at 300 nm, realized by the monochromator setup. At a wavelength of 300 nm, an intensity of approx. 3 mW/cm² reached the sample surface.

6.4.1 Influence of the electrolyte in photoassisted electrolysis

GaN samples were studied with the H₂O/300nm/+3V/24h and NaCl/300nm/+3V/24h method. Photos of the samples as well as light microscopy images are shown in figure 6.29. On the n-GaN samples in both H₂O and NaCl, a whitish layer on the surface can

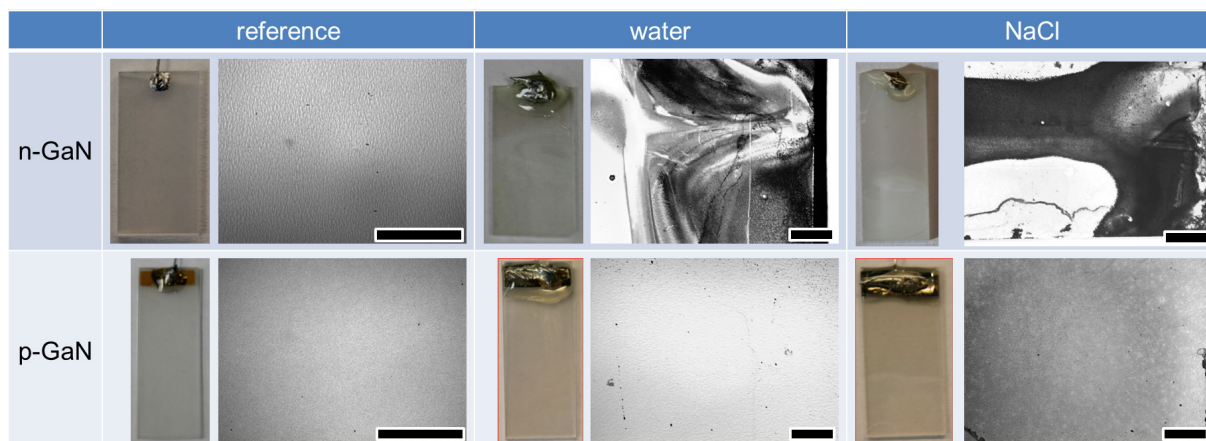


Figure 6.29: Photos and light microscopy images of reference and stressed GaN samples, treated with the $\text{H}_2\text{O}/300\text{nm}/+3\text{V}/24\text{h}$ or $\text{NaCl}/300\text{nm}/+3\text{V}/24\text{h}$ method. The n-GaN surfaces were attacked in the electrolytes, whereas the p-GaN samples remained unchanged. Scale bars: 1 mm.

be seen – by eye as well as under the microscope, probably a Ga_2O_3 phase. The p-GaN samples in figure 6.29 on the other hand showed no phenomenological changes (except for NaCl, where again the border of dried whitish NaCl crystal layer can be seen on the surface).

EDX measurement data are presented in table 6.9. For H_2O , the nitrogen content slightly decreased to 40.2 at%, whereas for NaCl it decreased even more to 32.1 at%. The oxygen content increased minimal to 3.7 at% for H_2O and even more to 10.5 at% for NaCl. This is a sign for oxidation of the n-GaN surfaces. In case of n-GaN, where photogenerated holes accumulate at the interface (cf. figure 2.1 (a)), an increased photo-oxidation reaction is expected, intensified by the additional applied anodic potential. The depletion of the space charge region is caused since the applied potential is greater than the flat band potential of n-GaN. Thus, gaseous N_2 evolves, and the dissolved Ga^{3+} ions in solution form Ga_2O_3 . The excess electrons diffuse into the bulk of n-GaN and thus are transported by the electrical contact to the CE, where they are consumed by the corresponding reduction

reaction. Compared to the photoinduced degradation experiments in section 6.1 on pure n-GaN samples, where a beginning oxidation was quantitatively observed for n-GaN in H₂O, photo-oxidation of n-GaN takes also place under an additional applied potential of +3 V in NaCl. Obviously, the Cl⁻ ions which provided protection due to the reaction with the holes at the surface, still react to form gaseous Cl₂ according to equation 2.7, since during CA measurements in NaCl, a chlorine smell could be determined. Huygens *et al.* reported that an applied anodic potential is strongly connected with the evolution of gaseous Cl₂ [111]. But simultaneously, also N₂ can evolve due to an increased number of holes, which are additionally generated by the anodic potential. Probably because the overpotential of the N₂ evolution is smaller than the protective Cl₂ evolution under the applied anodic potential of +3 V, photo-oxidation takes also place in case of n-GaN in NaCl. Several groups report from anodic etching of n-GaN [111, 115, 127, 134, 142, 187]. In our case, due to the pH value of the electrolytes, the n-GaN samples were not etched since the grown Ga₂O₃ layers did not dissolve. The p-GaN samples on the other hand under this photoassisted electrolysis conditions did not show any changes in their elemental composition.

The corresponding calculated electric charge densities, which are also presented in table 6.9, were magnitudes higher under 300 nm illumination,

This indicates the big importance of UV light on driving reactions at the GaN–electrolyte interface compared to the electric charge densities calculated for dark conditions as shown in table 6.7. The lower charge densities for p-GaN, compared to n-GaN, are due to the generally very low flowing current densities as already discussed when applying p-GaN as WE in section 5.2.2.

Figure 6.30 exemplarily shows recorded CA curves for GaN samples under dark conditions and 300 nm illumination under an applied potential of +3 V. A current density drop of approx. factor four can be seen for n-GaN under 300 nm illumination whereas it was half as

Table 6.9: EDX data measured on GaN samples, stressed with the H₂O/300nm/+3V/24h or NaCl/300nm/+3V/24h method. While n-GaN samples show sign of oxidation, the p-GaN samples remain stable in their elemental composition. The determined electric charge densities are higher for n-GaN than for p-GaN.

	n-GaN			p-GaN		
	reference	H ₂ O	NaCl	reference	H ₂ O	NaCl
charge density (C/cm ²)		28.68	21.28		0.143	0.880
Ga (at%)	47.1	47.4	45.1	50.1	51.3	49.2
N (at%)	45.1	40.2	32.1	43.1	43.0	40.2
O (at%)	1.5	3.7	10.5	1.1	0.4	1.9

much under dark conditions. This strong decrease under 300 nm is probably due to the fact that only a small fraction of photogenerated charge carriers can contribute to the photocurrent due to the blocking oxide layer. The recorded current densities for p-GaN were at a constant level, but generally much lower than in case of n-GaN.

Analogous to figure 6.5 in section 6.1.3, a photo from a stressed sample under the UV lamp was taken. In figure 6.31, exemplarily in this case, an n-GaN sample treated with the H₂O/300nm/+3V/24h method is shown. The part of the stressed sample, which was immersed in the electrolyte and also refers to the active area, shows a significantly lowered or almost not existing emission, compared to the reference n-GaN sample, which emits light homogeneously. This again is evidence of the attack of an n-GaN sample under above conditions.

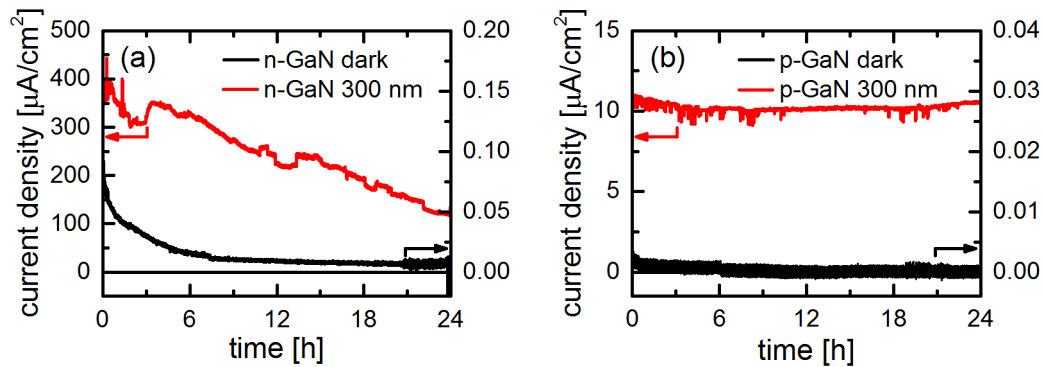


Figure 6.30: CA curves of n-GaN (a) and p-GaN samples (b), stressed with the NaCl/dark/+3V/24h and NaCl/300nm/+3V/24h methods (black and red curves, respectively). The current densities are orders of magnitudes lower for p-GaN. The influence of UV light on the current density can be clearly seen. The measured photocurrent density is in the $\mu\text{A}/\text{cm}^2$ region, whereas under dark conditions the current density is in the nA/cm^2 range. This is also reflected in the generated charge densities shown in the corresponding tables.

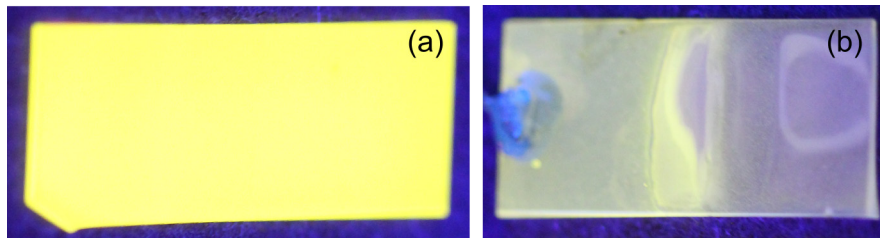


Figure 6.31: Photos taken under a UV lamp from an n-GaN reference (a) and an n-GaN sample stressed with the $\text{H}_2\text{O}/300\text{nm}/+3\text{V}/24\text{h}$ method (b). The emission is uniform on the reference sample and clearly weakened on the active area of the stressed sample where it was in contact with the electrolyte and excited with 300 nm.

6.4.2 Influence of metal coating in photoassisted electrolysis

Beneath pure samples, also the behavior of GaN samples with 100 nm thick silver stripes were investigated. They were stressed with the 100nmAg/H₂O/300nm/+3V/24h or 100nmAg/NaCl/300nm/+3V/24h method.

The corresponding results are presented in figure 6.32. The surface of n-GaN in H₂O appears to be more attacked than in NaCl solution. The whitish precipitations, probably Ga₂O₃, spread more intense across the n-GaN surface, whereas for NaCl they seem to be thinner. The light microscope images show that the n-GaN surface in H₂O shows cracks on the Ga₂O₃, whereas the sample which was stressed in NaCl solution appears to be roughened. Obviously, different thick Ga₂O₃ layers have formed. Peng *et al.* observed cracks on thicker Ga₂O₃ layers which had a thickness of approx. 450 nm. They reported that they are formed due to strain relief during the oxide growth [128]. The silver stripes in both H₂O and NaCl as electrolytes partially tarnished and simultaneously were covered by whitish Ga₂O₃ in the same extent. The tarnishing of silver on the n-GaN surfaces might have similar reasons as for dark conditions under an externally applied potential: the n-GaN surface under UV excitation works as photoactive anode and due to the additional applied anodic potential, the by contrast negatively charged silver more or less detached from the positively charged n-GaN surface. In case of p-GaN, the surfaces remained unchanged for both H₂O and NaCl as electrolytes. The metals almost (H₂O) or completely (NaCl) tarnished from the p-GaN surface.

Table 6.10 shows the results of the EDX measurements on the GaN surfaces after experiments. The n-GaN samples clearly underwent photo-oxidation, proven by a nitrogen content of 8.4 at% and an oxygen content of 44.6 at% in H₂O. In NaCl, these changes of the elemental composition were less distinct. But also there, an increased

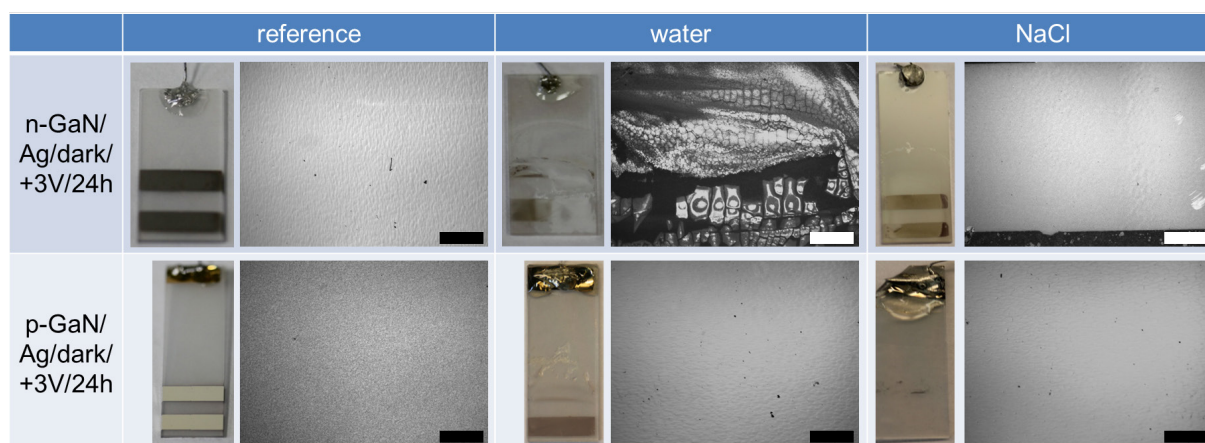


Figure 6.32: Photos and light microscopy images of GaN samples, stressed with the 100nmAg/H₂O/300nm/+3V/24h and 100nmAg/NaCl/300nm/+3V/24h method. The n-GaN surface in water was clearly more attacked than in NaCl visible by a whitish layer on the sample. The silver stripes in both electrolytes slightly tarnished. The p-GaN surfaces remained unchanged, whereas the deposited silver stripes partially or almost completely detached. Scale bars: 500 μ m.

oxygen content of 7.5 at% indicates a beginning oxidation of the surface. The detected content for p-GaN on the other hand did not show any changes compared to the reference sample. Due to the additionally applied potential, holes in a higher rate are generated, forming a thick Ga₂O₃ layer on the n-GaN surface close to the metals (compare with principle in figure 6.24). The p-GaN samples on the other hand remained unchanged under the applied stress conditions.

Since both n-GaN and p-GaN surfaces were positively charged at +3 V, the silver stripes showed negative characters. In case of n-GaN, the applied potential of +3 V intensified the photoanodic behavior of n-GaN, leading to a blast away of the silver from the n-GaN surface. Due to the anodic potential it could not re-deposit on the n-GaN surface again. Despite of the metal tarnishing, no silver traces could be detected on n-GaN. This was also the case for p-GaN: since p-GaN naturally works as photocathode under UV light excitation, showing

Table 6.10: EDX data measured on GaN samples treated with the 100nmAg/H₂O/300nm/+3V/24h and 100nmAg/NaCl/300nm/+3V/24h methods. Changes in the elemental compositions show the tendency towards an photo-oxidation of n-GaN samples, whereas the elemental composition for p-GaN remained unchanged. Only low silver content was found on the p-GaN surfaces. The generated electric charge densities are higher in H₂O than in NaCl. They are in the same range for n-GaN and p-GaN in H₂O.

	n-GaN			p-GaN		
	reference	Ag, H ₂ O	Ag, NaCl	reference	Ag, H ₂ O	Ag, NaCl
charge density (C/cm ²)		18.96	$4.71 \cdot 10^{-3}$		2.20	$1.24 \cdot 10^{-1}$
Ga (at%)	47.1	36.9	48.6	50.1	50.0	52.2
N (at%)	45.1	8.4	35.9	43.1	43.7	43.0
O (at%)	1.5	44.6	7.5	1.1	2.2	0.4
Ag (at%)	–	0.0	0.0	–	0.3	0.1

a negative character, the more positively charged metals are oxidized under UV excitation and get reduced elsewhere on the p-GaN sample, leading to their re-deposition. Now, p-GaN is due to the potential of +3 V driven as an anode. Thus, the silver stripes probably show a negative potential compared to the p-GaN surface, resulting in a detachment of the metals from the p-GaN surface in a similar way as it worked for n-GaN. Consequently, only very little silver species could be measured by EDX on the p-GaN surface. The generated charge densities are also enlisted in table 6.10. For n-GaN in H₂O, the generated charge density under 300 nm excitation, is approx. three orders of magnitudes higher than under dark conditions (cf. table 6.8). In NaCl, there was no difference in the charge densities between UV excitation and dark conditions. In case of p-GaN, an excitation

with 300 nm led to two to three orders of magnitude higher charge densities in H₂O and NaCl, compared to dark conditions.

SEM images were taken on both n-GaN and p-GaN surfaces, which were stressed under the influence of different electrolytes and with or without the presence of silver stripes. Figure 6.33 shows pictures of n-GaN, stressed with the (100nmAg/)/H₂O/300nm/+3V/24h method and the (100nmAg/)/NaCl/300nm/+3V/24h method. The stressed surfaces clearly changed – all of them more or less appear to be roughened. For n-GaN with silver stripes in H₂O, a Ga₂O₃ layer with cracks has formed, indicating a relatively thick oxide layer according to [106]. On top of the oxide layer, some rod-like structures as seen before on n-GaN samples, have formed (cf. figure 6.3 (b)). On the n-GaN samples in NaCl solutions, sedimented NaCl crystals can be seen which arbitrarily cover the n-GaN surfaces.

Figure 6.34 shows SEM images recorded on p-GaN surfaces which were treated analogous to n-GaN with the (100nmAg/)/H₂O/300nm/+3V/24h or (100nmAg/)/NaCl/300nm/+3V/24h methods. In contrast to n-GaN, no changes of the p-GaN surface could be proven by EDX measurements. The p-GaN surface next to the crumb sedimentation remained unchanged and was not attacked. The small crumbs on the p-GaN surfaces in figure 6.34 (a, b) were detected as GaN compound. Why this GaN component appears as crumb is not clear. In case of NaCl as electrolyte, shown in figure 6.34 (c, d), dried NaCl crystals aligned on the p-GaN surfaces, proven by EDX measurements.

Precipitation analysis

In case of 300 nm illumination and an applied potential of + 3 V, sometimes white sedimentation was at the ground of the PEC, which was only observed for n-GaN. These sedimentations were collected with a syringe and bottled, thus keeping them in solution. Afterwards they were dried and analyzed. Analysis carried out by centrifugation and subsequent decanting of the left-over solutions did not work, since

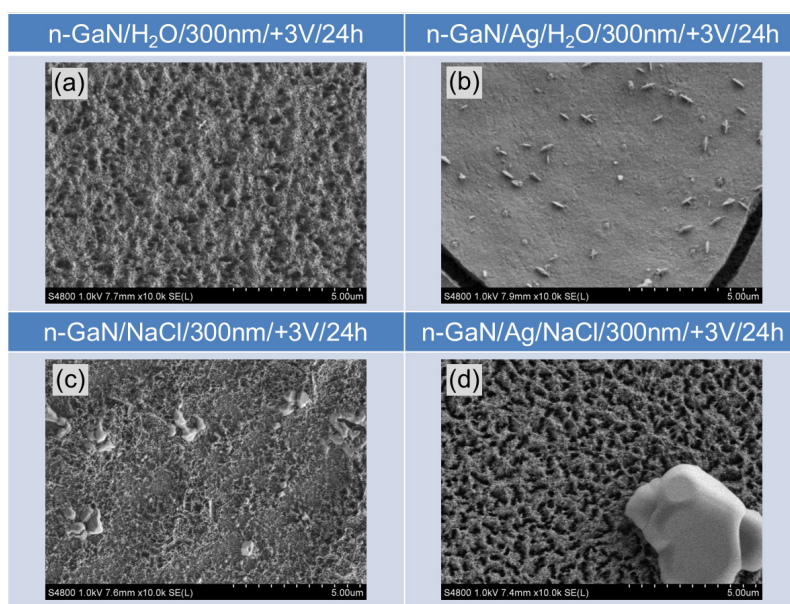


Figure 6.33: SEM images of n-GaN surfaces which were stressed with the $\text{H}_2\text{O}/300\text{nm}/+3\text{V}/24\text{h}$ (a, b) and $\text{NaCl}/300\text{nm}/+3\text{V}/24\text{h}$ (c, d) methods without (a, c) and with (b, d) the presence of 100 nm Ag. Clear surface changes can be seen on every sample – the surfaces all oxidized. In (b), cracks in the oxide layer are visible.

the deposits adhered too much to the centrifuge. Another approach which worked out was filtering the sediment with a frit that had a pore size of 10-16 μm . The filter cake was subsequently dried in the drying oven for two hours at 200°C and a very little amount of white powder was received. This powder was analyzed by EDX measurements. Figure 6.35 shows an example of such a precipitation which occurred in the case of n-GaN that was stressed with the $\text{NaCl}/300\text{nm}/+3\text{V}/24\text{h}$ method.

EDX analysis results of precipitations are listed in table 6.11. No nitrogen content was measured. The measured gallium content was at around 0.1 at%, i.e. insignificant low. Thus a compound, consisting of gallium and oxide can be excluded by this EDX measurement. The

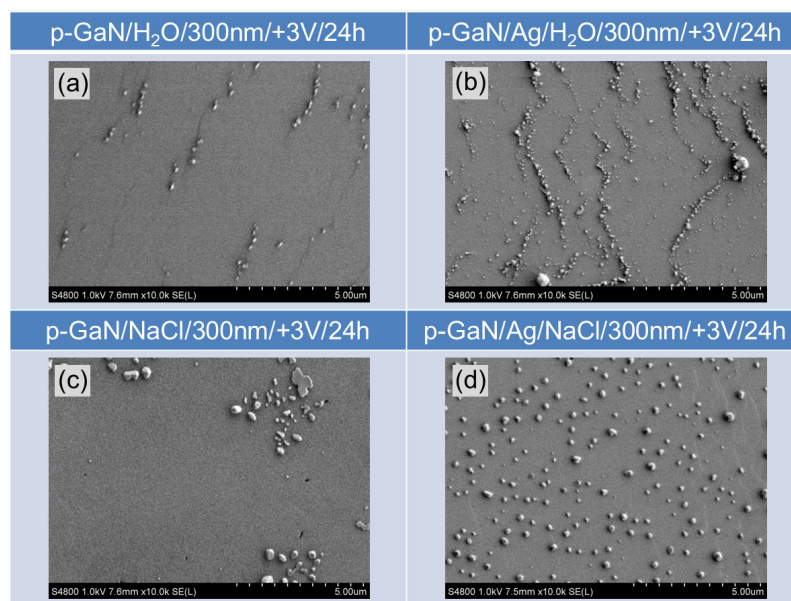


Figure 6.34: SEM images of p-GaN surface, which were stressed with the $\text{H}_2\text{O}/300\text{nm}/+3\text{V}/24\text{h}$ (a, b) and $\text{NaCl}/300\text{nm}/+3\text{V}/24\text{h}$ (c, d) methods without (a, c) and with (b, d) the presence of 100 nm Ag. The p-GaN surfaces showed no changes – only small grains appeared which correspond to deposits of the electrolyte.

silicon content probably originates from the doping of the n-GaN layer. It turned out, that the whitish powder is probably SiO_2 , precipitating from the n-GaN sample. It though is unclear, how the silicon dopants were exposed at the n-GaN surface to react with the oxygen species when the n-GaN sample was photo-oxidized.

As already mentioned, these sedimentations were only obtained for n-GaN in case of an anodic applied potential and under UV light illumination. Sedimentations were found for both NaCl and H_2O as electrolytes, although their appearance was quite arbitrary.

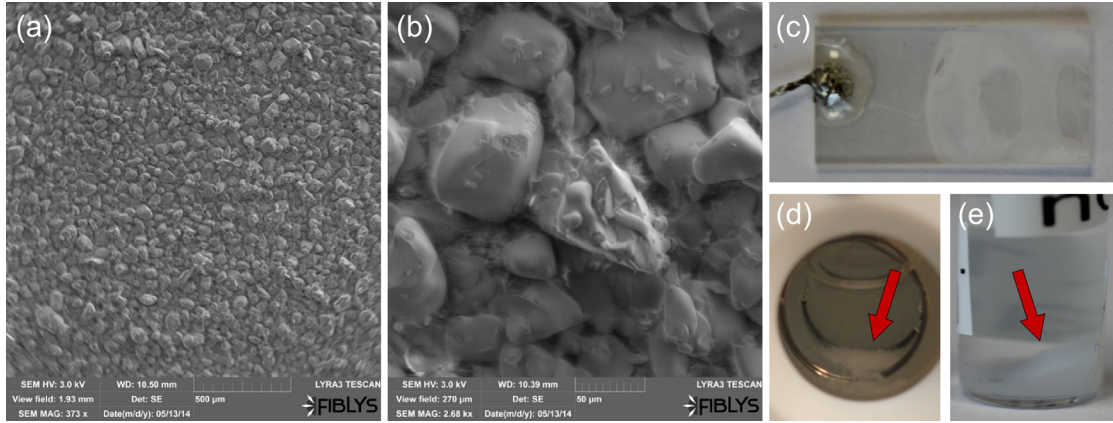


Figure 6.35: SEM images (a, b) of precipitations which originated from n-GaN samples stressed with the NaCl/300nm/+3V/24h method (c) and remained at the bottom of the PEC after the experiment (d). Precipitations were collected (e) and dried for the analysis by SEM/EDX. They mainly consisted of silicon and oxygen (see table 6.11) in grains with a diameter of approx. 50 μm .

Table 6.11: Results of EDX measurements on dried precipitation powder, originating from n-GaN samples stressed with the NaCl/300nm/+3V/24h method. As can be seen from the results, the precipitations are probably made of SiO_2 .

O (at%)	61.4
Si (at%)	25.7
Ga (at%)	0.1
N (at%)	0.0

6.4.3 Influence of long-term degradation stress in photoassisted electrolysis

To study, whether the time has an influence on the oxidation of GaN samples, a longer measurement period of was applied. Thus, GaN samples were stressed over 60 hours instead of 24 hours in the PEC

in aqueous solutions under an UV excitation with 300 nm and an applied potential of +3 V vs. Ag/AgCl. The changes on their surfaces, phenomenological and quantitatively, are discussed in this subsection.

Influence of long-term degradation stress on n-GaN

Figure 6.36 shows the phenomenological results for n-GaN, stressed with the (100nmAg/)/H₂O/300nm/+3V/60h and (100nmAg/)/NaCl/300nm/+3V/60h method. Clearly, the n-GaN surfaces are strongly attacked. Compared to the n-GaN images in figure 6.29, where the period of stress was only 24 hours, the changes have increased. The whitish Ga₂O₃ layer on the n-GaN surfaces in both H₂O and NaCl intensified. As stated before, the presence of metals in general accelerates the degradation of n-GaN. The images, as for pure n-GaN samples, show that the n-GaN areas, which were in contact with the electrolyte and excited with UV light, are attacked on a large-scale, forming an oxide layer on their surfaces, which as for pure n-GaN correspond to Ga₂O₃. Again, the metals partially or completely detached from the surfaces.

In table 6.12, the measured EDX data on the n-GaN surface with and without silver presence are enlisted. The oxidation of the samples can be clearly noticed.

The nitrogen content for pure n-GaN in H₂O decreased down to 4.4 at% (cf.: 40.2 at% for 24 hours) and the detected oxygen species increased to 52.6 at% (cf. 3.7 at% in H₂O). For n-GaN in NaCl for 60 hours, a nitrogen content of 32.0 at% (32.1 at% in 24 hours) and an oxygen content of 13.0 at% (10.5 at% in 24 hours) was measured – the surface attack did not further increase over a longer period of time. For n-GaN under the presence of silver stripes, the elemental composition in H₂O changed even more drastically: a nitrogen content of 1.8 at% was measured for 60 hours (8.4 at% in 24 hours) and the oxygen fraction increased up to 62.0 at% (44.6 at% in 24 hours). In NaCl, a value of 26.0 at% was measured (35.9 at% in 24 hours) and

6.4 Photo- and electrical stress on GaN (photoassisted electrolysis)

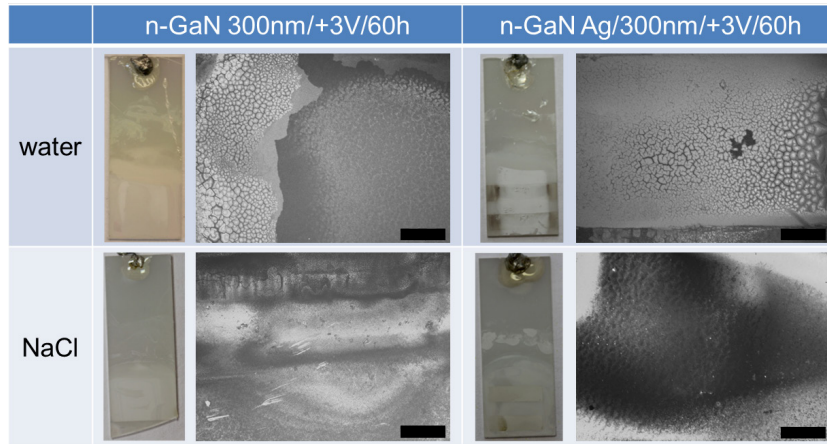


Figure 6.36: Photos and light microscopy images of n-GaN samples, stressed with the (100nmAg/) H_2O /300nm/+3V/60h and (100nmAg/) NaCl /300nm/+3V/60h method. The n-GaN surface for each sample showed a whitish oxide layer which also spread across the silver stripes which in turn slightly tarnished in both electrolytes. Scale bars: 500 μm .

the oxygen content was at 20.1 at% (7.5 at% in 24 hours). With the data in table 6.12 it can be concluded that for 60 hours of applied stress, the changes of n-GaN under the presence of silver are highest in H_2O . No traces of silver on the n-GaN surfaces could be detected by EDX. The generated electric charge densities, enlisted in table 6.12, are all in the same order, independent of the electrolyte or metal influence.

Figure 6.37 gives an overview of SEM images that were taken on n-GaN surfaces which were treated with the (100nmAg/) H_2O /300nm/+3V/60h and (100nmAg/) NaCl /300nm/+3V/60h method. The surfaces significantly changed in H_2O , cracks can be noticed, indicating thick Ga_2O_3 layers, as well as the formation of rod-like structures which appear more packed under influence of silver. These rod-like compartments again formed on the underlying oxidized n-GaN surface. In NaCl as electrolyte, the surfaces appeared roughened

Table 6.12: EDX data of n-GaN samples stressed with the (100nmAg/) H_2O /300nm/+3V/60h and (100nmAg/) NaCl /300nm/+3V/60h methods. An oxidation of the n-GaN surfaces was noticed for every stressed sample, but was strongest in H_2O under silver influence. The generated electric charge densities were all in the same range.

	reference	H_2O	Ag, H_2O	NaCl	Ag, NaCl
charge density (C/cm^2)		22.73	11.77	64.73	41.26
Ga (at%)	47.1	29.9	29.7	45.6	44.9
N (at%)	45.1	4.4	1.8	32.0	26.0
O (at%)	1.5	52.6	62.0	13.0	20.1
Ag (at%)	—	—	0.0	—	0.0

and baggy and no cracks or rod-like structures were obtained. This difference in morphology was already observed in case of 24 hours stress.

For these long-time photoassisted electrolysis measurements, the presence of metals induces a higher oxidation effect on n-GaN samples than under 24 hours stress. There is also a clear time dependence, since after a stress of 24 hours the elemental changes were not as distinct as for 60 hours. This is different to the photoinduced experiments on n-GaN in the previous section, where a longer time of applied stress does not significantly change the elemental composition any more. It thus can be due to the externally applied potential of +3 V, that triggers an increased oxidation reactions on the n-GaN surfaces.

Influence of long-term degradation stress on p-GaN

Figure 6.38 shows images on p-GaN samples that were stressed with H_2O /300nm/+3V/60h and NaCl /300nm/+3V/60h methods. The surface of p-GaN which was in H_2O looked roughened under the microscope. Already by eye, a color change of the p-GaN surface could

6.4 Photo- and electrical stress on GaN (photoassisted electrolysis)

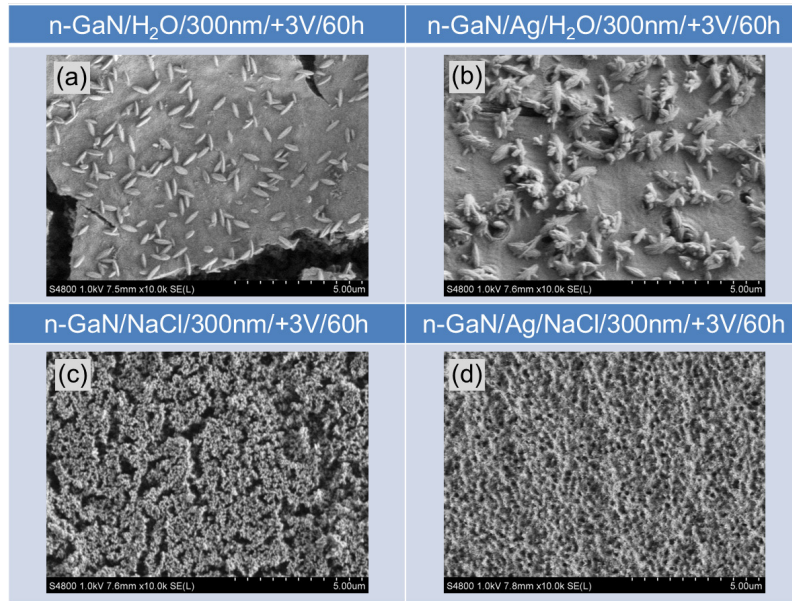


Figure 6.37: SEM images of n-GaN samples stressed with the (100nmAg/) $\text{H}_2\text{O}/300\text{nm}/+3\text{V}/60\text{h}$ (a, b) and (100nmAg/) $\text{NaCl}/300\text{nm}/+3\text{V}/60\text{h}$ (c, d) methods. In case of H_2O as electrolyte, rod-like Ga_2O_3 structures formed on an oxide layer which was quite thick and showed cracks as can be seen in (a). For n-GaN stressed in NaCl, the surfaces appeared strongly roughened.

be seen as it was only obtained in case of n-GaN so far. Obviously, the p-GaN surface showed sign of a photo-oxidation. On the other hand, p-GaN stressed in NaCl showed no changes besides some smears of the probably dried NaCl electrolyte.

Also, p-GaN samples were stressed under silver influence with the 100nmAg/ $\text{H}_2\text{O}/300\text{nm}/+3\text{V}/60\text{h}$ and 100nmAg/ $\text{NaCl}/300\text{nm}/+3\text{V}/60\text{h}$ methods which can be seen in figure 6.38. On the photos, a reddish color change between the silver stripes can be seen, probably a re-deposition of the silver. Under the light microscope, the p-GaN surfaces appear rather unchanged, in case of NaCl some sedimentations can be seen – probably silver or dried NaCl

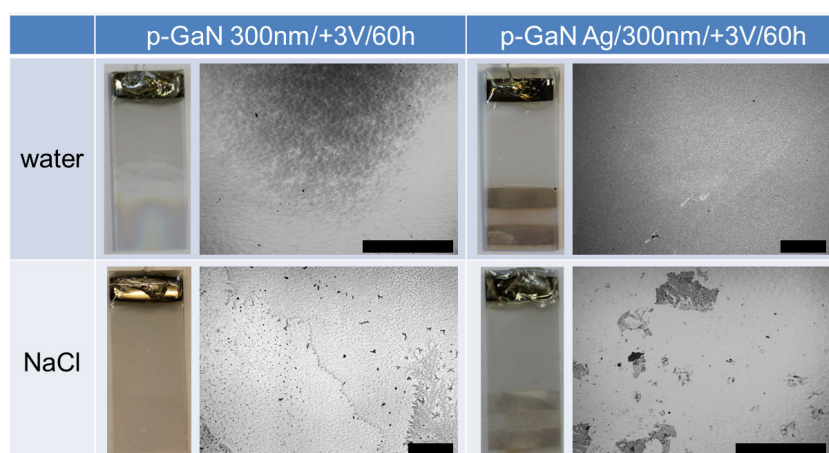


Figure 6.38: Photos and light microscopy images of p-GaN samples, stressed with the (100nmAg/) H_2O /300nm/+3V/60h and (100nmAg/) NaCl /300nm/+3V/60h method. Pure p-GaN in water showed significant changes, whereas no reactions were seen in case of NaCl. In the presence of silver the stripes tarnished and silver redeposited on the p-GaN surface in-between the stripes. Scale bars: 500 μm .

smears. The metals again started tarnishing, in NaCl stronger than in H_2O .

The results of EDX measurements are enlisted in table 6.13. No changes in the elemental composition were found – except for p-GaN stressed with the H_2O /300nm/+3V/24h method. It had a decreased gallium content and a slight increase of oxygen (37.6 at% and 4.2 at%, respectively).

As can be seen in figure 6.38, the reddish sedimentations in-between the silver stripes originate from a re-deposition of silver that tarnished in both H_2O and NaCl. EDX data showed in case of H_2O a silver content of 0.4 at% and for NaCl 2.8 at%. The higher amount for NaCl is probably due to the better conductivity, leading to a better distribution of the metal species. Even if the p-GaN surface remained

Table 6.13: EDX data recorded on p-GaN samples stressed with the (100nmAg/) H_2O /300nm/+3V/60h and (100nmAg/) NaCl /300nm/+3V/60h methods. No changes in the elemental composition were measured except of pure p-GaN in H_2O . Traces of silver could be measured on the p-GaN surface. The generated electric charge densities were all in the same range.

	reference	H_2O	Ag, H_2O	NaCl	Ag, NaCl
charge density (C/cm^2)		1.42	3.08	1.16	0.30
Ga (at%)	50.1	37.6	52.4	40.8	49.6
N (at%)	43.1	49.4	42.5	42.6	40.3
O (at%)	1.1	4.2	0.8	2.8	2.0
Ag (at%)	—	—	0.4	—	2.8

unchanged after 60 hours under the presence of silver, the mechanism of tarnishing and re-deposition took place, analogous to the photoinduced experiments in the previous section. Whereas there, a long-term stress of 72 hours led again to a detachment of the re-deposited silver (cf. table 6.13) due to the long time in the electrolyte, under 60 hours of photoassisted electrolysis, the re-deposited silver probably attached well to the p-GaN surface. This might be due to the additional applied anodic potential.

The generated electric charge densities for p-GaN under long-term conditions with and without silver in H_2O or NaCl were all in the same range and one order of magnitude lower than the charge densities determined for n-GaN under long-term conditions (cf. table 6.12). Since the function of p-GaN as weak photocathode played a minor role to the dominating applied anodic potential, higher charges can be produced. This effect was not as distinct under short stress times of 24 hours, but became clear for longer measurement times.

Figure 6.39 shows the corresponding SEM images of the stressed p-GaN samples. The surface of pure p-GaN in H_2O appeared to show slight cracks, which indicates a relatively thick Ga_2O_3 layer

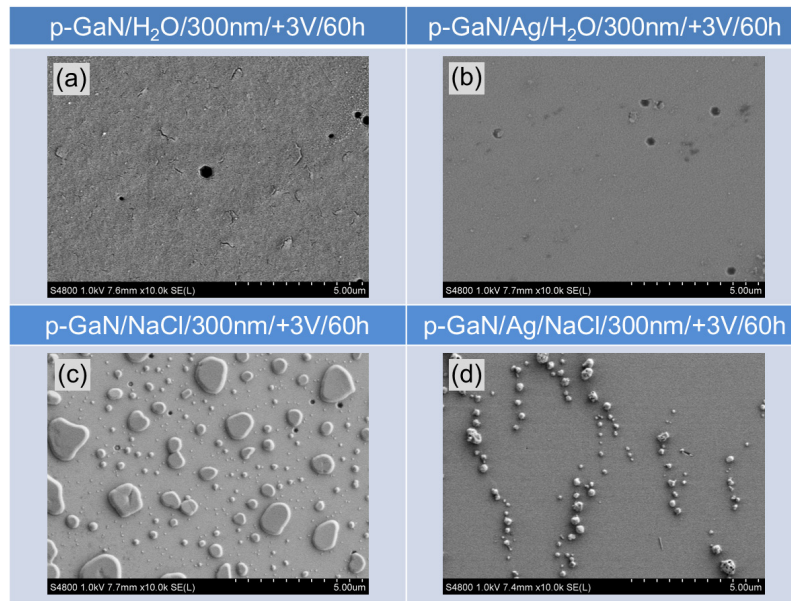


Figure 6.39: SEM images of p-GaN samples stressed with the (100nmAg/) $\text{H}_2\text{O}/300\text{nm}/+3\text{V}/60\text{h}$ (a, b) and (100nmAg/) $\text{NaCl}/300\text{nm}/+3\text{V}/60\text{h}$ (c, d) methods. No changes of p-GaN surfaces were observed (the deposits in (c) and (d) are dried NaCl crystals as can be seen in EDX). Only the p-GaN surface in (a) is roughened due to oxidation, as was shown by EDX measurements (cf. table 6.13).

and proves the finding of EDX (cf. table 6.13). Why especially for that constellation an oxidation occurred, it not certainly clear. The photo-oxidation of p-GaN might be associated with the band bending of p-GaN. For p-GaN, which works as photocathode, the applied anodic potential of +3 V is higher than the flat band potential of p-GaN. It thus is expected that crowding of photogenerated holes now takes place at the interface at the p-GaN surface due to the band bending under accumulation conditions. In the SEM images, also some hexagonal V-pits can be seen on the p-GaN surface. But no direct reference to the observation of rod-like formation on dislocations on n-GaN (as, e.g., in figure 6.37 (a, b)) can be made.

Since the photogenerated holes, which are responsible for the oxidation, are majority charge carriers in p-GaN and it is reported that only minority charge carriers contribute to the photo-oxidation of GaN, the process of photo-oxidation takes longer. It thus could be possible that some small concentration of holes at the surface drives the photo-oxidation, which indicates the initial step by evolution of N_2 , thus leading to the minimal decreased nitrogen content to 4.02 at%. Concluding, it thus could be indeed, that the p-GaN surface is oxidized, but it probably takes longer.

In case of H_2O with silver stripes and NaCl with and without silver stripes, no change of the p-GaN surface occurred – despite sedimentation of more or less big dried NaCl crystals, that spread across the p-GaN surfaces, as has been proven by EDX measurements. Some few V-Pits on p-GaN surfaces in H_2O can be seen.

In general, the influence of metals stripes in general protects the p-GaN surface – even if the samples would be stressed longer than 60 hours under an anodic potential. As already discussed for the photoinduced degradation experiments, they act as kind of photocatalysts on the p-GaN surface. It was reported that the role of metal catalysts which are applied to semiconductor surfaces improves the performance and efficiency of the PECs [188].

6.4.4 Photoelectrochemical CO_2 reduction of n-GaN with NiO co-catalysts

As motivated in the beginning of this work, one interesting application of GaN in energy conversion is the photoelectrochemical CO_2 reduction, where CO_2 is reduced to organic materials. For that purpose, n-GaN is used as photoanode which is excited with near-UV light. Samples with NiO particles are used therefore, since they showed a stable behavior under the presence of NiO co-catalysts (c.f. subsection 6.1.6), ensuring a reliable working system.

Experiments were carried out in the PEC with n-GaN as WE and a lead wire as CE. The RE was Ag/AgCl. 0.1 M KHCO_3 was used as electrolyte due to its high efficiency in forming hydrocarbons. Directly before the CA measurement started, the PEC was saturated with gaseous CO_2 for approx. 20 minutes – since the gas supply did not reach the electrolyte directly due to practical aspects of the PEC, a direct saturation of the electrolyte itself cannot be expected. The CO_2 flow rate through the PEC was controlled by a mass flow controller (MFK instruments). During the 24 hours experiment, the CO_2 flow rate was set to 5 sccm (i.e. 5 ml/min). The n-GaN sample was illuminated with 300 nm. The applied potentials were chosen on the one hand as the OCP at -0.2 V and on the other hand in the anodic potential region of +3 V to also study a possible oxidation of the n-GaN photoelectrode. In doing so, the behavior of the NiO co-catalysts on the stability on the n-GaN surface were brought into focus.

Figure 6.40 shows photos of the stressed n-GaN samples with an applied potential of -0.2 V and +3 V. It thus can be assumed that both samples were oxidized during the photoelectrochemical CO_2 reduction experiments. Also, photos of a reference and the stressed sample at +3 V are shown in figure 6.40. As for the images presented in figure 6.5 and 6.31, also here the reference sample (with NiO catalysts) emits light homogeneously in the greenish/yellowish spectral range. This was shown in the emission measurements in figure 5.6 in the previous chapter. The stressed active area of the n-GaN sample, which was illuminated and in contact with the electrolyte, does not emit light anymore (just as the insulated contact metal area on top) – a clear sign of the irreversible degradation of the stressed n-GaN sample. This behavior was the same for the sample stressed with the OCP potential of -0.2 V. Light is still emitted from the stressed sample areas, which were not in contact with the electrolyte and the 300 nm excitation spot.

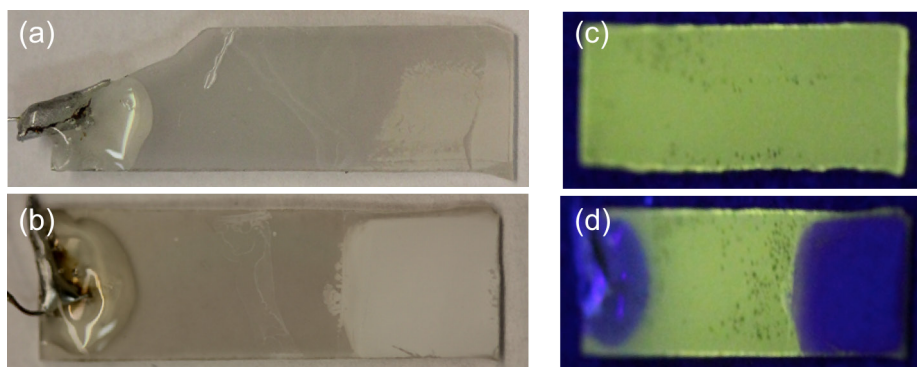


Figure 6.40: n-GaN samples with NiO co-catalysts after the photoelectrochemical CO₂ reduction experiments in the PEC with a CO₂ flow rate of 5 sccm under 300 nm excitation in 0.1 M KHCO₃, stressed for 24 hours at a potential of -0.2 V (a) and +3 V (b). Photos of a reference sample (c) and the stressed sample at +3 V (d) under an UV lamp are shown. The active area of the stressed n-GaN sample in (d) is attacked and does not emit light anymore – a clear sign for the damage of its surface. In contrast, the reference sample in (c) homogeneously emits light under UV excitation.

From this images it can be already seen that n-GaN with NiO particles is clearly attacked. This was confirmed by EDX measurements. Table 6.14 gives an overview of the elemental composition changes of stressed n-GaN sample surfaces with NiO particles, which were used for CO₂ reduction, compared to a reference sample. For both applied potentials of -0.2 V and +3 V the elemental composition of the n-GaN surfaces changed significantly. It can be concluded, that a photo-oxidation of the n-GaN anodes took place. The decrease of nitrogen is lower for -0.2 V (10.5 at%) than for +3 V (1.2 at%). Also the increase of the oxide content is higher for +3 V than for -0.2 V. This means that the applied potential of +3 V has more effect on the degradation on the n-GaN surfaces than -0.2 V, as expected. Thus, n-GaN samples are not stable even under NiO presence on

Table 6.14: EDX data of n-GaN samples with NiO co-catalyst particles on the surface. Data were determined from a reference as well as from stressed samples in 0.1 M KHCO_3 for a time of 24 hours at an excitation with 300 nm UV light. The CO_2 flow rate was 5 sccm. For applied potentials of -0.2 V or +3 V vs. Ag/AgCl clear changes in the elemental composition were detected. A clear change in the elemental composition took place.

	reference	KHCO_3 , -0.2 V	KHCO_3 , +3 V
charge density (C/cm^2)		8.41	9.77
Ga (at%)	55.4	29.7	30.6
N (at%)	42.2	10.2	1.5
O (at%)	0.5	47.8	59.5

their surfaces when such an extreme external anodic potential is applied. As could be seen in the photoinduced degradation experiments in aqueous solutions, pure UV light excitation has no effect on the elemental composition of n-GaN with NiO influence. But under an additional applied potential, degradation starts – slightly for the OCP value of -0.2 V, but stronger for +3 V which is in the high anodic range – although NiO co-catalysts are present on the n-GaN surface.

However, it needs to be considered that KHCO_3 as electrolyte was not used as aqueous electrolyte in the photoinduced and photoassisted electrolysis experiments before. It can be assumed that KHCO_3 in general shows a more aggressive behavior towards the GaN surfaces than H_2O or NaCl , due to the higher conductivity and simultaneously the missing Cl_2 evolution at discussed before, which protects the n-GaN surface from oxidation. The generated charge densities are also enlisted in table 6.14 and are nearly in the same range for both -0.2 V and +3 V. Thus, a more positive applied potential obviously has no influence on charge carrier generation.

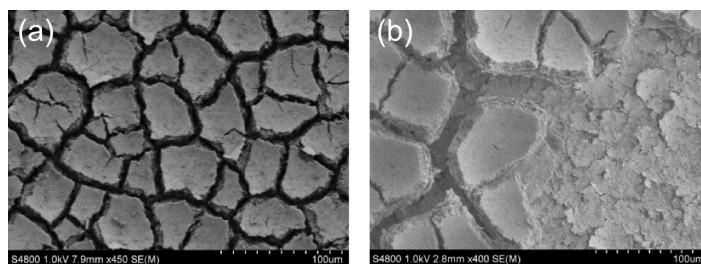


Figure 6.41: SEM images of n-GaN with NiO co-catalyst particles used as photoanode for photoelectrochemical CO₂ reduction under a potential of +3 V vs. Ag/AgCl. (a) The surface is covered by whitish Ga₂O₃, which shows deep cracks. (b) Border region of the active area covered with Ga₂O₃, showing cracks.

Figure 6.41 shows SEM overview screens of the stressed n-GaN samples with NiO particles under an applied potential of +3 V. Oxide formation with deep cracks in-between can be seen on the surface, corresponding to the whitish Ga₂O₃ which are visible on the n-GaN sample.

SEM images of n-GaN surfaces for both applied potentials of -0.2 V and +3 V are shown in figure 6.42. For -0.2 V, rod-like Ga₂O₃ structures that cover the whole active n-GaN surface can be noticed, whereas for an potential of +3 V, the active area surface already appears completely baggy. The influence of the extreme anodic potential of +3 V obviously causes more photo-oxidation of the n-GaN surface. Figure 6.42 also shows the measured CA curves for both potentials. As seen already in table 6.14, due to approx. similar generated electric charge densities, also the curve progressions are in the same range. The current densities drop more than one order of magnitude during the measurement time of 24 hours.

Besides the stability of the n-GaN photoelectrodes in the system, also the efficiency with respect to CO₂ reduction is studied. Since an analysis of the evolving gases is not possible because of low amounts, the KHCO₃ electrolyte after the 24 hours CA was analyzed. NMR

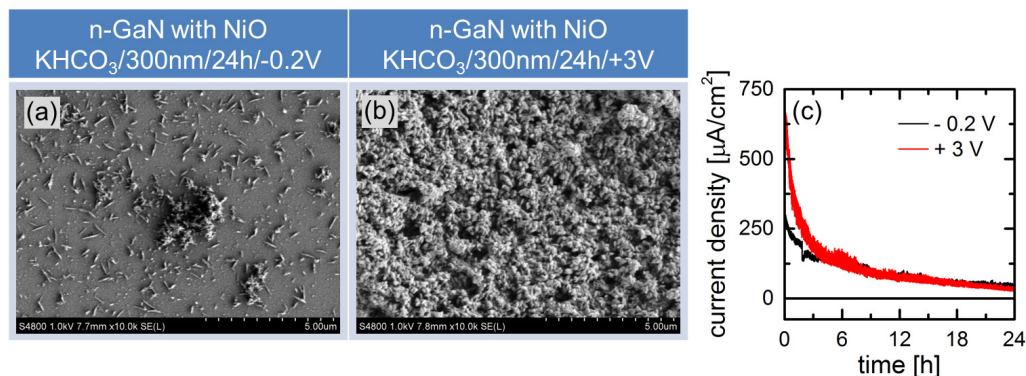


Figure 6.42: SEM images of n-GaN samples with NiO particles, stressed under 300 nm excitation for 24 hours in KHCO_3 with a CO_2 flow rate of 5 sccm at potentials of -0.2 V (a) and +3 V (b) vs. Ag/AgCl. In (c) the corresponding recorded CA curves are shown. The current density drop in case of +3 V at the beginning of measurements is stronger than for -0.2 V. Both applied potentials cause current densities in the $\mu\text{A}/\text{cm}^2$ range.

measurements were carried out at the institute for inorganic chemistry at the FAU Erlangen-Nürnberg. The electrolyte therefore was diluted with 1 M dimethyl sulfone in D_2O . Very small amounts of formic acid (HCOOH) could be detected. For the applied potential of -0.2 V vs. Ag/AgCl, an amount of $4.30 \cdot 10^{-6}$ M was measured and for a potential of +3 V vs. Ag/AgCl an amount of $7.96 \cdot 10^{-5}$ M formic acid was found. The corresponding FEs are around 1.0 %. Interestingly, there are, due to the similar generated electric charge densities, no differences in the achieved FE values, although very different potential values were applied. Compared to Yotsuhashi *et al.*, which gained a FE of 8.88 % with a copper CE [26], the achieved Faraday efficiencies in this work are approx. factor ten lower. The low efficiency is due to the low generated electric charge densities during experiments.

It is important to mention that the PEC consisted only of one chamber, where only one electrolyte could be filled in. This led to several disadvantages concerning the stability of the n-GaN anode

and other reactions. In Yotsuhashi *et al.* for example, a two chamber system was used, where KHCO_3 was the electrolyte at the cathode side (where also the CO_2 is introduced) and NaOH the electrolyte for anode i.e. GaN side [25–27]. Already here, a less aggressive electrolyte would ensure that the GaN electrode worked reliable due to less or almost none attack of the surface (as shown before under the influence of NiO particles) and still it would be guaranteed that the cathode (e.g., copper or lead) is working in KHCO_3 , where CO_2 could be reduced. Also, the two chambers were separated by a cation exchange membrane that blocks electrolytic intercommunication. This was not the case in this work.

6.5 Corrosion rate determination

A quantitative method to gain knowledge about the degradation of materials in general is the determination of a corrosion rate. The Tafel method as already described in section 2.2.3 was applied as analysis technique. The term corrosion in this case does not correspond to the formation of an oxide as considered in the GaN photo-oxidation reactions. It refers to the dissolution of the material – thus, the decomposition and dissolution of GaN in aqueous media. This would be caused by the dissolution of the grown Ga_2O_3 layer, leaving the underlying fresh n-GaN surface exposed and etched.

GaN samples were measured in the PEC in a 1 M NaCl solution and the OCP values were determined. A potential was applied starting approx. 200 mV in cathodic direction and ended approx. 1 V in anodic direction of the corresponding OCP. The scan speed was 1 mV/sec. The samples were measured under dark conditions but also under UV excitation with 300 nm. It was the first time that this measurement method was applied to GaN.

n-GaN

Measurements were carried out on pure n-GaN samples with and without illumination. Figure 6.43 shows the semi-logarithmic current density-potential curves for dark and 300 nm excitation together with the fitted Tafel lines. The determined OCP values were -0.06 V vs. Ag/AgCl for dark conditions and -0.6 V vs. Ag/AgCl for UV excitation. Compared to section 2.2.3, they have not changed significantly due to the higher concentration. This shows that the influence of the concentration of the electrolyte on the electrochemical reactions at the n-GaN–electrolyte interface has no big effect. The excitation with 300 nm causes a shift of the intersection of the Tafel lines to more negative OCP values as well as to higher currents due to the additional generated charge carriers, leading to an accumulation of holes at the n-GaN surface as discussed in the previous section, resulting in a decrease of the OCP value.

The evaluated corrosion rates are enlisted in table 6.15 and differ: n-GaN under dark conditions degrades with a corrosion speed of $5.13 \cdot 10^{-5}$ mm/y ($= 9.76 \cdot 10^{-5}$ nm/min), whereas illuminated n-GaN corrodes approx. three orders of magnitudes faster with $7.75 \cdot 10^{-2}$ mm/y ($= 1.47 \cdot 10^{-1}$ nm/min). It needs to be considered that due to the gentle measurement method, the samples are not oxidized during experiments. Thus, an idealistic case of immediate dissolution is expected without any disturbing intermediate steps.

Anyways, as seen in the corrosion rate, already under dark conditions, a corrosion takes place. For both photoinduced degradation and photoassisted electrolysis experiments in this work under dark conditions, no degradation of n-GaN was observed and the elemental composition did not change. Even so under the applied OCP potential to n-GaN in the PEC under dark conditions this was the case, but anyways, an electric charge was generated. Again, as already discussed, a degradation also takes place for n-GaN under dark conditions, but

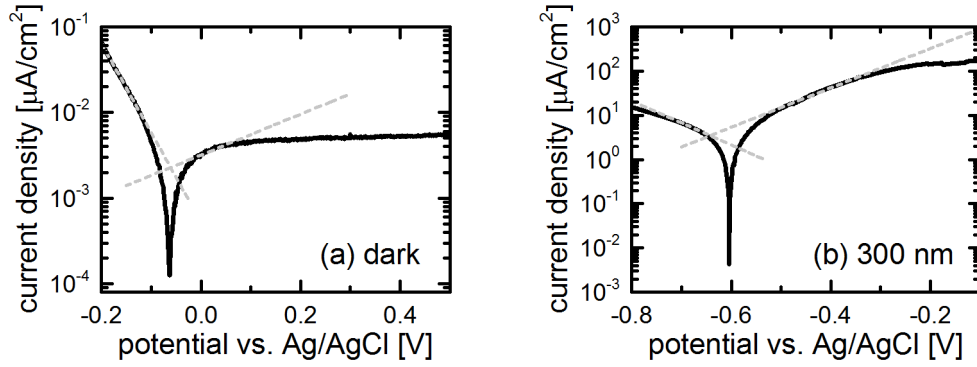


Figure 6.43: Current density vs. applied potential curves for pure n-GaN samples stressed in 1 M NaCl under dark conditions (a) and under 300 nm UV excitation (b) along with the corresponding Tafel plots. From the intersection of the Tafel lines, the corrosion rate of the samples could be estimated. The degradation rate of pure n-GaN under excitation is approx. three orders of magnitudes higher than under dark conditions.

it takes much longer than under additional UV excitation since not many free charge carriers are available to trigger this process.

The influence of 100 nm thick silver stripes on the corrosion behavior of n-GaN was also investigated. Figure 6.44 shows the current density-potential curves. The OCP changed from -0.09 V vs. Ag/AgCl under dark conditions to -0.56 V vs. Ag/AgCl under UV excitation. Again, n-GaN with silver influence degraded under dark conditions with a speed of $1.43 \cdot 10^{-4}$ mm/y ($= 2.72 \cdot 10^{-4}$ nm/min), which is three orders of magnitude slower than under 300 nm excitation, where a corrosion rate of $1.03 \cdot 10^{-1}$ mm/y ($= 1.97 \cdot 10^{-1}$ nm/min) was determined. The values are also enlisted in table 6.15. It can be seen, that the presence of silver in general accelerates the n-GaN corrosion by one order of magnitude for both dark conditions and 300 nm excitation. As discussed before, this again shows the influence of metals on the n-GaN surface influencing the reactions on the semiconductor-electrolyte interface.

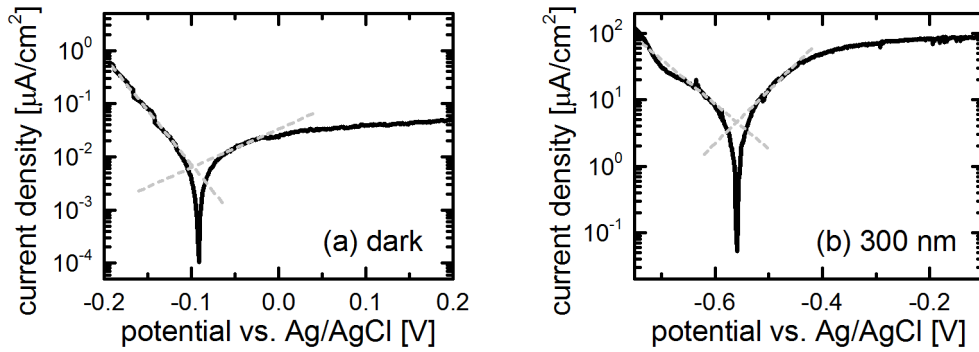


Figure 6.44: Current density vs. applied potential curves for n-GaN under the influence of silver stressed in 1 M NaCl under dark conditions (a) and under 300 nm UV excitation (b) along with the corresponding Tafel plots. From the intersection of the Tafel lines, the corrosion rate of the samples could be estimated. The degradation rate of n-GaN with silver under excitation is approx. three orders of magnitudes higher than under dark conditions.

When using the term corrosion in this subsection, it refers to the real exposure of the GaN material itself from the surface and not to an oxide formation on its surface. Because NaCl is commonly used as electrolyte for the Tafel measurements, it was also applied in case of GaN investigations. The n-GaN surface should be protected from any corrosion attack due to the competitive Cl_2 evolution in NaCl. But whitish precipitations on the active n-GaN area were visible, indicating an oxidation reaction which might took place due to the higher NaCl concentration. In presence of silver, the stripes also tarnished from the n-GaN surface or were partially covered by whitish oxide. Anyways, the determined data for the corrosion rates really refer to a exposure of the GaN surface itself.

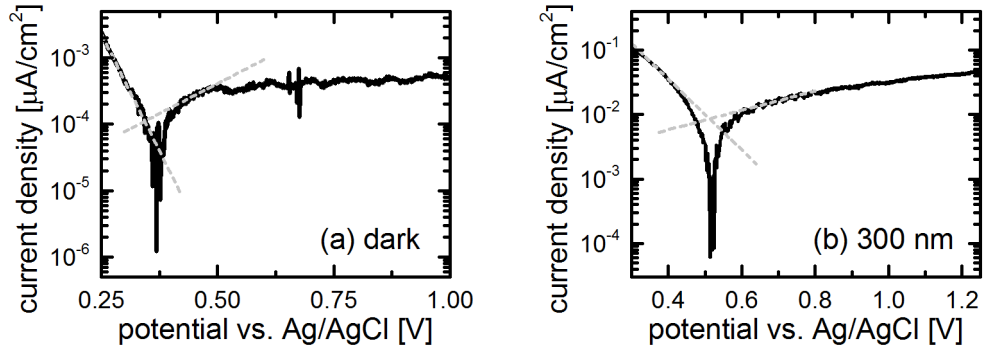


Figure 6.45: Current density vs. applied potential curves for pure p-GaN samples stressed in 1 M NaCl under dark conditions (a) and under 300 nm UV excitation (b) along with the corresponding Tafel plots. From the interception of the Tafel lines, the corrosion rate of the samples could be estimated. The degradation rate of pure p-GaN is approx. the same under dark conditions and illumination.

p-GaN

Analogous to n-GaN, the Tafel method was also applied to p-GaN samples with and without silver stripe influence in 1 M NaCl solution under dark conditions as well as 300 nm excitation. Figure 6.45 shows the corresponding semi-logarithmic current density-potential curves. Whether dark conditions or 300 nm excitation are applied, it has no big influence on the speed of corrosion. As characteristic for p-type semiconductors, the illumination with 300 nm causes a shift of the curves to more positive OCP values as well as to higher exchange current densities (from +0.37 V vs. Ag/AgCl under dark conditions to +0.52 V vs. Ag/AgCl under 300 nm excitation). The evaluated corrosion rates are in the same range: p-GaN under dark conditions degrades with a corrosion rate of $2.23 \cdot 10^{-6}$ mm/y ($= 4.25 \cdot 10^{-6}$ nm/min), whereas illuminated p-GaN corrodes slightly faster with $1.90 \cdot 10^{-4}$ mm/y ($= 3.61 \cdot 10^{-4}$ nm/min). These values are also enlisted in table 6.15.

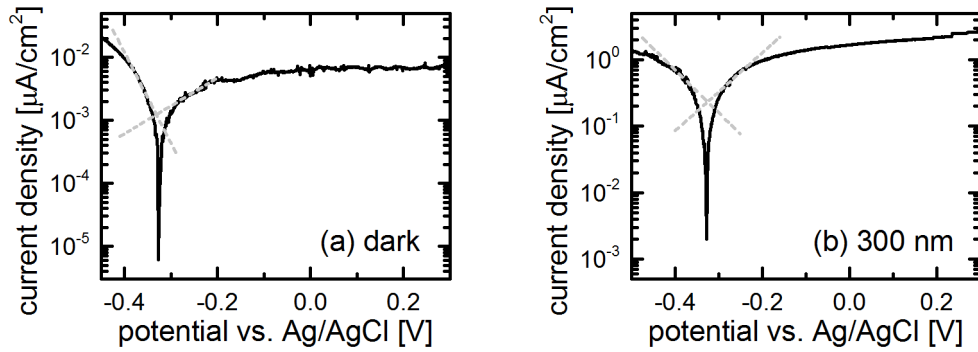


Figure 6.46: Current density vs. applied potential curves for p-GaN under the influence of silver stressed in 1 M NaCl under dark conditions (a) and under 300 nm UV excitation (b) along with the corresponding Tafel plots. From the intersection of the Tafel lines, the corrosion rate of the samples could be estimated. The degradation rate under excitation is approx. one order of magnitudes higher under dark conditions than under dark conditions.

The influence of 100 nm thick silver stripes on the corrosion behavior of p-GaN was also studied. Figure 6.46 shows the corresponding curves. The OCP was -0.33 V vs. Ag/AgCl for both dark conditions and 300 nm excitation. p-GaN with Ag corrodes under dark conditions with a speed of $2.68 \cdot 10^{-5}$ mm/y ($= 5.10 \cdot 10^{-5}$ nm/min) slower than under 300 nm excitation where it shows a corrosion rate of $5.20 \cdot 10^{-3}$ mm/y ($= 9.89 \cdot 10^{-3}$ nm/min). These values are also shown in table 6.15. The corrosion rate for p-GaN under the presence of silver is approx. two orders of magnitude higher under both dark conditions and 300 nm excitation. The p-GaN samples which were stressed with the Tafel method showed no changes on their surface and in case of metal influence, the silver stripes partially tarnished from the p-GaN surface.

Finally, table 6.15 shows an overview of the determined corrosion rates of all investigated samples and conditions.

Table 6.15: Overview of corrosion rates in mm/y, determined by the Tafel method from GaN samples in 1 M NaCl with and without silver stripes, stressed under dark conditions and with 300 nm UV light excitation (cf. figures 6.43, 6.44, 6.45, 6.46).

	n-GaN	n-GaN with Ag	p-GaN	p-GaN with Ag
dark	5.13×10^{-5}	1.43×10^{-4}	2.23×10^{-6}	2.68×10^{-5}
300 nm	7.75×10^{-2}	1.03×10^{-1}	1.90×10^{-4}	5.20×10^{-3}

In figure 6.47 (a) the current-density-potential curves of pure n-GaN and p-GaN samples under dark conditions and 300 nm excitation are compared. When comparing the corrosion rates of n-GaN and p-GaN without and with 300 nm illumination, there are big differences in the behavior of n-type and p-type GaN samples. The free corrosion potential or OCP is of special interest. The shift of the OCP values as described in section 5.2.2 is now presented graphically and it can be seen in the reversal point of the curves. For n-GaN under 300 nm excitation (green curve) the OCP value is shifted to more negative potentials compared to dark conditions (blue curve), whereas for p-GaN under 300 nm excitation (orange curve) it is shifted to more positive potentials compared to dark conditions (red curve).

The same comparison was applied to GaN samples with 100 nm thick silver stripes on their surfaces. Figure 6.47 (b) shows the corresponding current density-potential curves in a semi-logarithmic plot. For n-GaN under dark conditions (blue curve) the OCP is approx. -0.1 V and is shifted under 300 nm excitation to approx. -0.6 V (green curve). These are comparable values to pure n-GaN behavior. For p-GaN under metal influence, the dark OCP (red curve) is in the negative potential range at approx. -0.32 V and does not change significantly under 300 nm excitation (orange curve).

In this section, the corrosion rates of pure n- and type GaN samples as well as under the influence of silver stripes were determined. For

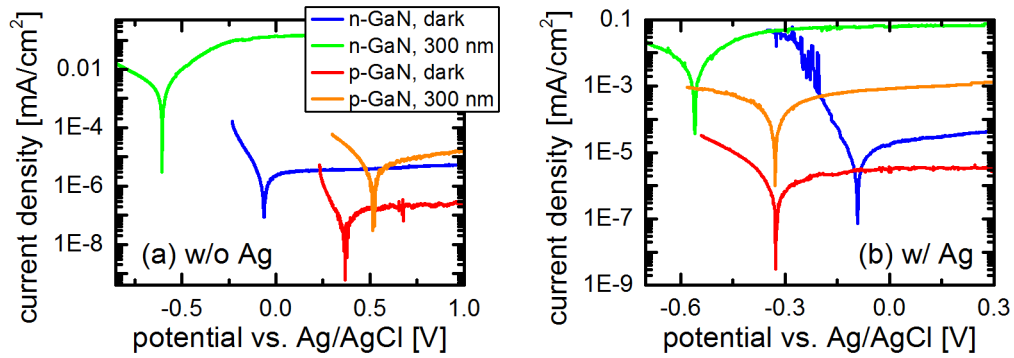


Figure 6.47: Current density vs. applied potential curves for GaN samples with and without excitation, pure GaN (a) and under the influence of 100 nm Ag (b). The OCP values can be read from the curves from their minima. (a) Under UV illumination, the corresponding OCPs are shifted to more negative potentials for n-GaN and higher potentials for p-GaN. (b) For n-GaN under UV illumination, the OCPs are shifted to more negative potentials whereas for p-GaN there is almost no difference between dark conditions or UV illumination.

pure p-GaN and n-GaN samples under dark conditions they are nearly in the same region as can be seen in table 6.15. For n-GaN samples under silver influence, the speed of corrosion was approx. one order of magnitudes higher than for pure n-GaN under dark conditions and 300 nm excitation, respectively. This was approx. also the case for p-GaN samples.

7 Fabrication of Mg_2Si Thin Films

GaN, which has a wide direct band gap of approx. 3.4 eV, is only excitable in the near-UV range, thus making pure GaN material not suitable for solar energy conversion in the visible range. Instead, Mg_2Si , belonging to the group of semiconducting silicides, was investigated as narrow band gap material. With its indirect band gap of approx. 0.78 eV [36] it has the ability of absorbing light in the visible range. Mg_2Si is the only possible stoichiometric stable compound in the Mg–Si phase diagram [51]. The fabrication of uniform Mg_2Si layers is less complex than the HVPE process for GaN.

7.1 Influence of the fabrication parameter on the material properties of Mg_2Si

Mg_2Si samples can be fabricated by several techniques as already mentioned in section 3.2. In this work, polycrystalline Mg_2Si thin films are formed either by evaporation of magnesium pellets to a silicon wafer or sputtering to a glass or silicon wafer from a Mg_2Si target. Details of the sample fabrications are explained in the following sections.

7.1.1 Evaporation of magnesium on silicon substrates

In this section, the formation of Mg_2Si thin films by evaporation of magnesium is studied. To receive a Mg_2Si phase, silicon wafers were used as substrates to enable diffusion reactions of both species. Therefore, magnesium pellets with a purity of 99.95 % were thermally evaporated on n-type and p-type silicon (100) wafers ($\rho_{\text{Si}} = 1 - 5 \, \Omega\text{cm}$, $n_{\text{Si}} = p_{\text{Si}} = 2 \cdot 10^{15} \, \text{cm}^{-3}$). Silicon wafers were cleaned before by a buffered oxide etch procedure, removing the native oxide layer from the silicon to avoid oxide impurities which would also influence the properties of the Mg_2Si layer. The final thickness of the magnesium layers was determined by a micro quartz balance that is placed in the evaporation chamber. Samples afterwards were annealed in a tube furnace under argon atmosphere in order to reduce oxidation of the magnesium film during the high temperature annealing and reduces the loss of magnesium due to magnesium desorption [38].

Figure 7.1 (a) shows an SEM image of the surface of a 280 nm thick magnesium layer directly after it was evaporated on a silicon wafer. The hexagonal crystal structure of the as-deposited magnesium plates is clearly visible. Since those plates cover the complete surface it can be concluded that magnesium aligns crystalline on the surface. After annealing the sample (cf. figure 7.1 (b)), a Mg_2Si phase developed as is evident from the diffractogram shown in figure 7.1 (c). Concerning to the XRD measurement, it is pure Mg_2Si , with a strong (220) peak, indicating the (220) preferential orientation of the Mg_2Si film (ICDD Card no. 35-0773). This was i.a. also reported in [152]. Also, the strong (400) peak of the underlying silicon wafer was measured. In the SEM image of the annealed sample, net-like structures are visible. Based on EDX measurements, those segregations have a four times higher magnesium content than the Mg_2Si layer itself. It thus is expected that those segregations mostly consist of non-transformed magnesium. Most likely they originate from non-converted magnesium

7.1 Influence of the fabrication parameter on the material properties of Mg_2Si

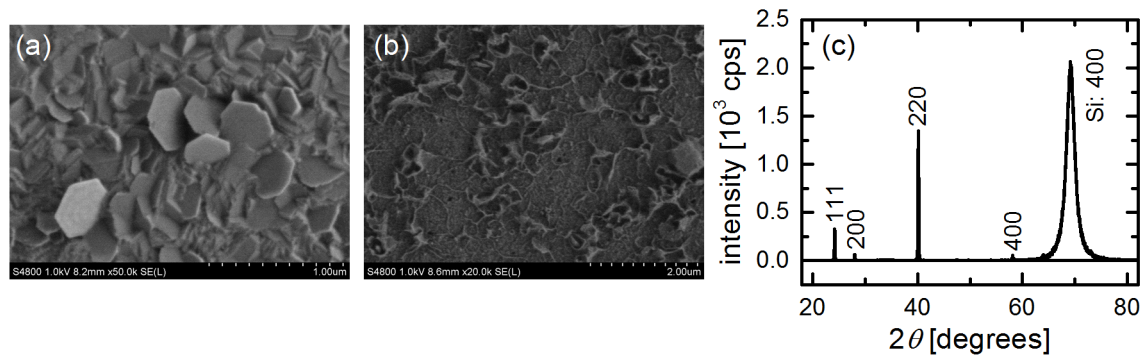


Figure 7.1: (a) SEM image of as-deposited magnesium on silicon by thermal evaporation. The hexagonal magnesium plates have a diameter of up to 400 nm and completely cover the surface. (b) After annealing the sample at 400°C for 1 hour, the hexagonal magnesium plates partially fused and formed a net-like structure on the surface. (c) XRD spectrum of the annealed sample confirming the presence of a pure Mg_2Si phase.

during annealing. No magnesium phase was detected, which might be due to the XRD measurements were performed in Bragg Brentano geometry, which is not sensitive enough to detect these surface-near segregations.

The goal of this section is to characterize the fabrication process of Mg_2Si in terms of varying fabrication parameters like the thickness of the evaporated magnesium, and the annealing temperature and time. With the help of these parameters, the transformation of the evaporated magnesium into Mg_2Si helps to understand and control the silicidation process at the interface of the magnesium–silicon system.

Variation of the thickness of the evaporated magnesium

Different thick magnesium layers were evaporated on silicon substrates, ranging from 50 nm up to 1000 nm.

Figure 7.2 exemplarily shows SEM images of 300 nm, 600 nm, and 1000 nm thick deposited magnesium films on silicon wafers which were subsequently annealed at 400°C for five hours. The temperatures of 400°C was chosen to be below the melting point of magnesium (which is at approx. 650°C).

XRD measurements confirmed the Mg_2Si phase. From the cross sections of the SEM images, the thickness of the grown Mg_2Si film can be determined with the help of a MATLAB routine. The thickness was measured at several positions in the SEM images and an average value for the thickness of the grown Mg_2Si layer was determined. This method is quite reliable, since the generated Mg_2Si layers are flat and homogeneous. It turned out that the thicker the deposited magnesium, the thicker the grown Mg_2Si layer was. The Mg_2Si fabrication process by evaporation is reproducible, as proven by many thickness measurements.

The resulting thicknesses for the grown Mg_2Si films are summarized in table 7.1. Furthermore, it needs to be considered that segregations have formed on the Mg_2Si surface, consisting of non-converted magnesium as identified by EDX measurements. The thickness of these segregations increased with the thickness of the deposited magnesium on silicon. The structure of the hexagonal magnesium crystallites on the Mg_2Si surface can be still seen in the SEM images shown in figure 7.2, although the samples were annealed. They cover the whole Mg_2Si surfaces and have no uniform height.

Additionally, the volumetric changes according to equations 3.10 and 3.11 are enlisted in table 7.1. Theoretically, the grown Mg_2Si film should be 38 % thicker than the deposited magnesium layer [38]. Actually, the grown Mg_2Si films in this work are approx. 12 % thicker than the proposed thicknesses in those equations, independent of the deposited magnesium layer. This might be due to differing values of the atomic density of the respective elements in the Mg_2Si phase, since the volumetric changes are calculated by these values. Probably the atomic packing factor of the grown Mg_2Si samples differs from the

7.1 Influence of the fabrication parameter on the material properties of Mg_2Si

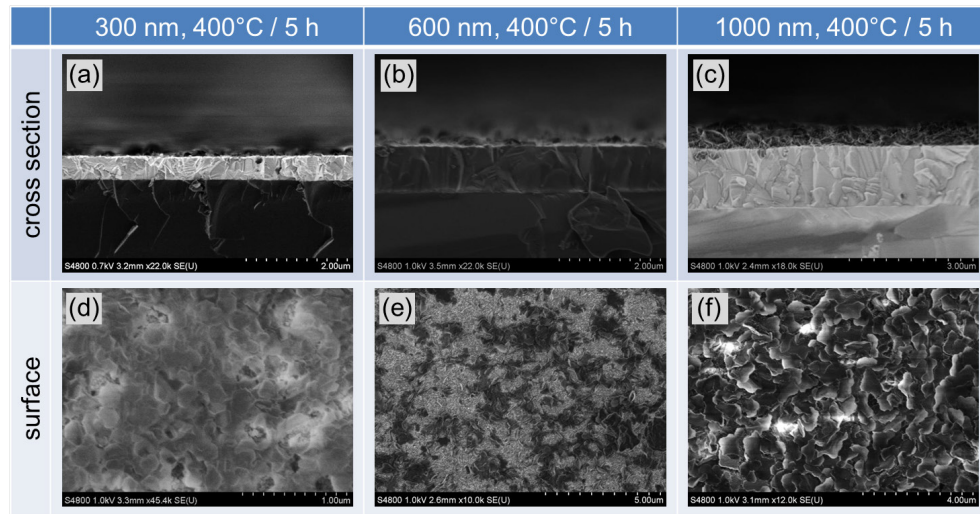


Figure 7.2: SEM images of cross sections (a–c) and surfaces (d–f) of Mg_2Si thin films formed by evaporating 300 nm (a, d), 600 nm (b, e), and 1000 nm (c, f) magnesium on silicon wafers with subsequent annealing at 400°C for five hours. The Mg_2Si layers appear flat and homogeneous. Segregation layers of non-converted magnesium covering the whole sample surface are clearly visible.

theoretical expected one. It also needs to be considered that equations 3.10 and 3.11 refer to the fact, that the whole deposited magnesium layer is consumed during silicide growth. It must be taken into account that some magnesium atoms might get lost due to desorption from the silicon surface during annealing because of the high vapor pressure of magnesium, [72]. Additionally, as can be seen from the SEM images, there are segregations on top of the Mg_2Si layers. EDX measurements confirmed that they consist of non-converted magnesium which thus does not involve in the calculation equations of the generated Mg_2Si layer. Finally in these calculations it needs to be considered, that there were also deviations in the homogeneity of the deposited magnesium layers during evaporation due to inaccuracies by the quartz

Table 7.1: Comparison of changes in layer thickness of Si, Mg and Mg_2Si after silicidation of magnesium layers of 300 nm, 600 nm, and 1000 nm thickness evaporated on silicon wafers and subsequently annealed at 400°C for 5 hours.

	thickness of deposited Mg layer d_{Mg}		
	300 nm	600 nm	1000 nm
predicted consumed Si according to equation 3.10 ($0.43 \cdot d_{\text{Mg}}$)	129 nm	258 nm	430 nm
predicted converted Mg_2Si according to equation 3.11 ($1.38 \cdot d_{\text{Mg}}$)	414 nm	828 nm	1380 nm
average measured thickness of grown Mg_2Si	463 nm	922 nm	1543 nm
deviation from predicted Mg_2Si thickness	11.8 %	11.4 %	11.8 %
thickness of segregations on Mg_2Si	138 nm	154 nm	443 nm

crystal. The deviations from the aimed magnesium film thickness are approx. ± 5 %, estimated by several calibrations of the tooling factor.

Variation of the temperature and annealing time of the samples in the tube furnace

Chu *et al.* reported that the formation of Mg_2Si films is already possible at temperatures of 200°C [149]. Figure 7.3 shows example SEM images of Mg_2Si layers which were formed from 1000 nm deposited magnesium on silicon wafers and subsequent annealing for five hours. The annealing temperatures were either 200°C or 400°C. In case of 200°C, the grown Mg_2Si film appears in the cross section view to be porous. Nevertheless, XRD measurements revealed a pure Mg_2Si phase.

7.1 Influence of the fabrication parameter on the material properties of Mg_2Si

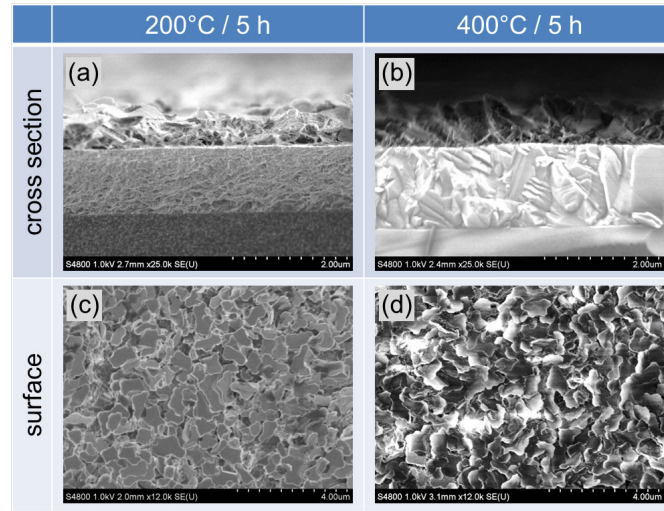


Figure 7.3: SEM images of cross sections (a, b) and surfaces (c, d) of Mg_2Si thin films formed by evaporating 1000 nm magnesium on silicon wafers with subsequent annealing at either 200°C (a, c) or 400°C (b, d) for five hours. The Mg_2Si films are flat and homogeneous for both temperatures.

Table 7.2 gives an overview of the measured Mg_2Si film thickness and the segregations on top as well as a comparison with the volumetric changes proposed in literature [38]. For the initial deposited magnesium thickness of 1000 nm, the grown Mg_2Si film under 200°C was 16 % thinner than proposed by equation 3.11. Obviously, less silicon was consumed during the silicidation process, which is probably associated with a slower diffusion of magnesium to the interface. In case of an annealing temperature of 400°C, a higher Mg_2Si film thickness was achieved than proposed. Again, segregations are present on top of the Mg_2Si layer. Since the Mg_2Si silicidation is proposed to be diffusion-controlled, it is unsurprising that the segregations are thicker in case of an annealing temperature of 200°C – at a higher temperature of 400°C, more magnesium was converted during the constant time of five hours.

Table 7.2: Comparison of changes in layer thickness of Si, Mg and Mg_2Si after silicidation of magnesium layers of 1000 nm thickness evaporated on silicon wafers and subsequently annealed at either 200 or 400°C for 5 hours.

	annealing temperature	
	200°C	400°C
predicted consumed Si according to equation 3.10 ($0.43 \cdot d_{\text{Mg}}$)	430 nm	430 nm
predicted converted Mg_2Si according to equation 3.11 ($1.38 \cdot d_{\text{Mg}}$)	1380 nm	1380 nm
average measured thickness of grown Mg_2Si	1159 nm	1543 nm
deviation from predicted Mg_2Si thickness	16.0 %	11.8 %
thickness of segregations on Mg_2Si	628 nm	443 nm

It thus can be concluded that 200°C are sufficient to provide silicidation and form Mg_2Si , but the consumption of the deposited magnesium occurs faster for higher temperatures. Also, an increase of the annealing temperature accelerates interdiffusion between the evaporated magnesium atoms and the silicon substrates.

Regarding the diffusion equation 3.12, it is obvious that also the time of annealing plays an important role in Mg_2Si silicidation [59]. Thus, for magnesium thicknesses of 300 nm, 600 nm, and 1000 nm respectively, the duration time of annealing was varied and the temperature in the furnace was kept constant at 400°C. In figure 7.4, three annealing times are shown exemplarily for a heating temperature of 400°C for a deposited magnesium layer of 1000 nm. In all cases, XRD measurements revealed the presence of a pure Mg_2Si phase. Surprisingly, even after a short annealing time of 10 minutes, a thick Mg_2Si layer has formed. The appearance of the Mg_2Si layers in the cross sectional view in terms of homogeneity is the same. This also

7.1 Influence of the fabrication parameter on the material properties of Mg_2Si

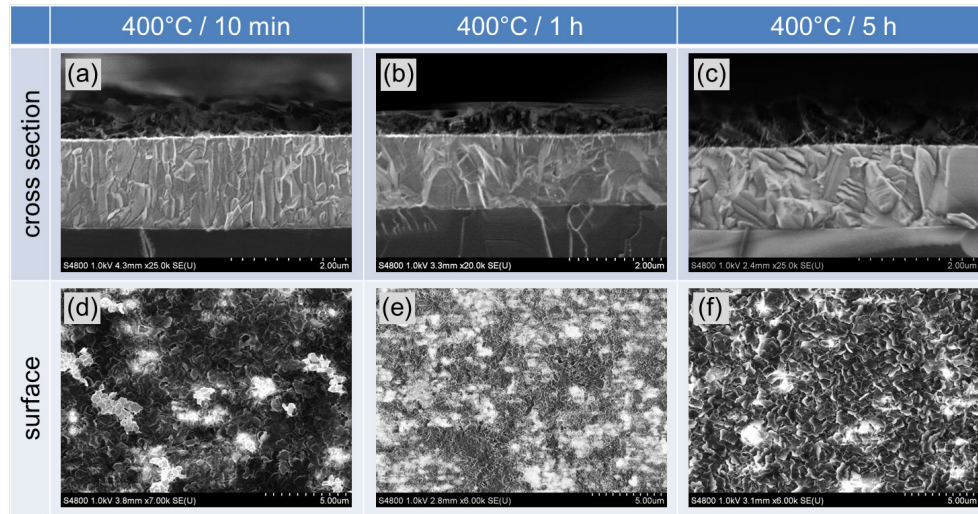


Figure 7.4: SEM images of the cross sections (a–c) and surfaces (d–f) of Mg_2Si thin films formed by evaporating 1000 nm magnesium on silicon wafers with subsequent annealing at 400°C for 10 min (a, d), one hour (b, e), or five hours (c, f). The resulting Mg_2Si layers all appear flat and homogeneous.

concerns the appearance of the segregations on the surface – there were obviously no differences between short or long annealing times – the segregations always covered the whole Mg_2Si surface.

The measured parameters for the annealing time variation are summarized in table 7.3. Surprisingly, already after an annealing time of 10 minutes, a relatively thick Mg_2Si layer has formed. Approximately the same Mg_2Si thickness was received after 5 hours of annealing. It can be concluded that already for a short time of annealing, a magnesium diffusion into silicon occurs, leading to the formation of Mg_2Si (as proven by XRD measurements). On the other hand, the segregation layers on the Mg_2Si surface after 10 minutes are higher than for a longer duration of annealing, which is probably due to the short annealing time.

In all XRD measurements of the formed polycrystalline Mg_2Si layers, the Mg_2Si phase was clearly present (see figure 7.1). The

Table 7.3: Comparison of changes in layer thickness of Si, Mg and Mg₂Si after silicidation of magnesium layers of 1000 nm thickness evaporated on silicon wafers and subsequently annealed at 400°C for either 10 min, 1 hour or 5 hours.

	duration of annealing		
	10 min	1 h	5 h
predicted consumed Si according to equation 3.10 ($0.43 \cdot d_{\text{Mg}}$)	430 nm	430 nm	430 nm
predicted converted Mg ₂ Si according to equation 3.11 ($1.38 \cdot d_{\text{Mg}}$)	1380 nm	1380 nm	1380 nm
average measured thickness of grown Mg ₂ Si	1531 nm	1542 nm	1543 nm
deviation from predicted Mg ₂ Si thickness	10.9 %	11.7 %	11.8 %
thickness of segregations on Mg ₂ Si	514 nm	515 nm	443 nm

diffractograms showed a strong (220) peak, revealing the (220) preferential orientation of the grown Mg₂Si films. The peak intensity of the signals was stronger, the more magnesium was evaporated. It was also stronger, the longer and higher the annealing time of the samples was. On the other hand, segregations were seen on each sample, independent of the fabrication process and varied parameters. They probably originate from non-converted magnesium and are proven to consist of magnesium by EDX measurements. They could not be explicitly determined by XRD measurements due to the non-surface sensitive Bragg Brentano geometry. This on the other hand is surprising, since the segregations reached thicknesses of up to 630 nm in average, which should be thick enough to be noticed in the diffractograms. Furthermore it needs to be considered that from XRD measurements, statements about the structure of the Mg₂Si phase can be made. An interdiffusion of silicon from the underlying

7.1 Influence of the fabrication parameter on the material properties of Mg_2Si

wafer to the Mg_2Si surface can be excluded, since magnesium is the predominant diffusion species in the Mg–Si silicidation system [149].

Note, that annealing of the samples was also performed on a hotplate which was located in a glovebox, but it turned out that the generated Mg_2Si layers were not as flat and homogeneous as in the tube furnace. Besides, the furnace provided a stable inert atmosphere by an adjustable argon flow through the furnace. Furthermore, the heating and cooling ramp of the furnace could be adjusted in order to control the Mg_2Si formation (5 K/min), which was not possible with the hotplate. Thus, the presented Mg_2Si layers in this work were all generated in the tube furnace.

For further characterization of Mg_2Si thin films in devices, which also included different Mg_2Si layer thickness dependencies, a standard fabrication routine was determined. It was decided to anneal the samples in the tube furnace at a temperature of 400°C for five hours, although already 10 minutes would have been sufficient to generate Mg_2Si films, leading to less energy consumption (cf. figure 7.4).

Additionally, the presence of segregations occurred in case of every chosen magnesium thickness and annealing temperature and duration – only by heating it longer, segregations would not disappear. But the 400°C / 5 h method was applied to every fabricated sample, since it showed the highest reproducibility thickness of the generated Mg_2Si films and lowest segregation thickness.

As mentioned before, the existence of segregations, probably due to a lack of magnesium conversion, is not greatly discussed in literature. Serikawa *et al.* also reported from magnesium rich grains which formed at the surface [70]. They also found an increased magnesium concentration at grain boundaries

Since the formation of Mg_2Si is diffusion-controlled, it is very sensitive to the annealing temperature and time. Measurements with changing annealing time were also carried out for other thicknesses of evaporated magnesium on silicon. The segregations were still present after annealing times of 10 hours, although the thickness growth of

Mg_2Si layers did not further proceed (results not shown). Thus it can be concluded, that magnesium films do not completely convert into Mg_2Si . It is also possible that even within the Mg_2Si layers both Mg_2Si and magnesium crystallites are present, although XRD measurements reveal only the Mg_2Si phase – these data therefore must be interpreted with caution.

One explanation is that although transport from the evaporation chamber to the tube furnace for annealing took place in inert atmosphere, the process anyways was interrupted. There was no smooth transition during silicidation process, although the silicon wafers with deposited magnesium were immediately transported to the tube furnace. But probably too much time passed until the tube furnace raised temperature. Other research groups anneal the silicon substrate in parallel during deposition of magnesium, which immediately formed Mg_2Si during the deposition process [59, 154, 156]. No findings of segmentations in literature for the evaporation method were made. It was reported that excess Mg atoms desorbed from the surface [70, 156, 189]. However, simultaneous heating of the silicon wafers was not performed in this work but for further applications of Mg_2Si in solar energy conversion devices, the removal of these metallic segregations was absolutely necessary to provide pure Mg_2Si thin films.

Ion beam etching of Mg_2Si

To ensure a characterization of pure Mg_2Si thin films, the removal of these segregations is realized by ion beam etching (IBE), which belongs to the dry etching methods under vacuum conditions. IBE was performed on every Mg_2Si sample, after it was fabricated by the evaporation of magnesium to a silicon wafer and subsequent annealing.

Figure 7.5 shows example SEM images of the general appearance of the Mg_2Si surface before and after IBE treatment. In Figure 7.5 (a), a Mg_2Si surface is shown which formed from 100 nm evaporated

7.1 Influence of the fabrication parameter on the material properties of Mg_2Si

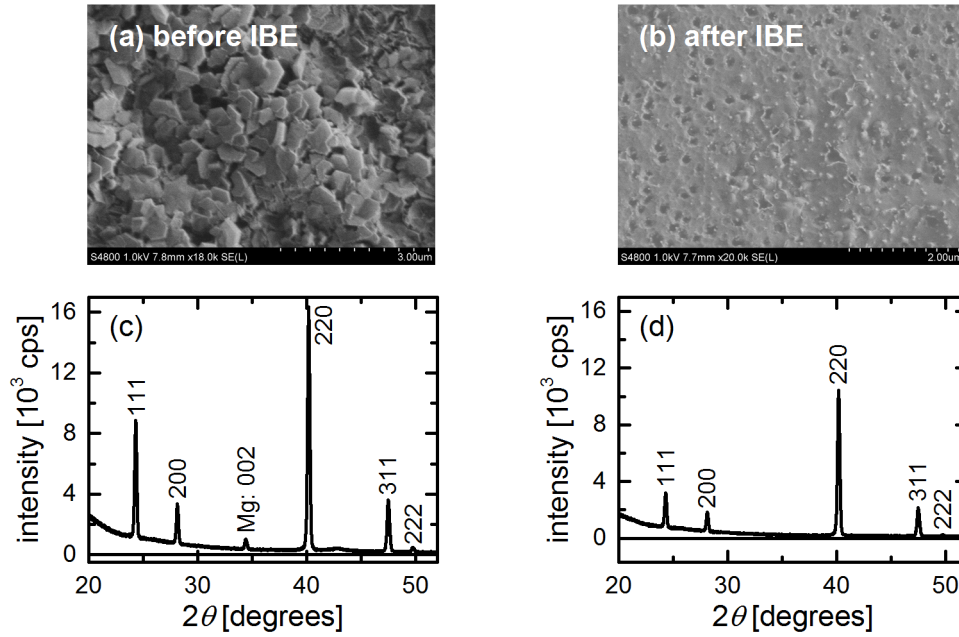


Figure 7.5: SEM images (a, b) and XRD spectra (c, d) of the surfaces of Mg_2Si before (a, c) and after IBE (b, d). The hexagonal, non-converted magnesium segregations were completely removed after IBE, leaving crater-like holes on the IBE-treated Mg_2Si surface. The magnesium peak visible in the XRD spectrum of the sample before IBE (c) is gone after IBE treatment (d).

magnesium on a silicon wafer with subsequent annealing at 400°C for 5 hours. The segregations, again visible by the hexagonal plates on the Mg_2Si surface, cover the whole Mg_2Si surface with different thicknesses – they do not have an uniform height. An average height of approx. 50 nm was estimated from the cross sectional SEM view (not shown here). IBE was applied to remove 60 nm with an etch rate of 10 nm/min to ensure the complete removal of segregations. As can be seen in figure 7.5 (b), segregations were obviously completely removed by IBE. Instead, the bullet holes of the ions can be clearly seen. These craters have a diameter of approx. 200 nm and homogeneously cover the complete Mg_2Si surface. The treated Mg_2Si surface now appears to be flat without bumps as before with segregations.

Due to a lack of sensitivity, segregations could not be detected by Bragg Brentano geometry. Thus, near-surface XRD measurements were performed (GIXRD) with the help of a Göbel mirror. Figure 7.5 (c) and (d) show diffractograms of Mg_2Si samples before and after IBE treatment, respectively. A magnesium (002) peak at 34.4° (ICDD Card no. 35-0821) was observed in the sample of the initial fabricated Mg_2Si film – this peak vanished after IBE etching, leading to the conclusion that excess magnesium could be removed. Also, the intensity of the XRD signal decreased after IBE, most likely due to the reduced thickness. Still, due to the distinct peak at (220), it is the preferred orientation.

The corresponding etch rate was adjusted for every single segregation height, which originated from the different evaporated magnesium thicknesses and measured from the SEM cross sections. They were removed generously to ensure complete removal of these disturbing metallic artifacts on the samples.

Figure 7.6 shows SEM images of approx. 473 nm Mg_2Si , which was fabricated by evaporating 300 nm magnesium on silicon with subsequent annealing at 400°C for 5 hours. The segmentations had an average height of approx. 112 nm. IBE was applied to remove 120 nm of the upper surface with an etch rate of 10 nm/min. This means that the complete segmentation area was removed, resulting in a homogeneous and uniform removal. The cross section of the Mg_2Si layer after treatment with IBE showed a homogeneous Mg_2Si film with an average thickness of approx. 360 nm. The impact of the ions on the surface of the sample after IBE can be clearly seen in figure 7.6 (d). The average diameter of these craters was approx. 200 nm. No traces of segmentation can be seen anymore. Only some left overs can be noticed in the background of the cross sectional SEM view. The same qualitative results were obtained for Mg_2Si layers of 914 nm thickness after IBE etching of approx 300 nm (cf. figure 7.7). For 1540 nm thick layers and etching of approx. 500 nm the sample

7.1 Influence of the fabrication parameter on the material properties of Mg_2Si

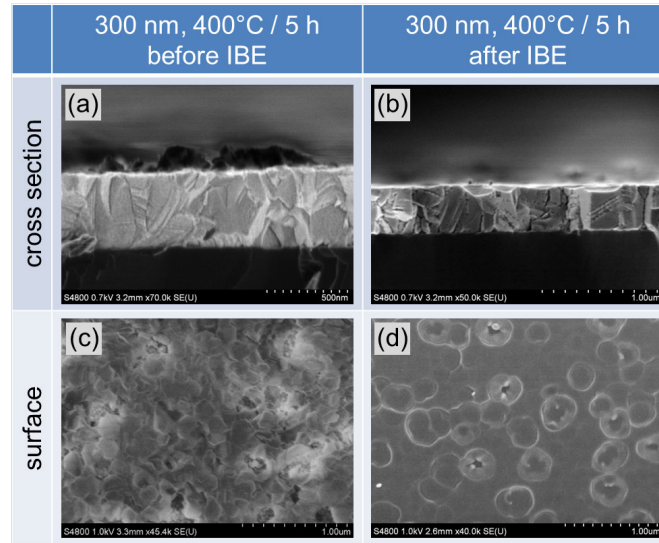


Figure 7.6: SEM images of cross sections (a, b) and surfaces (c, d) of Mg_2Si layers of approx. 473 nm thickness formed by deposition of 300 nm magnesium on silicon wafers and subsequent annealing at 400°C for 5 hours. Images are shown before (a, c) and after (b, d) IBE treatment. Before IBE the samples show segregations on the surface. After IBE etching with removal of approx. 150 nm the Mg_2Si layer was flat and homogeneous and free of segmentations. The craters of ion bombardment with diameters of about 200 nm can be clearly seen.

surface was left with a small amount of Mg left-overs covering the whole surface (cf. figure 7.8).

It could be proven, that ion beam etching successfully removed excess segregations from the Mg_2Si surfaces. Smooth and segregation-free Mg_2Si layers were guaranteed, existing of pure Mg_2Si phase as measured by XRD.

The advantage of fabricating Mg_2Si thin films by magnesium evaporation is the cheap manufacturing process. Also, for device fabrication, the underlying silicon substrate is already provided, thus enabling a direct characterization of Si- Mg_2Si junctions. On the other hand, although a reproducible process for Mg_2Si fabrication was found, there

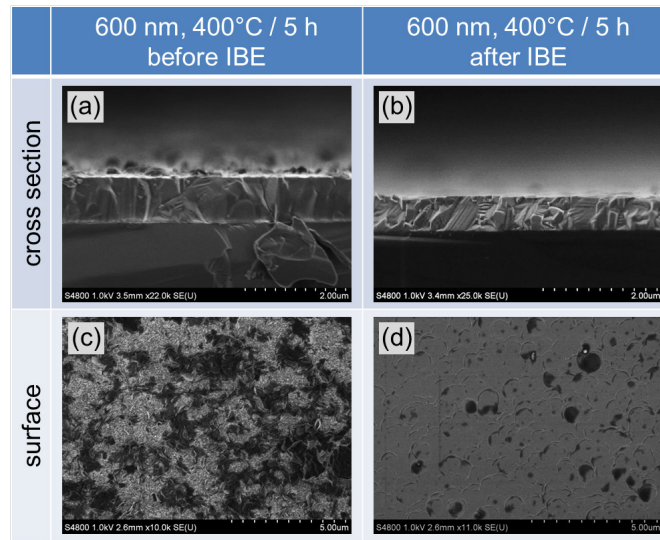


Figure 7.7: SEM images of cross sections (a, b) and surfaces (c, d) of Mg_2Si layers of approx. 914 nm thickness formed by deposition of 600 nm magnesium on silicon wafers and subsequent annealing at 400°C for 5 hours. Images are shown before (a, c) and after (b, d) IBE treatment. Before IBE the samples show segregations on the surface. After IBE etching with removal of approx. 300 nm the Mg_2Si layer was flat and homogeneous and free of segmentations.

are still fluctuations in the finally achieved thickness of the Mg_2Si layer which depend on deviations in the deposited magnesium film, and the adjusted temperature. Additionally, the non-uniform height of the segmentations makes a consistent etching procedure difficult. It also needs to be considered that IBE is a step backwards in Mg_2Si sample preparation. Mg_2Si films which have a higher thickness show also higher segmentations and thus require more etching. Thus, the waste of non-converted magnesium to gain thicker Mg_2Si films is higher. Finally, a characterization of pure Mg_2Si thin films is, due to the underlying silicon wafer, not possible – errors concerning a possible contribution or interaction with silicon can occur, leading to modified results in Mg_2Si characterization. In addition, a complete

7.1 Influence of the fabrication parameter on the material properties of Mg_2Si

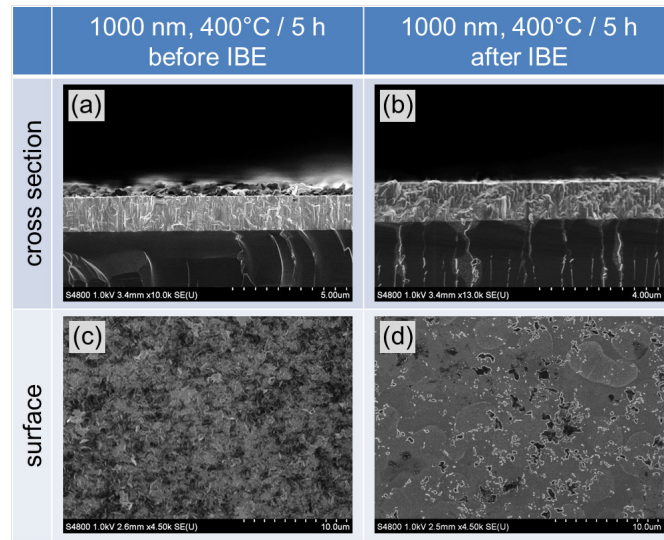


Figure 7.8: SEM images of cross sections (a, b) and surfaces (c, d) of Mg_2Si layers of approx. 1540 nm thickness formed by deposition of 1000 nm magnesium on silicon wafers and subsequent annealing at 400°C for 5 hours. Images are shown before (a, c) and after (b, d) IBE treatment. Before IBE the samples show segregations on the surface. After IBE etching with removal of approx. 500 nm the Mg_2Si layer was flat and homogeneous. The surface after IBE treatment still showed traces of magnesium left-overs, which spread across the sample surface.

segmentation-free pure Mg_2Si surface can not be provided, especially for thick evaporated magnesium (e.g., 1000 nm, cf. figure 7.8).

7.1.2 Sputtering of Mg_2Si on silicon and glass

All in all, the fabrication of Mg_2Si with the evaporation method, subsequent annealing and additional ion beam etching was quite extensive and, due to many parameters, partially unreliable. Thus, another diffusion synthesis method – sputtering – was applied.

The advantage of sputtering is, that Mg_2Si films were sputtered directly from a Mg_2Si sputter target (hot-pressed Mg_2Si granulate, 2N5 purity, FHR centrotherm group) on glass substrates. Glass substrates were cleaned in a sequential arrangement of ultrasonic baths in mucasol (0.2 %), acetone, isopropanol, and deionized water. Smears that were left on the substrates had an enormous influence on the attachment of the sputtered Mg_2Si layer – the smears showed through the deposited Mg_2Si layer and thus needed to be avoided by a thoroughly dry blowing of the glasses. Additionally, also silicon wafers were used as substrate material.

Sputtering was performed in a Kenotec sputtering system. Thin Mg_2Si layers were grown in the DC magnetron mode under argon atmosphere at a pressure of 2 mbar and a sputter power of 200 W. Before the deposition of Mg_2Si , the surfaces of Mg_2Si target and silicon or glass substrates were cleaned by argon ion sputtering for approx. 10 minutes. It was paid attention that a homogeneity in the thickness was adhered, but a deviation of approx. 25 % from the middle to the border (distance: 150 mm) was estimated from the calibration. The distance between the sputter target and the glass substrates was approx. 100 mm. Mg_2Si was sputtered from the target with a sputter rate of 28.7 nm/min.

Figure 7.9 shows XRD spectra taken on the surface of a 1000 nm Mg_2Si layer freshly sputtered on glass and after annealing. Before annealing, a broad peak at around 25° is observed which could stem from the underlying glass substrate, but is more likely from an amorphous Mg_2Si phase. Mg_2Si has probably adsorbed amorphously on glass during the sputtering process. In this context, Serikawa *et al.* [70] used a target composed of Si and Mg with various area ratios and discussed the formation of an Mg_2Si amorphous bottom layer and crystalline Mg_2Si upper layer. The Mg–Si phase diagram [51] indicates that Si and Mg have an insignificantly small solubility in each other at room temperature. When depositing Mg and Si from the sputter target, Si is supersaturated with Mg. Magnesium

7.1 Influence of the fabrication parameter on the material properties of Mg_2Si

migrates to the surface leading to a low concentration of Mg in the amorphous layer [70]. To receive crystalline Mg_2Si films, in the present work the sputtered Mg_2Si layers were annealed at 400°C for five hours. After annealing, the crystalline Mg_2Si phase formed as can be seen in the corresponding XRD spectrum in figure 7.9 (b). Already before annealing the preferential (111) orientation of Mg_2Si can be noticed. However, after annealing the broad amorphous peak almost completely vanished and the (111) signal is much more pronounced. This orientation was also mentioned in [40, 62, 63, 70, 145]. Figure 7.9 (c) and (d) shows SEM images taken from the cross section and surface of the sample after annealing. No segregations are present and the Mg_2Si layers are flat from the beginning. From the SEM image of the Mg_2Si surface in figure 7.9 (d), it can be seen that it appears to be grainy. This could be due to the growth of uniform columnar Mg_2Si grains, which were also obtained in [40, 152] by RF magnetron sputtering.

An explanation for the presence of sputtered Mg_2Si as amorphous phase concerns the fact that with increasing Mg_2Si thickness during the sputtering of magnesium-silicon films, the higher the compression of the accumulated film is. A detailed description is given in [70], where Serikawa *et al.* reported of magnesium segmentations on the Mg_2Si surface, which were obtained when sputtering was applied [70]. Obviously, the sputtered Mg_2Si films on glass consist of a crystalline Mg_2Si upper layer and an amorphous arranged bottom layer. During subsequent annealing, the weakly bonded magnesium atoms can diffuse easily to form highly stoichiometric Mg_2Si films. Interestingly, the sputtered Mg_2Si layers in this work did not show such segmentations. As for the evaporated magnesium layers in the previous chapter, an annealing temperature of 400°C for 5 hours was finally applied for all sputtered Mg_2Si thicknesses. Concerning to Xiao *et al.*, high quality sputtered Mg_2Si films were obtained by these parameters, independent of the thickness of the deposited Mg_2Si layers [152].

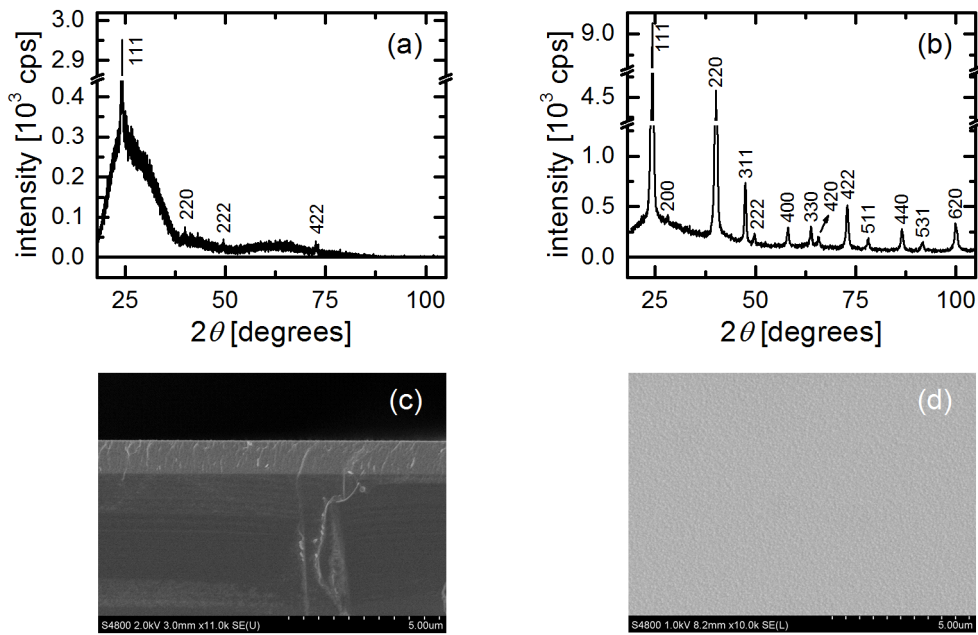


Figure 7.9: XRD spectra (a, b) and SEM images of the cross section (c) and surface (d) of Mg_2Si sputtered on glass before (a) and after (b–d) annealing at 400°C for 5 hours. After annealing the formerly amorphous Mg_2Si phase turned to a crystalline phase with a (111) texture and a flat and homogeneous Mg_2Si layer formed, which has no magnesium segmentations on its surface.

There are clear differences between the formation of Mg_2Si by evaporation and sputtering in this work. In case of evaporation, segmentation of non-converted magnesium on the surface was obtained. The preferential orientation was in (220) direction. On the contrary, by fabricating Mg_2Si with the sputtering technique, no segmentation, but rather a grainy Mg_2Si was achieved which was grown in (111) orientation. In general, various Mg_2Si orientations have formed for both fabrication techniques used in this work to receive polycrystalline Mg_2Si films. For further characterization, both fabrication techniques were applied, which both had advantages and disadvantages.

Having discussed how to fabricate Mg₂Si, the next section of this work addresses the preparation of the Mg₂Si samples for electrical and optical characterization.

7.2 Mg₂Si sample preparation

For most of the characterization methods applied to Mg₂Si as well as its usage as photoactive layer, an appropriate sample preparation of the fabricated Mg₂Si needs to be taken. For all kind of characterization measurements, a pure Mg₂Si surface needed to be ensured. Thus, dependent on the characterization method, either sputtered and annealed Mg₂Si samples or evaporated and annealed Mg₂Si samples with a subsequent ion beam etching were used.

Nickel, as mentioned in section 3.2 shows good ohmic properties as contact material and therefore was DC magnetron sputtered on the Mg₂Si layer under argon atmosphere at a pressure of 2 mbar and a sputtering power of 400 W. The nickel sputter rate was approx. 54.9 nm/min. Before, to guarantee as less contamination and disturbance in the ohmic contact formation, the Mg₂Si layers were slightly etched back in the sputtering chamber. This was done under argon atmosphere with a pressure of 12 mbar and a sputtering power of 50 W. The etch back rate was approx. 1 nm/min (calibrated for copper).

An ohmic contact of the deposited nickel on Mg₂Si was confirmed by two-point measurements. Additionally, aluminum was used as electrode material, which showed the same results in terms of resistivity and Hall parameters. It is not further mentioned in this work.

Figure 7.10 shows photos of the contacted Mg₂Si samples for their different applications. In figure 7.10 (a), Mg₂Si samples are contacted with four nickel electrodes for the van der Pauw measurements and Hall measurements. Figure 7.10 (b) shows the design for the measurements with the solar simulator. Copper stripes are glued with

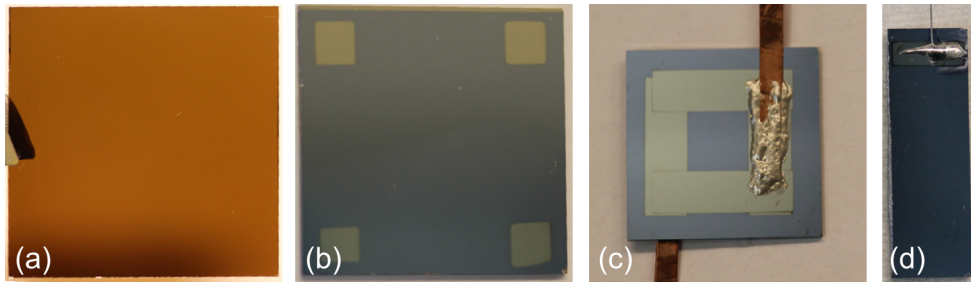


Figure 7.10: Photographs of Mg_2Si samples. (a) 50 nm Mg_2Si on glass; (b) 1 μm Mg_2Si on glass with four nickel electrodes for van der Pauw and Hall measurements; (c) 1 μm Mg_2Si on silicon with nickel surrounding an active area for solar simulator measurements; (d) 3 μm Mg_2Si on glass with an insulated nickel contact to be used as photoelectrode. All samples were sputtered and subsequently annealed.

a silver epoxy to the nickel electrode, which has an opening which forms the active layer of the Mg_2Si solar cell. These copper stripes are connected via crocodile clips to a Keithley source measurement unit. In figure 7.10 (c), a Mg_2Si photoelectrode is shown with an insulated nickel electrode.

8 Properties of Mg_2Si Thin Films

As pointed out in the introduction of this work, the use of Mg_2Si as photoactive material shows promising properties from a theoretical perspective, thus little is known about its applicability. This chapter describes and discusses the characterization of the Mg_2Si samples fabricated as described in the previous chapter. First, the electrical properties of Mg_2Si are investigated, giving i.a. information about resistivities and doping concentration of Mg_2Si samples. Afterwards, the usage of Mg_2Si in optoelectronic devices as well as its stability in aqueous media will be discussed.

8.1 Electrical properties

As was described in the previous chapter, Mg_2Si samples were contacted preferably with 300 nm thick nickel electrodes, providing a good ohmic contact. This contact ensures a proper characterization of the electrical properties of the Mg_2Si thin films, which, concerning to literature, have a relative high conductivity [57, 59].

Resistivities of Mg_2Si samples were measured in a van der Pauw setup. The basic principles were described in chapter 4.1. On the one hand, in order to guarantee a correct resistivity measurement, Mg_2Si layers were characterized on non-conductive substrates, as it is common practice. In that case, glass substrates were used – and thus the sputtered Mg_2Si were suitable. On the other hand, to also include characterization for the Mg_2Si layers which were fabricated

by evaporation of magnesium, Mg_2Si films on silicon substrates were also measured. Note, that due to the magnesium segregations, only IBE-treated samples were used. The silicon wafers had a resistivity of 1-5 $\Omega\text{ cm}$.

The measured resistivity of pure magnesium layers evaporated on silicon wafers without subsequent annealing is in the order of 10^{-6} $\Omega\text{ cm}$. This is also in accordance with the order of magnitude given in literature concerning metals in general, pointing out the high conductivity of metals. This measured value is also in agreement with the SEM image in figure 7.1 in the previous chapter, where hexagonal plates could be found on a magnesium layer which was not annealed.

Table 8.1 gives an overview of some of the measured resistivity values. In case of silicon wafers as substrates, the measured resistivities of the evaporated or sputtered Mg_2Si layers were in the range of 10^{-2} to 10^{-4} $\Omega\text{ cm}$.

The resistivities differed in orders of magnitudes from the resistivities of the underlying silicon substrates (which were in the range from 1-5 $\Omega\text{ cm}$). It thus is ensured that the pure Mg_2Si layer is measured and not the underlying silicon substrate. As mentioned before, all evaporated fabricated samples for electrical characterization were IBE-treated before electrical characterization. It thus was not possible to measure the influence of segregations on the Mg_2Si surfaces. Since those segregations consisted mainly of excess magnesium, a resistivity in the range of 10^{-6} $\Omega\text{ cm}$ should have been measured. This was not the case, excluding a contribution of magnesium left-overs on the surface. Variations of the measured resistivities in general are probably due to small differences in the fabrication process – but there were no huge deviations of the measured values. The determined resistivities from measurements of several Mg_2Si samples with the same fabrication properties were all in the same range, which illustrates the reproducibility of the Mg_2Si samples.

In case of the sputtered Mg_2Si layers on glass, the resistivities were orders of magnitudes higher compared to Mg_2Si samples grown on

Table 8.1: Overview of resistivity values for a number of different Mg_2Si samples with different film thicknesses and deposited either on silicon wafers ($\rho_{\text{Si}} = 1 - 5 \Omega\text{cm}$) or glass by either evaporation (e) or sputtering (s). All Mg_2Si samples were contacted with 300 nm nickel electrodes and measured in a van der Pauw setup.

	sample number									
	1	2	3	4	5	6	7	8	9	10
Mg_2Si thickness [μm]	0.1	0.3	0.6	1.0	0.3	3.0	3.0	3.0	3.0	3.0
substrate	p-Si	p-Si	p-Si	p-Si	p-Si	p-Si	n-Si	glass	glass	glass
deposition method	e	e	e	s	s	s	s	s	s	s
ρ [$10^{-3}\Omega\text{cm}$]	9.86	1.91	2.96	4.65	0.959	34.0	39.7	1160	1180	3530

silicon. It could be assumed that the pure Mg_2Si layer was measured, since glass is insulating and the Mg_2Si layers had no segregations on their surfaces. The different order of magnitudes of the given measurement values for the evaporated and sputtered Mg_2Si layers on different substrates may be due to different crystallization processes of Mg_2Si on glass and silicon and need to be studied in detail in future investigations.

It turned out that the selection of an appropriate contact metal is secondary, since the evaporated Mg_2Si layers are quite well conducting, enabling (almost) any metal to form a good ohmic contact with Mg_2Si . Samples that for example had 300 nm thick aluminum or magnesium electrodes, were also characterized by the van der Pauw method, leading to similar results in the same resistivity range of as nickel electrodes, although nickel was reported to have best ohmic properties [158, 159].

To gain information about a variety of electrical properties of the Mg_2Si samples, Hall measurements were carried out at a self-constructed setup at the i-Meet institute at room temperature. These

measurements were also interesting with respect to the further usage of Mg_2Si as optoelectronic device, where an n-doped or p-doped silicon wafer is necessary to ensure a heterojunction. The principles of Hall measurements and the received information as well as the experimental setup were explained in detail in chapter 4.1. The Hall measurements included also resistivity measurements of Mg_2Si , which were in good agreement with the data measured by the van der Pauw setup (cf. table 8.1).

By applying a magnetic field via Helmholtz coils to the measured samples, which were located perpendicular to the build up magnetic field, parameters like the doping concentration and mobility of the charge carriers in Mg_2Si could be determined. The corresponding formulas are listed in section 4.1. An overview of the obtained values is given in table 8.2, where a variety of Mg_2Si samples with different fabrication parameters and layer thicknesses were measured. Furthermore, the measured parameters enlisted in table 8.2 show a wide variety of orders of magnitude which is obviously independent on the film thickness of the measured Mg_2Si layers.

Contrary to literature, where intrinsic Mg_2Si is said to be n-type, no proper doping type can be defined for samples in this work. One reason could be due to impurities, which could be not proven by EDX measurements. These residual impurities may arise from an insufficient cleaning of the Si or glass substrate, insufficient purity of the Mg pellets or Mg_2Si sputter target as well as process impurities. This was also supposed in [40, 53, 190], where Al impurities were incorporated.

8.2 Photoactivity of Mg_2Si and its applicability as solar cell

In addition to the electrical properties, it is important to ask about the ability of Mg_2Si to absorb light for its use as optoelectronic device,

8.2 Photoactivity of Mg_2Si and its applicability as solar cell

Table 8.2: Overview of parameters determined from Hall measurements on Mg_2Si samples of different thicknesses and produced by either evaporation (e) or sputtering (s) of Mg onto either Si or glass substrates. The resistivity of the underlying Si substrates was $\rho_{\text{Si}} = 1 - 5 \, \Omega \text{ cm}$. Shown are the resistivity, ρ , the mobility of the majority carriers, μ , the charge carrier concentration of the majorities, n or p , as well as the doping type of the sample. All Mg_2Si samples are contacted with 300 nm nickel electrodes.

	sample number										
	1	2	3	4	5	6	7	8	9	10	11
film thickness [μm]	0.1	0.3	0.6	1.0	3.0	3.0	0.3	3.0	3.0	3.0	3.0
substrate	p-Si	p-Si	p-Si	p-Si	n-Si	p-Si	glass	glass	glass	glass	glass
deposition	e	e	e	s	s	s	s	s	s	s	s
ρ [$\text{m}\Omega \text{ cm}$]	0.227	1.64	1.55	46.3	13.0	9.75	695	356	656	2140	620
R_H [cm^3/C]	0.0337	0.238	0.215	0.186	-11.4	1.83	6.29	0.224	-0.596	15.8	-620
μ [cm^2/Vs]	149	146	138	4.00	875	187	9.05	0.63	0.91	7.40	7.98
n or p [10^{19} cm^{-3}]	18.6	2.62	2.91	3.37	0.055	0.342	0.298	2.80	1.05	0.0395	0.126
doping	p	p	p	p	n	p	p	p	n	p	n

e.g., in solar cells or as photoelectrode. As already reported by Scouler in 1969, Mg_2Si has a high absorption coefficient of $\alpha = 3.5 \cdot 10^5 \text{ cm}^{-1}$ at 2.5 eV [67]. At this energy (converted approx. 500 nm) the absorption coefficient is about 40 times higher than that of c-Si. Thus, already small thicknesses of Mg_2Si layers would be sufficient to absorb light. Due to its band gap, Mg_2Si is able to absorb the entire visible spectrum up to the near-IR region, making it an attractive candidate for solar energy conversion devices.

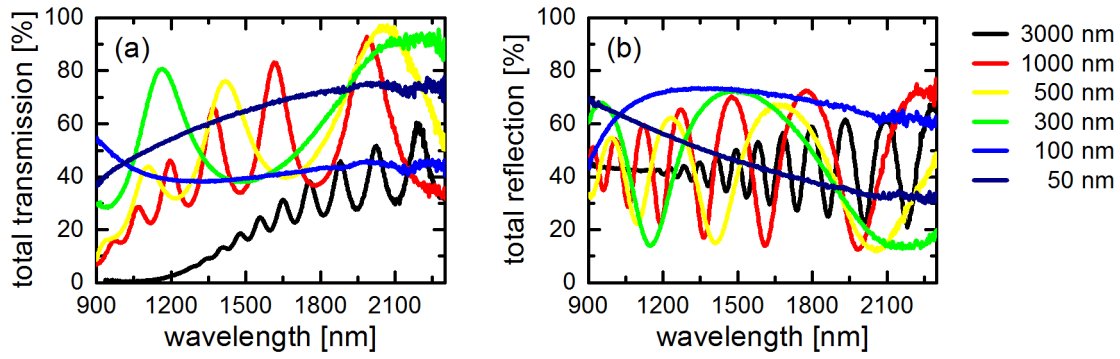


Figure 8.1: Spectra of total transmission (a) and reflection (b) of Mg_2Si films sputtered on glass substrates. Spectra were measured in an integrating sphere and Fabry-Perot interferences are clearly visible.

8.2.1 Transmission and reflection of Mg_2Si

Transmission and reflection measurements were carried out with the help of a UV/Vis spectrometer with an integrating sphere where it is distinguished between the total and diffuse part. Sputtered Mg_2Si layers with various thicknesses on glass were studied to gain information about the behavior of a pure Mg_2Si film without an interaction with an absorbing silicon substrate.

Figure 8.1 shows the total transmission and reflection spectra of Mg_2Si films with different thicknesses fabricated by sputtering on glass. Interferences in the spectra can be clearly seen. Those so-called Fabry-Perot interferences develop when light passes, e.g., through a thin film of a reflecting material. The incident light is reflected at both boundary layers (glass and Mg_2Si) a number of times, leading to either constructive or destructive interference, depending on the wavelength and the thickness of the reflective layer. Constructive interference arises when the thickness of the layer is a multiple of the half wavelength of the incident light. The Mg_2Si films are, due to the sputtering, highly reflective, thus presenting a resonator for

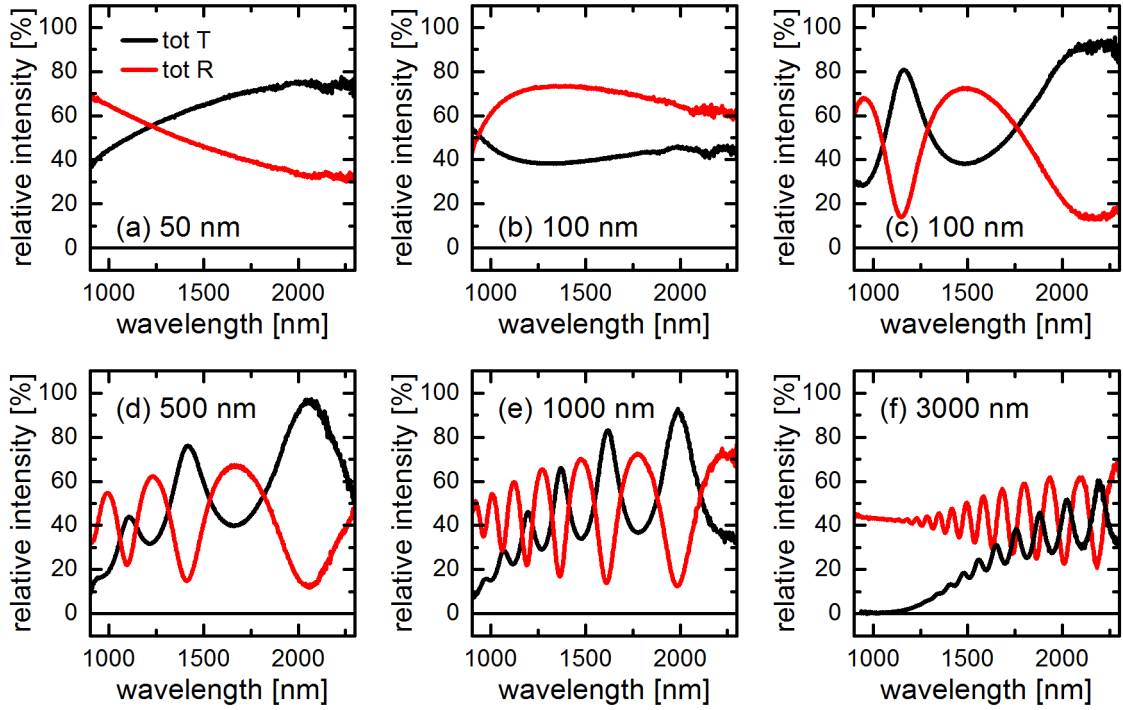


Figure 8.2: Transmission and reflection measurements for different film thicknesses of Mg_2Si as indicated in (a)–(f). Spectra include both the direct and diffuse part.

the formation of Fabry-Perot interferences. As can be seen from the spectra in figure 8.1, the interferences are obviously dependent on the thickness of Mg_2Si films. The higher the film thickness, the more interferences appear for both the transmission and the reflection spectra, whereas for 50 nm and 100 nm Mg_2Si films, there are almost no interferences visible anymore. A diffuse reflection of approx. 8 % was measured for all Mg_2Si thicknesses (spectra not shown). It furthermore can be concluded that the sputtered Mg_2Si samples show no scattering and that the direct transmission and specular reflection are the main contributions.

Figure 8.2 gives an overview of the total and diffuse transmission and reflection spectra for different thicknesses of Mg_2Si layers sputtered

on glass. In most cases (except for 3 μm thickness), the extreme values of the interferences are super-imposed.

Since the absorption is defined as $A = 100 \% - T - R$, it can be seen from the 500 nm, 1 μm , and 3 μm thick Mg₂Si layers that absorption occurs only until approx. 1300 nm. It shows the tendency to be higher in the visible range. In case of 3 μm thick films, Mg₂Si is furthermore able to absorb in the IR range.

Figure 8.3 gives an overview of the calculated refractive indices n for 500 nm, 1000 nm, and 3000 nm thick films. They were calculated based on the local extreme values in the transmission spectra by applying the so-called envelope method [191–194]. From that the refractive index is calculated as

$$n = \frac{\lambda_m \lambda_{m+1}}{2(\lambda_m - \lambda_{m+1})n_{\text{Si}}}, \quad (8.1)$$

where d is the thickness of the film and m is the order of the extreme value at the corresponding wavelength λ . As can be seen from the graphs, the values for the different thicknesses of Mg₂Si are in good agreement. For thinner deposited Mg₂Si layers, due to a lack of turning points, no calculation of n was possible anymore. A refractive index of $n = 3.591$ is given in literature [67].

From the measured transmission and reflection spectra, theoretically, the band gap of the Mg₂Si layers should be estimated according to equation 4.4 (cf. section 4.1). Since the band gap is indirect, it can be estimated from the intercept at $\alpha^{1/2} = 0$. But in this work, no indirect band gap could be determined from the absorption coefficient. From the plots it could be concluded that it probably concerns a smeared band gap (graphs not shown). Thus, the question arises, whether the sputtered Mg₂Si films have a distinct indirect band gap in the range of 0.78 eV – most likely not.

Furthermore, the transmission and reflection behavior of Mg₂Si on silicon wafers should be measured to see, whether a band gap determination was possible. Since there are obviously huge differences

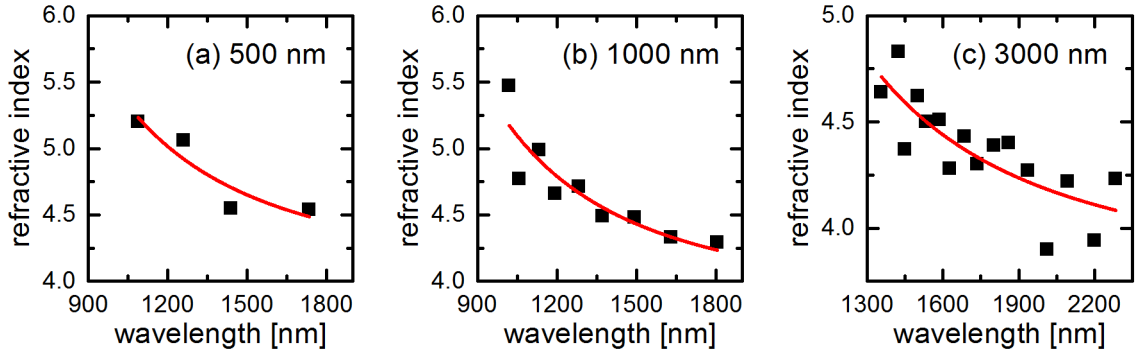


Figure 8.3: Estimated refractive indices for Mg_2Si films of 500 nm (a), 1000 nm (b) and 3000 nm (c) thickness as determined from the transmission spectra according to equation 8.1.

in the alignment and crystallization processes of evaporated and sputtered Mg_2Si films (as can be seen i.a. in the XRD measurements, where different preferred orientations occur), also different optical properties can be expected, as for the electrical characterization.

8.2.2 Mg_2Si as absorber material in heterojunction solar cells

In order to assess the ability of Mg_2Si as absorber material in solar cells, a heterojunction was realized by a stack consisting of Mg_2Si and a silicon wafer which both were electrically contacted. Measurements were performed by a solar simulator under AM 1.5.

The first photoresponse of bulk Mg_2Si was observed by Stella *et al.* which performed photoconductivity measurements at 90 K low temperature [195]. In [64, 196] the infrared photoresponsivity from a Mg_2Si p-n junction diode was investigated under zero potential conditions at room temperature. The disadvantage was that the gold electrode on p- Mg_2Si was opaque, thus blocking the incident light. By that the photoresponsivity of the Mg_2Si photodiode is significantly affected by the junction depth due to the absorption loss

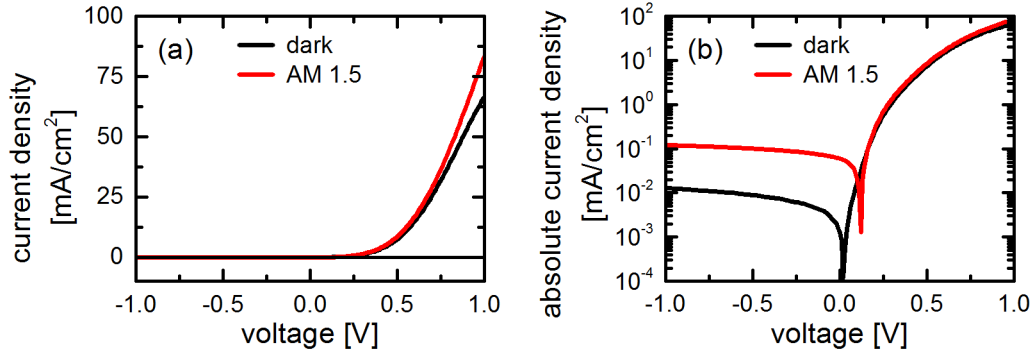


Figure 8.4: Current–voltage characteristics of a solar cell device consisting of 50 nm Mg_2Si sputtered and annealed on a p-Si wafer measured without (black curve) and with AM 1.5 illumination (red curve). An efficiency of 0.026 % was calculated. Both the linear (a) and logarithmic (b) representations are shown. On the logarithmic scale the absolute current density is plotted.

[196]. Daitoku *et al.* avoided that by applying a Au ring electrode on Mg_2Si and thus improved the ideality factor of the p-n Mg_2Si junction [65].

As shown before, Hall measurements indicated that the Mg_2Si thin films fabricated in this work are quite undefined concerning the doping. Different approaches were made to study the application of Mg_2Si in a solar cell device. Since it was not clear which doping type of Mg_2Si was existent (regarding also the predicted n-type behavior of undoped Mg_2Si layers from literature), several geometries concerning the composition of the solar cell devices were regarded to form a heterojunction solar cell device.

p-Si wafers as substrates were used, since it was assumed that Mg_2Si is n-type as mentioned in literature. The active area of the illuminated sample was always approx. 0.25 cm².

Figure 8.4 shows current–voltage characteristics for solar cell consisting of a sputtered 50 nm Mg_2Si (annealed at 400°C for 5 hours) on p-Si. The Mg_2Si layer was contacted with 300 nm nickel electrodes

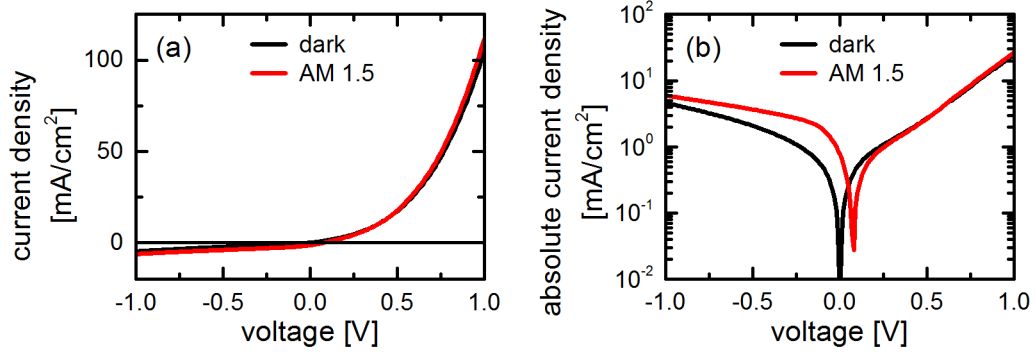


Figure 8.5: Current–voltage characteristics of a solar cell device consisting of 300 nm Mg_2Si formed by evaporation of Mg on a p-Si wafer and subsequent annealing and ion beam etching. Both the linear (a) and the logarithmic (b) representations are shown for the device without (black curve) and with illumination (red curve). An efficiency of 0.025 % was estimated. On the logarithmic scale the absolute current density is plotted.

and p-Si was supplied aluminum electrodes. The determined efficiency was 0.026 %, the open circuit potential, short current density, and fill factor were measured as 0.2 V, approx. 1.0 mA/cm², and 21.9, respectively.

Figure 8.5 shows linearly and logarithmically plotted I - U curves for a 300 nm Mg_2Si film which was formed by evaporation of magnesium on a p-Si wafer with subsequent annealing at 400°C for 5 hours and an ion beam etch treatment. A solar-to-energy efficiency of approx. 0.025 % was measured. The open circuit potential was 0.12 V and the short current density was approx. 0.4 mA/cm². The devices had a fill factor of 38.3.

All samples had rectifying behavior, which indicates the formation of a potential barrier and a depletion region. Apparently, the measured I - U curves show a diode-like behavior. It could be assumed that the Mg_2Si layer forms a p-n junction with the silicon substrate.

Due to the proposed narrow band gap, Mg₂Si can be applied as the bottom layer in solar cell devices to absorb light at higher wavelengths that transmits through the upper layer(s). Silicon, which is used as upper material in this work, has a band gap of approx. 1.1 eV which corresponds a wavelength of approx. 1100 nm. When silicon represents the upper layer this means that light with wavelengths higher than 1100 nm can reach the Mg₂Si layer. It turned out that it makes no difference whether the Mg₂Si or silicon side are illuminated.

It thus can be concluded that it is possible that the fabricated Mg₂Si layers (both the evaporated and sputtered ones) behave as p⁺ part of heterojunction solar cells. This explains why there is a diode-like current-voltage characteristic both for n-type and p-type silicon wafers. Either a sort of a p-n junction was formed (when n-Si was the substrate), or a p-p⁺ heterojunction formed (when using p-type Si). The response to light illumination was low in all cases, observable in low efficiencies. This leads to other possible applications of Mg₂Si, which could be used as near-IR absorber material in photodetectors.

In spite of everything it needs to be considered that these kind of solar cells are only “prototypes” without any improvements concerning their structure and contacting. For example, neither silicon nor Mg₂Si had an anti-reflection coating on their surfaces. A detailed study is necessary to concretely test Mg₂Si layers in photoactive devices and their response to light.

Fourier transform photocurrent spectroscopy (FTPS) measurements were additionally carried out in order to characterize thin microcrystalline solar cells. Therefore, the output light beam of a Fourier transform infrared spectrometer (FTIR) is used to illuminate the photovoltaic device and the spectral dependence of the incident light is measured with a photodetector and was converted to light irradiation power. Thus, a photocurrent spectrum can be measured. When the Mg₂Si-Si optoelectronic devices were illuminated from the silicon side, no photocurrent was measured, indicating that the interface of silicon to Mg₂Si did not react to light. On the other hand, when the

light beam was half on the silicon and half on the aluminum metal, a small photocurrent was measured, indicating a Schottky-contact like behavior (results not shown). It could be, however, that the very small currents which were measured under the solar simulator, are due to this Schottky contact formation, although only the active area of silicon or Mg_2Si was exposed to the light. This is very reasonable, since Schottky contacts are quite sensitive to light. For the future, IR measurements at deep temperatures are necessary to see a response of the Mg_2Si –Si interface to light.

8.3 Stability of Mg_2Si as photoelectrode

The usage of Mg_2Si in electrolytes as photoelectrodes is an interesting subject to study. A stable Mg_2Si which can convert visible light would find an application as bottom layer in photoelectrode tandem devices. The aim of this section is to investigate the stability and function of Mg_2Si thin films in solution. This has not been reported so far and was tested in this work. Mg_2Si films were sputtered on glass substrates and were subsequently annealed at 400°C for 5 hours. They were afterwards contacted as described in section 7.2.

8.3.1 Electrolysis and photoassisted electrolysis

For the measurements in aqueous solution, relatively thick Mg_2Si layers were fabricated. Mg_2Si was sputtered with a thickness of $3\text{ }\mu\text{m}$ on glass and was subsequently annealed. The active area of the Mg_2Si electrode was approx. 1 cm^2 . Figure 8.6 shows CV curves of Mg_2Si in H_2O and 0.1 M NaCl , stressed over a potential range of 6 V vs. Ag/AgCl . Despite the fact that the measured curves do not show any features, there is also no big difference between dark conditions

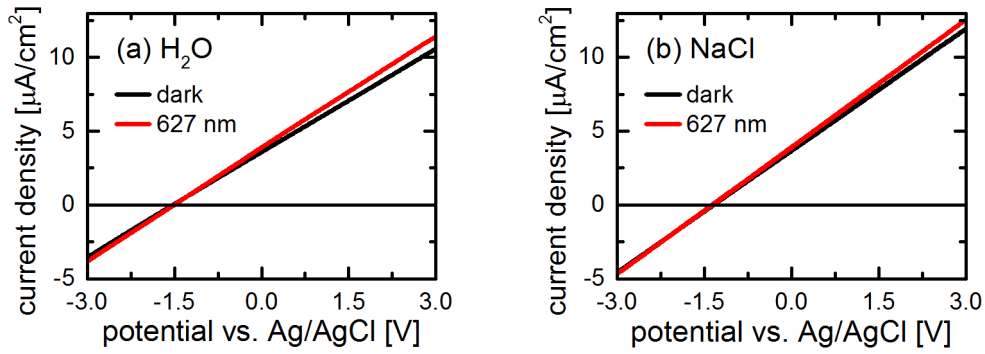


Figure 8.6: CV curves of 3 μm thick Mg_2Si sputtered on glass in H_2O (a) and 0.1 M NaCl (b), stressed over a potential range of 6 V with and without illumination (red and black curve, respectively). Measured currents in both electrolytes showed no response to light. It can be clearly seen that the current is linear with the potential and shows no additional features.

and 627 nm illumination. Furthermore, the currents were in the same range for H_2O and NaCl. No photocurrent could be determined. The fact that the CV curves are only straight lines indicates that only the resistance of the electrolyte is measured. The Mg_2Si film still adhered to the glass substrate after measurements, but showed signs of an attack and beginning dissolution. Measurements were also performed using other wavelengths (365 nm, 525 nm, 940 nm), but no difference between dark conditions and illumination could be determined (data not shown).

Additionally, CA measurements on Mg_2Si samples were performed. Figure 8.7 shows CA curves for Mg_2Si electrodes in H_2O and 0.1 M NaCl under dark conditions and 627 nm, measured for 10 minutes, respectively, and driven under different potentials. The flowing currents were in general higher according to amount for NaCl as electrolyte.

In figure 8.7 (a), a cathodic potential of -3 V vs. Ag/AgCl was applied. In case of H_2O , a slight jump of the current from approx.

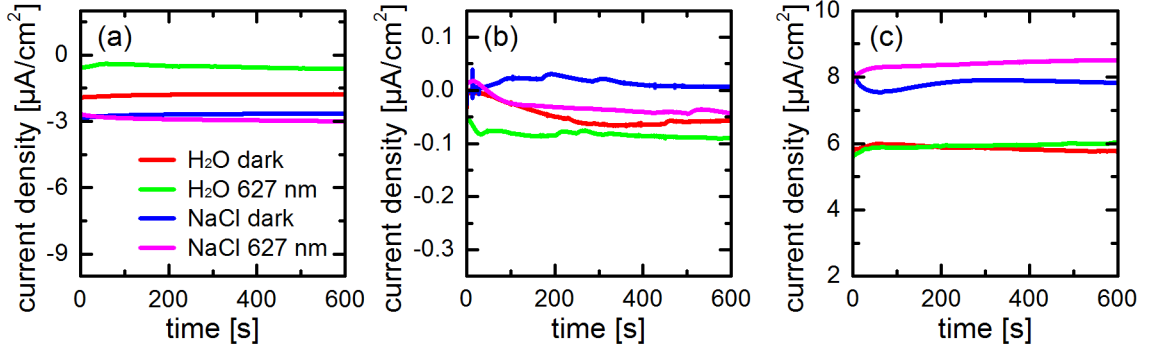


Figure 8.7: CA measurements of 3 μm thick Mg_2Si (sputtered on glass) stressed in H_2O (red and green curves) and 0.1 M NaCl (blue and magenta curves) for 20 minutes under dark conditions (red and blue curves) and under 627 nm illumination (green and magenta curves) carried out at externally applied potentials of -3 V (a), -1.5 V (OCP) (b) and +3 V (c).

-2 $\mu\text{A}/\text{cm}^2$ to -0.5 $\mu\text{A}/\text{cm}^2$ under 627 nm illumination was recorded. This is interesting, since this according to amount reduced current under illumination is not likely for semiconductors. In case of NaCl , no difference between dark and illumination conditions could be determined. The CA curves in figure 8.7 (b) correspond to OCP conditions. The OCP value of -1.5 V vs. Ag/AgCl for both dark conditions and 627 nm illumination was the same. Again, no difference in the recorded CA curves between dark conditions and 627 nm illumination was observed.

For an applied anodic potential of +3 V vs. Ag/AgCl as is shown in figure 8.7 (c), there was a difference of about 2 $\mu\text{A}/\text{cm}^2$ between H_2O and NaCl . Again, Mg_2Si electrodes did not respond to 627 nm illumination – the currents ran on a constant level.

To conclude, the flowing currents are quite low in the μA region, but they run stably at a constant level without additional features for 20 minutes of measurement time. Under the applied anodic potential, the current densities were slightly higher than in the cathodic region. No response to light (except for H_2O at -3 V) was determined. A

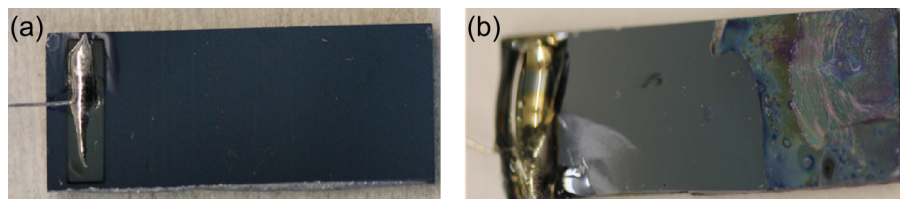


Figure 8.8: Photographs of an Mg_2Si photoelectrode ($3\ \mu\text{m}$ Mg_2Si sputtered on glass) before (a) and after (b) CA measurements with an applied potential of $+3\ \text{V}$ vs. Ag/AgCl in $0.1\ \text{M}$ NaCl . The active area which was in solution is clearly attacked.

longer CA measurement period was not applied due to the stability of the Mg_2Si electrodes, which started to extremely dissolve after approx. one hour in solution (already in H_2O).

Figure 8.8 shows photos of $3\ \mu\text{m}$ thick Mg_2Si photoelectrodes sputtered on glass before and after CA measurements in the PEC in $0.1\ \text{M}$ NaCl . The active area is clearly attacked and the generated colors indicate a change in the thickness and dissolution of Mg_2Si in the electrolyte. The applied potential was $+3\ \text{V}$ vs. Ag/AgCl , but the active area in general looked the same also for $-1.5\ \text{V}$ and $-3\ \text{V}$ vs. Ag/AgCl .

8.3.2 Corrosion rate determination

Statements about the dissolution of Mg_2Si in aqueous solutions are expected from linear polarization measurements with the Tafel method which was applied the first time to Mg_2Si films. The corrosion rate was determined for Mg_2Si in the same way as it was determined for GaN – with help of the Tafel plot method. The Mg_2Si samples were placed in $1\ \text{M}$ NaCl solution, where they remained stable without dissolving during the measurement time.

The changes of the corrosion rates under the influence of dark conditions and illumination with a $627\ \text{nm}$ LED were studied. Figure 8.9

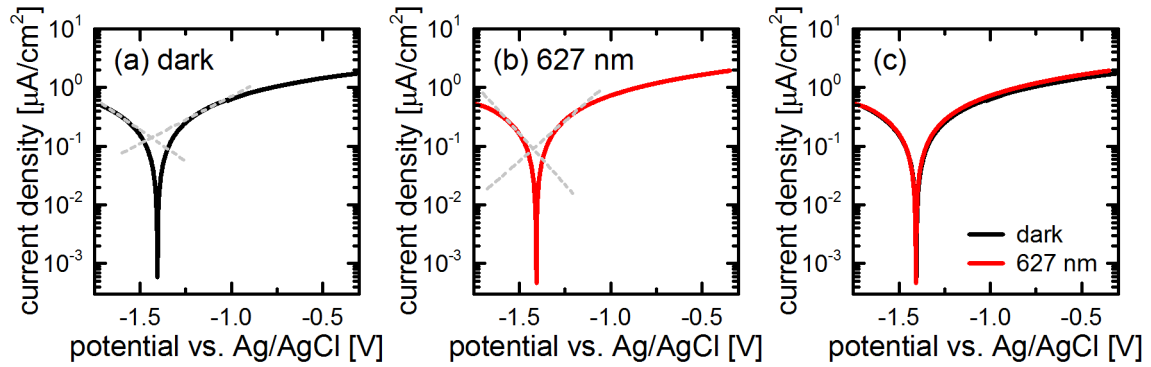


Figure 8.9: Tafel plots for an Mg_2Si photoelectrode ($3\ \mu\text{m}$ Mg_2Si sputtered on glass) for dark conditions (a) and for illumination with a 627 nm LED (b) in 0.1 M NaCl. (c) Comparison of dark and 627 nm plots – the two curves are almost identical and no shift of the OCP values is detected.

shows the current density-potential curves for dark and illuminated conditions. By determining the intersection of the anodic and cathodic Tafel plots, the corrosion rate could be calculated. Without illumination, the corrosion rate of Mg_2Si was determined as $1.06 \cdot 10^{-2}$ mm/y ($= 2.02 \cdot 10^{-2}$ nm/min) and under 627 nm excitation it was calculated to be $8.89 \cdot 10^{-3}$ mm/y ($= 1.69 \cdot 10^{-2}$ nm/min). The OCP of Mg_2Si is not shifted under illumination, probably Mg_2Si does not respond to illumination. Figure 8.9 (c) shows the direct comparison of the measured curves under dark conditions and 627 nm illumination at all. The OCP and currents did not change under illumination. As observed for the measurements with the solar simulator in the previous section, Mg_2Si is obviously not really excitable.

8.3.3 Photoinduced degradation

In chapter 6, GaN was investigated with respect to its stability in aqueous media. The same procedure was done with Mg_2Si . It was illuminated with light in the UV, visible and IR range, since the

material covers the whole spectral range due to its proposed narrow band gap. Several parameters were varied to get an overview of the behavior of Mg_2Si in aqueous media. Thus the wavelength, the time of stress in solution, and the type of electrolyte were varied. Concerning the electrolytes, the focus was put on H_2O and 0.1 M NaCl solution to have comparable electrolytes with respect to the GaN degradation experiments. As has been already recognized by the CV and CA measurements, Mg_2Si layers start to dissolve from the glass substrates during experiments. In the following, photos of 3 μm thick Mg_2Si layers are shown that were sputtered on glass substrates and annealed at 400°C for 5 hours. A stripe of pure glass was left free during sputtering to have a reference area on the sample. Samples were taken out of solution after every ten minutes and dry blown for taking a photo and they afterwards were put again into solution.

Influence of the wavelength on Mg_2Si degradation

Mg_2Si was illuminated in the crystallizing dishes containing the corresponding electrolytes with different wavelengths to gain broad statistics concerning the response to light over a wide spectral range. High power LEDs with wavelengths of 365 nm, 525 nm, 660 nm, and 940 nm were used. Also, Mg_2Si was investigated under dark conditions. In case of Mg_2Si which responds and absorbs already room light it is especially important to accurately cover the Mg_2Si sample, to exclude external influences. This was done with a black lid which was put over the crystallizing dish containing the Mg_2Si sample in the aqueous electrolyte.

It is observed that illumination of Mg_2Si samples with visible light could slightly accelerate degradation reactions, whereas the dissolving of Mg_2Si occurs slower under dark conditions. But these observations are more or less subjective since it was not possible to measure an exact degradation of the Mg_2Si thickness. Referring to previous observations of the response of Mg_2Si to light, it could be rather

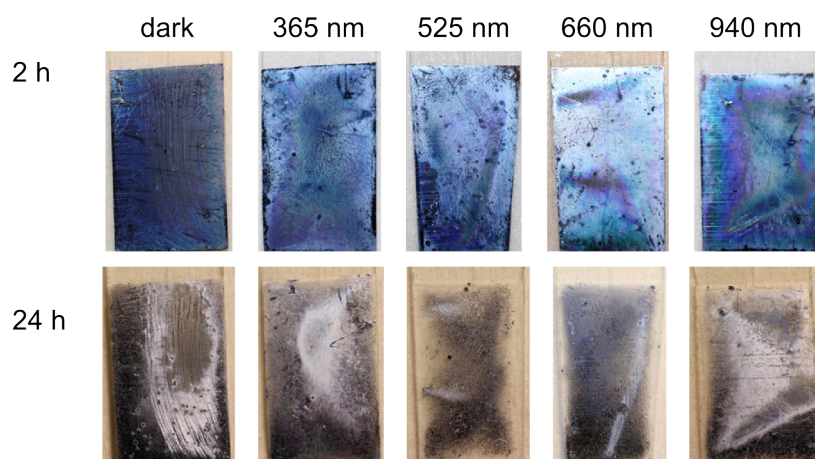


Figure 8.10: Influence of illumination with different wavelengths on the dissolution of 3 μm thick Mg_2Si samples in 0.1 M NaCl. The Mg_2Si surface was damaged in all measurements, irrespective of the illumination. Also dark conditions led to a dissolution of Mg_2Si .

expected, that there is no difference, whether the Mg_2Si samples were stressed in the dark or under illumination.

Figure 8.10 gives an overview of Mg_2Si samples which were illuminated with light of different wavelengths. Exemplarily, photos of Mg_2Si layers on glass were shown after a stress period of two hours and 24 hours. For all wavelengths, the Mg_2Si films showed clear changes due to dissolution of the layers in aqueous solutions.

Comparing the observed changes of these experiments with the results of the Tafel plots recorded under dark conditions and 627 nm illumination (cf. figure 8.9), one can conclude that there is no difference between dark conditions and illumination with light in the visible range.

Influence of the time of applied stress on Mg_2Si degradation

Figure 8.11 shows photos of stressed Mg_2Si samples under dark conditions and 525 nm illumination that were in 0.1 M NaCl solution

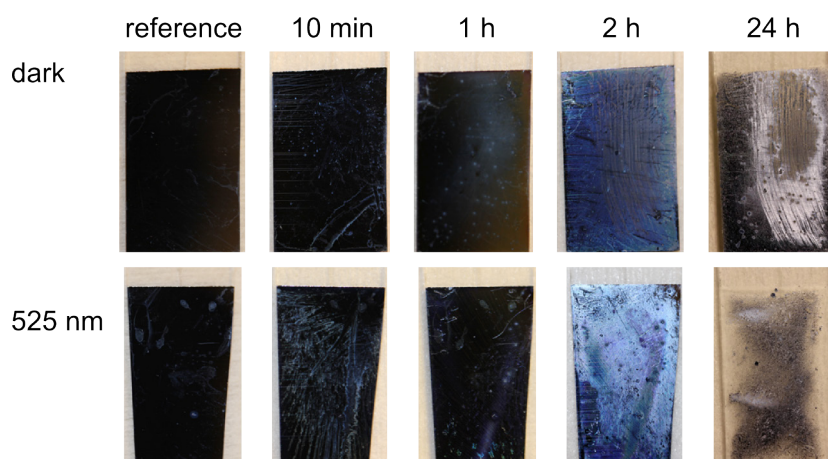


Figure 8.11: Time series of photographs of Mg_2Si degrading in a 0.1 M NaCl electrolyte. Already after 2 hours, the sample surfaces under both dark conditions and 525 nm illumination were clearly attacked and started to dissolve.

for at least two hours. For both illumination conditions, the Mg_2Si films started to visibly dissolve already after approx. one hour. This process seemed to occur with a constant dissolution rate. After 24 hours, the Mg_2Si layer under dark conditions was attacked but still covered the glass substrate, whereas under 525 nm illumination the Mg_2Si layers dissolved stronger and spatially, from all sides of the sample. Obviously, Mg_2Si under illumination dissolved slightly faster than under dark conditions.

Influence of the electrolyte on Mg_2Si degradation

The influence of different electrolytes on the degradation tendency of Mg_2Si was studied. Figure 8.12 shows Mg_2Si photos after 30 min in different electrolytes, stressed under dark conditions and 525 nm illumination. Mg_2Si samples in H_2O and NaCl solution still adhered properly, in case of 0.1 M KHCO_3 after 30 minutes, the Mg_2Si film dissolved, leaving back a thinned out film. It can be concluded that Mg_2Si is not stable in aqueous solutions. The observations concerning

the photoinduced degradation experiments with Mg_2Si are more or less randomly. Statements about photo-oxidation or reactions at the Mg_2Si –electrolyte interface as made in chapter 6 for GaN cannot be made, since the Mg_2Si films do not react to light and furthermore are not as stable as GaN.

Regarding the time of applied stress, the dissolution is more distinct over a longer time and runs with a continuous degradation of Mg_2Si . The Mg_2Si layer itself is obviously not stable in any solution and dissolves easily. It easily dissolves due to bad adhesion on the glass substrates in solution, whereas GaN from the beginning adheres stably on the sapphire substrate. To summarize, it obviously plays no role which wavelength is used to excite Mg_2Si – in aqueous solution it anyways dissolves. The process of additional generated charge carriers has no influence in the whole Mg_2Si dissolution process, since Mg_2Si shows no reaction to light takes place at all – neither under dry conditions, nor in aqueous solutions.

Additionally it needs to be mentioned that Mg_2Si not only as thin film is dissolving in aqueous solutions, but also in bulk form. Mg_2Si with a purity higher than 99 % from Sigma Aldrich was investigated, which was delivered as powder-like bulk. When putting a fingernail big piece into solution, it also dissolved. The effects that occurred during dissolution were dependent on the type of electrolyte that was used. Already in H_2O , the dissolution of Mg_2Si bulk material begins – recognizable by bubbling gases evolving from the Mg_2Si surface. Also NaCl solution causes this behavior. In a (highly) concentrated NaOH solution, Mg_2Si bulk pieces first seems to be stable since no bubbles escape from the bulk surface. Due to OH^- ions that attach and thus passivate the bulk surface, the process of dissolution is slowed down, but after a while bubble formation begins. Also NH_3 and KHCO_3 solutions caused bubble formation. What is left is a bluish shimmering Mg_2Si bulk piece – a sign for oxide formation on the Mg_2Si surface. Putting a Mg_2Si bulk piece in 37 % HCl for example, it is well known

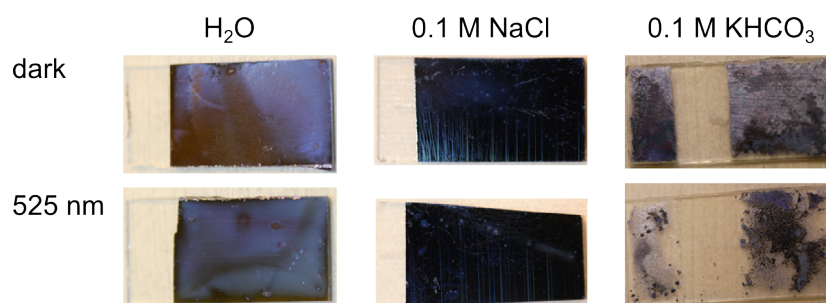


Figure 8.12: Influence of different electrolytes on Mg_2Si degradation under dark conditions and 525 nm illumination after 30 minutes. Mg_2Si samples in 0.1 M KHCO_3 dissolved strongest, whereas in H_2O and 0.1 M NaCl the Mg_2Si films were not yet visibly attacked.

that the formation of silane occurs – going along with cracking noises. Most likely, magnesium chloride (MgCl_2) remains.

Serikawa *et al.* sputtered Mg-Si on glass substrates either by DC or RF sputtering. They found out that RF fabricated Mg-Si films from a target, consisting of 25 % magnesium and 75 % silicon, showed superior corrosion resistance under the salt spray test with 5 % NaCl carried out at 308 K for 100 hours [81]. The high corrosion resistance is explained by amorphous phases in the Mg-Si film. On the other hand, Mg-Si films fabricated by DC sputtering from a target, consisting of 50 % magnesium and 50 % silicon, were fully removed, due to poor crystalline and coarse columnar structure and excess metallic magnesium in the Mg-Si film. The dissolution of Mg_2Si layers from the glass substrates in this work thus could be due to the elemental composition of the Mg_2Si target, the metallic magnesium in the Mg-Si film by all means is higher than 25 %, thus enabling corrosion and fully removal of the Mg_2Si film. Furthermore, Mg_2Si layers were annealed, thus the amorphous structure has vanished.

9 Conclusions and Outlook

9.1 GaN

The behavior of n-GaN as photoanode and p-GaN as photocathode was investigated. Since the band edge positions of n-GaN and p-GaN are the same [33, 105] they have similar capabilities for water splitting. But, as was also demonstrated in the present work, their stability in electrolytes is different.

Photoinduced degradation experiments were conducted in aqueous solutions under UV light excitation without the influence of a second electrode or an externally applied potential. Clear differences in the stability of n-type and p-type GaN were observed. This is caused by different charge transfer mechanisms of the photogenerated charge carriers. Further detailed investigations need to be carried out in order to gain a fundamental understanding of the charge transfer kinetic processes occurring at the GaN–electrolyte interface.

n-GaN samples undergo photo-oxidation due to accumulated photo-generated holes at the surface. These holes act as strong oxidizing agents leading to a photo-oxidation during which gaseous nitrogen evolves from the n-GaN surface. These findings are in accordance with previous studies [28, 31, 111]. In case of ultrapure water as electrolyte, a gallium oxide layer is formed as can be concluded from the elemental ratios in EDX measurements as well as from XPS spectra. Surprisingly, a gallium oxide phase on n-GaN samples illuminated with UV light in water could not be detected by GIXRD measurements – only the GaN phase was detected.

Furthermore, n-GaN samples showed elemental changes under an externally applied anodic potential under UV illumination. In the presence of a metal coating on the n-GaN sample the degradation was strongly increased both in the presence and absence of an externally applied potential.

These changes in elemental composition of stressed n-GaN samples due to photo-oxidation were successfully proven by EDX measurements on a large set of samples in a large parameter space which was not done so far in previous studies.

The question arises how degradation of the GaN samples can be avoided. It was found that photo-oxidation can be reduced in the presence of chloride-containing electrolytes such as NaCl, where the photo-generated holes preferably react with the chloride ions to form gaseous chlorine. On the other hand, the presence of metal stripes on the n-GaN surface leads to an increased change of the elemental composition of n-GaN under UV illumination, even in the presence of NaCl. This finding needs to be taken into account for the design of devices in photoelectrochemical applications – a proper insulation of the contact-metal is crucial for the longevity of the device.

Another approach to stabilize n-GaN against degradation is the presence of NiO co-catalyst particles on the n-GaN surface which are oxidized instead of the GaN surface. With NiO present, stressed n-GaN surfaces showed no changes in their elemental composition – even if they were coated with silver stripes.

Furthermore it is reported that gallium oxide can act as surface photocatalyst [197, 198]. Thus, once it formed on the GaN surface, the oxide layer could be advantageous by providing an improved charge transfer at the semiconductor–electrolyte interface.

Different to n-GaN, p-type samples inherently offer self-protection against photocorrosion since photogenerated electrons accumulate at the surface. Due to the behavior of p-GaN as photo-active cathode, hydrogen evolution can occur without applying an external potential. Since semiconductors in general are more resistant to reduction than

oxidation reactions in aqueous solutions, p-type GaN is an ideal photoelectrode [113, 199].

p-GaN samples in this work remained unchanged even for applied extreme anodic or cathodic potentials of -3 V or +3 V vs. Ag/AgCl, respectively. An exception was when the H₂O/300nm/+3V/60h stress method was applied. There, p-GaN showed signs of photo-oxidation as was verified by EDX measurements and SEM images. This is a reproducible result which should be studied in detail in future research.

One drawback of p-GaN are the low efficiencies compared to n-GaN which were also observed in this work as lower measured photocurrents. This is due to the inefficient charge separation of photo-generated carriers. Furthermore the p-type doping with magnesium is difficult [22].

However, first approaches exist in engineering a GaN photocathode providing higher cathodic currents than p-GaN and which is furthermore stable in aqueous solutions. It consists of an undoped GaN layer with a few nm thick AlN layer beneath [121].

If GaN is not illuminated or is illuminated with light below the band gap energy, GaN cannot be excited and no surface changes were detected. This was also true if additionally anodic potentials were applied. Also other groups, who studied the etching properties, confirm that dark conditions have no effect on GaN etching (see, e.g., [28]).

The concentration of the NaCl solution was not varied in this work – it was always 0.1 M. It thus would be interesting to study the effect of varying that concentration. Especially since a comparison of the results obtained in the present work to previously published results is difficult because of very specific choices of parameters in the various studies – apart from the electrolyte concentrations, also the time of the applied stress as well as the electrolyte types are different from the present work. Currently, the main focus is on basic and acidic solutions like KOH or HCl since they provide better efficiencies

[32, 105]. Less investigations are made for solutions with neutral pH values or naturally occurring aqueous solutions. Furthermore, in literature, a wide range of illumination strategies was employed.

Due to practical reasons, two different irradiation sources were used in this work. On the one hand, photoinduced degradation measurements were carried out with a 365 nm LED which is close to the band edge of GaN (approx. 367 nm) and which had a light intensity at the GaN surface of approx. 3.6 mW/cm^2 . Measurements in the photoelectrochemical cell, on the other hand, were carried out using 300 nm excitation with an intensity at the sample surface of about 2.8 mW/cm^2 . This probably leads to small deviations in the magnitude of degradation. Again, since every research group uses different settings, a quantitative comparison of results is not possible.

It needs to be considered that the pH value for ultrapure water and NaCl in the present work (approx. 5) does not correspond to more natural conditions like, e.g., the pH value of tap water or seawater, which are more in the neutral-basic range. Thus, the results of this work cannot be transferred one-to-one to these more realistic conditions. For later applications, the use of seawater which is safe and available would be desirable for studying the stability of GaN [107].

In order to determine corrosion rates of stressed GaN the Tafel plot method was employed. Based on the measurement results, n-GaN has an approximately three orders of magnitude lower corrosion rate under dark conditions ($9.76 \cdot 10^{-5} \text{ nm/min}$) than under 300 nm excitation ($1.47 \cdot 10^{-2} \text{ nm/min}$). Pure n-GaN corrodes faster than p-GaN. Note that these corrosion rates correspond to the pure dissolution of the GaN material but do not take into account an oxidation of the sample which, on the other hand, cannot be excluded in case of n-GaN. In previous studies etch rates were determined by ICP-MS, i.e. determining the dissolved Ga^{3+} content, or analyzing the removal of material from the sample surface. Compared to the present work, these rates are much higher – for example, in [28] a photo etch rate

of 400 nm/min in KOH and 40 nm/min in HCl was determined for n-GaN, compared to $1.69 \cdot 10^{-2}$ nm/min in NaCl in this work. As already mentioned above, the different measurement conditions (electrolytes, excitation wavelength, intensity, etc.) need to be taken into account.

Unfortunately, an analysis of the evolved gases during measurements could not be carried out. Even though hydrogen was surely produced during CA experiments, the generated amounts were too low to be measured by a gas-phase chromatograph. Thus, quantitative statements about the efficiency of water splitting, which most likely occurred during the CA measurements on n-GaN under an anodic potential, could not be obtained.

In the present work, KHCO_3 was used as electrolyte for CO_2 reduction at a lead counter electrode, where an Faraday efficiency of approx. 1.0 % was achieved for the generation of HCOOH . This is one order of magnitude lower than reported in [26]. One reason for this might be the geometry of the photoelectrochemical cell by which no appropriate CO_2 reduction experiments could be carried out. In case of a copper counter electrode the complete n-GaN electrode was damaged due to the missing cation exchange membrane. Greenish copper oxide adsorbed on the GaN surface and falsified results. The n-GaN WE surface was oxidized, thus not allowing a reliable measurement. Another disadvantage of the photoelectrochemical cell is the insufficient saturation of the electrolyte with gas, since the gas inlet leads to the volume above the electrolyte and not into the electrolyte directly.

For future CO_2 reduction and also water splitting experiments in the photoelectrochemical cell, a two-chamber photoelectrochemical cell would be advisable to avoid back reactions within the cell like oxidation of the counter electrode by introducing a cation exchange membrane. The cell should furthermore include in- and outlets to collect the evolving gases. Photoinduced degradation as well as photoassisted electrolysis studies and surface analysis of GaN samples

in KHCO_3 would then need to be carried out to understand the degradation mechanisms in this electrolyte, since it is typically used for CO_2 reduction experiments.

According to Peng *et al.* [106] the solvent plays an important role in the photo-oxidation of GaN. It would be interesting to study the stability of GaN in other solutions than aqueous media. Peng *et al.* dissolved KOH in ethanol instead of water as solvent and observed no etching of GaN [106]. Furthermore it would be interesting to study the stability of n-GaN in ionic liquids instead of aqueous solutions.

Due to the big band gap of GaN (3.4 eV) only near-UV light can be absorbed. There are strategies to shift the spectral response of GaN into the visible by tuning the band gap of GaN. One example is the incorporation of indium to form InGaN which is also reported to have a higher stability against photocorrosion [14, 22, 122–125]. By changing the content of indium, the band gap can be varied from 0.7 to 3.4 eV, which makes those $\text{In}_x\text{Ga}_{1-x}\text{N}$ samples also interesting candidates for the absorption of light in the visible region. This is an experimental challenge and the application would be mostly restricted to n-GaN since the fabrication of p-type InGaN is very difficult [22]. It would be of great interest to apply the measurement methods used in this work to InGaN samples and to analyze the elemental compositions, e.g., by EDX afterwards.

9.2 Mg_2Si

The formation of polycrystalline Mg_2Si thin films was realized in the present work by evaporation of Mg onto Si wafers or sputtering of Mg_2Si onto Si or glass with subsequent annealing. In the former case, magnesium segmentations developed which probably originated from non-converted magnesium. So far, no findings of such segmentations had been reported in literature for the evaporation method since in most cases a parallel annealing was performed during evaporation

as well as co-evaporation of silicon and magnesium [59, 63, 154, 156]. It thus might be considered to include a substrate heater into the evaporation chamber to enable parallel annealing of the deposited magnesium layer.

Nevertheless, it was possible to fabricate Mg_2Si layers by the evaporation technique by employing a subsequent annealing of evaporated magnesium at 400°C for five hours. This was performed independently of the evaporated thickness of Mg. Afterwards, an ion beam etching procedure was applied to remove magnesium segmentations from the surfaces. Contrary to the evaporation method, sputtering of Mg_2Si films on glass substrates with subsequent annealing showed no segmentations, although this was reported by other groups for sputtered films [70]. Finally, smooth Mg_2Si films were fabricated with both deposition methods. In case of the evaporation method, XRD measurements revealed a (220) texture whereas a (111) orientation was present in case of sputtered samples.

Contacting Mg_2Si with nickel has proven to be ohmic. Van der Pauw measurements showed resistivity values in the range of 10^{-2} to $10^{-4} \Omega\text{cm}$ for Mg_2Si films fabricated on silicon wafers which is also consistent with the results of other research groups [57, 59, 200]. Layers deposited on glass substrates had lower conductivities in the range of $1 \Omega\text{cm}$.

Mg_2Si was proposed to intrinsically show n-type conductivity [36, 40, 49, 52–56]. This property could not be clearly proven in this work. Instead, Hall measurements revealed either n-type or p-type conductivity for different samples, independent of the fabrication method or film thickness. The reasons for this discrepancy are not clear. Measured samples were free of defects and showed a pure Mg_2Si phase in XRD measurements. One explanation might be the fact that in previous studies the n-type doping was measured mostly for bulk Mg_2Si crystals. In general, bulk properties cannot simply be transferred to thin films. On the other hand, nevertheless, Mg_2Si films should at least have a consistent doping behavior. Reasons for

the varying doping properties could be the low purity of the Mg_2Si target or Mg pellets, leading to the incorporation of impurities like Al into Mg_2Si and thus to not well-defined doping. This needs to be further investigated. Moreover, due to the low band gap of Mg_2Si , measurements need to be carried out under low temperature to block the thermally activated charge carriers. Therefore, low temperature Hall measurements might be helpful to accurately measure the charge carrier concentration and mobility of Mg_2Si .

For thermoelectric materials it is reported that higher efficiencies can be achieved by doping. A p-type doping of Mg_2Si , e.g., with silver [59], could be performed for electric characterization in general to study the properties of systematically doped Mg_2Si films.

In order to test the applicability of Mg_2Si in photovoltaic applications, an optoelectronic device was made consisting of Mg_2Si on silicon wafers. It showed diode characteristics under dark conditions and illumination. The diode behavior was found for both n-type and p-type silicon wafers. Therefore, in agreement with the discussion above, possibly different types of junctions formed (e.g., n-p, p-p⁺, Schottky). Under AM 1.5 conditions no clear photoresponse was observed for deposited Mg_2Si on both n-Si and p-Si wafers as substrate. Very small efficiencies of approx. 0.025 % were achieved for 50 nm and 300 nm Mg_2Si films. Higher film thicknesses showed no response to light at all. From Fourier transform photocurrent spectroscopy measurements a slight response to light is detected when additionally to Mg_2Si a part of the nickel metal contact is illuminated, indicating a Schottky diode behavior. This could be also transferred to the diode curves measured under dark conditions. It is not exactly clear which type of junction exists and thus it is recommended to intensively study the reactions at the Mg_2Si –Si interface to gain knowledge about transport processes and life times of charge carriers.

Since the indirect band gap of Mg_2Si is very small at around 0.78 eV [36] it is recommended to use the silicide as bottom layer in multijunction cells [40]. The transmission and reflection of sputtered Mg_2Si

layers on glass substrates was measured, showing strong interferences from which the refractive index could be determined. It was between 4 and 5 in the near-IR range. In [201] it was predicted to be 4.0 from first principle calculations and in [67] it was measured as approx. 3.6.

The use of the Mg_2Si layers as photoelectrode in aqueous solution turns out to not be practical. Like already under dry conditions, photoelectrochemical measurements in solution showed no reaction of Mg_2Si to light.

Like for GaN, the Tafel plot method was applied to determine corrosion rates of Mg_2Si , resulting in values of approx. $2 \cdot 10^{-2}$ nm/min for both dark conditions and 627 nm illumination which is surprisingly slow compared to the dissolution of Mg_2Si from underlying glass substrates. The determined values thus need to be considered with care.

Polycrystalline Mg_2Si has a poor stability in aqueous solutions which obviously does not make it a suitable candidate for photocatalytic purposes. In order to be able to use them in photocatalytic applications efforts must be undertaken to stabilize Mg_2Si thin films in aqueous solutions. In the present work, the idea was to employ the annealing steps after evaporation or sputtering in order to obtain a flat and homogeneous polycrystalline Mg_2Si layer. On the other hand, since a more stable behavior of amorphous Mg_2Si layers was reported [70, 71] it might be more advisable to repeat the measurements of the present work for amorphous Mg_2Si films. Furthermore, Mg_2Si sputter targets with various area ratios could be applied [70] to exactly adjust the composition of Mg_2Si and to study the influence of the ratio of magnesium and silicon and their amorphous phases and crystallinity to Mg_2Si thin film formation. This could potentially be a first step in fabricating Mg_2Si detectors for the infrared range [64, 72] or Mg_2Si tandem solar cells [40] or Mg_2Si photoelectrodes [71].

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List of abbreviations

Ag/AgCl	silver chloride electrode
CA	chronoamperometry
CE	counter electrode
CV	cyclic voltammetry
EDX	energy-dispersive X-ray spectroscopy
EIS	electrochemical impedance spectroscopy
EQE	external quantum efficiency
FE	Faraday efficiency
GIXRD	grazing incidence X-ray diffraction
HVPE	hybrid vapor phase epitaxy
IBE	ion beam etching
IR	infrared
LED	light-emitting diode
MC	Monte Carlo
NHE	normal hydrogen electrode
OCP	open circuit potential
PEC	photoelectrochemical cell
RE	reference electrode
RSF	relative sensitivity factor
SCR	standard calomel electrode
SEM	scanning electron microscopy
ToF SIMS	Time-of-Flight Secondary ion mass Spectroscopy
UV	ultraviolet
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
WE	working electrode

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Gallium nitride (GaN) is a well-established semiconductor in opto-electronic applications. It has a wide band gap of 3.4 eV and is thus excitable in the near-UV range. A promising application of GaN is its use as a photoelectrode driving photocatalytic reactions such as water splitting for generation of H₂ without consumption of fossil fuel or emission of CO₂. For such applications the corrosion resistance of the photoelectrodes in aqueous media is one of the main factors determining their lifetimes and thus plays an important role for their applicability for highly efficient solar energy conversion. It has been demonstrated in photocatalytic experiments that under UV-illumination n-type GaN acts as oxygen-evolving photoanode and p-type GaN as hydrogen-evolving photocathode. In the present work, the degradation of GaN under various conditions is investigated. Specifically, the corrosion resistance of pure and metal-coated GaN photoelectrodes in aqueous media is studied by electrochemical measurements. Furthermore, the influence of an externally applied potential under light excitation as well as the effect of long-term photoinduced stress are investigated. It is observed that without illumination the GaN surfaces and GaN-metal interfaces are rather stable for a broad potential range, whereas they undergo degradation when exposed to UV light.

Parallel to the III-V semiconductor GaN, semiconducting magnesium silicide (Mg₂Si) presents an alternative material type which is not as well characterized as GaN in its use as photoelectrode. It is a promising candidate for low-cost and efficient absorber layers for solar energy conversion. Its main application so far is as a high-performance thermoelectric material. Little is known, however, about its applicability as a photo-active material. Semiconducting Mg₂Si is the only stable phase in the Mg₂Si system. It has a narrow indirect band gap of 0.78 eV. Its high absorption coefficient furthermore makes it an interesting material for the production of thin solar cells. In the present work, Mg₂Si thin films were produced by thermal evaporation of Mg on Si substrates and by sputtering from a Mg₂Si sputter target on silicon wafers or glass substrates with subsequent annealing. This results in the formation of smooth Mg₂Si layers, which can be adjusted in thickness by varying the annealing temperature, time as well as the amount of deposited magnesium. The Mg₂Si films are characterized in terms of morphological, electrical and optical properties. Furthermore, measurements on the photo-activity of Mg₂Si as well as its stability in aqueous media are discussed.

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