PECVD-Deposition and Characterisation of C-Si Thin Film Systems on Metals

Dissertation zur Erlangung des Grades eines Doktors der Naturwissenschaften an der Fakultät für Physik und Astronomie der Ruhr-Universität Bochum

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List of Abbreviations

$\alpha$ absorption coefficient
$\delta$ deflection
$\Delta$ ellipsometric angle
$\epsilon$ dielectric function
$\gamma$ surface energy
$\lambda$ wavelength
$\nu$ wavenumber
$\Psi$ ellipsometric angle
$\sigma$ stress
a-C:H hydrogenated amorphous carbon
AFM Atomic Force Microscope
a-Si:H hydrogenated amorphous silicon
a-Si:C:H hydrogenated amorphous silicon-carbon
CCP capacitively coupled discharge
$C_H$ hydrogen content
DC Direct Current
DLC Diamond Like Carbon
EMA Effective Medium Approximation
$E_{\text{gap}}$ energy of optical bandgap
ERDA Elastic Recoil Detection Analysis
ESCA Electron Spectroscopy for Chemical Analysis
FTIR Fourier Transformed Infra Red Spectroscopy
GCF Gas Correction Factor
GEC Gaseous Electronics Conference
HF High Frequency
HSM High Stretching Mode
<table>
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<tr>
<td>IR</td>
<td>infrared</td>
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<tr>
<td>$k$</td>
<td>index of absorption</td>
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<tr>
<td>$K$</td>
<td>kinematic factor</td>
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<tr>
<td>LSM</td>
<td>Low Stretching Mode</td>
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<td>MW</td>
<td>microwave</td>
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<tr>
<td>$n$</td>
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<td>$n_e$</td>
<td>electron density</td>
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<tr>
<td>$n_s$</td>
<td>atomic surface coverage</td>
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<td>$n_v$</td>
<td>atomic volume density</td>
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<tr>
<td>$p$</td>
<td>pressure</td>
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<td>P</td>
<td>polarisation</td>
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<tr>
<td>PAP</td>
<td>Plasma Absorption Probe</td>
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<tr>
<td>PECVD</td>
<td>Plasma Enhanced Chemical Vapour Deposition</td>
</tr>
<tr>
<td>PLC</td>
<td>Polymer Like Carbon</td>
</tr>
<tr>
<td>PSII</td>
<td>Plasma Source Ion Implantation</td>
</tr>
<tr>
<td>$\tilde{R}$</td>
<td>coefficient of reflection</td>
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<tr>
<td>$R_a$</td>
<td>roughness</td>
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<td>RBS</td>
<td>Rutherford Back Scattering</td>
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<tr>
<td>$rf$</td>
<td>radio frequency</td>
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<td>SEM</td>
<td>Scanning Electron Microscope</td>
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<td>SMA</td>
<td>Shape Memory Alloy</td>
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<td>$T$</td>
<td>transmission</td>
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<td>$T_s$</td>
<td>substrate temperature</td>
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<td>TMS</td>
<td>Tetramethyldisilane</td>
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Chapter 1

Introduction

A variety of medical devices are implanted into the human body, such as artificial hip and knee joints, coronary stents, heart valves, pacemakers or intraocular lenses. These devices are in contact with body cells and fluids and risk to corrode from the material of the body. Body fluids contain about 1 % NaCl and are therefore a corrosive environment for implants. Another problem – especially in the case of joints – is the sliding wear due to sliding movements. The interaction of implants with the body cells, the products of corrosion and wear debris may have harmful effects on both body and implants. These effects can be cellular damage, infections, blood coagulation or failure of the implants. In the case of stents, blood coagulation can lead to thrombosis. Metallic implants may release metal ions and also wear debris can lead to the surrounding tissue.

Total hip joint replacement is the largest area of tribological implants. Currently, the life expectancy of such joints is over 15 years which requires second replacement especially for younger patients. There are three main factors which limit the treatment to younger patients: 1) deficiencies in the wear resistance, 2) loosening of the stem to hip caused by wear particles, or 3) cement-to-bone interface failure or implant-to-bone interface failure [1].

Gutensohn et al. [2] report that atomic adsorption spectrophotometry analysis revealed a significant release of nickel and chromium metal ions by non-coated stents over a storage period of 96 hours in human plasma, leading to inflammations. In the case of implants the release of metal ions may result in inflammations and bone resorption, which leads to loosening and finally failure of the implant [3], [4].

Medical implants made of metal for the fixing or replacing of hard tissue as for example bones are widely produced from titanium or its alloys. Titanium shows excellent
biocompatibility, good corrosion resistance and passable mechanical properties. Regarding elastic modulus and strain behaviour, NiTi alloys seem to match much better than Ti, especially due to the superelastic properties of NiTi, resembling closely the hard tissue response [5]. An additional advantage is the shape memory effect of NiTi alloys [6]. This effect is a reversible transition from austenite to martensite, while the transition temperature is adjustable by the chemical composition and can easily be set at body temperature. The shape memory effect can therefore exert a constant force, for example for a more stable fixation of fractures. Unfortunately, the wear resistance of NiTi alloys is relatively low.

NiTi superelastic wires were first introduced into orthodontic use. Today, there are some commercial products available on world wide markets. Most times, NiTi is used in self-expandable stents, for example in narrowed arteries, where they expand and dilate the artery, or for oesophageal strictures and as urethral stents [7]. NiTi is also used for orthopaedics and bone-related application, such as fixations of small bone fragments and others. But the use of NiTi in this field is still very uncommon.

Today, there is still a controversial debate about the question whether nickel and its alloys are toxic in the human body or not. Whereas some authors report on the biocompatibility of NiTi [8], [9], [10], other publications show that NiTi is not biocompatible but toxic and allergenic [11], [12], [13]. In [8] and [9] the biocompatibility has only been tested \textit{in vitro} and not on a long term scale. In [10], NiTi test specimens have been implanted into rats and no difference between the inflammatory response of NiTi and stainless steel could be observed. [12] reports that a certain amount of Ni is released from 1- and 2-euro coins by sweat and that this amount is much higher than that of pure nickel. [11] summarises several studies that report on the cytotoxicity and inflammatory response around the Ni implants. In one study the implantation of NiTi in rabbits led to significant increase of the Ni concentration in the blood. It therefore appears that there are no available conclusive data on the biocompatibility of NiTi, but Ni is recognised as being potentially carcinogenic.

A promising solution of the problems described above could be the coating of the implant with a protective film, reducing corrosion and wear. Such a coating could extend the lifetime of implants, meaning that the implant has to be changed more rarely.

Mändl et al. [5] showed that the implantation of oxygen via plasma immersion ion implantation into NiTi leads to a nickel free layer on top of the surface. The material
shows a layered sequence of TiO$_2$-Ni$_3$Ti-NiTi, forming an effective diffusion barrier for Ni. This would solve the problem of Ni-release, but the problem of wear debris and corrosion is still open.

Diamond-like carbon (DLC) seems to be the best material for such a protective coating, since it is characterised by chemical inertness, corrosion and wear resistance and biocompatibility. In the last 15 years several *in vitro* and *in vivo* studies on the biocompatibility have been performed (see section 2.1). They all came to the conclusion that DLC is a biocompatible material without harm for blood, human cells, living animals and even human beings.

The main problem for the use of DLC as protective coatings for biomedical applications is the bad adhesion of DLC on most metals. This may be due to poor chemical binding between a-C:H and metal and/or high internal stresses inside the DLC film leading to flaking of the film.

The adhesion of the coating to the substrate is one of the crucial problems to overcome before a satisfactory surface behaviour can be achieved. One promising technique is the deposition of a very thin interface layer on the substrate before the coating is deposited on top. By a correct material choice such an interface can replace weak coating-to-substrate bonds with a strong coating to interface layer and interface layer to substrate bond. Another effect of the interface layer can be the reduction of internal stresses in the interface region. By the use of at least two layers on top of each other the probability of pinholes or defects going from the surface to the substrate is decreased. This is especially important if toxic substrates are to be coated.

Therefore, a thin amorphous hydrogenated silicon (a-Si:H) film will be used as an intermediate layer between metal and DLC film in this work. Due to the formation of strong silicide bonds the adhesion of DLC films on metal is expected to increase significantly. The aim of this work is to prove whether an intermediate layer of a-Si:H increases adhesion of DLC on metals and how film properties of a-Si:H and DLC influence the strength of adhesion. The a-Si:H films are only several 10 nm thick, whereas the DLC films are supposed to have a thickness of 100 nm or more. The influence of different parameters like applied power, substrate temperature, hydrogen content and others on the adhesion of the films also under durability tests are investigated.

For the deposition of a-Si:H and DLC films a plasma process is used. Plasma deposition is a common method for the production of thin films. One big advantage of this method are the relative low gas temperatures (room temperature or slightly above)
during the deposition process which even allow the coating of temperature sensitive materials. The high chemical activity due to fast electrons enables non-equilibrium processes in these low temperature plasmas. The average kinetic energy of the electrons is in the range of hundreds up to ten thousand K. In this work a capacitively coupled discharge (CCP) for the thin film deposition is used.

This work is organised as follows: the next chapter is concerned with the deposition of thin films. The properties of the two mainly used types of thin films in this work, amorphous hydrogenated silicon and amorphous hydrogenated carbon, are described in more detail in this chapter. Since they are deposited in a plasma assisted process, this process, called PECVD (plasma enhanced chemical vapour deposition), is specified in section 2.3. The main problems occurring in the deposition of thin films are internal stresses in the films and poor adhesion to the substrate. Different types of stress and attempts to improve the adhesion are discussed in section 2.4. In the last section of chapter 2 binary phase diagrams of different elements being part of the films and substrates are presented. The formation of stable compositions between elements in films and substrates is important for a good adhesion of the film on the substrate. In chapter 3 different thin film diagnostics employed in this work are introduced. The main diagnostic method used is optical ellipsometry. With this technique, film thickness and optical constants of the films can be determined. Therefore, this diagnostic is described in more detail in this chapter. Other diagnostics give insight into the chemical composition of the films. These are FTIR, XPS, SIMS, and RBS. With atomic force microscopy the surface of the samples can be imaged. Two other diagnostics dealt with in this chapter are a method to measure the intrinsic stress of the film and cavitation erosion. With the latter mechanisms of failure of the film systems can be investigated.

In chapter 4 the experimental set-up used throughout this work is presented. Two main properties of the plasma, namely self-bias and plasma density, are characterised. The pretreatment of the samples is crucial for the deposition of good films. The standard procedure used in this work is treated in the last section of this chapter. Chapter 5 deals with the deposition and characterisation of a-Si:H films. These films will be used as intermediate layers between metal and DLC films. Their properties are decisive for the adhesion and should therefore be known very well.

In the next chapter (chapter 6) the deposition of DLC films is described and their
properties relevant for applications as biocompatible wear resistant coatings are characterised.

When two gases are used simultaneously in a plasma, new films with particular properties can be produced. The deposition and properties of amorphous films containing silicon, carbon, and hydrogen are described in chapter 7. This kind of film can be used in form of a gradient layer to enhance the adhesion between DLC film and metal.

In chapter 8 the deposition of film systems consisting of a-Si:H and DLC films on metals is described. With TOF-SIMS depth profiles of the chemical composition of the film systems are measured. Their adhesion to different metal substrates is investigated and mechanisms of failure of the films are analysed. Results from measurements of the internal stress in such film systems will be shown as well as results from tensile tests to investigate the behaviour of the film systems under strain.
Chapter 2

Deposition of thin films

Thin-film technology is simultaneously one of the oldest arts and one of the newest sciences. Involvement with thin films dates back to the metal ages of antiquity. Since then, the ancient craft of gold beating has been practised continuously for at least four millennia. Its great malleability enables gold to be hammered into very thin leafs while its beauty and chemical resistance feature it for durable decoration and protection purposes.

Today, thin films of any material are widely used in electrical, optical, thermal, and protective applications. Surface properties such as corrodibility, wear resistance, hardness, and wettability can be changed fundamentally due to coatings with thin films. The coating can result from wet-chemical or electrolytic procedures or out of the gas phase.

In this chapter, two prominent thin films, namely amorphous hydrogenated silicon and amorphous hydrogenated carbon are introduced as well as one of the most frequently used thin film deposition method, the PECVD process.

This chapter is organised as follows. In section 2.1 the growth and properties of diamond-like carbon films are presented and the question of biocompatibility of DLC is treated. Section 2.2 deals with the growth mechanisms and properties of amorphous hydrogenated silicon films. Both these films are deposited via the PECVD process, therefore the principles of this method are dealt with in section 2.3. One important point in the deposition of thin films is the adhesion of the films, which may be limited by the internal stress occurring in the films. The phenomenon of intrinsic stress and efforts to improve the adhesion of thin films to the substrate are treated in section 2.4.
2.1 Growth and properties of diamond-like carbon (DLC) films

Carbon forms a great variety of crystalline and disordered structures because it is able to exist in three different hybridisations, namely sp$^3$, sp$^2$ and sp$^1$. These different forms of hybridisations lead to totally different configurations of carbon. In diamond the four valence electrons of the carbon atom are each assigned to a tetrahedrally directed sp$^3$-orbital. The sp$^2$ configuration characterises a graphite-like structure. DLC is a metastable form of amorphous carbon containing a significant fraction of sp$^3$ bonds. At sp$^3$ sites each of the four valence electrons of a carbon atom is assigned to a tetrahedrally directed sp$^3$ hybrid which forms σ bonds to four adjacent carbon atoms. These bonds give diamond its rigidity and wide bandgap. At sp$^2$ sites, as in graphite, three of the valence electrons are assigned to trigonally directed sp$^2$ hybrids which form σ bonds such as the strong intra layer σ bonds of graphite. The fourth electron is placed in a π orbital lying normal to the layer and this forms weaker π bonds which give rise to the anisotropic metallic character of graphite [14]. The term a-C:H as an abbreviation for amorphous, hydrogenated carbon describes a system which covers a wide range of properties depending on deposition parameters.

A rough classification of a-C:H films is given by the fractions of hybridisation type and hydrogen content. Hydrogen rich films with a hydrogen content of 40 at.% or more, usually deposited with low ion energies, are often so called polymerlike (soft) a-C:H films, whereas dense, sp$^3$ rich (hard) a-C:H films with a hydrogen fraction lower than 40 at.% are called diamond-like carbon (DLC) films [14], [16]. Films containing less then 1 at.% hydrogen are so called a-C films. The phase diagram of carbon-containing materials (with and without hydrogen) can be seen in figure 2.1. The properties of different carbon-containing materials are compared in table 2.1. More about carbon films (both amorphous and crystalline) can be found in [17].

In DLC there is no three-dimensional network of tetrahedrally bonded sp$^3$ carbon incorporated in these films but an amorphous network of graphite-like clusters interconnected by sp$^3$ bonds. The properties of the films are determined by the relative ratio of the two hybridisations. Angus and Jansen [18] have described the structure of hydrogenated DLC by a random covalent, fully constrained, network model. In this model, the DLC structure can be described as a three-dimensional array of mostly
Figure 2.1: Phase diagram of carbon-containing materials (from [15]). The three corners correspond to diamond (sp$^3$), graphite (sp$^2$) and pure hydrogen. In the shaded area in the right corner no film deposition is possible, because volatile hydrocarbon products are build.

Robertson [14] modelled the structure of DLC as a random network of covalently bonded carbon atoms in different hybridisations, with a substantial degree of medium range order on the 1 nm scale. In a refined model of Robertson [25] he described the structure of DLC as being controlled by the energy of the $\pi$ bonding of the sp$^2$ sites. This bonding of the sp$^2$ carbon favours clustering of sp$^2$ sites to maximise the $\pi$-bonding energy. The sp$^2$ sites can gain further energy by forming sixfold planar "aromatic" rings and fusing the rings into larger graphite-like clusters [26]. Robertson presents a two-phase model of amorphous carbon. The first phase is the $\pi$-bonded clusters which determine the electronic properties. This phase is embedded in a second phase. Usually this phase is the minor phase and consists of a rim of defect or possibly sp$^3$ sites, as in hard forms of a-C:H, or a more hydrogenated phase, as in softer, polymer-like forms of a-C:H. The second phase largely determines the mechan-
Chapter 2 Deposition of thin films

<table>
<thead>
<tr>
<th>Material</th>
<th>density [g/cm(^3)]</th>
<th>hardness [GPa]</th>
<th>sp(^3) [%]</th>
<th>H [at. %]</th>
<th>bandgap [eV]</th>
<th>n</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>diamond</td>
<td>3.52</td>
<td>100</td>
<td>100</td>
<td>0</td>
<td>5.5</td>
<td>2.4</td>
<td>[19], [20]</td>
</tr>
<tr>
<td>graphite</td>
<td>2.27</td>
<td></td>
<td>0</td>
<td>0</td>
<td>-0.04</td>
<td>2.15</td>
<td>[14], [21]</td>
</tr>
<tr>
<td>a-C (MSIB(^1))</td>
<td>3.0</td>
<td>30-130</td>
<td>90±5</td>
<td>0</td>
<td>0.5-1.5</td>
<td></td>
<td>[22], [23]</td>
</tr>
<tr>
<td>a-C:H (hard)</td>
<td>1.6-2.2</td>
<td>10-20</td>
<td>30-60</td>
<td>10-40</td>
<td>0.8-1.7</td>
<td>1.9-2.4</td>
<td>[20], [24]</td>
</tr>
<tr>
<td>a-C:H (soft)</td>
<td>0.9-1.6</td>
<td>&lt;5</td>
<td>50-80</td>
<td>40-65</td>
<td>1.6-4</td>
<td>1.6-1.9</td>
<td>[20], [24]</td>
</tr>
</tbody>
</table>

Table 2.1: Comparison of properties of DLC with diamond, graphite, soft a-C:H films and a-C.

ical properties of the material. Robertson also found that the optical bandgap of all types of DLC, with or without hydrogen, depends mainly on the sp\(^3\) fraction in the films and decreases with increasing sp\(^2\) fraction.

The excellent physical and mechanical properties of DLC due to the high fraction of sp\(^3\) type C bonds (30-60 %) are to a certain extent similar to those of diamond. DLC films are characterised by high hardness and a high elastic modulus, but also by high internal stress. The hardness of DLC lies in the range of 10-30 GPa (diamond 100 GPa), with a corresponding Young’s modulus 6-10 times larger [14], [15]. Many applications exploit the low friction coefficients and high wear resistance of this material. The density of DLC is about 1.6-2.2 g cm\(^{-3}\). The films are characterised by internal compressive stresses in the range of 0.5-7 GPa. Efforts have been made to reduce the internal stress by the incorporation of N, Si, O or metals in the film. Hong [27] successfully incorporated carbon-nanoparticles into DLC films leading to a lowering of the intrinsic stress. Details about stress in thin films can be found in section 2.4.

DLC is a metastable material which will change its structure to graphite-like carbon by thermal activation or irradiation with energetic photons or particles. Heating of hydrogenated DLC films results in the loss of hydrogen and CH\(_x\) species, starting at about 400 °C, or even lower, depending on deposition conditions. Heating leads to changes in dimensions and properties of the material and limits the use of DLC in applications involving temperatures above 400 °C. The thermal instability of DLC films is generally associated with the loss of hydrogen, resulting in a collapse of the

\(^1\)Mass Selected Ion Beam deposition
structure into a mostly sp$^2$-bonded network. Memming et al. [28] report that after annealing at 600 °C all the hydrogen had disappeared and a pure carbon layer was left.

It is possible to produce DLC with a variety of deposition methods like plasma enhanced chemical vapour deposition (PECVD) or physical vapour deposition techniques (sputtering or ion beams) with different precursors such as acetylene or methane. The choice of the source gas has influence on film properties like optical constants. Amorphous hydrogenated carbon films deposited from acetylene have the highest refractive index $n$, the lowest hydrogen content and also the highest mass density compared to others deposited under the same conditions but with different source gases [29].

In the PECVD process, the substrates have to be at a negative bias relative to the plasma to achieve ion bombardment during film growth. This is usually given by the negative self-bias arising in capacitively coupled discharges. With higher ion energy the film is packed more dense and contains less hydrogen. When the deposition is performed in hydrogen-containing environments, the DLC films contain 10-50 at.% hydrogen. The hydrogen is needed to obtain the ”diamond-like” properties in the DLC. It determines the film structure, controls the optical and electrical properties and passivates the dangling bonds in the amorphous structure, which affects the internal stress of the film.

A more recent technique for the deposition of DLC films is the plasma source ion implantation (PSII). In this technique, the substrate or workpiece to be coated is placed directly in a plasma source and then pulse-biased. This technique enables the coating of complex 3d-structures because it is a non-line-of-sight one. Another non-line-of-sight technique for the deposition of DLC films has been performed in an ionnitriding tool in which DLC has been deposited by bipolar-pulsed DC PECVD [15]. The films have been found to have properties similar to films deposited by RF PECVD.

In this work the DLC films are deposited by PECVD with acetylene ($\text{C}_2\text{H}_2$) as precursor gas. More about the PECVD process can be found in chapter 2.3. The growth and properties of DLC films are controlled by substrate temperature and bias $V_b$, whereupon the latter has the dominant control. $V_b$ is a measure of the mean ion energy $E_i$ and at typical operating pressures (about 3 Pa) $E_i \approx 0.4V_b$ [25]. Hardness, density and refractive index of the films increase with increasing substrate bias. Additionally the growth rate usually increases with increasing bias, but only up to a certain value where the limit of precursors for the growing of the film is reached.
In acetylene, the $\text{C}_2\text{H}_2$ molecules are dissociated due to collisions with electrons:

$$e^- + \text{C}_2\text{H}_2 \rightarrow \text{C}_2\text{H} + \text{H} + e^- \quad (2.1)$$

$\text{C}_2\text{H}$ is able to react with other molecules in the gas phase:

$$\text{C}_2\text{H} + \text{C}_2\text{H}_2 \rightarrow \text{C}_4\text{H}_2 + \text{H} \quad (2.2)$$

$$\text{C}_2\text{H} + \text{C}_4\text{H}_2 \rightarrow \text{C}_6\text{H}_2 + \text{H} \quad (2.3)$$

The $\text{C}_2\text{H}$ radicals adsorb at the surface and lead to film growth [30]. But also other radicals like $\text{C}_2\text{H}_3$, $\text{C}_4\text{H}_3$ and $\text{C}_6\text{H}_3$ react with the surface and contribute to the growth of the film. However, the $\text{C}_2\text{H}$ radical is the dominant growth precursor in acetylene [30].

In contrast to that the dominant growth precursor for DLC in a methane ($\text{CH}_4$) plasma is the $\text{CH}_3$ radical [31]. Open bonds at the surface act as chemisorption sites for incoming $\text{CH}_3$ radicals. These open bonds can be created by the ion bombardment during growth. The $\text{CH}_3$ radicals first adsorb in a weakly-adsorbed state and reside on the surface until they desorb via thermal activation or chemisorb at a dangling bond [31].

DLC films have been produced and investigated since 1971, when Aisenberg and Chabot first prepared such films [32]. Today the growth mechanism is well understood and the sophisticated properties of DLC films are used in many industrial and technical applications. Via different vapour deposition methods non-crystalline carbon films which are smooth, mechanically hard, IR transparent and chemically inert are produced. These films are much easier to deposit than diamond and their properties are already sufficiently good for some applications such as corrosion protection coatings for magnetic disk drives and magnetic heads, tribological coatings for metal bearings, gears and seals, antireflective and scratch-resistant wear-protective coatings for IR optics and, as a recent application, wear-resistant coatings of razor blades (MACH3 by Gillette). The low deposition temperatures of DLC allows its use as a wear-protective layer on products made of plastics, for example of sunglass lenses made of polycarbonate. Additionally, DLC is chemical inert and impermeable to liquids. DLC films can therefore protect biological implants against corrosion and serve as diffusion barriers [15].
**Biocompatibility of DLC**

In the last 15 years several *in vitro* and *in vivo* studies on the biocompatibility of DLC have been performed. The *in vitro* studies have been realised in environments which simulate the human body including macrophage cells (white blood cells), fibroblast (connective tissue forming cells) and osteoblasts (bone-forming cells) [3]. Several studies showed that DLC does not induce inflammatory reactions in the cells or cytotoxicity. DLC films deposited on polystyrene tissue culture plates have been compared with uncoated plates in osteoblast-like cell lines for periods up to 72 hours [33]. The DLC coating had no adverse effect on any of the measured parameters, namely production of three osteoblast-specific marker proteins. Cui *et al.* [34] showed that fibroblast and osteoblast cells attach to DLC coatings and that osteoblast cells spread well on the DLC surface. This enhances the potential of the bone to grow over a DLC-coated implant, giving the implant a better hold in the bone. Alanazi *et al.* [35] investigated the blood compatibility of DLC coated polymeric material. The results indicated that DLC could be used as a coating material in implantable blood contacting devices, as for example artificial hearts, pacemakers and others. In studies of Gutensohn *et al.* [2], [36] intracoronary stents were coated with DLC, which significantly improved their biocompatibility, because it contributes to a reduction in thrombogenicity (occurrence of thrombosis). The incorporation of different elements in the film can alter the bio-characteristics of the DLC coatings. The addition of Ti to the DLC film caused an enhanced differentiation of bone marrow cells from rats in osteoblasts and reduced osteoblast-like activity on the coated surface [4]. Thus, a-C:H/Ti could be a valuable coating for bone implants due to its enhancement of bone ingrowth through osteoblast differentiation and reduction of bone resorption through osteoblast inhibition without the release of Ti. Si or F containing DLC films have shown good biocompatibility in cell culture tests with fibroblasts and the behaviour showed no dependence of the Si or F content [37].

There are much less reported *in vivo* test of DLC. In one study DLC-coated CoCr cylinders were implanted in intramuscular locations in rats and in transcortical sites in sheep [33]. The specimen were retrieved 90 days after surgery and their histologic analysis showed that the DLC-coated specimen were tolerated well in both body sites. Implants of DLC-coated devices in the human body have also been reported [3]. DLC-coated steel rods were implanted in a human body for seven months to fixate a fractured bone. The coating prevented corrosion of the rods, metalosis (loss of metal),
and formation of local cells, thus preventing inflammation and enabling the healing of a complicated bone fracture.

All these studies show that DLC is biocompatible and can therefore be used for the coating of biomedical devices and implants.

### 2.2 Growth and structure of amorphous hydrogenated silicon (a-Si:H) films

The fabrication and investigation of amorphous hydrogenated silicon (a-Si:H) films began in the late 1960s. Researchers documented the superior properties of the amorphous silicon like fairly high carrier mobility and strong photoconductivity resulting from a very low defect density [38]. In 1975 Spear and Le Comber [39] reported on n-type or p-type doping of a-Si:H by adding phosphine or boroethane to the deposition gas. Paul’s group at Harvard recognised that the high defect density of amorphous silicon and amorphous germanium prevented these materials from being useful for electronic devices and that the addition of hydrogen into the material increased the photoconductivity and lowered the defect density [40]. In 1976 Carlson and Wronski started to develop photovoltaic devices made of a-Si:H [41]. The first use of a-Si:H solar cells was in hand-held calculators. Today big solar cell arrays are widely used for power generation on house tops or in isolated regions with high solar irradiation. Other applications include crystal displays and optical scanners.

The disorder of the atomic structure is the main feature that distinguishes amorphous from crystalline material. But amorphous materials are not completely disordered. The covalent binding between silicon atoms are almost the same as in crystalline silicon, having the same number of neighbours and the same average bond lengths and bond angles. Thus the amorphous material has the same short range order as the crystal but lacks the long range order. This leads to similar material properties of amorphous and crystalline semiconductors.

The growth of a-Si:H in a plasma is mainly determined by radicals. Investigations of the ion chemistry by Kessels et al. showed that the contribution of Si\(_n\)H\(_m^+\) ions is less than 10 % [42], [43].

Due to the collisions of silane molecules with electrons the gas molecules are dissoci-
ated in the plasma. Two main reaction paths are:

\[ e^- + \text{SiH}_4 \rightarrow \text{SiH}_2 + \text{H}_2 + e^- \]  
(2.4)

\[ e^- + \text{SiH}_4 \rightarrow \text{SiH}_3 + \text{H} + e^- \]  
(2.5)

which require electron energies between 2 and 4 eV [38], [44]. The SiH$_2$ molecule is not very important for the film growth because of its high reaction probability with other molecules building silane molecules, more SiH$_3$ radicals or larger molecules, such as:

\[ \text{SiH}_4 + \text{SiH}_2 \rightarrow \text{Si}_2\text{H}_6 \]  
(2.6)

\[ \text{Si}_2\text{H}_6 + \text{SiH}_2 \rightarrow \text{Si}_3\text{H}_8. \]  
(2.7)

These molecular species lead to the formation of macroscopic particles in the gas which interfere with growth. Thus reactions building higher silanes should be suppressed because they act as precursors for dust particles.

The radical mainly responsible for the growth is the SiH$_3$ radical [31], [38], [45], [46]. This radical does not react with SiH$_4$, unlike radicals with fewer hydrogen atoms, because Si$_2$H$_n$ structures are possible only with \( n \leq 6 \). In a pure silane plasma at least 80\% of the gas radicals are SiH$_3$, in an argon diluted silane plasma this number gets smaller [38], [45]. Thus, SiH$_3$ radicals can diffuse to the surface without undergoing reactions in contrast to the SiH$_2$ radical. This and the fact that SiH$_3$ is the radical produced in the largest quantities is the reason why it is the main molecule responsible for deposition [45].

The radicals arriving at the surface bring far more hydrogen than is later found in the film. Thus hydrogen must be released from the surface during growth. A surface completely terminated by Si-H bonds can not take up SiH$_3$ radicals. Bonding of SiH$_3$ can only occur at any unterminated silicon bond with the reaction [47]

\[ \equiv \text{Si} - + \text{SiH}_3 \rightarrow \equiv \text{Si} - \text{SiH}_3. \]  
(2.8)

Here \( \equiv \text{Si} - \) denotes a silicon atom bonded to the surface with a dangling bond. Therefore the removal of hydrogen from the surface is an important step in the deposition of films. The hydrogen can be released spontaneously by thermal excitation either as atomic or molecular hydrogen (this is especially important for heated substrates) or it can be stripped from the surface by gas radicals or ions. Two main reactions are [47]:

\[ \equiv \text{Si} - \text{H} + \text{SiH}_3 \rightarrow \equiv \text{Si} - + \text{SiH}_4 \uparrow \]  
(2.9)
or

\[ \equiv \text{Si} - \text{H} + \text{H} \rightarrow \equiv \text{Si} - + \text{H}_2 \uparrow \]  

(2.10)

where \( \equiv \text{Si-H} \) represents silicon at the surface which is bonded into the network. \( \uparrow \) denotes that the respective molecule goes into the gas phase. Reaction 2.9 leads to the formation of a dangling bond with the release of a silane molecule whereas reaction 2.10 leads to the desorption of a \( \text{H}_2 \) molecule while forming a dangling bond. Another important reaction is the dangling bond recombination leading to crosslinking of the silicon network:

\[ \equiv \text{Si} - + - \text{Si} \equiv \rightarrow \equiv \text{Si} - \text{Si} \equiv. \]  

(2.11)

Von Keudell et al. propose another mechanism for the film growth by \( \text{SiH}_3 \) radicals. They found experimentally that \( \text{SiH}_3 \) is directly inserted into strained Si-Si surface bonds forming metastable pentacoordinated Si-SiH\(_3\)-Si sites \([31]\). These metastable sites can further reconstruct by directly forming a surface monohydride and releasing two \( \text{H}_2 \) molecules. The reactions going on look as follows:

\[ \text{SiH}_3 + \text{Si} - \text{Si} \rightarrow \text{Si} - \text{SiH}_3 - \text{Si} \]  

(2.12)

\[ 2(\text{Si} - \text{SiH}_3 - \text{Si}) \rightarrow \text{Si}_2 - \text{SiH} - \text{SiH} - \text{Si}_2 + 2\text{H}_2. \]  

(2.13)

When the plasma is diluted with argon there are secondary processes in which energy is transferred from the excited argon to the silane, causing dissociation. This leads to the production of more highly reactive species in the discharge. \( \text{SiH}_3 \) is no longer the dominant radical and the plasma contains many others, such as \( \text{Si}, \text{SiH}, \text{SiH}_2 \). Each of these is able to react directly with the hydrogen-terminated surface, inserting into the Si-H bonds. The result is a high sticking coefficient and a low surface mobility.

## 2.3 Basic principles of the PECVD process

The PECVD (Plasma Enhanced Chemical Vapour Deposition) process is the commonly used technique for the deposition of thin films. Sometimes it is also called "glow discharge" deposition because of the clearly observable glowing of the plasma. One important advantage of the PECVD process are the relatively low gas temperatures inside the reactor during deposition making it suitable for a variety of substrates. The energy for the dissociation is mainly put in the electrons in the plasma (electron
temperature $\sim 3$ eV) while the gas remains relatively cold (typically room temperature or slightly above).
The plasma is created through inelastic collisions between gas molecules and electrons which gain adequate kinetic energy in the electric field inside the discharge chamber. The electric field for the acceleration of the electrons can be provided via direct current (DC), a high frequency alternating voltage (HF) or via microwaves (MW). Usually the HF excitation at 13.56 MHz is used because DC discharges are not feasible for dielectric films. It is allocated as a free frequency for industrial applications all over the world. But in principle all frequencies can be used for the deposition of thin films. The electric field in an rf plasma initially accelerates a few free electrons present in the gas. Although the electric field also acts on the ions, they remain relatively immobile because of their much higher mass. The accelerated electrons do not lose much energy in elastic collisions with gas species because of the large mass difference. They also do not lose much energy in inelastic collisions (excitation and ionisation), until their energies reach the necessary threshold energies. As a consequence, these accelerated electrons gain energy quickly from the electric field. When these electrons acquire enough energy, their collisions with gas species result in excitation and ionisation. The latter process generates additional electrons, that are again accelerated by the electric field. This process avalanches quickly, creating a steady state glow discharge. In this state, loss (electrodes and walls and in the volume) and gain (ionisation) of charges are equal.

Inelastic collisions between electrons and gas species give rise to highly reactive species, such as excited neutrals and free radicals, as well as ions and more electrons. The reactive species are used to deposit thin films at low temperatures, because the gas temperature does not raise significantly during these processes. Possible inelastic collisions between electrons and gas species in the PECVD process are: Excitation, ionisation, dissociation, electron attachment and dissociative attachment. Other important reactions are photoemission and charge transfer [48].

\[
\begin{align*}
\text{Excitation:} & \quad A + e^- &\rightarrow A^* + e^- \\
\text{Ionisation:} & \quad A + e^- &\rightarrow A^+ + 2e^- \\
\text{Dissociation:} & \quad A_2 + e^- &\rightarrow 2A + e^- \\
\text{Electron attachment:} & \quad A + e^- &\rightarrow A^- \\
\text{Dissociative attachment:} & \quad A_2 + e^- &\rightarrow A + A^- 
\end{align*}
\]
Although DLC and a-Si:H films are both deposited by PECVD, the conditions in both processes are considerably different. Common in both processes is that the gas is decomposed between two electrodes in a low pressure plasma (p < 100 Pa). To obtain hard a-C:H films, ion bombardment during deposition is required, meaning the substrate is placed on the cathode (to receive positive ions). Also a high rf power (for a high self-bias), a low gas pressure (for high ionisation) and low substrate temperatures (to minimise self-annealing) are needed for the deposition of good DLC films. a-Si:H in contrast is deposited from silane plasmas under conditions which minimise the concentration of defect states due to silicon dangling bonds. That means that sufficient hydrogen must be present to passivate the dangling bonds but not so much that polymeric SiH$_2$ groups are common. This requires low rf power, a moderate gas pressure and an anodic substrate (to minimise ion bombardment) and a substrate temperature of about 250 $^\circ$C to give optimum self-annealing.

In the following the PECVD process is described for a silane plasma. One prominent gas for the deposition of amorphous hydrogenated silicon thin films is silane (SiH$_4$). Figure 2.2 shows a sketch of the PECVD process which can be decomposed into four steps: 1) the dissociation of the gas precursors, 2) the plasma physics and chemistry, which determine the flux and nature of reactive species to the substrate, 3) the plasma-surface interactions, and 4) the reactions taking place in a growth-zone where cross-linking reactions result in the formation of the film [49].

The silane gas is decomposed into reactive neutral fragments (e.g. SiH, SiH$_2$, SiH$_3$, Si$_2$H$_6$, H, H$_2$, etc.) and into positively charged ions (e.g. H$^+$, SiH$^+$, SiH$_2^+$, SiH$_3^+$). The neutral fragments diffuse with thermal velocity to all surrounding walls, including the substrate whereas the positive ions are accelerated in the space charge sheaths in front of the electrodes leading to a bombardment of the electrodes and the substrate with positive ions. Depending on their adhesion coefficient all fragments are deposited onto the surfaces they hit and are incorporated into the film with the probability $s$.

The production of reactive species can result from either primary or secondary reactions (see Figure 2.2). Primary reactions are inelastic collisions between electrons and gas molecules. The results of the primary reactions are the radicals and ions re-

Table: 17

Photoemission: \[ A^* \rightarrow A + h\nu \]
Charge transfer: \[ A^+ + B \rightarrow A + B^+ \]
Figure 2.2: Schematic representation of the PECVD process involved in a-Si:H deposition, after [49].

Responsible for the deposition of a-Si:H as described before. At low pressure, low silane dissociation and/or temperatures above 200° C primary reactions alone are sufficient to describe a-Si:H deposition. Under these conditions the SiH₃ radical is responsible for a large fraction of the deposition. Going to higher power, higher pressure and/or lower temperature the formation of particles inside the plasma can be observed. The formation of particles can lead to macroscopic defects in thin films, but today there are also efforts to incorporate nanoparticles into a-Si:H films with improved properties compared to a-Si:H [49].

In this work the formation of nanoparticles has been avoided to obtain good quality films. The discharge conditions where no dust particles could be observed are shown in chapter 5.1.
2.4 Stress and adhesion of thin films

Most surface coatings suffer from intrinsic stress. These stresses can be of great relevance, since they may have influence on e.g. the resistance of the coating to wear and fatigue crack propagation. But the more significant problem is the danger of debonding and destruction of the film due to intrinsic stress. This danger increases as the thickness of the coating is increased, since the release of stored elastic strain energy as the stresses become relaxed can drive this debonding. Additionally the quantity of energy released, per unit area of interface, normally rises more or less linearly with coating thickness [50].

There are two main sources of stress in general: 1) differential thermal contraction and 2) phenomena occurring during deposition. The first one is usually referred to as extrinsic stress, the second one to as intrinsic stress.

The stress due to differential thermal contraction develops when the substrate and the deposited film have different expansion coefficients. At higher deposition temperatures, meaning higher expansion mismatch, this stress will be more pronounced. When the films, as mostly is the case in this work, is deposited at room temperature, this kind of stress can be neglected.

The second type of stress, intrinsic stress due to phenomena occurring during deposition, is more important in this work. These stresses can arise in different ways during the thin film deposition from the vapour phase. Molecular species arriving with high energies at the surface can become implanted within the film, where they may occupy interstitial sites and therefore produce compressive stress. Also the bombardment with energetic species which are not deposited into the film can promote such site occupancy and have a similar effect. Tensile stress on the other hand is generated when processes during the deposition take place which produce excess vacancies.

a-C:H films also usually possess considerable intrinsic, compressive stresses which limit the adhesion of thicker films. DLC films are typically found to have high internal stresses, usually in the range of 0.5-7 GPa [15], [51]. This property is directly correlated to the fraction of sp³-bonded C in the films [51]. The high intrinsic stresses limit the thickness of films that can be used for any application usually to less than 1 µm. Robertson and Grill [14], [51] report that the intrinsic stress of a-C:H films deposited from methane is a function of the bias voltage. For low bias the stress is compressive and becomes lower and at least tensile at high bias. This is the result of
pronounced implantation of bombarding carbon ions, once they have enough energy to penetrate the structure. A further increase in the ion energy leads to intensive local heating and consequent reduction in the compressive stress until it becomes tensile as the structure undergoes thermal relaxation.

When the intrinsic stress of a film is too high, the film flakes off the substrate directly after the deposition process. The work $W_A$ required to separate a unit area of two phases forming an interface is expressed by [21]:

$$W_A = \gamma_f + \gamma_s - \gamma_{fs}.$$  

(2.14)

The quantities $\gamma_f$ and $\gamma_s$ are the specific surface energies of film and substrate, and $\gamma_{fs}$ is the interfacial energy. A positive $W_A$ denotes attraction (adhesion) while a negative $W_A$ implies repulsion (de-adhesion). $W_A$ is largest and adhesion strongest when materials of high surface energy come into contact. When the energy density in the film exceeds that which is needed to create two new surfaces of surface energy $\gamma$, the stress $\sigma$ leads to delamination of the film of thickness $h$. Adhesion of the film requires [14]:

$$\frac{\sigma^2 h}{2E} < 2\gamma,$$  

(2.15)

where $E$ denotes Young’s modulus.

To act as a protective coating, the films have to adhere very well to the substrate. Therefore the adhesive forces have to overcome the internal stresses in films, which will otherwise cause the films to delaminate from the substrate.

Other effects having influence on adhesion of films on a substrate beside intrinsic stress are contamination and chemical bonding between the film and the substrate and physical properties and roughness of the substrate. To provide equal conditions for the deposited films, the roughness of the substrate was kept smaller than the film thickness. Therefore, the metal substrates used in this work are ground and polished before deposition.

Another limitation of the adhesion of films on metal substrates are native oxide layers which usually form on metal. Morshed et al. [52] showed that the adhesion of DLC films on stainless steel is improved significantly when the substrate is pre-etched with
Figure 2.3: Different interfacial layers formed between film and substrate: 1) abrupt interface, 2) compound interface, 3) diffusion interface, 4) mechanical anchoring at interface.

argon before the deposition of the DLC film. Due to the etching the composition of the surface oxide is altered and partially removed. Additionally, the etching minimises the intrinsic stress without significantly affecting the film hardness.

Ohring [21] distinguishes between four types of interfaces as depicted in figure 2.3.

1. The *abrupt* interface is characterised by a sudden change from the film to the substrate material within an atomic spacing distance (~1-3 Å). Such interfaces arise because of the lack of interaction between film and substrate atoms and low interdiffusion rates. Film adhesion in this case will be low because of easy interfacial-fracture modes.

2. The *compound* interface is characterised by a layer or multilayer structure many atomic dimensions thick which is created by chemical reaction and diffusion between film and substrate atoms. This type of interface usually suffers from high stresses generated by accompanying reaction leading to volumetric changes.
Adhesion is generally good if the interfacial layer is thin, but poorer if thicker layers are formed.

3. The diffusion interface is characterised by a gradual change in composition between film and substrate. Mutual solubility of film and substrate precludes the formation of interfacial compounds. These layers usually show good adhesion.

4. The mechanical interface is characterised by interlocking of the depositing material with a rough substrate surface. In this case the adhesion strength depends primarily on the mechanical properties of film and substrate as well as interfacial geometry. A tortuous fracture path induced by rough surfaces and mechanical anchoring leads to high adhesion.

It is known that DLC films do not adhere well on most metals. Peng and co-workers [53] found out that a thin (80 nm) layer of aluminium deposited on titanium and steel substrates prior to DLC deposition raised the interfacial toughness substantially. Simultaneously, a pre-cleaning process, involving bombardment of the substrate by argon ions, improved the adhesion of the DLC film strongly. Peng et al. associated this effect with the removal of the native oxide layers. Grill et al. [54] propose an intermediate amorphous silicon layer between the metal surface and the DLC film since most metals are able to form silicides. This silicon layer improved the adhesion of the films to the substrates. He deposited DLC films (thickness 50 nm) onto silicon substrates coated with Co, Cr, or their alloys. With an adherence tester, consisting of aluminium studs precoated with epoxy, the adhesion of the films to the substrate was tested. These studs were pulled with a continuously increasing load until fracture occurred. The DLC films adhered very well to pure silicon substrates, but not at all to the metallic layer some silicon substrates were coated with. They even cracked immediately after removal from the chamber and could be wiped off easily. When he used a thin (several atomic layers to 4 nm thick) a-Si film between metal and DLC, the films adhered very well and fracture was only observed in the silicon substrate or inside the metallic layer. Grill assigned the significant improvement in adhesion when using the amorphous silicon interfacial layer to the formation of strong Si-C and Si-metal bonds. Herd et al. [55] report that amorphous silicon crystallises in contact with certain metals at relatively low temperatures, forming silicides.
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Ianno et al. [56] followed a similar method as Grill. They tried to improve the adhesion of DLC films on titanium containing alloys with the help of a thin silicon layer on the substrate. PECVD deposited DLC films showed almost no improvement of the adhesion when using a silicon layer. But the adhesion of reactive magnetron sputter deposited DLC films was strongly improved by using an intermediate silicon layer.

In this work the attempt of using a thin adhesive layer of amorphous hydrogenated silicon to improve the adhesion of DLC on different metals is chosen. The a-Si:H film is only several 10 nm thick, whereas the DLC film is supposed to have a thickness of 100 nm or more. The influence of different parameters like applied power, substrate temperature, hydrogen content and others on the adhesion of the films also under durability tests are investigated.

2.5 Binary phase diagrams of different metal-, Si-, and C-systems

At the interface substrate–film different mixtures of the participating metals (iron, nickel, titanium, copper, chromium) and of the constituents of the films (carbon or silicon) appear. The stability of the resulting phase has strong influence on the adhesion of the film on the substrate. With the help of binary phase diagrams it is possible to determine stable and non-stable compounds of the different systems. In the following, the most important phase diagrams are shown and discussed. These phase diagrams are all valid for the case of thermodynamic equilibrium. The plasma enhanced deposition is a non-equilibrium method. Thus, non-equilibrium processes

![Figure 2.4: Scheme of the film system consisting of a-Si:H and DLC on metals.](image)
are enabled which under equilibrium conditions are only possible under significantly higher temperatures or pressures. The phase diagrams show whether a generated phase is thermodynamical stable or not after the deposition. The shown phase diagrams are taken from [57].

**Carbon-Iron**

Figure 2.5 shows the phase diagram of carbon-iron on the at. % scale. The phase relations are presented in form of the generally accepted double diagram. The curves of the metastable system Fe-Fe$_3$C are drawn in solid lines and those of the stable system Fe-graphite in dashed lines except for the stable equilibria between melt and the phases $\delta$ and $\gamma$. Under normal conditions there are only two stable compounds, namely Cementite, Fe$_3$C (orthorhombic) and the so called "Hägg-carbide". The latter only exists between room temperature and 230 $^\circ$C with the empirical formula Fe$_{2.2}$C. Since the solubility of C in bcc $\alpha$-Fe is very small, the ferrite phase has practically the lattice constant and the magnetic transition temperature (768 $^\circ$C) of pure $\alpha$-Fe. At low temperatures this phase exists only for carbon contents below 0.3 at. %.

**Carbon-Copper**

In [57] the solubility, in wt. % C, was determined to be about 0.0001 at 1100 $^\circ$C, 0.00015 at 1300 $^\circ$C, 0.0005 at 1500 $^\circ$C, and 0.003 at 1700 $^\circ$C. As carbon does not
diffuse through solid copper, the solubility must be exceedingly small.

**Carbon-Nickel**

The phase diagram of carbon and nickel is shown in figure 2.6. Molten Ni can dissolve substantial amounts of C, which precipitate as graphite on cooling. The composition of the point where the solubility of C in molten Ni changes in slope at 2100 °C coincides nearly with that of Ni$_3$C. Therefore, Ni$_3$C exists but is stable only at these high temperatures and decomposes already on quenching from the molten state. In general, a stability limit for Ni$_3$C between 400 and 500 °C is found. Below these temperatures nickel and amorphous carbon are assumed to be the decomposition products of Ni$_3$C.

**Carbon-Chromium**

Since steel consists also of Cr, the system C-Cr is shortly treated here. The phase diagram shows the existence of three carbides, namely Cr$_{23}$C$_6$, Cr$_7$C$_3$, and Cr$_3$C$_2$. The monocarbide CrC does not exist. The solubility of C in Cr is exceedingly small, it decreases from 0.32 wt. % at 1498 °C to 0.006 wt. % C at 900 °C.

**Carbon-Titanium**

The phase diagram of carbon-titanium reveals as the only stable compound TiC, whose structure is of the NaCl type. The melting point has not been clearly estimated yet and lies somewhere between 3030 and 3250 °C.
Carbon-Silicon

There exist two possible phase diagrams for the system carbon-silicon which differ slightly, presented in figure 2.8. The only chemically stable compound is silicon carbide, SiC. The decomposition temperature of SiC lies at about 2700 °C. SiC exists as a thermodynamic more stable hexagonal α-phase and as a cubic β-phase. The transition from the β- to the α-phase occurs at temperatures higher than 1414 °C. SiC shows strengths at high temperatures, refractoriness, and high thermal conductivity. Additionally, it has a low coefficient of linear thermal expansion and a high degree of chemical stability. SiC exists in many crystal modifications, so called polytypes. These polytypes are distinguished by just the vertical stacking of SiC bilayers with an otherwise identical bond coordination.

The covalent Si-C-bindings have a very high binding energy. This leads to rather low chemical reactivity of a-C/Si:H coatings compared with the chemical erosion yields of a-C:H films, tested with hydrogen ions with effective impact energies of 180 eV. The chemical erosion rate of a-C/Si:H is about 30 times lower than that of a-C:H [58].
Iron-Silicon

The phase diagram of iron-silicon (figure 2.9) is well investigated and today essentially established. In approaching the composition Fe$_3$Si, ordering takes place. In the region of low silicon content three phases, $\alpha$, $\alpha'$, and $\alpha''$ can be found. The $\alpha$-phase is disordered. The phases $\alpha'$ and $\alpha''$ differ in composition having identical bcc lattice structure. The $(\alpha+\alpha')$ field is very narrow. The solubility of Si in $\alpha$-Fe decreases from 25 at. % at 1250 °C to 14 at. % Si at 700 °C and 9.5 at. % Si at room temperature. However, in the range up to 25 at. % silicon miscibility of silicon and iron in one of the three phases exists. The $\eta$-phase is indicated with Fe$_5$Si$_3$ and stable in the temperature range from 825-1030 °C. It can, however, be retained metastable at room temperature and is ferromagnetic below about 90 °C. Fe$_5$Si$_3$ has a hexagonal structure. The composition of the FeSi phase ($\epsilon$-phase) was found to be variable within narrow limits. The homogeneity range extends from 49 to 50.5 at. % Si. The structure of FeSi constitutes the cubic B20 prototype. In the partial system FeSi-Si, only one intermediate phase, $\zeta$, exists. It has a tetragonal structure and 3 atoms per unit cell.

Nickel-Silicon

The system nickel-silicon is also well investigated. The phase diagram is depicted
in figure 2.10(a). In this system, several stable phases exist, namely Ni$_3$Si, Ni$_5$Si$_2$, Ni$_2$Si, Ni$_3$Si$_2$, NiSi, and NiSi$_2$. In the past, Ni$_3$Si was assumed to be stable only above 1100 °C, but it was clearly shown that Ni$_3$Si exists down to room temperature. It undergoes two transformations at about 1120 °C and 1040 °C; the three modifications are designated $\beta_3$, $\beta_2$, and $\beta_1$ in the diagram. The composition of these phases alters slightly with temperature. Ni$_5$Si$_2$ shows an orthohexagonal cell containing 91 atoms. Ni$_2$Si(L) is orthorhombic and 12 atoms per unit cell, whereas Ni$_2$Si(H) is hexagonal and 6 atoms per unit cell. Ni$_3$Si$_2$ has an orthohexagonal cell with 45 atoms. Ni$_2$Si is always the first phase to form during low-temperature annealing [21]. But Ni$_2$Si is not in thermodynamic equilibrium with either Ni or Si according to the phase diagram. What happens next depends on whether Si or Ni is present in excess. When a thin Ni film is deposited on a massive Si wafer, the sequence proceeds first to NiSi.
and then to NiSi$_2$ at elevated temperatures. However, when a film of Si is deposited on a thicker Ni substrate (as is the case in this work), then the second and third compounds formed are Ni$_5$Si$_2$ and Ni$_3$Si at temperatures above about 400 °C. At elevated temperatures the resulting two-phase equilibrium, either Si/NiSi$_2$ or Ni/Ni$_3$Si, develops, in agreement to the phase diagram.

Copper-Silicon
The phase diagram of the system copper-silicon is depicted in figure 2.10(b). It shows several crystalline phases. The $\alpha$-phase is almost pure copper. The $\kappa$-phase is hcp, the $\beta$-phase bcc. The $\gamma$-phase is cubic of the $\beta$-Mn type. The high-temperature $\delta$-phase is considered to be a Cu$_{31}$Si$_8$ compound. The $\epsilon$-phase (Cu$_{15}$Si$_4$) has a bcc lattice structure with 76 atoms per unit cell. The $\eta'$-phase (Cu$_3$Si) has a slightly distorted $\gamma$-brass structure.

Silicon-Titanium
According to the diagram of Si-Ti, there are three compounds in this system: Ti$_5$Si$_3$, TiSi, and TiSi$_2$. The phase coexisting with the $\alpha$ and $\beta$ solid solutions extends over a range of compositions, whereas heterogeneous microstructures below 37.5 and above 40 at. % Si have been observed. The crystal structure of this phase is based on the
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composition Ti$_5$Si$_3$. The structure of TiSi$_2$ forms the orthorhombic ZrSi$_2$ prototype.

**Chromium-Silicon**

In this system the following Cr silicides can be found: Cr$_3$Si, CrSi, and CrSi$_2$. There is still dispute over the existence of Cr$_2$Si and Cr$_3$Si$_2$.

**Figure 2.11:** Phase diagram of Si-Ti.

**Figure 2.12:** Phase diagram of Cr-Si.
Conclusion
The examined phase diagrams reveal that carbon does not build stable phases with copper and nickel at all and no stable phases at lower temperatures with iron. Therefore, no adhesion of carbon films on these materials is expected. Later experiments will confirm this fact also under non-equilibrium plasma conditions.

Silicon, in contrast, forms stable silicides with all considered metals. Those silicides exist down to low temperatures and should therefore lead to good adhesion of silicon-containing films on these metals.

In the case of silicon-carbon, the especially stable SiC is formed. This leads to good adhesion of the carbon-containing DLC film on the a-Si:H film. The formation of SiC under plasma conditions is confirmed in chapter 7. The quality of the adhesion of the film system metal–a-Si:H–DLC will be investigated in chapter 8.
Chapter 3

Thin film diagnostics

In this chapter the diagnostics used for the investigation and characterisation of the thin films are described. Most of them are used \textit{ex situ} meaning that the measurement is performed outside the plasma reactor after the deposition of the thin films with the sample stored at ambient air.

The main diagnostics used throughout this work is optical ellipsometry. Therefore, this diagnostic method is described in more detail than the others in section 3.1. Ellipsometry is very powerful because it can measure the film thickness of even very thin films as well as the optical properties of these films like indices of refraction and absorption. Other methods like reflectometry are not able to measure the film thickness of such thin films (down to about 50 nm) as precisely as ellipsometry does. The optical constants are important to know because they give information about the composition of the thin films.

Ellipsometry can be used both \textit{in situ} and \textit{ex situ}. Both methods are used in this work and are therefore described in the following chapter. With \textit{in situ} ellipsometry the growth behaviour of thin films can be monitored during the growth process.

For the analysis of the chemical composition and the bonding configuration of the atoms in a thin film Fourier Transformed Infrared Spectroscopy (FTIR), Time of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) and X-ray Photoelectron Spectroscopy (XPS) are used. While XPS can only investigate the surface of a sample, FTIR and TOF-SIMS can probe the whole depth of the film. Especially with FTIR the hydrogen content of the films can be determined as described in section 5.2. In sections 3.2 (FTIR), 3.3 (XPS), and 3.4 (TOF-SIMS) these methods are presented. Atomic concentrations in a material can be measured with the help of Rutherford-Backscattering (RBS), which is explained in section 3.5.
The roughness both of the substrates and the deposited films is measured with the help of an Atomic Force Microscope (AFM). The mode of operation of the AFM will be dealt with in section 3.6.

The intrinsic stress inside a thin film is decisive for the adhesion of the film on the substrate. The method for measuring the intrinsic stress inside a film is described in section 3.7.

One method used for the determination of the adhesion of the film system on the samples is the cavitation erosion admission. Chapter 3.8 explains the setup and the principle of measurement of the cavitation erosion method.

The RBS and XPS measurements have been performed in cooperation with different institutes at the Ruhr-Universität Bochum whereas the TOF-SIMS measurements have been made as remittance work at the Forschungszentrum Jülich. All other measurements have been carried out by the author.

### 3.1 Ellipsometry

Optical ellipsometry is a sensitive method for the investigation of surfaces and thin films. It works in measuring the relative change of the phase angles in the reflected beam of polarised light. These angles that define the state of polarisation of light are named $\Psi$ and $\Delta$. $\Psi$ and $\Delta$ are related with Fresnel’s coefficient of reflection $\tilde{R}_p$ and $\tilde{R}_s$ (p for parallel and s for perpendicular [German ”senkrecht”] polarised light) via:

$$\rho = \frac{\tilde{R}_p}{\tilde{R}_s} = \tan(\Psi)e^{i\Delta}. \quad (3.1)$$

The measurement of the ratio of two numbers makes this method very precise and reproducible. The value of $\rho$ is complex so that the measurement becomes very sensitive due to the phase information.

Ellipsometry is used to measure the film thickness or optical constants of a thin film or even both simultaneously, if possible. The optical constants can be estimated in the UV, the visible and the IR range. But there are also limits of this method. To gain useful information the film thickness should be in the range of the wavelength. The roughness of the sample surface or of an intermediate layer should be smaller than 10% of the wavelength to avoid diffuse scattering of the incident light beam and
depolarisation of the reflected light beam. Finally the film thickness in the area of the light beam should not vary more than 10% because otherwise the assumption of parallel film boundaries is not valid anymore, leading to deviation of the calculated data from the measured ones.

The principle of optical measurements will be described in the following. Instead of measuring quantities of interest like film thickness or index of refraction directly quantities which are a function of the parameters of interest are measured in optical experiments. With the help of a model the parameters giving the best results for the measured quantities when inserted into the model are estimated. Thus first the state of polarisation (\(\Psi\) and \(\Delta\)) of the reflected beam as a function of wavelength and/or angle of incidence is measured. Then a model is created which connects the known quantities – state of polarisation, wavelength, and angle of incidence – with the unknown quantities like film thickness and optical constants. The unknown parameters are varied as long as the calculated values for \(\Psi\) and \(\Delta\) fit best to the measured optical values. When the physical parameters are estimated so that the calculated values are as close as possible to the measured ones, it has to be proven that this set of parameters is physically meaningful and does not correlate strongly. If so, the estimated parameters can be considered to reflect the real physical state of the sample. The choice of the adequate model is critical to obtain the correct quantities.
3.1.1 Kramers-Kronig relation

Real and imaginary part of the complex index of refraction are not independent quantities, nor are the real and imaginary part of the complex dielectric function. In the Kramers-Kronig correlation the real and imaginary part of the index of refraction respectively the dielectric function are connected as follows:

\[ n(E) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{E' k(E')}{E'^2 - E^2} dE' \]  
\[ \epsilon_1(E) - 1 = \frac{2}{\pi} P \int_0^\infty \frac{E' \epsilon_2(E')}{E'^2 - E^2} dE'. \]  

(3.2)

(3.3)

Here \( E \) denotes the energy of the incident photon.

The Kramers-Kronig correlation results from the condition that a material can not respond to an applied electric field prior to the application of the electric field. The polarisation \( \vec{P} \) can only be induced after an electromagnetic wave with frequency \( \omega \) and electric field \( \vec{E} \) interacted with the solid.

With the help of the Kramers-Kronig correlation the refractive index \( n \) can be calculated from the known absorption coefficient \( k \) and vice versa. For this the absorption coefficient has to be known in the whole spectral range. This is not the case in most cases because of the used light source. However, \( n \) is only changed in the region near \( \omega_0 \) due to absorption at frequency \( \omega_0 \). The influence of the absorption in distant spectral regions can be corrected by a factor \( n_{\infty} \) and \( \epsilon_{\infty} \), respectively:

\[ n(E) = n_{\infty} + \frac{2}{\pi} P \int_0^\infty \frac{E' k(E')}{E'^2 - E^2} dE'. \]  

(3.4)

All optical constants calculated from a model have to be controlled by the Kramers-Kronig correlation. If they do not satisfy the Kramers-Kronig correlation they are not the true optical constants of the sample.

The Kramers-Kronig correlation is already inherently fulfilled in the optical models used in this work meaning that the control of the Kramers-Kronig consistency ”by hand” after the fitting procedure can be omitted.
3.1.2 Configuration of the used ellipsometer

In this work an ellipsometer with rotating analyser was used. The configuration of the components in this kind of ellipsometer is as follows:

Source $\Rightarrow$ polariser $\Rightarrow$ sample $\Rightarrow$ rotating analyser $\Rightarrow$ detector.

A Xenon lamp was used as the light source. The detectable wavelength range lies between 245 and 999 nm. The light source is the main source of error in optical ellipsometry. Thus attention has to be paid to use a good, stable light source.

The main drawback of a rotating analyser ellipsometer is that it measures the most accurate when the beam entering the detector is nearly circularly polarised ($\Delta \approx 90^\circ$). The measurement gets more and more inaccurate when the incident beam of light is nearly linearly polarised ($\Delta \approx 0^\circ$ or $180^\circ$). Another, less critical problem is that $\Delta$ ranges from $0^\circ$ to $360^\circ$. The ellipsometer can not distinguish between left- and right-circularly polarised light meaning that $\Delta$ is always mapped into the $0^\circ - 180^\circ$ range.

Adding a variable compensating element, for example a $\lambda/4$ plate, into the beam of light, one is able to distinguish between the two states of polarisation and the measurement gets more accurate. The variable retarder is placed between polariser and sample into the course of beam and moved in and out controlled by a computer. Thus, the input polarisation may be adjusted to provide a reflected beam which is always close to circularly polarised. With the help of this system $\Delta$ can be measured accurately over the entire range of $0^\circ - 360^\circ$.

3.1.3 Tauc-Lorentz model

For the amorphous silicon films in this work the Tauc-Lorentz model was used. This model is especially appropriate for amorphous layers. It models the dielectric function of a film or substrate as a linear summation of real and complex terms (or "oscillators"), each of which is a function of wavelength or photon energy. The Tauc-Lorentz model looks as follows [59]:

$$\epsilon_{nT-L} = \epsilon_{n1} + i\epsilon_{n2},$$

(3.5)

where

$$\epsilon_{n2} = \frac{A_n(E - E_{gn})^2 \Theta(E - E_{gn})}{(E^2 - E_0^2) + C_n^2 \frac{\Theta(E - E_{gn})}{E}},$$

(3.6)
and
\[ \epsilon_{n1} = \frac{2}{\pi} P \int_{R_g}^{\infty} \frac{\epsilon_{n2}(E')}{E'^2 - E^2} dE'. \] (3.7)

The fit parameters are \( A_n, E_{0n}, C_n \text{ und } E_{g_n} \), denoting amplitude, position, and width of the oscillator and the energy of the bandgap. \( \Theta \) stands for the theta-function. The Kramers-Kronig correlation is already included in this model and is solved analytically by the used computer program (see [60]). The whole dielectric function results in:

\[ \epsilon = \epsilon_{n1} + i\epsilon_{n2} = \epsilon_{1\text{offset}} + \text{Pol#1}(\text{Pos}, \text{Mag}) + \text{Pol#2}(\text{Pos}, \text{Mag}) + \text{Tauc} - \text{Lorentz}(A_n, E_{0n}, C_n, E_{g_n}). \] (3.8)

The offset term \( \epsilon_{1\text{offset}} \) is a real number and was mentioned as \( \epsilon_{\infty} \) in section 3.1.1. The two poles are two zero-width Lorentz oscillators (or poles). They are defined by position (centre energy) and magnitude (strength) and simulate the dispersion in \( \epsilon_1 \) created by absorption that occurs outside the measured spectral range. The dielectric function for a pole-oscillator looks as follows:

\[ \epsilon_{n\text{-Pol}} = \frac{A_n}{E_n^2 - E^2}. \] (3.9)

In the fitting procedure whether \( \epsilon_{\infty} \) or one or two poles with \( A_n \) and \( E_n \) are activated. Thus this model consists of minimum five maximum eight fit parameters.

3.1.4 Parametric DLC-Model

The deposited DLC films were modelled with a parametric semiconductor-layer model. Parametric dispersion models oppress parametric correlation and enforce Kramers-Kronig consistency of the model. The parametric DLC model consists of an oscillator whose amplitude, position, width, and exact form left and right of a critical point are used as fit parameters for the model. Additionally, a pole oscillator above the measured spectral range occurs.
3.1.5 In situ ellipsometry

With in situ ellipsometry the film growth can be followed during deposition. For this purpose an ellipsometer consisting of polariser and analyser was flanged on two opposite windows of the chamber under an angle of 76 degree to the axis of symmetry of the chamber. The ellipsometer was equipped with a rotating compensator. The light of a He-Ne laser (632 nm) is polarised and detected after reflection on the sample. Although only two values ($\Psi$ and $\Delta$) are measured in the case of a single wavelength ellipsometer, it is possible to determine three quantities ($n$, $k$, and film thickness). This is due to the fact that the initial values for $\Psi$ and $\Delta$ for a bare substrate are known and because $\Psi$ and $\Delta$ develop with time due to increasing film thickness. The principle of measurement is the same as in ex situ ellipsometry. The values are measured every 1000 ms. For the analysis the same models as used for ex situ ellipsometry have been applied. One disadvantage of the used in situ ellipsometer is the fact that $n$ and $k$ can only be measured at one specific wavelength. Therefore, all samples were measured ex situ after deposition to obtain $n$ and $k$ over the whole visible wavelength range.

3.2 Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared Spectroscopy (FTIR) is one of the few techniques that is able to provide information about the chemical bonding in a material. This technique is, in contrast to others, non-destructive, meaning that the properties of the sample will not be subjected to any chemical changes by the measurements. Infrared spectroscopy detects the vibration characteristics of functional groups in a sample. When infrared light interacts with the material, chemical bonds will stretch, contract, and bend. As a result, a chemical functional group absorbs infrared radiation in a specific wave number range regardless of the structure of the rest of the molecule.

To measure spectra either dispersive spectrometers or Fourier-Transform (FT) spectrometers can be used. For measurements in the IR range mostly FT spectrometers are employed today. The instrument first scans and records the transmittance of the radiation source through pure substrate and air column within the instrument, which is then subtracted from the samples measurement. The spectrum is calculated via the Fourier transformation of the measurement signal of a Michelson interferometer, the
so called interferogram. A schematic drawing of a Fourier transform infrared spectrometer is displayed in figure 3.2.

A thermal radiation source is used to produce IR radiation. Depending on the interesting spectral range (far, mid or near IR) different sources are utilised. The emitted radiation is directed towards the interferometer and goes through a beam splitter with, in ideal case, 50 % transparency. The two resulting beams are reflected by two mirrors, of which one is movable along the optical axis. After reflection the two beams recombine at the beam splitter and interfere. Half of this radiation leaves the interferometer and is directed and focused onto the sample and subsequently falls into the detector. The other half moves towards the radiation source and is lost for the measurement.

During the measurement, the movable mirror is moved a distance $x$ from the position $x = 0$, where both mirrors have the same distance to the beam splitter. This leads to an optical retardation $d = 2 \times x$. The intensity of the radiation is measured by the detector in dependence of $d$. When a polychromatic radiation source is used, the signal is a superimposition of cosine functions of all present wavelength in the spectrum. At zero the cosine for all wavelength is one, leading to a pronounced maximum.

**Figure 3.2:** Principle of a Fourier transform infrared spectrometer.
at this position. Moving away from the zero point the amplitude decreases fast due to destructive interference.

The interferogram is not recorded continuously but in distinct points. The interference pattern of an additional He-Ne laser in the path of beam is used to measure the optical retardation. The IR interferogram is recorded in every zero-crossing or multiple zero-crossing of the sinusoidal laser signal. The distance $\Delta x$ between two points in the interferogram determines the maximal frequency that can be detected unambiguously. The Nyquist criterion gives the spectral bandwidth within a spectrum that can be displayed depending of the interval $\Delta x$ in the interferogram:

$$\tilde{v}_{\text{max}} - \tilde{v}_{\text{min}} = \frac{1}{2\Delta x}. \quad (3.10)$$

In our case a He-Ne laser with a wavelength of 633 nm is used ($\Delta x = 316.5 \text{ nm}$) and the interval from 0 to 15800 cm$^{-1}$ can be detected.

Fourier Transformation Spectrometers have several advantages compared to dispersive instruments [61]. The first advantage is the fact that all wavelengths are measured simultaneously leading to a higher signal-to-noise ratio. The second advantage, the so called "Throughput-Advantage", is the fact that the light throughput of a FT spectrometer with its circular aperture is much higher than of a dispersive instrument with two slits. Thus more radiation power can be detected. The third point is the wavelength stability of spectra measured with an interferometer which is clearly higher than those of dispersive spectrometers. This is due to the fact that the frequency scale is measured with the help of a He-Ne laser giving an internal reference for each interferogram.

In this work an "Equinox 55" FTIR by Bruker has been used. It is equipped with a MIR source and a beam splitter made of KBr. The measurement volume is flushed with dried air to avoid spurious water bands.

### 3.3 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is used to analyse the chemical composition of a sample. In older literature this technique is called electron spectroscopy for chemical analysis (ESCA). For this method X-rays are used to excite photo emission and
the energy of the electrons ejected from the solid is analysed. The energy of the X-ray photons lies in the range of inner-shell electrons. When a solid absorbs a photon with an energy higher than the binding energy of an electron, a photoelectron is emitted and its kinetic energy is related to the energy of the photon. The energies of inner-shell electrons are characteristic of the atom from which they originate. Thus, elemental analysis with the help of XPS is possible. In principle all elements, apart from H and He, can be detected. Due to their very small cross section for ionisation H and He can not be identified by XPS.

The principle of measurement of XPS is displayed in figure 3.3. Figure 3.4 shows a typical energy spectrum of a XPS measurement of an a-Si:C:H film on a silicon wafer. The main peaks can be attributed to silicon, carbon and oxygen.

Not only the composition of a sample can be identified, but it is also possible to determine the composition quantitatively. For quantitative analysis, the XPS peak areas are proportional to the amount of material in the sample because the photoionisation cross-section of inner shell levels is almost independent of the chemical environment surrounding the element. But the detection volume is limited to a region near the surface (depth about 10 nm) due to the limited mean free path of the electrons. This is one source of error, because the surface composition may differ from the composition of the bulk material, especially when the surface is oxidised due to storage in air.
Due to the bonding environment around the atom the binding energies of an atom are shifted clearly. Thus even the binding state of an atom can be estimated, for example whether Si is bonded in SiO$_2$ or SiC. These shifts, called chemical shifts, are tabulated, for example in [62]. A more detailed description about XPS can be found in [63].

The measurements in this work have been performed in the Institute for Physical Chemistry I at the Ruhr-Universität Bochum. An Al K-alpha X-ray source with an energy of 1486.6 eV was used. The emitted photoelectrons have therefore kinetic ener-

<table>
<thead>
<tr>
<th>compound type</th>
<th>binding energy</th>
<th>state</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (Carbide)</td>
<td>281-283 eV</td>
<td>1s</td>
</tr>
<tr>
<td>C (Carbon)</td>
<td>284-285 eV</td>
<td>1s</td>
</tr>
<tr>
<td>Si (Silicon)</td>
<td>$\approx$ 99 eV</td>
<td>2p</td>
</tr>
<tr>
<td>Si (Carbide)</td>
<td>100-101 eV</td>
<td>2p</td>
</tr>
<tr>
<td>Si (SiO$_2$)</td>
<td>103 eV</td>
<td>2p</td>
</tr>
</tbody>
</table>

Table 3.1: Binding energies of carbon and silicon atoms.
gies up to maximum 1480 eV. The analysed atoms were Si and C, present in different binding states. The binding states of these atoms with the related binding energy are listed in table 3.1 [62].

3.4 Secondary Ion Mass Spectrometry

In the secondary ion mass spectrometry (SIMS) the sample is bombarded by high energetic primary ions (in the range of 20 keV) to analyse its surface. Due to its high specificity and sensitivity and also because of the low penetration depth of the primary ions the SIMS is well suited especially for chemical analyses of the top most atomic layers of solid state surfaces. The formation of neutral, positive and negative particles, which are further detected, gives information about the composition of the sample. The registered secondary ions reflect the element concentration in the sample. The depth resolution is smaller than 1 nm, the lateral resolution in the range of 1 µm. The sensitivity of SIMS is in the ppm range for all elements, but the disadvantage of this method is the fact that the sample gets destroyed by the measurement: despite the removal of material the composition and morphology of the sample is changed due to insertion of primary ions.

Bonding of atoms from the sample can also occur due to mixing of atoms in the collision cascade. These have to be distinguished from compositions present in the sample. In the following the set-up of the SIMS technique used will be explained in principle (after [64]). An ion source produces high energetic ions which are guided to a mass separator to guarantee proper bombardment conditions. The sample holder and manipulator is placed in ultra high vacuum. After the bombardment of the sample the energy of the generated secondary ions is analysed to separate a certain energy interval or to record an energy distribution. Subsequently the ions are mass-analysed with the help of quadrupole or time of flight (TOF) spectrometers. The secondary ions are detected with Faraday cups or single particle counting with channeltron or secondary electron multipliers. The signals are then processed by special computer programs.

Care in the interpretation of the data must be taken because of the so called ”matrix effect”. This means that the ion beams interact with the sample surface in different ways. For example, the positive metal ion yield of an oxidised surface is typically enhanced tenfold and even more, relative to a clean surface [21]. This effect usually
leads to an increase of the signal of different elements near interfaces.  
The so called TOF-SIMS (time of flight secondary ion mass spectrometry) is a special type of SIMS. While SIMS only detects single atoms (chemical elements and their isotopes) the TOF-SIMS also detects whole molecules [65]. This leads to knowledge not only about the chemical composition but also about the chemical bonding of the surface. As well as in SIMS the surface is bombarded with a primary ion beam. But in difference to SIMS this beam is not continuous but pulsed and also weaker, leading to a removal of only the topmost layer of atoms. When the ion beam for analysis is off, a second ion beam sputters the surface to ablate the sample layer by layer. This method is also able to provide depth profiling for thin film characterisation showing the distribution of the chemical elements or bondings in the sample. The secondary ions coming from the sample are separated and detected in the flight tube where they are reflected at the upper end of the tube to correct for different velocities. They are mass analysed by measuring their time-of-flight from the sample surface to the detector. Depth profiling by TOF-SIMS allows monitoring of all species of interest simultaneously, and with high mass resolution.

TOF-SIMS measurements were performed at the ”Forschungszentrum Jülich, Zentralabteilung für Chemische Analysen”. The used sputter ions were O$_2^-$ ions with an energy of 2 keV, resulting in a current of 346 nA, scanning an area of 300 µm × 300 µm. The ions for the analysis were Bi ions with an energy of 25 keV, resulting in a current of 1.5 pA and a scanning area of 100 µm × 100 µm.

With TOF-SIMS depth profiles of different samples are measured. Here, the intensity of the different elements and molecules are plotted versus the sputter time in seconds. This time is related to the depth, but not in a linear way, since different materials are worn away due to the sputtering faster than others. The intensities of different elements can not be absolutely compared to each other because different elements have different sputter yields.

### 3.5 Rutherford Backscattering Spectrometry

Rutherford Backscattering Spectrometry (RBS) is a method for the investigation of thin films with the help of ion beams. This method was discovered in 1911 during an experiment suggested by Lord Ernest Rutherford. In this experiment alpha particles were directed towards a thin gold foil where they were scattered by the atomic nuclei.
Today the analytical technique which is named after Rutherford is very similar to that first experiment. For the measurement high energetic ions (1-4 MeV) of low mass (hydrogen or helium) are directed onto the sample. Most of these ions are implanted into the sample, however some of these ions are scattered back from the atomic nuclei in the near surface (1 to 2 µm) of the sample. The energy of these backscattered ions is related to the mass of the target element from which the ion is scattered back. The energy of the backscattered ions is measured by a detector under a certain angle, usually 170 degrees. With the known scattering cross sections the concentration of the elements of the sample can be estimated without using a calibrated sample with known composition.

RBS is an elastic collision between energetic ions and target nuclei. Thus, the mass of the target atom \( M_2 \) can be determined by measuring the kinetic energy of the scattered atom. The collision is insensitive to the electronic configuration or chemical bonding of target atoms, but depends only on the masses and energies involved. After the collision the incident atom (mass \( M_1 \), energy \( E_0 \)) has been scattered with a scattering angle \( \theta \), having now an energy \( E_1 \). The kinematic factor \( K \) relates the backscattered energy to the incident energy of the ion [21]:

\[
E_1 = KE_0
\]  

With known energy and mass of the incident ion and known angular position of the ion detector, \( K \) only depends on the atomic weight of the target atom.

RBS is often used to measure the stoichiometry of thin films. A model based on the actual scattering cross section and the stopping power is used to generate a theoretical spectrum which is then adjusted until a fit is obtained to the experimental data. When the ion beam impinges on a thin film consisting of two components on a Si wafer, the majority of the ions penetrates below the film surface, where they continuously lose energy at a linear rate with distance travelled. At any film depth they can suffer an atomic collision. The scattered ion energy is still given by equation 3.11, but \( E_0 \) is now the incident ion energy at that point in the matrix. Some of the energy-attenuated
ions can reach the film/substrate interface where they may be backscattered and again lose energy in traversing the film backward until they finally exit. Other ions can even penetrate the Si substrate where they eventually are backscattered. It is important to realise that in the course of passage through the film, the ion beam can be thought of as splitting into two separate elemental components, each spanning a different range of energies. For each broad elemental peak detected, the highest and lowest energies correspond to atoms on the front and back film surfaces, respectively.

Assuming constant values for the energy losses in the target $\Delta_{\text{in}}$ and $\Delta_{\text{out}}$:

$$\Delta_{\text{in}} \approx \frac{t}{\cos \phi_1} \left. \frac{dE}{dx} \right|_{\text{in}}$$  \hspace{1cm} (3.13)$$

and

$$\Delta_{\text{out}} \approx \frac{t}{\cos \phi_2} \left. \frac{dE}{dx} \right|_{\text{out}}.$$  \hspace{1cm} (3.14)

The energy of an ion scattered in a depth $t$ is therefore:

$$E'(t) = K(E_0 - \Delta_{\text{in}}) - \Delta_{\text{out}}.$$  \hspace{1cm} (3.15)

The area under a spectral peak represents the total number of atoms of a given element present in the probed region or layer. The peak height is directly proportional to the atomic concentration. Since the peak width is dependent on the maximum
length traversed by the ions in the layer, it is directly proportional to the layer or film thickness if the ion energy attenuation with distance is known. The concentration ratio of two elements A and B is therefore given by:
\[
\frac{C_A}{C_B} = \frac{\sigma_B H_A \Delta E_A}{\sigma_A H_B \Delta E_B}
\]  
with \(\sigma\) the scattering cross section, \(H\) the peak height and \(\Delta E\) the peak width.

The measurements in this work have been performed at the "Dynamitron Tandem" laboratory at the Ruhr-Universität Bochum. Single charged He-ions with an energy of 2 MeV and a current between 10 and 20 nA have been used. The backscatter-spectra have been detected with a surface barrier detector under a backscatter angle of 160° in Cornell geometry. The resolution was 15 keV. For some measurements the samples have been inclined under an angle of up to 40° relativ to the incident beam to achieve a better depth resolution. The spectra have been analysed with the computer programm RBX [66].

### 3.6 Atomic Force Microscopy

The atomic force microscope (AFM) was developed to mechanically scan the surface of materials on a nanometer scale. During the measurements the surface is scanned by a very thin tip of silicon, diamond, silicon nitride or other materials. Depending on the radius of curvature of the tip and of the roughness of the surface lateral resolutions of 0.1-10 nm are possible. Thus even single atoms can be pictured. The repulsive force between surface and tip is of the order of \(10^{-9}\) N. Via a piezo-electric crystal the surface can be moved in all directions. During the measurement the tip scans the surface moving the sample under the tip. The tip is located at the end of a cantilever. The deflection of the cantilever is detected with a laser light beam and converted into a DC voltage. A feedback control systems controls the movement of the scanner and of the tip and analyses the signals. Figure 3.6 shows the functional principle of an AFM.

There are three different modes to operate an AFM: contact mode, non-contact mode and tapping mode.

In the contact mode the tip is in direct contact to the surface. The contact mode can
be operated in the constant height mode where the control system holds the height of the tip constant in adjusting the height of the sample or in the constant force mode were the mounting point of the cantilever is adjusted that way that the force between tip and surface stays constant.

In the non-contact mode, the cantilever is externally oscillated through an external periodical force slightly above its resonance frequency. When the tip gets closer to the surface the oscillation gets damped due to the attractive forces, especially van-der-Waals forces, and the amplitude as well as the frequency of the oscillation decrease. This makes the tip oscillating in a small distance to the surface.

The tapping mode is similar to the non-contact mode but with the excitation frequency slightly below the resonance frequency of the cantilever. This means that more energy can be transferred into the cantilever and due to the higher amplitude the tip touches the surface at each minimum of the oscillation.

In this work the roughness of the samples is measured by the contact mode in the constant height mode. This method is especially useful for hard materials and can be used with high measurement velocities. The used AFM tips are made of silicon with the backside coated with aluminium. The size of the cantilever is 125 µm × 35 µm with a thickness of 1 µm. The typical resonance frequency is 80 kHz with a force constant of 0.6 N/m.

The dimension of the scanned area depends on the applied scanner and is 90 µm ×
3.7 Measurement of the intrinsic stress

Stress in internally stressed films is normally revealed by measuring the strain it induces. The bipolar intrinsic stress of a film on a substrate causes an elastic bending of the substrate. A prior flat surface becomes convex or concave due to the stress with equal curvature in each direction leading to a spherical surface [50]. The amount of bending depends on the thickness and biaxial modulus $E/(1 - \nu)$ of the substrate. $E$ denotes the Young’s modulus and $\nu$ the Poisson’s ratio. When the layer is much thinner than the substrate, the radius of curvature $R$ of the substrate is related to the biaxial stress via Stoney’s formula [67]:

$$\sigma_f = \frac{1}{6} \left( \frac{E}{1 - \nu} \right) \frac{h_s^2}{h_f R}.$$  

(3.17)

Here, $h_s$ denotes the thickness of the substrate and $h_f$ the film thickness. For (1 0 0) silicon $E/(1 - \nu) = 1.805 \times 10^{11}$ N/m$^2$ [68].

The radius of curvature $R$ is measured indirectly via the deflection $\delta$ of the wafer (radius $a$) in the middle.

$$R = \frac{a^2}{2\delta} + \frac{\delta}{2}.$$  

(3.18)

The second term can be neglected compared to the first one giving:

![Figure 3.7: Deflection of the wafer due to intrinsic stress.](image)
Figure 3.8: Schematic configuration of the device to measure the deflection of a wafer.

\[ \sigma_f = \frac{1}{3} \left( \frac{E}{1 - \nu} \right) \frac{h_s^2 \delta}{h_f a^2}. \]  

(3.19)

Usually, the deflection is measured via a laser beam reflection method. The set-up used in this work works without laser and has been developed in our institute. It has been tested carefully and can measure the deflection in a wide range (up to several mm). The deflection is measured with the help of a micrometre screw. The wafer is placed in a holder directly below the micrometre screw. With the help of a telescope the tip of the micrometre screw is observed until it just touches the middle of the wafer without pressing it down. Screwing the micrometre screw further down the middle of the wafer touches the base at a certain hight. The difference of the two read off values corresponds to the deflection \( \delta \).

The reading accuracy of the deflection is 5 \( \mu \text{m} \). This corresponds to an error of 1.7 % with a deflection of \( \delta=300 \, \mu \text{m} \). To take into account the initial deflection of the wafer that was present before the deposition, this value has been subtracted from the measured value.

3.8 Cavitation erosion admission

To measure the wear resistance of the film systems the samples have been investigated by cavitation erosion admission. Since the films are very thin, other methods to measure the hardness of films like scratch tests or indenter methods are of limited use because the penetration is usually higher than the film thickness. These tests only provide meaningful results when used on films of more than 1 \( \mu \text{m} \) thickness. In
contrast, cavitation admission is a suitable testing method for sub-micrometer films because the size of the micro-jets developing during cavitation is in the micrometer range. This method gives qualitative knowledge of deterioration mechanisms by determining the surface damage as well as a quantitative measure of the bond strength between coating and substrate, and the intrinsic strength of the film.

The cavitation erosion test should be performed after all other measurements of the thin film because afterwards the film will be totally destroyed.

Figure 3.9 shows a sketch of the used cavitation erosion system. It consists of a piezoelectric vibrating device placed in distilled water at 20 °C. The tip of the so called sonotrode moves with a frequency of 20 kHz and an amplitude of 40 µm up and down. The frequency and amplitude are reproducible in the used configuration and held constant throughout all experiments. A sample holder with dial gauge guarantees a constant distance between sample and sonotrode and therefore a reproducible intensity of the cavitation attack.

Due to the vibrating tip of the sonotrode periodical shock waves are produced in the water. Imploding bubbles produce micro jets due to the local subsidence of the hydrostatic pressure of the water below the saturation vapour pressure [69]. Close-by a solid this implosion leads to a formation of a high-energetic liquid jet towards the
solid’s surface.
During the process the material suffers from pressure loads up to $10^5$ bar. Due to the cavitation exposure the surface of the material will be removed or shows modifications like cracks or topography changes. For thin films deposited on substrates different mechanisms of failure can be observed due to the influence of the high energetic micro jet on the interface between substrate and film. These different mechanisms are: a) adhesive failure at the interface between substrate and film, b) cohesive failure due to low intrinsic stability of a film, c) mixture of adhesive and cohesive failure and d) formation of a network of cracks.

The damage of the surface is determined by quantitative image analysis of a macroscopic image of the sample. With a special software regions of different colours on the sample can be separated and their area can be measured. This leads to determination of the fraction of damaged surface.
Chapter 4

Experimental set-up and characterisation of fundamental plasma properties

In this chapter the experimental set-up of the experiment is presented and the plasma properties present during film deposition are described. The films under investigation are deposited in a slightly modified GEC cell, equipped with a load lock chamber to avoid impurities in the deposition chamber. The exact configuration of the chamber and the employed in situ diagnostics are presented in section 4.1.

A critical parameter for the film deposition in the PECVD process is the self-bias. The self-bias determines the energy of the ions impinging on the surface of the growing film, leading to film growth. Measurements of the self-bias are presented in section 4.2 were its influence on the film growth is discussed.

Another critical parameter in the PECVD process is the plasma electron density. Measurements of the plasma density are presented in section 4.3.

Special care must be taken in the pretreatment of the used substrates. The surface configuration of a sample such as roughness, contamination, oxide film etc. has strong influence on adhesion and growth of the thin film. To obtain good quality films and to be able to compare films deposited on different substrates, a standard procedure for the grinding, polishing and subsequent cleaning of the substrate was developed. This procedure will be described in section 4.4.
Chapter 4 Experimental set-up and plasma properties

4.1 The deposition chamber

The investigated thin films are deposited in a capacitively coupled discharge chamber with two electrodes. This chamber is a slightly modified GEC cell. The ”gaseous electronics conference (GEC) reference cell” was developed on this conference to make experimental and theoretical data and results from different research groups comparable [70]. A schematic drawing of the used set-up including the GEC cell is displayed in figure 4.1. The electrodes are placed parallel with a distance of 3 cm, their diameter is 10 cm. The cylindrical vacuum chamber (diameter 25 cm) offers eight flanges for the access of diagnostic accessories. The two DN 150 CF, DN 100 CF, DN 63 CF and DN 40 CF flanges are placed pairwise vis-a-vis. The two DN 63 CF flanges are mounted in 75 degree to plumb line, the others are horizontal. This assembly, which allows optical access to the substrate laying on the lower electrode, differs from the original GEC cell.

The electrodes are isolated electrically from the chamber via Teflon and can selectively be grounded or set on high-frequency potential. In this work the upper electrode
was grounded and the lower electrode, with the substrate laying on it, was powered with rf voltage. To maintain a homogeneous plasma between the electrodes and to prevent the isolator material from being sputtered, it is protected with a grounded shielding made of stainless steel.

Silane (SiH₄, ultra high purity, diluted to 10 % in argon 5.0) and acetylene (C₂H₂, solubilized in acetone, CH₃-CO-CH₃) have been used for the deposition of a-Si:H and DLC films, respectively. The gases were introduced through a ring with a diameter of 23.2 cm (diameter of pipe: 6.35 mm) situated as high as the upper electrode. In this ring 36 holes are drilled which point to the middle of the lower electrode. This is another deviation from the original GEC cell.

The gas flows are controlled via mass flow controllers; subsequently the gases are mixed in one pipeline to achieve a homogeneous mixture already before the discharge chamber. Each gas flowing through the mass flow controller requires its own gas correction factor (GCF). The gas correction factor for argon is 1.39, for silane it is 0.6, for example. For gas mixtures, like the used mixture of silane and argon, which are already mixed in the gas bottle, the gas correction factor is not simply the weighted average of each component’s GCF. Instead, the GCF (relative to nitrogen) is calculated by the following equation (for n gases) [71]:

\[
GCF = \frac{0.3106(a_1s_1 + a_2s_2 + \ldots + a_ns_n)}{a_1d_1c_{p1} + a_2d_2c_{p2} + \ldots + a_nd_nc_{pn}}. \tag{4.1}
\]

Here, \(a_1\) through \(a_n\) are the fractional flows of gas 1 through n, \(s_1\) through \(s_n\) are the molecular structure factors, \(d_1\) through \(d_n\) are the standard densities, and \(c_{p1}\) through \(c_{pn}\) are the specific temperatures. The values for \(a_1\) through \(a_n\) depend upon the application and must add up to 1. The molecular structure factors are:

- 1.030 for monoatomic gases
- 1.000 for diatomic gases
- 0.941 for triatomic gases
- 0.880 for polyatomic gases (four or more atoms).

The standard densities are \(d_1=1.782\) g/l and \(d_2=1.433\) g/l and the specific temperatures are \(c_{p1}=0.1244\) cal/(g °C) and \(c_{p2}=0.3189\) cal/(g °C) for silane and argon, respectively. With \(a_1=0.9\) and \(a_2=0.1\) the gas correction factor for the used gas mixture results in 1.29.
The gases are pumped with a forepump and a turbo molecular pump. Without gas flow pressures clearly below \(1 \times 10^{-6}\) mbar are obtained. With the help of a butterfly valve the pumping speed and therefore the pressure inside the chamber at a certain gas flow can be varied.

Since the used silane gas is flammable, pyrophoric and toxic, it is kept in a special locker under low pressure. Additionally, the laboratory is equipped with several gas sniffers sensitive especially to silane. When they detect silane in even very small concentrations, the whole gas supply is shut down and an alarm is given.

The plasma is operated at a frequency of 13.56 MHz. The power is coupled into the plasma via a matching box, consisting of two variable capacitors and a coil with centre tap. The matching box adjusts the impedance of the whole system, consisting of plasma, discharge chamber, power supply and matching box, to 50 \(\Omega\), in order to avoid power reflection back to the generator and to ensure maximal power coupling into the plasma. The capacitance and inductance are adjusted until the reflected power is zero.

The lower electrode can be heated with the help of an integrated heating wire made of nickel-chrome (80/20). Hereby the substrates can reach temperatures up to 320 °C. The temperature of the substrate has been measured with a fluoroptic thermometer under vacuum. This thermometer consists of a fibre optic made of glass. At the sensing end of the fibre optic a phosphor compound is encapsulated. This probe is immune to EMI and radio-frequency noise. The phosphor is excited with a burst of light sent through the fibre optic cable. The instrument determines the temperature of the sensor by measuring the decay time of the emitted light. It is a persistent property of the sensor that its decay time varies precisely with temperature. The decaying light signal returns through the fibre to the instrument where it is processed by converting the analogue signal into a digital value which is then converted into a calibrated and corrected temperature. Unfortunately, this thermometer only works up to 295 °C. For higher temperatures, a K-type thermocouple has been used to measure the temperature.

The samples are inserted into the discharge chamber via a load lock chamber to avoid impurities in the plasma and therefore in the deposited films. Between load lock
Chapter 4 Experimental set-up and plasma properties

Figure 4.2: Set-up of the lower electrode with three different removable sample holders, see text for description.

chamber and deposition chamber a vacuum shutter is placed. To insert the sample, the shutter is opened. The top part of the lower electrode can be removed and serves as sample holder (see figure 4.2).

Depending on the task three different sample holders have been used. The first one is a simple rectangle with planar surface made of stainless steel on which the sample is placed. The second one offers a quadratic hole, were the sample is mounted from behind with the help of a thick block of copper, which is screwed on the sample holder from behind. This block of copper assures good heat transport from the heated electrode to the sample. The third sample holder shows three even round cavities in which the circular metal substrates can be placed. They are covered with a flat sloping, sharp edge made of metal, so that only part of them can be coated. The resulting sharp edge of the film can be used to measure the film thickness with the help of a profilometer.

The sample holders are screwed on a magnetically-coupled transporter which can be moved from the load lock chamber to the deposition chamber and back. The transporter is in vacuum and runs on ball-bearing. To move and turn it from outside a magnetic holder is placed round the metal cover which can move the transporter inside. When the sample holder is placed into the electrode, the transporter can be released and removed from the deposition chamber. To remove the sample after the deposition, the vacuum shutter is closed, as soon as the sample holder is back in the load lock chamber. The load lock is then vented with nitrogen and can be opened to
extract the sample holder.

4.2 Self-bias in an asymmetric capacitively coupled discharge

The higher mobility of the electrons in the plasma, due to their small mass compared to the ions, leads to a characteristic potential distribution in the discharge chamber. If the rf frequency is higher than the ion plasma frequency (2-5 MHz) the electrons can follow the rf voltage, but the ions cannot. During each half cycle the electrons touch one of the electrodes leading to negatively charged electrodes in average. The potential of the plasma, $V_p$, is always positively related to the ground and is typically several Volts. The jump in potential in the space charge sheath in front of the powered electrode is called sheath potential $V_s$.

Most capacitive discharges are driven asymmetrically, because more electrode surfaces are grounded (electrode and walls) than driven. Due to the capacitor in the matching network the powered electrode cannot unload in contrast to the grounded electrode. The DC voltage between the plasma and the driven electrode is larger than the DC voltage between the plasma and the grounded electrode [72]. An easily measurable DC bias voltage, the so called self-bias is set up at the driven electrode with respect to ground which is negative when the powered electrode is smaller than the grounded one. The ratio of the sheath potentials of the two electrodes $V_{s,a}$ and $V_{s,b}$ varies with the ratio of the electrodes areas $A_a$ and $A_b$ [73]:

$$\frac{V_{s,a}}{V_{s,b}} = \left(\frac{A_b}{A_a}\right)^q.$$

Depending on experimental conditions, different values for $q$ can be found in literature. In [73] $q \approx 1 - 1.4$, in [72] $q \leq 2.5$. However, if the smaller electrode is powered, the sheath potential of the driven electrode is much higher than the sheath potential of the grounded electrode. That means that ions hit the powered electrode with a much higher energy than the grounded electrode. This is the reason why the substrates in this work are placed onto the powered electrode. Due to the high ion energy the films are packed more dense and are therefore harder. When the substrates are placed on the grounded electrode, the films become softer and less dense packed. In the case of
acetylene, placing the substrate on the powered electrodes leads to hard, diamond like a-C:H films (DLC, see chapter 6), placing it on the grounded electrode gives much softer, polymer like a-S:H films (PLC). But also for a-Si:H films it makes a difference on which electrode the substrate is placed.

The surface area ratio between grounded electrode (electrode plus wall) and driven electrode is about 16 in the used set-up. Thus almost the whole voltage supplied by the power generator drops in the sheath of the driven electrode.

Figure 4.3 shows the self-bias voltage (black squares) of the powered electrode for different powers provided by the rf generator at a pressure of 3 Pa in silane. The self-bias voltage $V_b$ varies with rf power $W$ and operating pressure $p$ as follows [14]

$$V_b = k \left( \frac{W}{p} \right)^{1/2}$$ (4.3)

where $k$ depends on different factors such as the electrode areas. In figure 4.3 the self-bias voltage has been calculated using equation 4.3 with a pressure of 3 Pa and a $k$ of 67. It is obvious that the measured values are in good agreement with the
calculated ones.

The energy $E_i$ of the ions depends on the self-bias voltage and can be assumed as $E_i = 0.6V_b$ for a pressure of 3 Pa [14]. This leads to an ion energy of about 111 eV for a 20 W silane plasma at 3 Pa.

4.3 Plasma density

Beside the self-bias the plasma density is a critical parameter in the PECVD process. Density and kinetic energy of the electrons have strong influence on chemical processes and composition of the plasma and on growth rate during film deposition.

In this work the plasma density is measured by C. Scharwitz, using a plasma absorption probe (PAP). It has the advantage that it can be used even in reactive plasmas without damaging the probe. A coating on the surface of the probe has no influence on the measurement signal. The plasma absorption probe was contrived by Sugai [74],[75] and enhanced by Scharwitz [76]. It consists of a dielectric tube made of quartz in our case, a coaxial cable inside the tube and a network analyser. The naked centre conductor of the coaxial cable serves as an antenna for radiating electromagnetic waves where a frequency-swept signal of about 1 mW is fed in a frequency range of 5 MHz to about 1.5 GHz from the network analyser (Rohde & Schwarz, vector network analyser ZVC, 20 kHz to 8 GHz). The inner of the tube is at atmospheric pressure whereas the whole probe is inserted into the plasma and connected via vacuum feedthrough with the network analyser. The network analyser measures the power reflection coefficient defined as the ratio of the reflected power to the incident power. At a certain frequency the power reflection spectrum shows a dip indicating that at this frequency the applied power is absorbed by the plasma. The plasma density (in m$^{-3}$) is connected with the absorption frequency $f_{abs}$ (in GHz) via:

$$n_e = 2.94 \times 10^{16} f_{abs}^2.$$  (4.4)

The pre factor depends on the dielectric constant $\varepsilon_d$ of the dielectric and on the geometrical conditions of the probe. A derivation of this equation can be found in [74].

Figure 4.4 presents the measured plasma density versus applied power for different
probe positions in the discharge chamber for a silane plasma at 3 Pa. The plasma density has been measured in steps of 1 cm, starting in the centre of the electrode ($r=0$ cm) and going outwards. In the middle, the electron density is highest, far outside the electrodes it is almost zero. The plasma density increases with increasing power. At about 50 W an abrupt rise towards higher densities can be observed, showing a transition into a new mode. Radio frequency capacitive discharges usually operate in one of two totally different modes, the so called $\alpha$ and $\gamma$ modes. These modes differ in the intensity and luminosity distribution along the discharge length and especially in the ionisation processes in the electrode sheaths. In the $\alpha$ mode the discharge shows a relatively low intensity with two weak maxima near the electrodes. Between plasma and electrodes two distinct dark space charge sheaths can be observed. In the middle between the electrodes a relatively homogeneous plasma forms which is maintained by a more or less uniform rf field. In this mode only displacement current flows through the capacitor formed by the two electrodes. In the $\alpha$ mode the electrons acquire energy for ionising gas atoms in the rf field in a quasi neutral plasma and the emission of electrons from the electrode surfaces does not play a major role.

**Figure 4.4:** Electron density versus discharge power for different probe positions in a 3 Pa argon-silane plasma.
in sustaining the plasma. The conductivity of the electrode sheaths is small, and the circuit between the plasma and the electrodes is closed mainly by the bias current [77]. With larger voltage, the current rises and the voltage drops and an abrupt restructuring of the discharge occurs. In the $\gamma$ mode electron avalanches develop in the electrode sheaths, ionisation of the gas atoms by electron impact takes place mainly near the boundaries between the electrode sheaths and the quasi neutral plasma. In this mode one can see well defined bright regions of ”negative glow” and the ”Faraday dark space”. The positive column at the gap centre is much brighter than the $\alpha$ discharge. In this form of rf discharge the ions produce secondary electrons when they reach the electrode. These electrons mainly sustain the discharge. Because of this effect this form of discharge is called $\gamma$ discharge, because the letter $\gamma$ symbolises the contribution of secondary emission ($\gamma$-process). The voltage at which the transition from $\alpha$ to $\gamma$ mode occurs is dependent on gas, pressure and electrode spacing. More about the $\alpha$-$\gamma$ transition can be found in [73].

In figure 4.5 the plasma density is plotted versus the radial probe position, starting in the centre of the electrode. The plasma density for low powers is quite low (about

![Figure 4.5: Electron density in dependence of the radial probe positions for different discharge powers in a 3 Pa argon-silane plasma.](image-url)
2 \times 10^{15} \text{ m}^{-3}), but it is, in contrast to higher powers, quite homogeneous in the middle of the electrode \((r=0-4 \text{ cm})\). Therefore most thin films have been deposited with a power of 20 W, ensuring that the plasma conditions are equal for inner and outer samples when more than one sample is placed on the electrode.

### 4.4 Sample pretreatment

The films have been deposited on pieces of polished silicon wafers \((1 0 0)\) and on different metal substrates made of stainless steel, copper, nickel and an alloy of nickel and titanium. The nickel sheets are 0.4 mm thick, all other sheets have a thickness of 0.5 mm. The austenitic stainless steel \((1.4541)\) is characterised by high corrosion resistance and consists of \(\leq 0.08\% \text{ C, 17-19 \% Cr, 9-12 \% Ni and up to 0.7 \% Ti.}\) Nickel with the pureness \text{BR-NI 99.6} and the identification 2.4060 has been used. NiTi has been used in two different configurations. One type of used NiTi is a standard alloy for higher temperature actuation with an austenit finish temperature of about 98 °C and an Ni content of 49.4 to 49.6 at.%. The other used NiTi type is a superelastic standard alloy with an austenit finish temperature of around 0 °C consisting of about 51 at.% Ni.

The pretreatment of the samples is one critical point in the deposition of thin films. The roughness of the surface for instance has a strong influence on quality and adhesion of the films as well as have impurities on the surface. Also the native oxide layer on metals can have influence on the adhesion of the films. Different sample pretreatments before the thin film deposition can therefore lead to total different results and characteristics of the films.

To attain comparable and good quality results all substrates in this work have been treated the same way before they were deposited with thin films. The metal substrates have first been ground and polished before they have carefully been cleaned in an ultrasonic bath in pure ethanol. To remove remaining impurities and the native oxide layer the metals have been sputtered in an argon plasma directly before the deposition of the thin films.

The used silicon wafers were carefully cut into pieces of \(2 \text{ cm} \times 2 \text{ cm}\) and then blown with pure nitrogen to remove small silicon particles resulting from the cutting. Since they were already polished and thoroughly cleaned by the manufacturer, no further treatment of the silicon wafers was performed.
In the following the pretreatment of the metal substrates will be explained in more detail. In section 4.4.3 the special properties of shape memory alloys and especially NiTi are treated.

### 4.4.1 Grinding and polishing

The metal substrates were blanked from sheet metal. After the blanking they show a very rough, irregular surface. To achieve good adhesion of the films and to have reproducible results the substrates have been ground and polished before they were plasma treated. For this purpose a standard procedure has been used which will be described in more detail below.

The metal plates were initially face-ground and fine-ground with wet emery paper with graining of 320, 500 and 1000, each for about three minutes. The emery paper was fixed on a rotating disc with 250 rotations per minute. After each grinding process the metal substrates were cleaned in an ultrasonic bath with ethanol for ten minutes to remove residues from the emery paper.

After the grinding the metal plates were polished. For this purpose a special rag (MD Mol) and a suspension with diamond-grains of 3 µm size (DiaPro Mol) have been used for three minutes of polishing. The final polishing was accomplished with another special rag (MD Nap) and a suspension with diamond-grains of 1 µm size (DiaPro Nap B), for two minutes. Both rags were also fixed on a rotating disc. Polishing (LaboPol 5) and grinding (LaboPol 21) machines as well as rags and suspensions are from Struers company.

After each polishing step the metal plates were also cleaned in the ultrasonic bath to

![Figure 4.6: Definition of roughness $R_a$.](image-url)
Table 4.1: Roughness of the metal substrates after polishing.

<table>
<thead>
<tr>
<th>Sample</th>
<th>stainless steel $R_a$ in nm</th>
<th>copper $R_a$ in nm</th>
<th>nickel $R_a$ in nm</th>
<th>NiTi $R_a$ in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>1.5</td>
<td>3.1</td>
<td>3.4</td>
<td>6.7</td>
</tr>
<tr>
<td>#2</td>
<td>4.3</td>
<td>4.8</td>
<td>3.1</td>
<td>9.7</td>
</tr>
<tr>
<td>#3</td>
<td>2.4</td>
<td>3.9</td>
<td>2.1</td>
<td>4.5</td>
</tr>
<tr>
<td>#4</td>
<td>3.5</td>
<td>3.0</td>
<td>4.9</td>
<td>7.7</td>
</tr>
<tr>
<td>#5</td>
<td>2.7</td>
<td>4.2</td>
<td>4.9</td>
<td>5.6</td>
</tr>
<tr>
<td>#6</td>
<td>4.3</td>
<td>2.4</td>
<td>5.4</td>
<td>5.3</td>
</tr>
</tbody>
</table>

avoid transfer of bigger grains onto the next rag. The roughness of the metal substrates after polishing was measured with an AFM (Atomic Force Microscope, see chapter 3.6). The measurements were operated in contact-mode, meaning that the surface is scanned by the tip in close contact with the surface. For the determination of the roughness of the metal substrates a square of $20 \mu m \times 20 \mu m$ has been scanned. The arithmetic mean of the profile-ordinate $Z(x)$ (height of the measured profile at any position $x$) was used for the degree of roughness $R_a$. It is given in one dimension after [78] as follows:

$$R_a = \frac{1}{L} \int_{x=0}^{x=L} |Z(x)| \, dx.$$  \hspace{1cm} (4.5)

The definition of $R_a$ is shown in figure 4.6. Here $L$ denotes the scan length.

The measured roughness of six randomly chosen substrates for each different type of metal are summarised in table 4.1. It is obvious that the roughness of the substrates is clearly below 10 nm thus the coating with very thin films even in the range of several 10 nm is possible.

### 4.4.2 Argon sputtering

Before depositing the a-Si:H films on the metal substrates the substrates have been cleaned with an argon plasma to remove impurities on their surfaces and to sputter
Chapter 4 Experimental set-up and plasma properties

Figure 4.7: AFM images of stainless steel, before and after Ar-sputtering.

the native oxide film which usually grows on metal surfaces.

It was observed before that there was almost no adhesion of the film system without this argon pretreatment. This can be explained with the removal of the oxide layer which prevents the a-Si:H films from sticking on the surface [53], [52]. Peng and Clyne report that the adhesion of DLC films on metals, especially on steel substrates, increases strongly when an argon pre-cleaned substrate is used for deposition. They presume that the argon bombardment of the substrate for in their case 10 minutes is associated with the effective removal of the oxide layer [53]. Morshed et al. also found that argon pre-treatment of stainless steel increases the adhesion of DLC films on the substrate and that the adhesion depends on plasma etching time. By FTIR studies they showed that the composition of the surface oxide is altered during argon sputtering [52]. A second explanation is the change in topography of the surface. Figure 4.7 demonstrates that the micro-roughness of the surface increases after the argon sputter process. That means that the growing a-Si:H film has more surface to grow on and is coupled to the surface more strongly. More about the effect of argon sputtering of metal substrates can be found in [79]. TOF-SIMS measurements revealed that a lot of contaminations, for example Na or K, are present on non-sputtered samples. These contaminations are reduced after the argon sputtering.

The parameters for the argon sputter process in this work were a 30 sccm argon flux at a pressure of 2 Pa with a power of 50 W and 10 minutes discharge time.

To show the influence of the Ar-sputter process metal substrates have been treated for one hour in an Argon plasma with a power of 50 W. During the plasma process the samples were placed in the third sample holder described in chapter 4.1, meaning that one part of the sample was covered by the sharp edge. After the plasma treatment the developed step was measured with the AFM. Figure 4.8 shows the step on
Figure 4.8: Copper sample treated with argon plasma for one hour, one part has been covered. Left hand side: 3d representation, right hand side: height profile.

A copper substrate. The step height is about 100 nm. That means that the substrate is sputtered with a sputter rate of about 1.7 nm per minute. The standard sputter process of 10 minutes leads therefore to a removal of about 17 nm or several 10 atomic layers during the process.

The change in the topography of the surface of the sputtered samples can be seen in figure 4.9. It shows the histograms of the surface height of different metal substrates before and after the sputter process. Although the roughness almost stays constant, the height distribution gets more narrow after the sputtering. Thus the surface is more homogeneous leading to a better adhesion of the film.
Chapter 4 Experimental set-up and plasma properties

Figure 4.9: Histograms for different metal substrates before and after cleaning in an argon plasma. The height distribution after the argon cleaning process is more narrow than before the argon cleaning although the roughness keeps almost constant.
4.4.3 Shape memory alloys

There exists a variety of metallic alloys which demonstrate shape memory and/or pseudoelastic effects such as FePt, FeNiC, NiFeAlB, AuCd, NiAl, NiTi, and CuZnAl. The ability to revert to the original shape after reheating of a metallic object which has been given a particular shape at higher temperature before provides the name for this class of metals – shape memory alloys (SMA). SMA are ordered and exist in two crystalline phases. The low-temperature phase is called martensite (M) and the high-temperature phase is called austenite (A) [80]. Phase A has a higher degree of symmetry than phase M. There is a phase transition governing the $A \leftrightarrow M$ transformation (from A to M, and vice versa), illustrated in figure 4.10. The hysteresis is characterised by four temperatures ($A_s$, $A_f$, $M_s$, and $M_f$) which indicate the initial and final transformation temperatures. Two stable transformation phases are present at different temperatures: the martensite phase is stable at low temperatures in contrast to the austenite one which is stable at high temperatures. These two transformations are reversible without inducing any diffusion between the existing phases.

Three different effects of SMA can be observed:

- The one-way shape memory effect, where the change in shape is regulated by the transition from martensite to austenite. The material is deformed in the martensitic state due to an external stress field and takes its original shape after

![Figure 4.10: Austenite transformation and hysteresis following a temperature change. $A_s$=Austenite start, $A_f$=Austenite finish, $M_s$=Martensite start, and $M_f$=Martensite finish.](image-url)
annealing. This original shape has been applied permanently in the austenitic state.

- The two-way shape memory effect, with the learning process by mechanical cycles and the one-way shape memory effect, where the changes in shape are regulated by the phase transition (martensite-austenite followed by austenite-martensite). This effect works without external stress fields. The material takes one shape at low temperature and another shape at high temperature.

- The superelastic effect, where the deformations are regulated by the phase transitions (austenite-martensite, then martensite-austenite) due to external stress fields.

NiTi is a nickel-titanium alloy of near-equal-atomic composition, meaning that nickel represents approximately 50% of its chemical composition. Variations of the ratio nickel-titanium can vary the transformation temperatures in a wide range. The NiTi alloy cover as much as $-100 \pm C$ up to $+100 \pm C$ for the $A_s$ temperature [6]. In particular blood temperature ($37 \pm C$) as transformation temperature can be adjusted by the chemical composition.
Chapter 5

Deposition and characterisation of amorphous hydrogenated silicon (a-Si:H) films

The amorphous hydrogenated silicon films are designated to act as intermediate layers between metal and DLC film to significantly improve the adhesion between metal and DLC. Therefore, the growth conditions and properties of these films are discussed in more detail in this chapter since they may have strong influence on the adhesion. For the ease of investigations and to perform the ellipsometric measurements more precisely, the a-Si:H films have been deposited on pieces of silicon wafers in a first step. A Tauc-Lorentz oscillator has been used to model the a-Si:H films.

In the first section (5.1) of this chapter the growth of a-Si:H films is investigated and the chemical conditions of the employed plasma are characterised. Since the presence of dust particles in the plasma volume is critical for good quality films, the conditions under which the formation of dust particles is suppressed, are defined.

The hydrogen content of a-Si:H is a critical parameter for the structural and mechanical properties of the material. Therefore special attention is laid on the investigation of the hydrogen content of the films. The hydrogen content is estimated via FTIR measurements. In section 5.2 the absorption modes occurring in a-Si:H are presented. In the following section (5.3) the absorption strength is correlated to the hydrogen content and results of the hydrogen content of a-Si:H obtained from FTIR measurements for different deposition conditions are shown.

The substrate temperature has strong influence on the hydrogen content and also on
optical properties of amorphous silicon films. This item is dealt with in section 5.4. The optical properties of a-Si:H are discussed in more detail in the last section (5.5).

5.1 Growth of a-Si:H films

One common method of depositing hydrogenated silicon is by plasma decomposition of silane (SiH₄). Most properties of the a-Si:H network, e.g. the hydrogen content, are defined at the time of growth and therefore depend on the details of the deposition process. Amorphous hydrogenated silicon can contain up to 50 at. % hydrogen [38]. To obtain the desired material characteristics many variables in the deposition process have to be controlled. These variables are named and discussed in the following.

The gas pressure determines the mean free path for collisions of the gas molecules and influences whether the reactions are at the growing surface or in the gas, leading to the formation of nanoparticles in the used set-up. Figure 5.2 shows the pressure range in which no dust particles are formed.

The gas flow rate determines the residence time of the gas species in the reactor. With a volume of the reactor of 13 l, a pressure of 3 Pa and a flow of 50 sccm the residence time in the used set-up is calculated to be 0.5 s at room temperature.

The rf power controls the rate of dissociation of the gas and therefore also the film growth rate. The dependence of the growth rate on power will be shown in figure 5.3. The growth rate \( v \) for a given gas varies with self-bias voltage \( V_b \) and gas pressure \( p \) as [14]

\[
v = k \ V_b \ p.
\]  

(5.1)

The temperature of the substrate controls the chemical reactions on the growing surface. The influence of the substrate temperature on the material will be discussed in chapter 5.4.

The silane gas is dissociated in the plasma chamber through electron collisions. To get more insight into the plasma chemistry, the gas composition in the vacuum chamber has been monitored and analysed by a residual gas analyser. Figure 5.1 shows the mass spectrum of the argon/silane gas mixture with a flow of 50 sccm at 3 Pa compared with a plasma at 20 W at the same conditions. Without plasma, argon
Figure 5.1: Mass spectrum of silane/argon mixture at 50 sccm, 3 Pa, with and without plasma at 20 W.

(m/q=20, 36, 38, and 40), nitrogen (m/q=14, 28), and water vapour (m/q=18) can be observed. Silane (m=32) is dissociated in the mass spectrometer into several decay products (m/q= 1, 2, 28, 29, 30, and 31). When the plasma is ignited, several changes in the mass spectrum can be observed. The value of m/q=2 increases by one order of magnitude due to the dissociation of SiH$_4$ in the plasma. The intensities of the silanes (m/q=28-32) decrease because the dissociated molecules of silane are deposited on the walls and therefore less of them can be found in the plasma volume. The values for argon (m/q=20, 36, 38, and 40) nearly stay constant, only the intensity for m/q=41 increases by one order of magnitude due to the formation of ArH$^+$ ions inside the mass spectrometer.

The most obvious change is the formation of higher silanes when the plasma is ignited (m/q=57-62). In the plasma volume Si$_2$H$_n$ molecules with n=1-6 are formed. These molecules are not present in the pure gas but occur in the plasma because the dissociation of SiH$_4$ only takes place when electrons are present. Si$_2$H$_2$ (m=58) and Si$_2$H$_4$ (m=60) are the most prevalent higher silane molecules inside the plasma. These molecules are the precursors for the formation of macroscopic dust particles.
Figure 5.2: Parameter range of dust particle production in a silane plasma depending on pressure and applied power. The conditions on the right hand side of the red line lead to particle formation, the conditions on the left hand side show no particle formation.

[81]. Their formation should therefore be suppressed. But no molecules with higher masses and no dust particles at all could be observed under these conditions.

To find conditions were a-Si:H films can be deposited without the formation of dust particles, power and pressure have been varied. Figure 5.2 shows the parameter range in which dust particles could be observed in the used experimental set-up. Each symbol denotes that under these parameters dust particles inside the plasma have been observed. The dust particles were made visible with the help of a He-Ne laser whose light was scattered by forming dust particles. Additionally, the self bias has been monitored which starts to oscillate when dust particles are created [82].

The region left hand side of the red line shows the parameters under which no dust formation has been observed. Going to higher pressure and/or higher power (right hand side of the red line) the formation of dust particles could be noticed. To avoid the formation of dust particles during film deposition, the pressure of 3 Pa has been
chosen throughout all experiments. For lower pressures it was not possible to ignite the plasma at low powers.

During deposition the film of course does not only grow on the substrate, but on all surfaces present in the chamber. Since the growth-process is not ion-driven, but dominated by radicals, even surfaces far away from the powered electrode are coated. In ion-dominated growth processes like those of DLC films, a more directed growth towards the powered electrode is achieved. The resulting film on the chamber walls could not easily be sputtered or etched like a-C:H films. To remove a-Si:H films, fluororic gases can be used. But the problem then is to remove the fluorine afterwards out of the chamber. In this work, the a-Si:H film on the walls has not been removed and after a while a thin film on the walls became visible through interference colours. One can assume that after several deposition processes stable conditions have developed without differences for the following films. Equal film results and plasma parameters are evidence for this assumption.

The deposition rate of a-Si:H films is dependent of the particle flow impinging on

\[ \text{Figure 5.3: Growth rate of a-Si:H films for different substrate temperatures versus applied power at 3 Pa.} \]
the substrate, the surface reaction and incorporation probability and of sputter processes of the growing film due to ion bombardment. It is the net effect of film growth through incorporation of silicon and hydrogen atoms and of sputtering and etching of the film due to argon ions and radicals, respectively. Figure 5.3 shows the growth rate versus applied power for different substrate temperatures. With increasing power the electron density increases, leading to a higher dissociation of the precursor gas. Thus, the concentration of ions and radicals responsible for the film growth increases and the film grows faster. 

The growth rate for unheated substrates lies in the range from about 6 nm/min for 20 W to \( \sim 14 \) nm/min for 120 W. It increases for lower power and then tends to saturate for higher power. With higher power more silane molecules can be dissociated leading to a higher amount of SiH\(_3\) radicals in the gas phase and thus to faster film growth. At a certain power the point of maximal dissociation is reached (in our case at \( \sim 100 \) W) because of total consumption of the precursor gas and the growth rate can only be increased further by increasing the gas flow. But since a high growth rate is not of interest here, because we need only very thin films (several 10 nm), the gas flow was held constant at 50 sccm.

The growth rate for heated substrates is much lower than for unheated ones. At 320 °C a maximum growth rate of about 7 nm/min can be achieved. Also here a saturation effect can be observed. The growth rate at a substrate temperature of 100 °C is first even higher than of unheated samples but at powers higher than 60 W the growth rate decreases sharply going to similar values like the samples at higher substrate temperature. A more detailed explanation of the influence of the substrate temperature is given in section 5.4.

5.2 IR absorption spectroscopy on a-Si:H

The concentration and bonding state of hydrogen in a-Si:H have a major influence on the structural and electronic properties of this material, for example on the optical bandgap or the density of dangling bonds [83]. Infrared absorption is the predominant method to characterise the amount and the bonding configurations of hydrogen incorporated into a-Si:H thin films. In the following the method to derive the hydrogen concentration of a-Si:H films from IR spectroscopy measurements will be explained. The underlying principle is that hydrogen which bonds to the a-Si network produces a
local vibrating dipole because of the electronegativity difference between the hydrogen atom (slightly negatively charged) and the neighbouring silicon atom (slightly positively charged). In the harmonic oscillator picture, this Si-H dynamic dipole moment is changed when a resonant infrared photon is absorbed by the oscillator, exciting it to the next higher vibrational state with a larger dynamic dipole moment due to the increased vibrational amplitude. This change of the dynamic dipole moment between the initial and the final state and the number of bonded hydrogen atoms contributing to a specific spectral line determine the intensity of the corresponding infrared absorption.

Infrared spectra of a-Si:H show three main absorption regions: one bending mode at
640 cm\(^{-1}\), a doublet at 840-890 cm\(^{-1}\) due to dihydride bending or scissoring modes and two stretching modes at about 2000 and 2100 cm\(^{-1}\) \cite{83}, \cite{85}, \cite{86}, \cite{87}. Figure 5.4 shows the different modes in a-Si:H. The lower stretching mode (LSM) at 2000 cm\(^{-1}\) is usually attributed to isolated monohydrides (SiH) and the higher stretching mode (HSM) at 2100 cm\(^{-1}\) to clustered monohydrides as well as to dihydrides (SiH\(_2\)) and trihydrides (SiH\(_3\)) \cite{85}. In \cite{87} the HSM is also attributed to hydrogen on the surface of voids.

The mode at 850 cm\(^{-1}\), attributed to the bending mode of SiH\(_3\) groups could not be observed in the measurements. Thus, no trihydrides are present in the a-Si:H films under investigation.

The amount of IR absorption of these modes is related to the hydrogen content in the film through the oscillator strengths. The hydrogen concentration \(N_x\) is related to the integrated absorption coefficient via \cite{84}:

\[
N_x = A_x \int \omega^{-1} \alpha(\omega) d\omega. \tag{5.2}
\]

The proportionality constant \(A\) is inverse proportional to the oscillator strength, \(\omega\) denotes the wave number in cm\(^{-1}\), \(\alpha\) the absorption coefficient and the integral is over the absorption band of interest \(x\). The absorption coefficient \(\alpha\) is connected to the transmission \(T\) via:

\[
T = e^{-\alpha d}, \tag{5.3}
\]

where \(d\) denotes the film thickness. With known film thickness and transmission measured via ellipsometry and FTIR, respectively, the absorption coefficient can be calculated:

\[
\alpha = -\frac{1}{d} \ln(T). \tag{5.4}
\]

The proportionality constant \(A_x\) depends on the effective dynamical charge \(e^*\) of the Si-H dipoles and is given by \cite{83}:

\[
A_x = c \, n \, \mu \, \omega_0/(2 \, \pi^2 \, e^*). \tag{5.5}
\]
Here $c$ is the velocity of light, $n$ the refractive index, $\mu$ the reduced mass of the vibrating atom, $\omega_0$ the centre frequency of the mode, and $A_x$ is obtained in units of $\text{cm}^{-2}$ if atomic units are used for $c$, $n$ and $\mu$. The proportionality constants $A_x$ are determined empirically by different methods like nuclear-reaction analysis, hydrogen evolution, $\alpha$ particle scattering, secondary ion mass spectrometry, and nuclear elastic scattering. To determine $A_x$ the IR stretching or wagging mode absorbance are correlated with the measured hydrogen content. Due to the different methods the values for $A_x$ differ in literature. Due to the fact that every bonded hydrogen atom in a-Si:H contributes to the 640 cm$^{-1}$ wagging mode this peak can be used to determine the total hydrogen density of the a-Si:H film. The value for the $A_{640}$ constant has been calibrated by various of the above mentioned techniques. Values reported in literature vary between $1.6 \times 10^{19} \text{ cm}^{-2}$ and $2.1 \times 10^{19} \text{ cm}^{-2}$ [83], [85], [86], [88]. Regarding the complex dependence of $A_x$ on refractive index, the effective dynamical charge, and the eigen frequency, the range of $A_{640}$ values are surprisingly consistent. The $A_x$ values for the proportionally constant of the stretching modes have also been determined, showing, in contrast to the wagging mode, more inconsistency. Some authors found that $A_{LSM} = A_{HSM}$ whereas others report that $A_{LSM} < A_{HSM}$. Reported values for $A_{LSM}$ vary from $2.2 \times 10^{19} \text{ cm}^{-2}$ to $14 \times 10^{19} \text{ cm}^{-2}$ and the reported $A_{HSM}$ values vary from $9.1 \times 10^{19} \text{ cm}^{-2}$ up to $22 \times 10^{19} \text{ cm}^{-2}$ [83], [85], [86].

5.3 Fourier Transform Infrared (FTIR) absorption spectroscopy on a-Si:H

The hydrogen content of the a-Si:H films is obtained from FTIR measurements in transmission using a Bruker Equinox 55 Fourier Transform Infrared spectroscope. The IR spectra are measured in the range from $\omega=400 \text{ cm}^{-1}$ up to $3000 \text{ cm}^{-1}$ on samples deposited on crystalline silicon substrates. Crystalline silicon is almost transparent in the near and mid IR range down to about 500 cm$^{-1}$ and can therefore be used as substrate for IR spectrometric measurements of amorphous silicon. Below 500 cm$^{-1}$ the range of silicon one-phonon lattice oscillations begins. Before deposition of the a-Si:H films no extra treatment has been performed to remove
the native oxide layer on the surface of the silicon wafers. From the IR transmission spectra referenced to a plain silicon wafer the absorption coefficient has been calculated according to equation 5.4 using the film thicknesses determined from optical ellipsometry measurements. Special care was taken to ensure that the substrate and the reference wafer were from the same charge to match them perfectly and to avoid a contribution from the substrate c-Si phonon mode at 615 cm$^{-1}$ [89].

The hydrogen content is determined using both the wagging and the stretching mode described in chapter 5.2. The hydrogen content is defined as $C_H = N_H/(N_{Si} + N_H)$ where $N_{Si} + N_H \approx 5 \times 10^{22}$ cm$^{-3}$, $N_{Si}$ denotes the number of silicon atoms and $N_H$ the number of hydrogen atoms [85], [88], [89].

It must be mentioned that IR spectroscopy only detects the bonded hydrogen, whereas other methods like ERDA (elastic recoil detection analysis) is sensitive to all the hydrogen. Measurements with ERDA determine a higher hydrogen content than the IR measurements because ERDA additionally detects the molecular hydrogen trapped in internal micro voids or micro cavities present in the material. It has been shown that the molecular hydrogen in a-Si:H films can attain substantial amounts [89]. It is estimated that there are about ten hydrogen molecules in each void [38]. Annealing to high temperature which tends to remove bonded hydrogen from the a-Si:H network even increases the amount of molecular hydrogen in the voids.

**Figure 5.5:** Absorption coefficient obtained from FTIR measurements for three different substrate temperatures, left hand side: wagging mode, right hand side: stretching mode. Deposition at 3 Pa, 50 sccm, 20 W.
For the determination of the hydrogen content the constants of proportionality $A_{640}=1.6 \times 10^{19} \text{ cm}^{-2}$ and $A_{LSM}=A_{HSM}=9.1 \times 10^{19} \text{ cm}^{-2}$ are used in this work. The fact that $A_{LSM}=A_{HSM}$ is based on the fact that $e_{LSM}^*=e_{HSM}^*$ shown in [90]. It appears that the results obtained with this assumption fit well (figure 5.6). This leads to the relation between the constant of proportionality of the wagging and the stretching mode:

\[ N_H = A_{640}I_{640} = A_{LSM}I_{LSM} + A_{HSM}I_{HSM} \] (5.6)

where $I_x = \int \omega^{-1} \alpha(\omega) d\omega$ is the integrated absorption at peak $x$. This means that every bonded hydrogen atom contributes to the wagging mode and every bonded hydrogen atom contributes to either the LSM or the HSM.

Since the value of the constant of proportionality $A_{640}$ for the wagging mode at 640 cm$^{-1}$ was found to be independent of the hydrogen content as well as film preparation method [91], and due to the fact that the constant of proportionality $A_{640}$ is more consistent in literature (see chapter 5.2), this mode is used to determine $C_H$ in this work. A comparison with the results obtained from the stretching modes will however also be given.

Figure 5.5 shows fitted absorption coefficients for both the wagging and the stretching mode for different substrate temperatures obtained from FTIR measurements. They have been calculated from the transmission $T$ measured by FTIR and normalised on 1 nm film thickness. The areas of both peaks decrease with increasing substrate temperature due to the decreasing hydrogen content. It is clearly observable that the stretching mode absorption consists of two peaks. For low substrate temperatures the LSM dominates in contrast to higher substrate temperatures where the HSM is dominant. The connection between relative peak heights of LSM and HSM with the hydrogen bonding structure of a-Si:H will be dealt with further down.

The left hand side of figure 5.6 shows the total hydrogen content in the a-Si:H films obtained from the wagging mode at 640 cm$^{-1}$ versus applied power. It is obvious that the hydrogen content decreases slightly with increasing power. This can be explained with the higher substrate temperature when the applied power is increased. Measurements with an optical fiber thermometer show that the substrate temperature of a non heated sample increases from 25 °C at 20 W to 36 °C at 100 W for a silane plasma
at 3 Pa. A similar increase in temperature may be obtained for a heated sample.
The hydrogen content is highest for the non heated sample (about 25 to 30 at. %) and
decreases for increasing substrate temperature (15 at. % at 320 °C). The influence of
the substrate temperature on hydrogen content and other film properties will be dealt
with in the next chapter.
The hydrogen content results obtained from the stretching mode (right hand side of
figure 5.6) show similar behaviour like that of the wagging mode. These results are
quite consistent regarding the uncertainty concerning the constants of proportionality
$A_{LSM}$ and $A_{HSM}$.

Figure 5.7 shows the $C_{H,LSM}=A_{LSM}I_{LSM}$ and $C_{H,HSM}=A_{HSM}I_{HSM}$ hydrogen con-
tents plotted versus the total hydrogen content density $C_{H,wagging}=A_{640}I_{640}$. The sum
of $C_{H,LSM}+C_{H,HSM}$ would again give the total hydrogen content obtained from the
stretching mode. It is obvious that the LSM dominates over the HSM meaning that
most hydrogen in the a-Si:H films is bonded in monohydrides. Only one to seven per-
cent of all atoms are hydrogen atoms bonded in dihydrides. The amount of hydrogen
in dihydrides stays constant over the whole range of hydrogen content whereas the
amount of hydrogen in monohydrides decreases with decreasing hydrogen content. It
may be supposed that for $C_H < 10$ at. % the contribution of the LSM absorption
is even smaller than the contribution of the HSM absorption meaning that for very
small hydrogen contents more hydrogen is bonded in dihydrides than in monohydrides. This is at first sight in contrast to results from other groups [86], where at low hydrogen contents all hydrogen is bonded in monohydrides. But reference [84] reports that using high substrate temperatures ($T_s \geq 250 ^\circ C$) and without dilution of silane the films only contain Si-H groups. Going to lower substrate temperatures and/or with dilution of silane with for example argon, higher order bonding groups like SiH$_2$, (SiH$_2$)$_n$ or SiH$_3$ appear [86]. Also the use of high plasma power and other deposition conditions outside the normal range (substantially higher or lower pressure, etc.) can lead to the appearance of higher order bonding groups [91]. This can also be observed in our measurements since all films show both LSM (SiH) and HSM (SiH$_2$, (SiH$_2$)$_n$ or SiH$_3$) absorptions. Even at substrate temperatures higher than $T_s \geq 250 ^\circ C$ HSM absorptions are present because of the dilution of silane with argon.

Figure 5.8 shows the peak position of the LSM and HSM depending on the hydrogen content. The peak position of the HSM is almost constant whereas the peak position of the LSM increases with increasing hydrogen content, especially for low hydrogen
contents. Lucovsky [86] reports that the peak position of the lower stretching mode is not always detected at the same wave number but that it may be shifted. He attributes this shift to a change in electronegativity (due to impurities) of the atoms adjacent to the vibrating hydrogen atom.

5.4 Influence of the substrate temperature

The substrate temperature is one of the main parameters which controls the properties of the deposited thin films. More precisely the substrate temperature has influence on the plasma reactions (see figure 5.10) as well as on surface reactions and cross-linking processes of the atoms and molecules contributing to the film growth. As can be seen later the substrate temperature also modifies the onset of nanoparticle formation in the plasma volume. In figure 5.9 the growth rates of a-Si:H films for different deposition conditions are plotted versus substrate temperature. It is obvious that the growth rates show an approximately exponential decrease with increasing substrate temperature for temperatures below 300 °C and get saturated for higher temperatures. The

Figure 5.8: Peak position of the low stretching mode (LSM) and high stretching mode (HSM) versus total hydrogen content.
deposition rate is about 8-15 nm/min for deposition at room temperature, depending on the applied power. At temperatures above 300 °C the growth rate decreases to 5-7 nm/min. This decrease is due to the higher mobility of the deposited species. The activation of the surface mobility and the increase of the diffusion length of the deposited species favours the surface rearrangement and therefore leads to a better film microstructure. The deposited films are more dense and less surface roughness is obtained leading to a lower growth rate.

Another explanation for the lower growth rate with higher substrate temperature is given by Andújar et al. [92]. The relevant parameter in gas-phase processes is not the pressure $p$ but the gas density $N$. With the assumption that with increasing substrate temperature also the gas temperature (at least near the substrate) increases and with the ideal gas law

$$ p = N k T \quad (5.7) $$
an increase of $T$ at constant $p$ results in a decrease of $N$ and therefore in decreasing film growth.

A third explanation is given by Myburg [93] who found similar results like those presented here. He ascribes this behaviour to the increase in the kinetic energy on the surface of the substrate. At high surface temperature, the thermal desorption becomes too rapid, meaning that the precursors have no time to reach the chemisorption sites at surface steps via surface diffusion [31].

However, one can also assume that with increasing gas temperature the plasma chemistry is changed leading also to a lower growth rate. To estimate the influence of the substrate temperature and therefore higher gas temperature on the plasma chemistry, mass spectrometer measurements have been performed. The results are presented in figure 5.10.

Both spectra have been measured at the same conditions, namely 50 sccm SiH$_4$ flow at 3 Pa with a power of 20 W. The only difference is the substrate temperature and therefore the gas temperature. In one case the substrate is not heated (black
Figure 5.11: Hydrogen content obtained from the wagging mode versus substrate temperature for different plasma powers.

line) meaning the gas temperature is about room temperature. The red line shows the spectrum with a substrate temperature of about 300 °C leading to a significant higher gas temperature. The most obvious feature is the absence of higher silane molecules \((m/q=54-64)\) at higher gas temperature. The formation of \(\text{Si}_2\text{H}_n\) molecules is suppressed due to the high gas temperature since higher silanes are thermally unstable. Since the reaction of \(\text{Si}_2\text{H}_n\) molecules with other silane molecules leads to the formation of macroscopic particles (see subsection 5.1) it can be assumed that the formation of nanoparticles is reduced or even suppressed with higher substrate temperatures. Apart from that signals from all other masses are clearly lower when the gas is heated and the pressure is hold constant. This is one explanation for the decreasing growth rate when the substrate is heated (see figure 5.9).

Figure 5.11 shows the total hydrogen content obtained from the wagging mode peaks at 640 cm\(^{-1}\) versus the substrate temperature for different deposition conditions. Since the growth rate at constant temperature increases with increasing power, the total hydrogen content depends both on substrate temperature and on growth rate. In
general the hydrogen content decreases with increasing substrate temperature. One explanation that can be found in literature is the thermal activated desorption of hydrogen [38], [94]. The high temperature provides the low energy (<0.25 eV) which is necessary for the diffusion of H\textsubscript{2} from the growing surface. For this process two neighbouring SiH molecules bond by cross-linking and release one H\textsubscript{2} molecule. In this case the contribution of SiH\textsubscript{3} radicals is increased because they require a hydrogen-free surface to be incorporated and contribute to film growth. The activation of hydrogen removal from the growing surface reduces the hydrogen content of the film. Another explanation is the thermal activated diffusion of precursors and hydrogen on the surface [46]. This diffusion leads with increasing substrate temperature to a more perfect amorphous network, meaning that less hydrogen is needed for the relaxation of intrinsic stress. The actual mechanism for the decrease of hydrogen content with increasing substrate temperature may be a combination of improved growth due to increased surface diffusion and an eased hydrogen desorption.

In figure 5.12 the refractive index $n$ obtained by \textit{ex situ} ellipsometry is plotted versus
Figure 5.13: Hydrogen density $N_H$ (squares) versus refractive index $n$. The black line shows the empirical relation between $N_H$ and $n$ after [95], the red line shows the linear fit by hand of $N_H$.

The substrate temperature. For the determination of the optical properties as well as the film thickness the Tauc-Lorentz model, described in chapter 3.1.3, has been used to simulate the experimental data.

The refractive index $n$ (at 632 nm) increases with increasing substrate temperature corresponding to an increase of the density of the films. For unheated substrates it is about $3.85$, almost independent of the applied power. After a small decrease at $100$ °C it increases again up to $4.05$ at $320$ °C for high powers. The refractive index $n$ of amorphous silicon without hydrogen (a-Si) for comparison is $4.2$ at $632$ nm. In [96] it is reported that the film density of a-Si:H increases with increasing substrate temperature respectively with decreasing hydrogen content.

The increase of $n$ with increasing plasma power is also supposed to be due to the higher film density. With higher power the ions gain more energy in the electric field of the sheath and thus can be incorporated into the film deeper making the film more dense.

Van de Sanden et al. [95] even found a linear correlation between refractive index
Chapter 5 Deposition and characterisation of a-Si:H films

Figure 5.14: AFM images of a-Si:H films deposited under similar conditions, left hand side without heating, right hand side heated at 320 °C. The strong peak represents a dust particle on the surface.

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$\textit{n}$ (at 632.8 nm) and the atomic hydrogen density $N_H$ with elastic recoil measurements (ERDA) to show that there is no density gradient present in a-Si:H films. In figure 5.13 this correlation between $N_H$ and $n$ is plotted (black line). For comparison the obtained data of this work (red squares) and the resulting fit (red line) are also plotted. Although the obtained data are quite disperse a clear linear trend can be observed. The empirical relation between $N_H$ and $n$ of the data in this work is $N_H= (9.75-2.2 \, n) \times 10^{22}$. In general the hydrogen density in this work is higher than in [95] for one defined refractive index but also the slope is steeper.

Although the a-Si:H film is not in contact with blood or tissue of the human body, the smoothness of the surface may be critical for the adhesion of the DLC film. Figure 5.14 shows AFM images of a-Si:H films deposited on silicon wafers, one without heating of the substrate, the other one with a substrate temperature of 320 °C. The film deposited on the unheated sample is very smooth (apart from the dust particle on the surface), its roughness is $R_a= 1.6$ nm (figure 5.14 (a)) . Deposited with a higher substrate temperature, the film gets a little bit more rough, as depicted in figure 5.14 (b). The roughness in this case is $R_a=2.4$ nm, which is not much higher than the unheated case. However, the microstructure of the surface is more distinct. It should be noticed that a higher roughness of the film can be expected when the roughness of the substrate is higher. Thus, the roughness of the a-Si:H films deposited on polished
metal substrates is expected to be higher, depending on the roughness of the substrate (usually below 10 nm).

### 5.5 Optical properties of a-Si:H films

Although the optical properties of the a-Si:H films are of no interest for the target application they will be discussed in this subsection. The optical properties of a thin film are closely associated with the chemical composition, density and mechanical

![Figure 5.15: Optical constants $n$ and $k$ as a function of wavelength for different powers of a-Si:H films deposited at room temperature.](image1)

![Figure 5.16: Optical constants $n$ and $k$ as a function of wavelength for different substrate temperatures deposited with a power of 100 W.](image2)
properties like hardness of the film. Therefore the knowledge of the optical properties can give insight into the above mentioned features. Measurement and monitoring of these properties enables easy control of these features.

Figure 5.15 shows the optical constants $n$ and $k$ as a function of the photon wavelength of a-Si:H films deposited with powers from 20 W to 100 W at room temperature. The variation of $n$ and $k$ with power is not very pronounced in contrast to a-C:H films. For a-C:H films the power and therefore the self-bias which accelerates the ions onto the substrate have more influence on the optical properties of the films because a higher ion energy leads to a more dense packed film [97]. The growth of a-Si:H is by contrast not mainly driven by ions but by radicals. In these films, no competition between sp$^2$ and sp$^3$ sites occurs. Thus the higher energy does not have much influence on the density and consequently on the optical properties of the film.

The substrate temperature has more influence on the optical properties of a-Si:H films. Figure 5.16 shows the optical constants $n$ and $k$ as a function of the photon wavelength of a-Si:H films deposited with different substrate temperatures at a power of 100 W. It is obvious that $n$ and $k$ differ for different substrate temperatures, especially $k$.

Although the influence of the power on the refractive index is not significant, looking closer at the refractive index $n$ at 632 nm provides interesting results. This is the standard wavelength of a He-Ne laser and is usually used to compare refractive indices. In figure 5.12 the refractive index is displayed versus substrate temperatures for different applied powers. For low substrate temperature (without heating) $n$ decreases slowly with increasing power. For high substrate temperatures (210 °C and 320 °C) the refractive index increases strongly with increasing power. For medium temperatures (100 °C) a transition between both cases can be observed: the refractive index first decreases and than increases again.

The optical bandgap of the a-Si:H films is obtained by the Tauc method [98]. Tauc describes the relation between the absorption coefficient $\alpha$, the incident photon energy $E = h\nu$ and the bandgap $E_{gap}$ as follows:

$$\sqrt{\alpha E} \approx B(E - E_{gap}).$$  \hspace{1cm} (5.8)

The absorption coefficient $\alpha$ can be obtained from the extinction coefficient $k$, measured by optical ellipsometry, via:
Figure 5.17: Extrapolation of $\sqrt{\alpha E}$ down to zero to obtain the optical bandgap.

$$\alpha = \frac{4\pi k}{\lambda}, \quad (5.9)$$

where $\lambda$ is the wavelength.

To obtain the optical bandgap, $\sqrt{\alpha E}$ is plotted versus the photon energy $E$ in eV. The extrapolation of the linear part down to zero gives the optical bandgap. An example for the determination of $E_{\text{gap}}$ from $\sqrt{\alpha E}$ is shown in figure 5.17. The extrapolation down to zero leads to a relatively high error of the bandgap (assumed as 10 \%).

The bandgap for amorphous hydrogenated silicon films is plotted versus the refractive index $n$ in figure 5.18. The optical bandgap for all investigated films lies in the range from 1.65 eV to 1.95 eV. It slightly decreases with increasing refractive index $n$ respectively substrate temperature $T_s$. The gap narrowing with increasing substrate temperature is attributed to the decrease in the hydrogen content in the film (see figure 5.11).
5.6 Summary

In this chapter the deposition of a-Si:H films has been investigated. To obtain good quality films, the parameter range of power and pressure, where no dust particle formation is observed, has been identified.

Via FTIR the hydrogen content $C_H$ of films deposited with different substrate temperatures has been determined. Without heating $C_H$ is in the range of 30 at. % and decreases down to about 15 at. % for samples heated at 320 °C. The hydrogen of films with a high $C_H$ is mainly bonded in monohydrides whereas the ratio of monohydrides and dihydrides in films with lower hydrogen content is almost equal.

The growth rate decreases significantly with increasing substrate temperature mainly due to thermal desorption of growth species on the surface. With less hydrogen in the amorphous silicon film the refractive index $n$ increases due to a higher film density. The bandgap decreases with increasing $n$ and lies in the range of 1.8 eV.
Chapter 6

Deposition and Characterisation of diamond-like carbon (DLC) films

In this chapter the deposition of diamond-like carbon (DLC) films in a capacitively coupled GEC-cell is described and the deposited films are characterised by several diagnostics. Since the deposition and properties of DLC are well investigated by several authors [14], [15], [16], [25], [26], and also by a recent dissertation in our institute [27], this chapter will only present some selected items which are important for the desired application.

The deposited DLC films are intended to be used as wear resistant protective coatings and should therefore be as hard as possible to protect possible implants against wear and damage. By optical ellipsometry the refractive index $n$ is measured which is a good indicator for the hardness of the film. A parametric model for DLC has been used to fit the measured data.

Implantation into the human body and the contact with blood or other fluids require a smooth surface. Therefore the surface roughness of the films is analysed by AFM. The biocompatibility will not be investigated in this work, since it has been tested and proven in a series of publications summarised in chapter 2.1.

In section 6.1 the growth process of DLC films is described and monitored by \textit{in situ} ellipsometry. Via \textit{ex situ} ellipsometry the optical constants $n$ and $k$ are determined as a function of the wavelength. The choice of acetylene as the precursor gas for DLC films will be justified. Results from optical ellipsometry and Rutherford Backscattering (RBS) are shown and the deposited DLC films are characterised. Section 6.2 gives an overview about the temperature dependence of surface roughness and optical constant of the DLC films since the films will also be deposited at higher temperatures.
6.1 Growth and properties of DLC films

With PECVD different types of a-C:H films can be deposited, as described in chapter 2.1. The properties can be varied from soft, polymer-like carbon to hard diamond-like carbon [99]. When the substrate is placed on the grounded electrode, the ion energies are relatively low, resulting in a soft, loose packed film. This film can easily be scratched and even wiped off the substrate. These films are not useful to build a wear resistant coating for biomedical devices or other applications. The second type of a-C:H films are hard, dense packed films (DLC). For the deposition, the substrates have to be placed on the powered electrode. The bombardment with high-energetic ions due to the self-bias leads to the film properties mentioned in chapter 2.1. An explanation of the self-bias is given in section 4.2. In this work the substrates were always placed on the powered electrode to gain as hard films as possible.

The DLC films have been deposited on test-pieces of polished silicon wafers (1 0 0). They have been inserted into the deposition chamber through the load-lock chamber introduced in chapter 4.1. The silicon substrates were placed on the sample holder with planar surface. Acetylene (C₂H₂) has been used as precursor gas with a standard flow of 20 sccm at a pressure of 1 Pa. Applied powers were between 20 and 140 W.

The growth of the DLC films was monitored by in situ ellipsometry measurements.

![Graphs](image)

(a) Measured \( \Psi \) and \( \Delta \) versus time

(b) Behaviour of \( \Psi \) and \( \Delta \)

**Figure 6.1:** In situ ellipsometric measurements of the growth of a 280 nm thick DLC film at a wavelength of 632 nm.
Chapter 6 Deposition and characterisation of DLC films

Figure 6.1 shows an ellipsometric measurement of a DLC film of 280 nm thickness deposited with 30 sccm acetylene flow at a power of 140 W. When the plasma is switched on, $\Psi$ and $\Delta$ immediately start to increase and later to decrease again, showing an oscillating curve with decreasing magnitude. This gives the typical elliptic curve in the $\Psi$-$\Delta$ plane turning into the centre. To obtain a film having a certain thickness, the corresponding $\Psi$ and $\Delta$ values have to be known. The plasma and therefore film growth can be stopped when these $\Psi$ and $\Delta$ values are reached.

After each deposition of a DLC film the chamber has been cleaned with the help of an oxygen plasma to guarantee similar deposition conditions for each process and to avoid the formation of flake-like particles peeling off the electrodes and walls after several deposition processes. For this purpose 50 sccm of oxygen were led into the chamber and a discharge with a power of 60 W was ignited for several hours. The generated oxygen radicals react with the carbon atoms to form volatile CO$_2$ which is then pumped out of the chamber.

Certainly, the formation of nanoparticles in acetylene plasmas is also possible. But the probability of volume polymerisation is much lower compared to a silane plasma. The dilution with argon even increases the tendency of dust particle formation. But

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure6.2.png}
\captionsetup{justification=centering}
\caption{Comparison of optical constants $n$ and $k$ for diamond-like carbon (DLC) and polymer-like carbon (PLC), deposited from acetylene and methane at equal deposition conditions.}
\end{figure}
since the acetylene gas was not diluted in argon in contrast to silane and since the pressure was kept quite low (1 Pa), no particle formation could be observed. This has been confirmed by \textit{ex situ} ellipsometric measurements which usually reveal even small dust particles in thin films as well as with optical (laser light scattering) and electrical (control of the self-bias) methods.

Figure 6.2 shows the optical constants $n$ and $k$ versus wavelength for hard and soft a-C:H films deposited on silicon wafers with methane ($\text{CH}_4$) and acetylene ($\text{C}_2\text{H}_2$) as precursor gases. It is obvious that both hard films (DLC), which were deposited on the powered electrode, have a much higher refractive index than soft films (PLC), which were deposited on the grounded electrode. This is due to the higher energy of the ions as mentioned above. Furthermore, the refractive indices of the films deposited from acetylene are higher than those deposited from methane. This effect is due to the higher amount of hydrogen in the growth precursor in methane ($\text{CH}_3$) than in the growth precursor in acetylene ($\text{C}_2\text{H}$) leading to the incorporation of more hydrogen into the film and making the film less dense. The hydrogen content is strongly
correlated with the refractive index $n$ and hardness of the film (see table 2.1). Both hardness and refractive index increase with decreasing hydrogen content. Thus the optical constants are an indirect measure for the mechanical properties of a-C:H films. For the desired applications the films should be as hard as possible, meaning that a refractive index as high as possible is preferable. This is the reason why the DLC films in this work are deposited from acetylene instead of methane. Another reason for this choice is the much higher growth rate for acetylene-deposited films. While acetylene-grown films have e.g. a growth rate of 18 nm/min, methane-grown films under the same deposition conditions (flux, power) have a growth rate of only 4.7 nm/min.

Figure 6.3 shows the growth rate for acetylene deposited DLC film versus applied power for two different flow regimes. The growth rate increases with increasing power due to higher dissociation of the precursor gas in the plasma. This fact leads to a higher concentration of ions and radicals responsible for the film growth in the plasma and thus enhanced growth speed. Since the self-bias goes with the square root of the applied power, the deposition rate is proportional to the square root of the power,
as predicted by equation 5.1. Additionally, a higher gas flow and therefore higher pressure also leads to faster film growth because more molecules are present in the plasma volume to be dissociated and their products incorporated into the film.

The optical constants $n$ and $k$ of DLC films measured by optical ellipsometry are plotted versus applied power in figure 6.4. The refractive index is quite high (between 2.18 and 2.34), meaning the film is very dense, very hard and contains little hydrogen (see chapter 2.1). It increases with increasing power, respectively self-bias. The value of the negative self-bias increases in this case from 190 to 450 V. The index of absorption $k$ also increases slightly with increasing power.

From RBS measurements the area density of a DLC film deposited at 20 W is estimated to be $0.8 \times 10^{18}$ at/cm$^2$. With known film thickness of 57 nm a volume density of $1.4 \times 10^{23}$ at/cm$^3$ can be calculated. This corresponds to a mass density of $2.8$ g/cm$^3$ with neglected mass of the hydrogen atoms. The refractive index of this film is 2.17.

### 6.2 Influence of the substrate temperature

The deposition of DLC films is usually performed at relatively low temperatures. But due to the fact that the DLC films are deposited onto the a-Si:H films directly after the deposition of these, the substrate is still hot during the deposition of the DLC films when the a-Si:H film has been deposited at higher substrate temperatures. This high substrate temperature may have influence on growth and properties of the DLC films. Therefore, the influence of the substrate temperature on the DLC films has been investigated and the results are presented in this section.

In figure 6.5 the deposition rate of DLC films versus applied power is depicted for unheated and heated substrates. It is obvious that there is almost no difference in deposition rate, except maybe for higher powers where a higher growth speed for unheated samples may be expected due to smaller chemical erosion [100]. Thus, no significant influence of the substrate temperature on growth rate can be identified.

In contrast to that, a strong influence on the optical properties of the DLC films can be seen in figure 6.6. Both $n$ and $k$ increase significantly with increasing substrate temperature. This can be explained with a lower hydrogen content in the film, since the refractive index $n$ increases with decreasing hydrogen content (see section 2.1). Grill et al. [101] report that the hydrogen content of DLC films decreases with in-
The area density of a DLC film deposited at 20 W on a heated substrate has been estimated from RBS measurements to be $1.1 \times 10^{18}$ at/cm$^2$. With a film thickness of 65 nm the volume density can be calculated to be $1.7 \times 10^{23}$ at/cm$^3$. Neglecting the mass of the hydrogen atoms, this corresponds to a mass density of the film of 3.4 g/cm$^3$. This film has a higher refractive index of 2.36 compared to the film deposited at room temperature mentioned in the previous section ($n=2.17$, density 2.8 g/cm$^3$).

The influence of the substrate temperature on the internal stress of the DLC films has not been investigated in this work. But all DLC films deposited at higher temperatures showed excellent adhesion to the substrate directly after deposition and days and weeks later. Additionally, they could not be scratched with a sharp object.

In [101] it is reported that the internal stress in DLC films strongly decreases when the film is annealed at temperatures between 200 and 500 °C. This effect may be due
to relaxation of the network. In [101] the stress has been measured by curvature measurements. This paper reports also that the wear of DLC films decreases with higher temperatures during deposition. But the wear increases when the film is annealed after deposition to temperatures higher than 440 °C.

The last item to be investigated in this section is the influence of the substrate temperature on the surface properties of the DLC films. In figure 6.7 the AFM images of the surfaces of two DLC film deposited on silicon wafers under the same conditions except substrate temperature are shown. Both films appear to be very smooth. The roughness of the unheated film is about 1 nm, measured by AFM. $R_a$ even increases for the heated substrate down to 0.6-0.7 nm. Thus, higher substrate temperatures do not have negative influence on the smoothness of DLC films.

The investigations show that the deposition at higher substrate temperatures exhibits no negative influence on the desired properties of the DLC films. The films are still hard and wear resistant and the stress even decreases with higher temperatures. It is expected that DLC films deposited at high substrate temperatures are applicable for the use as wear resistive protective coatings.
Chapter 6 Deposition and characterisation of DLC films

Figure 6.7: AFM images of DLC films deposited under similar conditions, left hand side without heating, right hand side heated at 250 °C.

In chapter 8, heated and unheated metal substrates coated with the combination of a-Si:H and DLC films are investigated under durability tests to study the performance under load.

6.3 Summary

Hard (diamondlike) a-C:H films (DLC) have been deposited from acetylene plasmas. Acetylene has been chosen because it leads to harder films than the deposition with methane. Besides, the growth rate for acetylene-deposited DLC films is higher than for methane-deposited ones. The refractive index of the deposited films lies in the range of 2.18 to 2.34, which is quite high for DLC films and an indicator for very hard films.

Higher substrate temperatures have no influence on the growth rate, but on optical constants of the DLC films. Refractive index and index of absorption increase significantly with heating due to a lower hydrogen content and a higher film density. The film density of DLC films deposited on unheated samples was estimated to be 2.8 g/cm³ ($P=20$ W, $n=2.17$). The density increases to 3.4 g/cm³ for films deposited on heated samples ($P=20$ W, $n=2.36$).

The surface roughness of deposited DLC films is about 1 nm, for heated and unheated substrates, and is therefore suitable for applications with blood or tissue contact.
Chapter 7
Deposition and characterisation of amorphous hydrogenated silicon-carbon (a-Si:C:H) films

When silane and acetylene are used simultaneously in a plasma, films with new properties can be deposited. The result is an amorphous network consisting of carbon, silicon and hydrogen in the form of a-Si$_{1-x}$C$_x$:H. These amorphous hydrogenated silicon-carbon films are of great interest for technological applications, for example as p-type layers in photovoltaic devices like solar cells, for flat panel displays and for optical and solar selective coatings [102], [103]. But there is also fundamental interest regarding to understand how the local silicon, carbon, and hydrogen bonding configurations act on film properties.

The composition of amorphous hydrogenated silicon-carbon films depends on the gas composition flowing into the plasma. It ranges from hydrogenated amorphous silicon, a-Si:H ($x=0$), deposited in pure silane (plus argon) to hydrogenated amorphous carbon, a-C:H ($x=1$), deposited in pure acetylene.

In a-Si:H, where Si is tetrahedrally coordinated, the hydrogen serves to passivate dangling bonds and also to relax the strained a-Si network. This leads to a more "ideal" tetrahedrally coordinated Si network with obvious technological applications [102].

In a-C:H, the situation is more complex due to the fact that C can be bonded in either trigonal (graphitic) or tetrahedral (diamond-like) coordinations. The hydrogen in a-C:H also plays an important role in passivating dangling bonds and in promoting tetrahedral coordination for the C atoms to which it is bonded. The properties and
applications of the so called "diamond-like" a-C:H films have been pointed out in chapter 6. One problem for a-C:H has been the preparation of films which are both hard and optically transparent. The difficulty has been due to the (relatively small) volume fraction of graphite-like bonded carbon which remains in the films [102]. In a-Si:C:H films, carbon and silicon form carbide-like Si-C bonds and hydrogen is attached both to carbon and to silicon [58]. In order to enhance tetrahedral coordination for C in the films, thereby enhancing their diamond-like properties, a-Si$_{1-x}$C$_x$:H films are prepared and characterised in this work.

For a far better adhesion between DLC and amorphous silicon film one could think of an a-Si:C:H gradient layer going from 100 % amorphous silicon to 100 % DLC. These films can be deposited in changing the gas flows continuously from pure silane to pure acetylene. Therefore, these films are investigated in more detail in this chapter.

This chapter is organised as follows. In section 7.1 the deposition of a-Si:C:H films is described. The chemical composition of these films is investigated in section 7.2 and the optical properties of a-Si:C:H films are characterised in section 7.3.

### 7.1 Deposition of a-Si:C:H films

The a-Si:C:H films have been deposited in the GEC-cell described in chapter 4.1. Pieces of Si(1 0 0) wafers (2 cm × 2 cm) have been used as substrates and placed on the lower, powered electrode. Acetylene and silane (ultra high purity, diluted to 10 % in argon 5.0) have been mixed to the desired [C$_2$H$_2$]/[SiH$_4$] ratios in a tube before entering the discharge chamber being homogenously mixed. Both flows were controlled by individual mass flow controllers.

It should be noted that a-Si$_{1-x}$C$_x$:H films can also be deposited from other gases, for example with methane instead of acetylene or with tetramethylsilane (TMS, C$_4$H$_{12}$Si) which contains both carbon and silicon. But in the case of TMS the ratio of C/Si can not be varied as wide as in the case of for example silane/acetylene mixtures. In this work the deposition of a-Si$_{1-x}$C$_x$:H films is performed with acetylene and silane, diluted in argon.

During the deposition of the mixed layers the silane/argon flow and the pressure in the chamber have been held constant at 50 sccm and 3 Pa, respectively. The flow of acetylene has been varied between 0 and 10 sccm. In two cases the flow of the silane/argon mixture was only 30 and 40 sccm. Since silane is diluted in argon at
Table 7.1: Gas flows in sccm, gas composition, film thickness, optical constants, and carbon concentration $x$ of the a-Si:C:H films.

<table>
<thead>
<tr>
<th>sample #</th>
<th>[SiH$_4$]+[Ar]</th>
<th>[C$_2$H$_2$]</th>
<th>$r_{{C_2}H_2}$</th>
<th>d/nm</th>
<th>$n$</th>
<th>$k$</th>
<th>$x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>115</td>
<td>0</td>
<td>30</td>
<td>1</td>
<td>79.2</td>
<td>2.05</td>
<td>0.05</td>
<td>1.00</td>
</tr>
<tr>
<td>107</td>
<td>30</td>
<td>20</td>
<td>0.87</td>
<td>148.7</td>
<td>2.09</td>
<td>0.03</td>
<td>0.85</td>
</tr>
<tr>
<td>114</td>
<td>50</td>
<td>10</td>
<td>0.67</td>
<td>108.9</td>
<td>2.16</td>
<td>0.01</td>
<td>0.76</td>
</tr>
<tr>
<td>126</td>
<td>50</td>
<td>7.5</td>
<td>0.60</td>
<td>128</td>
<td>2.19</td>
<td>0.03</td>
<td>0.72</td>
</tr>
<tr>
<td>109</td>
<td>40</td>
<td>5</td>
<td>0.56</td>
<td>125.5</td>
<td>2.28</td>
<td>0.01</td>
<td>0.73</td>
</tr>
<tr>
<td>125</td>
<td>50</td>
<td>5</td>
<td>0.50</td>
<td>113</td>
<td>2.33</td>
<td>0.01</td>
<td>0.67</td>
</tr>
<tr>
<td>124</td>
<td>50</td>
<td>3.5</td>
<td>0.41</td>
<td>112</td>
<td>2.22</td>
<td>0.02</td>
<td>0.62</td>
</tr>
<tr>
<td>110</td>
<td>50</td>
<td>2</td>
<td>0.29</td>
<td>90.9</td>
<td>2.79</td>
<td>0.02</td>
<td>0.50</td>
</tr>
<tr>
<td>111</td>
<td>50</td>
<td>1</td>
<td>0.17</td>
<td>101.3</td>
<td>3.30</td>
<td>0.14</td>
<td>0.40</td>
</tr>
<tr>
<td>112</td>
<td>50</td>
<td>0.5</td>
<td>0.09</td>
<td>92.6</td>
<td>3.72</td>
<td>0.26</td>
<td>0.31</td>
</tr>
<tr>
<td>116</td>
<td>50</td>
<td>0</td>
<td>0</td>
<td>63</td>
<td>3.97</td>
<td>0.20</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The real silane flow has to be calculated by dividing the total flow by a factor of 10.

Table 7.1 shows the flows for silane and acetylene and the acetylene fraction during deposition of the a-Si:C:H layers, film thickness, optical constants $n$ and $k$ and the carbon concentration $x$ obtained by RBS (see next section) of the films. The column $r_{{C_2}H_2}$ denotes the fraction of acetylene in the gas flow calculated by the ratio of acetylene to the sum of acetylene and silane (without argon) flows:

$$
  r_{{C_2}H_2} = \frac{[C_2H_2]}{[C_2H_2] + [SiH_4]}.
$$

The carbon concentration $x$ of the films is defined as the relative atomic concentration of carbon referred to the total concentrations of carbon plus silicon, neglecting hydrogen:

$$
  x = \frac{c_{carbon}}{c_{carbon} + c_{silicon}},
$$

where $c_{carbon}$ and $c_{silicon}$ denote the relative carbon and silicon concentration, respec-
Chapter 7 Deposition and characterisation of a-Si:C:H films

All films have been deposited for 10 minutes at a power of 20 W. The substrates have not been heated from outside and had a temperature of about 25 °C. The resulting films are amorphous, homogeneous and semitransparent and can therefore be investigated by optical ellipsometry. Additionally, these films are quite hard and non abrasive and show good adhesion to the substrate.

7.2 Chemical composition of a-Si:C:H films

For the investigation of the chemical composition of a-Si:C:H films Rutherford Backscattering (RBS), Fourier Transformed Infrared Spectroscopy (FTIR) and X-ray photo-electron spectroscopy (XPS) have been used. While RBS can measure the whole film depth, XPS can only detect atoms at the surface of the film (up to 10 nm deep). The penetration depth is determined by the mean free path of the electrons. Due to the fact that the surface composition of a deposited film may differ from the volume composition the RBS measurements have been used to determine the carbon concentration of the films because they are more reliable. But in order to double-check these values and to get more insight into the binding configuration, which is only possible with XPS measurements, both types of measurements have been performed.

With the help of the RBS measurements the concentration of carbon atoms in the deposited a-Si:C:H films has been determined. Figure 7.1 shows a typical energy spectrum of a Rutherford backscattering measurement of an a-Si:C:H film. The film has been deposited with \( r_{C_2H_2} = 0.87 \) leading to a carbon concentration of \( x = 0.85 \). With the help of a simulation (red line) of the measured data the relative contents of different elements can be determined. The carbon concentration is calculated after equation 7.2 from the silicon and carbon content. In all films also argon atoms could be detected. But since its concentration was in the range of 1 % of the carbon content, it was ignored.

The carbon concentration \( x \) of the deposited films is plotted in figure 7.2 versus the gas composition \( r_{C_2H_2} \). The carbon concentration increases from 0 for a pure silane plasma to 1 for a pure acetylene plasma. Since both carbon and silicon are four-fold coordinated, carbon atoms are simply more and more replaced by silicon atoms going from a pure acetylene plasma to a pure silane plasma. The carbon concentration does not show a linear behaviour since there are twice as much carbon atoms present in the
Figure 7.1: Energy spectrum of a Rutherford Backscattering measurement of an a-Si:C:H film on a silicon substrate, measured yield (black dots) and simulation (red line).

gas than silicon atoms. To check if the probability to be incorporated into the film for both silicon and carbon atoms is equal, the resulting carbon concentration in the film was modelled for the case that the probability for both carbon and silicon to be incorporated is equal (red line in figure 7.2), assuming that the formation of reactive radicals is directly proportional to the concentration in the gas phase.

Up to a gas mixture of 50 % silane and 50 % acetylene the measured carbon concentration is higher than the modelled one meaning that the probability for carbon atoms to be incorporated is higher than for silicon atoms. When more acetylene than silane is present in the gas \( r_{C_2H_2} = 0.5 - 1 \), the measured values are lower than the calculated ones, meaning that in this case the probability for silicon molecules to be incorporated into the film is higher. When the ratio of silane flow and acetylene flow is 1 \( r_{C_2H_2} = 0.5 \) the measured carbon concentration is 0.67 and equal to the calculated one meaning that the probability for carbon atoms to be incorporated into the film is as high as the probability for silicon atoms.

The atomic surface coverage \( n_s \) (silicon and carbon) of the film shown in figure 7.1 is
Figure 7.2: Atomic carbon concentration $x$ of the films deposited with various gas flow ratios $r_{\text{C}_2\text{H}_2}$, obtained from RBS measurements

$2.5 \times 10^{18}$ atoms/cm$^2$. With the known film thickness of 148.9 nm the volume density of the film $n_v$ can be calculated, giving $1.7 \times 10^{23}$ cm$^{-3}$. The values for atomic density $n_a$ and volume density $n_v$ for all deposited films are listed in table 7.2. It is obvious that the volume density decreases with decreasing carbon concentration leading to a less dense packed network.

With XPS the chemical composition of the films can be measured as well as the binding states of the atoms in the material. In this work the binding energies of Si and C for different film compositions have been measured. The binding energies of these atoms in different binding conditions are listed in table 3.1 on page 42. In figure 7.3 two examples for different film compositions are given. It shows the intensity of the XPS measurement depending on the binding energy. The first sample was deposited with 44 % silane and 56 % acetylene in the gas phase. Most of the silicon in the film is bonded in SiC, meaning that the Si 2p peak is shifted towards 100.2 eV. Some Si atoms are bonded in SiO$_2$, this explains the shoulder of the Si 2p peak at 103.3 eV.
Table 7.2: Carbon concentration $x$, atomic surface coverage $n_s$, and atomic volume density $n_v$.

<table>
<thead>
<tr>
<th>$x$</th>
<th>$n_s / \text{atoms} \text{cm}^{-2}$</th>
<th>$n_v / \text{atoms} \text{cm}^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85</td>
<td>$2.50 \times 10^{18}$</td>
<td>$1.7 \times 10^{23}$</td>
</tr>
<tr>
<td>0.76</td>
<td>$1.85 \times 10^{18}$</td>
<td>$1.7 \times 10^{23}$</td>
</tr>
<tr>
<td>0.72</td>
<td>$1.80 \times 10^{18}$</td>
<td>$1.4 \times 10^{23}$</td>
</tr>
<tr>
<td>0.73</td>
<td>$1.30 \times 10^{18}$</td>
<td>$1.0 \times 10^{23}$</td>
</tr>
<tr>
<td>0.67</td>
<td>$1.30 \times 10^{18}$</td>
<td>$1.1 \times 10^{23}$</td>
</tr>
<tr>
<td>0.62</td>
<td>$1.20 \times 10^{18}$</td>
<td>$1.1 \times 10^{23}$</td>
</tr>
<tr>
<td>0.50</td>
<td>$1.00 \times 10^{18}$</td>
<td>$1.1 \times 10^{23}$</td>
</tr>
<tr>
<td>0.40</td>
<td>$0.75 \times 10^{18}$</td>
<td>$0.7 \times 10^{23}$</td>
</tr>
<tr>
<td>0.31</td>
<td>$0.65 \times 10^{18}$</td>
<td>$0.7 \times 10^{23}$</td>
</tr>
</tbody>
</table>

Figure 7.3: (a) Example for one measured XPS peak and its fit with three gaussians, (b) XPS measurement for two different films deposited with different gas compositions.
Figure 7.4: Atomic carbon concentration $x$ of the films deposited with various gas flow ratios $r_{C_2H_2}$, obtained from XPS measurements.

The oxidation occurs because the samples are stored in ambient air and the topmost surface is able to oxidize. The second sample has been deposited in 91% silane and only 9% acetylene. In this film most silicon atoms can not find a carbon atom to build SiC meaning that the Si 2p peak is maximum at 99.2 eV, the binding energy of pure silicon. The SiO$_2$ peak is here clearly observable.

The area under the peak for one binding energy is proportional to the volume fraction of the corresponding atoms.

The carbon concentration $x$ is obtained by calculating the integrated intensity of C 1s and Si 2p peaks and using equation 7.2. Figure 7.4 shows the carbon concentration as a function of the gas flow ratio $r_{C_2H_2}$ obtained from the XPS measurements in comparison with those obtained by the RBS measurements. The values of the XPS measurement are a bit lower than those of the RBS measurement but show the same behaviour. The reason why they are lower is the already mentioned difference between the chemical composition of the surface and the volume of a deposited film due to contamination, oxidation etc. But the results from the XPS measurements support
Figure 7.5: Deposition rate of the a-Si:C:H films versus carbon concentration.

The film deposition rate in figure 7.5 shows a linear increase with increasing carbon concentration in the film. Only the values for $x=0.5$ and $x=0.75$ deviate from the linearity. The value for $x=1$ is not shown here because this film has been deposited with a different pressure (1 Pa instead of 3 Pa) and can therefore not be compared with the other values. The growth rate for the pure amorphous silicon film is 6.3 nm/min and it increases up to 14.9 nm/min for $x=0.84$.

The variation in deposition rate results from the competition between deposition due to active species and hydrogen etching. The available reactive species contributing to film growth are limited by the gas flow of SiH$_4$ and C$_2$H$_2$. The amount of dissociated hydrogen atoms can simultaneously etch off weak bonds during film deposition [104].

In order to analyse not only the composition but also the bonding configuration of the films, FTIR measurements have been performed on each of them. The results are shown in figures 7.6 and 7.7. Here the absorption coefficient $\alpha = -\frac{1}{d} \ln(T)$ is plotted versus wavenumber in cm$^{-1}$ while $d$ denotes the film thickness and $T$ the transmission measured by FTIR. Thus, all results are independent of the different film thicknesses...
Figure 7.6: Absorption coefficient versus wavenumber obtained by FTIR measurement for $x=0.85$.

It is obvious that there are a lot of spurious bands visible in all spectra. Even with high flushing of the sample ambient with dry air these bands could not be suppressed. The broadest band can be found between 1280 and 2000 cm$^{-1}$ which is attributed to water vapour. In this region water shows many sharp, relatively strong bands [105]. The two overlapping dips around 2360 cm$^{-1}$ are attributed to atmospheric CO$_2$ bands as well as the sharp dip at 665 cm$^{-1}$. Here the absorption coefficient is negative because there was more CO$_2$ in the sample ambient during the measurement of the pure substrate than later, when the samples were measured. The striking peak at about 1100 cm$^{-1}$ is due to SiO$_2$ [105]. This band can occur if the native oxide layer on the deposited silicon wafer is thicker than on the silicon wafer used for the background measurement. Other peaks like those at 610 cm$^{-1}$ and 740 cm$^{-1}$ could not be identified in a unique way. But since they occur at exactly the same frequency with the same peak form and approximately the same intensity for all samples, they also seem
Figure 7.7: Absorption coefficients versus wavenumber obtained by FTIR measurements for different gas flow ratios.

to be spurious bands which are not attributed to characteristics of the films. A very weak peak can be found at \( \sim 640 \text{ cm}^{-1} \) corresponding to the SiH\(_n\) wagging mode. It diminishes gradually with increasing \( x \) and totally disappears for \( x=1 \). The peak at around 2100 cm\(^{-1}\) is related to SiH\(_n\) stretching modes in hydrogenated amorphous silicon thin films (see chapter 5) with \( n=1, 2 \) or 3. This peak has it strongest intensity when \( x=0 \). In general, this peak corresponds to the SiH stretching mode in hydrogenated amorphous silicon films and can be found the most in the films with less or no carbon. It can be seen that this peak shifts slightly towards higher wave numbers with increasing \( x \). Yu et al. [104] attribute this effect to the increase in the sum of electronegativity around silicon atoms when carbon atoms are incorporated into the microstructure of the films.

The peak at 1290 cm\(^{-1}\) can be attributed to CH sp\(^2\) bending [83]. The absorption band at 2800-3000 cm\(^{-1}\) corresponds to the stretching modes of sp\(^3\) CH\(_n\) bonds [83], [104]. This band is not visible in the films with \( x=0.24 \) and below, but appears in the
spectra of films with higher carbon concentration. The 3000 cm$^{-1}$ band related to sp$^2$ CH$_n$ bonds [104] is not seen in these spectra.

The influence of the chemical composition of the films on optical properties can not only be seen in the refractive index $n$ (see figure 7.10) but also in the optical bandgap. The optical bandgap is determined after the Tauc method as described in chapter 5.

The optical bandgap of the a-Si:C:H films versus the gas flow ratio is plotted in figure 7.8 (black squares). It is minimal for pure DLC and a-Si:H films respectively and shows a maximum for a gas mixture with about 50 % acetylene and 50 % silane. This gas composition leads to a carbon concentration of about 67 % (see figure 7.4). The bandgap of the pure a-Si:H film is 1.6 eV for our deposition conditions. In general it lies between 1.5 and 2 eV, depending on substrate temperature, applied power and gas composition (e.g. hydrogen dilution) [106]. For the pure DLC film a bandgap of about 1.95 eV is found. In literature values of 1 to 2 eV – depending of the self-bias voltage – can be found [14], [16]. In our case the self-bias was quite low (-180 V) leading to a rather high bandgap. Usually the bandgap is lower than 1.6 eV for hard a-C:H films.
The question why the bandgap of the material with carbon and silicon mixed in one phase is higher than in the two pure materials with only carbon or silicon can only be answered by assuming the formation of bonds between carbon and silicon, namely SiC. The optical bandgap for SiC is tabulated in [107]. Depending on the polytype it is 2.46 eV for 3C-SiC, 3.28 eV for 2H-SiC, 3.35 eV for 4H-SiC and 3.10 for 6H-SiC. The maximum value of the a-Si:C:H films investigated here is 2.6 eV. This leads to the assumption that not all but a certain amount of the silicon and carbon atoms are bonded into SiC. To verify this, the relative SiC content of the a-Si:C:H films has been determined from XPS measurements. The results are plotted in figure 7.8 (red circles). It can be seen that SiC is formed in all films which have been deposited with acetylene and silane simultaneously in the plasma. The SiC content is maximum for a gas flow ratio \( r_{\text{C}_2\text{H}_2} \) of about 0.3-0.4 leading to a carbon:silicon ratio of about 1:1 in the gas and also in the film (see table 7.1). With this gas composition in the plasma the maximum SiC content in the films can be achieved. Starting from pure silicon films the increasing SiC content leads to the increase of the optical bandgap from 1.6 eV to 2.6 eV. Going from the maximum of SiC in the films towards pure DLC films, the optical bandgap decreases again until the value for a pure DLC film is reached.

### 7.3 Optical properties of a-Si:C:H films

For the determination of the optical constants \( n \) and \( k \) and the film thickness \( d \) optical ellipsometry has been used \textit{ex situ} as described in chapter 3.1. 

As for the pure a-Si:H films the Generalized Oscillator Layer with a Tauc-Lorentz Oscillator has been used. This model is described in more detail in chapter 3.1. The Tauc-Lorentz Oscillator is a good model for amorphous films [59], thus as well for a-Si:C:H films.

Figure 7.9 shows optical constants \( n \) and \( k \) for different carbon concentrations. It is evident that the refractive index \( n \) increases strongly with increasing silane fraction in the gas flow. The imaginary part of the optical constant, \( k \), initially shows a small decrease at about 400 nm, as silane is added to acetylene. This decrease in absorption results from the replacement of strongly absorbing graphitic C–C bonds by Si–C bonds which absorb at higher energies. At higher Si concentration, \( k \) increases again as Si–C
bonds are replaced by Si–Si bonds which absorb at lower energies [102].

Figure 7.10 shows the refractive index $n$ at 632 nm versus carbon concentration in the film. The refractive index increases monotonically from about 2 for a pure DLC film to about 4 for a pure amorphous silicon film. The refractive index for pure SiC is 2.6 at 632 nm. Thus, the refractive index depends on the composition of the film. A change of the gas composition leads to a change in composition of silicon and carbon of the film and so any refractive index between 2 and 4 can be set.

It is also possible to model the a-Si:C:H films with an Bruggemann effective-medium approximation (EMA) combining the different components the films consists of. The EMA provides a method to mix two or three sets of optical constants together. The usual interpretation of the EMA theory is that small particles of one material are suspended in a matrix of the host material. Under that approximation the optical constants can be mixed in a way that satisfies certain electromagnetic equations. In practice it is just a reasonable way to mix optical constants together [59].

The deposited films are proposed to be macroscopically homogeneous, but having a heterogeneous microstructure. Mui et al. propose the films to consist of an amorphous polymeric (a-CH$_m$, $m\approx2$) component, an amorphous graphite-like (a-C) one and an amorphous tetrahedral (a-Si:C:H) one, plus voids (porous structure) [102]. In this work, the films are considered to be composed of three components: a-C:H in the form of DLC, a-Si:H and SiC. This is a better reflection of the real film composition and leads to a better understanding of the results of optical properties and optical
For the DLC component, the parametric DLC model giving the best results for a pure DLC film is chosen, while all fit parameters are held constant. For a-Si:H the Generalized Oscillator Layer in the form of a Tauc-Lorentz Oscillator, fitted for a pure a-Si:H film has been used. For the SiC component the tabulated optical constants of the model "Cubic Silicon Carbide" from Palik [108] have been used. Modelling the experimental results for $\Psi$ and $\Delta$ with the EMA Modell consisting of these three components, it is possible to determine the volume fractions of the three proposed components in the a-Si$_{1-x}$C$_x$H films as a function of the carbon fraction $x$. Although it is a very rough model, it describes the reality of the composition quite well.

In figure 7.11 the volume fractions of the three considered components DLC, a-Si:H and SiC are plotted as a function of the fraction of acetylene in the gas flow $r_{C_2H_2}$. It is evident that the DLC component increases with increasing acetylene flow and the a-Si:H component decreases with decreasing silane flow. The SiC component is maximum in a mixture of 71 % silane and 29 % acetylene. This agrees very well with
Figure 7.11: Volume fractions of DLC, a-Si:H and SiC as a function of acetylene fraction in the gas, obtained by the EMA-model.

the results from the XPS measurements in figure 7.8.

7.4 Summary

a-Si_{1-x}:C_x:H films with different carbon concentrations have been deposited in various mixtures of silane and acetylene. The carbon concentration varies from 0 to 1 and the resulting refractive index from 3.97 to 2.05.

The chemical composition of the deposited a-Si:C:H films has been measured via RBS and XPS. Results from both measurement methods coincide quite well. With XPS additionally the different binding states of C and Si atoms have been investigated. The formation of SiC in these films has been shown. The bonding configuration of the films has been measured via FTIR and compared for different film compositions. The influence of the film composition becomes apparent in the optical constants as well as in the optical bandgap which strongly depend on chemical composition of the films. The refractive index n decreases with increasing carbon content, whereas the
optical bandgap increases with increasing SiC content.
Chapter 8

DLC/a-Si:H film systems deposited on metal substrates

In the previous chapters the constituents of the film system, a-Si:H and DLC films, have been analysed, as well as the surface of the substrate. In this chapter these elements are joined together and their interaction is investigated. The deposition of a-Si:H/DLC film systems on different metal substrates is described and adhesion and failure mechanisms of the film system are analysed.

In section 8.1 the process of depositing DLC/a-Si:H films on metal substrates is described and a depth profile of the film system is presented.

The reduction of the intrinsic stress of DLC films using an intermediate layer of a-Si:H is shown in section 8.2. The adhesion and mechanisms of failure are investigated in this section. Additionally, results from cavitation erosion measurements and tensile tests are presented.

8.1 Deposition and characterisation of DLC/a-Si:H film systems on metals

The aim of this work is to deposit DLC films on metal substrates such as stainless steel, copper, nickel or NiTi. In an incipient experiment, it has been tried to deposit a thin DLC film (55 nm) directly on a polished plate made of Ni. But directly after removal of the sample out of the reactor, delamination of the DLC film could be observed. The film simply flaked off the substrate, showing no adhesion at all.

When a thin amorphous silicon film (30 nm) was used as intermediate layer between
metal and DLC, the film adhered much better to the substrate. Even after months no delamination could be observed. Photos of this first test are displayed in figure 8.1. Therefore, the use of an intermediate layer of hydrogenated silicon seems very promising in improving the adhesion between metal and DLC.

In the previous chapters the films under investigation have only been deposited on silicon wafers to study the characteristics of the films themselves and to make measurements with the ellipsometer more comfortable. Although the metal substrates are thoroughly polished, they show a remaining roughness greater than the roughness of the silicon wafers, which leads to slightly diffuse scattering of the light beam of the ellipsometer. The second point is that there exist perfected optical models used for ellipsometric measurements for crystalline silicon, but optical models for metals like copper, stainless steel, nickel and NiTi are not well validated or simply do not exist. Therefore, a piece of silicon wafer was usually placed next to the metal substrates during the deposition process to enable measurements of film thickness and optical properties afterwards.

Nevertheless, the metal substrates have also been modelled to measure the properties of film deposited directly on the metal substrate. For copper a model made by Palik [59] has been used, for stainless steel a model consisting of three Lorentz oscillators. Both models are available in the used software. For nickel and NiTi, new models had

Figure 8.1: Ni coated with a 55 nm DLC film, left hand side with, right hand side without intermediate layer of a-Si:H (30 nm).
to be established, which also consist of three Lorentz oscillators. For the determination of the parameters of the model, well polished metal substrates without coating have been measured and the data have been fitted.

To examine the influence of the substrate material on the deposition rate, three different film systems consisting of a-Si:H film and DLC film have been deposited on four different substrate materials (copper, nickel, stainless steel and silicon). For one deposition condition, all four substrates have been placed in the deposition chamber at the same time, to guarantee equal deposition conditions. The thickness of the amorphous silicon films shows a strong dependence of the substrate material. While the film thickness on copper is only 20.3-22.5 nm, the film on silicon is 28.5-32.6 nm thick (see figure 8.2). This effect is due to different sticking probabilities of the different materials. For amorphous silicon it is more easy to grow on crystalline silicon than on copper or other metals. The DLC film on the other hand shows no dependence of the substrate material because it grows on the already grown silicon film. Here, only a dependence of the applied power can be observed.

The results show that the deposition conditions of the intermediate layer have to be
adjusted individually for each different substrate material. This is of course not only true for the thickness of the adhesive layer, but also for other properties that influence adhesion.

The growth of the film system consisting of a-Si:H and DLC film can be monitored by in situ ellipsometry. Figure 8.3 shows the evolution of $\Psi$ and $\Delta$ during growth of the film system on a silicon wafer. Here, a 100 nm DLC film has been deposited on a 30 nm a-Si:H layer. The initial $\Psi$ and $\Delta$ values for native SiO$_2$ on top of the silicon wafer change rapidly and saturate after few minutes when the argon plasma is ignited. The native oxide layer of approximately 2 nm is sputtered quite fast by argon ions. It may be supposed that a sputter time of 10 minutes is sufficient to remove the top oxide layer on metal substrates completely. After the sputter process $\Psi$ and $\Delta$ values for a pure silicon wafer at 632 nm and 76° angle of incidence are obtained. During the deposition of the amorphous silicon film $\Psi$ and $\Delta$ change slightly until the end of the deposition process. The most significant change of $\Psi$ and $\Delta$ is observed during deposition of the DLC film. The values now follow the already known curves for DLC films presented in figure 6.1.
During plasma-off time (time between different discharges) the values for $\Psi$ and $\Delta$ stay almost constant. This time is needed to pump down remaining gases before the new gas is led into the discharge chamber.

Depth profiles of the chemical composition of the films on different metals have been measured by TOF-SIMS. Figure 8.4 shows the depth profile of a 100 nm DLC film and a 30 nm a-Si:H film deposited on polished NiTi. The films have been deposited under similar conditions as described in chapters 5 and 6 and have therefore the same characteristics as previous investigated films. The abscissa shows the sputter time in seconds which is correlated with the depth but not in a linear way. Different layers can be sputtered faster or slower than others and can therefore not be compared with each other, while staying within one layer, the time has a constant proportionality to the depth. Depicted in the graph are elements and their compounds which are present in the films (H, C, Si) and in the metal substrate (Ni, Ti). It should be noted that the intensities for Si, Ti, and Ni in figure 8.4 are divided by a factor of 100 for clarity since their intensity is much higher than of the other elements.

Since four different metal substrates have been placed side by side on the lower electrode to be coated simultaneously, metal atoms of the other samples such as Fe, Co and Cr can be found in this sample as well. They have been sputtered during the argon sputter phase previous to the deposition process and subsequently been redeposited on all samples. But their amount is quite small compared to other intensities. To avoid this contamination, only one sample at once was placed in the reactor in the remaining investigations.

Other contaminations like Na, Ca or K could also be found on the samples but are not displayed here. They result from contaminations in the reactor or from the tweezers contaminated with sweat and are usually found in SIMS measurements. For clarity they are not displayed in the graph as well.

One important result of these measurements is the fact that carbon and hydrogen in the DLC film are distributed homogeneously as can be seen in figure 8.4. That means that on top and bottom of the DLC film the composition is the same. This can not be said definitely for the amorphous silicon film since this film is quite thin. At the interface silicon–metal the matrix effect can be observed leading to a higher intensity for silicon. The high peak results from a better yield for silicon atoms in the different matrix present here.
Figure 8.4: TOF-SIMS depth profile of a-Si:H/DLC on NiTi.
The intensity of hydrogen in the silicon film is higher than in the carbon film. This does not mean necessarily that there is more hydrogen present in the a-Si:H film than in the DLC film. In fact, both hydrogen contents are supposed to be equal (about 30 at. %). The discrepancy results from a higher sputter rate in silicon and therefore higher intensities for hydrogen in this region.

At the interface carbon–silicon a small overlap of these two elements can be observed. Additionally, a small peak for SiC (blue curve) is present. As shown in section 2.5 SiC is the only chemically stable compound of silicon and carbon existing even at room temperature. The (predicted) formation of stable SiC leads to good adhesion of the DLC film on the amorphous silicon film.

There exists also an overlap of Si and Ni and Ti, respectively, at the interface silicon-NiTi. Also here the formation of silicides, namely SiTi and SiNi, can be observed. These silicides are responsible for the good adhesion of the amorphous silicon film on NiTi. SiTi and SiNi are stable compounds which can be found in the binary phase diagrams presented in section 2.5. Other compounds like NiSi\textsubscript{2} or TiSi\textsubscript{2} could not be observed by TOF-SIMS measurements.

The formation of SiTi and SiNi might also be due to sputter-mixing of the atoms. But since the deposition of the films was a non-equilibrium process as well, the formation of SiTi and NiTi at the interface may be assumed.

Surprisingly, the distribution of Ni and Ti in the NiTi substrate is not homogeneously throughout the depth. The intensity of Ni increases by a factor of two from 100 to 250 s whereas the intensity of Ti slightly decreases. One may think that the depletion of Ni in the top most zone of NiTi is due to selective sputtering of Ni during the argon sputter process. But since similar results can also be observed in polished NiTi samples which have not been exposed to plasma, there has to be another reason for this effect. It is likely that this depletion is inherent of the base material and arises from the production process.

The results for measurements of film systems on stainless steel, nickel, and copper substrates are displayed in the addendum. Similar results as found for NiTi are observed here. At the interface carbon–silicon significant amounts of SiC have been detected as well. Depending on the type of metal, different silicides at the interface silicon-metal have been found. On the stainless steel sample, for example, a quite high peak depicting FeSi is visible, and also CrSi can be observed.

Stainless steel and NiTi samples heated at 250 °C during deposition have also been
investigated. No drastic difference between heated and non-heated samples can be observed in the a-Si:H and DLC film. This is astonishing because at least the intensity of hydrogen should decrease when the sample is heated. The amount of hydrogen in the a-Si:H and also in the DLC films decreases significantly when the substrate is heated, as shown in chapters 5 and 6. This decrease was expected to be observed by TOF-SIMS measurements. But since the diagnostic was not absolutely calibrated a direct comparison of the counting rates is misleading.

8.2 Adhesion and failure of a-Si:H/DLC film systems

Adhesion to the substrate is certainly the first attribute the investigated films must possess before any of their other properties can be exploited. After each deposition process it was checked whether the film adhered to the substrate at all. The DLC films which were deposited directly on the metal substrate without a-Si:H intermediate layer generally did not stick on the metal, independently whether the substrate had been cleaned by argon sputtering or not. The DLC films simply released in flakes and fell off the substrate. Microscope images of such films can be seen in figure 8.5. Only few films deposited on stainless steel showed poor adhesion under certain conditions. This means that the film starts to release at the edge of the substrate but still sticks to it in the middle.

When an amorphous silicon layer was used between metal and DLC, the film system always adhered very well, if the substrate has been cleaned in an argon plasma beforehand. No difference for different substrate temperatures could be observed and adhesion was good for a wide range of power and deposition time. Without cleaning in argon, only some films adhered slightly.

8.2.1 Intrinsic stress of DLC/a-Si:H film systems

Decisive for the adhesion of a film to the substrate in addition to the strength of the interfacial bonds is the intrinsic stress inside the film leading to delamination of the film when the stress is too high. To measure the intrinsic stress of the DLC films and
to study the effect of the intermediate a-Si:H layer on the intrinsic stress of the DLC film, different films were deposited on pure silicon wafers and the stresses of the films were measured as described in chapter 3.7. The results are displayed in figure 8.6. The compressive stress of two DLC films different in thickness and deposited with unequal self-biases is plotted versus the thickness of the intermediate a-Si:H layer between DLC film and silicon wafer. Although compressive stresses are by convention negative and tensile stresses positive, the compressive stresses measured here are displayed with positive values.

Without intermediate a-Si:H film the stress is 2.9 GPa for the 325 nm thick DLC film (red squares) and 1.6 GPa for the 235 nm thick DLC film (black squares). Both films were deposited for 40 minutes, the thinner one at 20 W, the thicker one at 40 W. It is obvious that the stress is higher for the thicker film even though the self-bias is higher in this case than for the thinner film.

The presence of the amorphous silicon film lowers the compressive stress bit by bit until it saturates. This means that although the total film thickness increases the compressive stress of the film system decreases. This observation can be explained with the fact that the amorphous silicon film somehow absorbs the intrinsic stress of the DLC film. The amorphous network leads to cushioning of the strains between surface and DLC film. This is a reason for the better adhesion of (thin) DLC films on metals when an a-Si:H intermediate layer is used. When the DLC film is thicker (~ 1 µm) it may not work since the influence of the interface DLC-a-Si:H is to small in this case. It may be assumed that a ratio of DLC film thickness to a-Si:H film thickness of 2 is optimum.
8.2.2 Results from cavitation erosion measurements

To get more insight into the quality of the adhesion of the films and into the mechanism of failure, cavitation erosion measurements have been performed on selected film systems deposited on metal. a-Si:H/DLC double layers with different film thickness have been deposited on three polished nickel substrates. The thickness of the amorphous silicon film on the first sample was 26 nm and the thickness of the DLC film 58 nm. On the second sample the thickness of the a-Si:H film was held constant and that of the DLC film was almost twice the thickness of the first sample. On the third sample the thickness of the silicon film was only half that of the first silicon film and the thickness of the DLC film was equal compared to the first sample. All three samples have been tested with the cavitation erosion. The aim was to detect correlations between film thickness and bonding strength. The area of damaged regions versus film thickness is depicted in figure 8.7. No dependence of the thickness of the DLC film can be observed, samples one and two show almost equal damaged areas after 5000 s cavitation. In contrast to that an a-Si:H film half of thickness (sample three)
leads to significantly higher area damage. This film is responsible for the adhesion of the film system on the metal substrate. It seems that the bonding strength of a thin a-Si:H film is much lower than for a film twice as thick. This effect might occur due to the higher intrinsic stress in case of the thin a-Si:H film (see figure 8.6).

To investigate the mechanism of failure of the a-Si:H/DLC films on metals, Scanning Electron Microscope (SEM) images of a-Si:H/DLC on a stainless steel sample in different stages of damage have been taken. The thickness of the a-Si:H film was 29 nm, the thickness of the DLC film 92 nm. Figure 8.8 shows the surface damage after one hour of cavitation. It is obvious that the film is still on the metal substrate and that neither adhesive nor cohesive failure of the film can be observed. Instead, the formation of cracks due to curvature of the substrate is visible. Since the a-Si:H/DLC layer is very thin the metal below suffers from cavitation admission showing deformation and damage. This leads to topology changes of the metal surface which has influence on the thin film on top. A stronger deformation of the surface leads to formation of cracks in the film.

**Figure 8.7:** Influence of the film thickness on the damaged area for different film systems after cavitation tests of 5000 s.
In [109] the damage of different metals due to cavitation erosion has been investigated. In this work, similar plastic deformation of the surface of different steels and other metals have been observed. This is the first step out of four characteristic levels of the damage due to cavitation erosion. In this step, no mass loss (of the metal substrate) can be observed.

With proceeding cavitation more damage and mass lost of the substrate can be observed. Stronger erosion of the metal leads to removal of the film system of the surface. In figure 8.9 strong damage of the metal surface can be observed after five hours of cavitation. The a-Si:H/DLC layer has been removed in large surfaces. Only in small areas remaining film fragments are visible (darker areas). They are characterised by distinctive cracks. Thus, the adhesion of the film system on the substrate in principle is good and its destruction is only due to deformation and damage of the substrate. Increasing a-Si:H film thickness leads to longer resistance of the substrate and thus better adhesion of the film.

To evade the problem of substrate destruction and to characterise the mechanism of failure of the film system itself cavitation admission on a-Si:H/DLC films deposited on a silicon wafer has been performed. In this case the thickness of the amorphous silicon film was 28 nm and of the DLC film 56 nm. Damage due to erosion developed much slower in the case of a silicon substrate because no deformation of the substrate like in the case of metal occurred. After 20000 s of cavitation first removal of the film system could be observed by eye. At this stage the silvery silicon wafer appeared in
some areas of the sample, giving a good contrast to the brownish film.

SEM images in this area reveal sharp defined holes in the range of several μm in diameter where the film system has been totally removed. This is clearly adhesive failure, meaning that the film does not fail itself and is removed bit by bit (cohesive failure), but is removed as a whole because of failure of the bonding to the substrate. That means that as long as the bonding between metal substrate and a-Si:H intermediate layer is strong enough and the load of the metal substrate is low enough no damage of the film system can be expected. This is especially important for biomedical applications where wear debris of the coating could lead to inflammation or failure of the implant. Of course, good adhesion of the coating as a whole to the metal substrate
has to be guaranteed to extend the lifetime of the implant.

The adhesion between a-Si:H and DLC is achieved through the strong bonding of forming SiC. The formation of SiC in a plasma process has been shown in chapter 7. With a gradient layer going from 100 % silicon to 100 % DLC the bonding strength at this interface could even be increased.

In regions of strong cavitation exposure the formation of so called whiskers can be observed (figure 8.11). Whiskers usually are tiny, filiform hairs in a crystalline form. The effect is primarily seen on elemental metals but also occurs with other materials such as graphite, silicon and iron. The material of the whiskers found here is probably silicon. The mechanism behind whisker growth is not well understood yet, but seems to be encouraged by compressive mechanical stresses which appear during cavitation admission.

8.2.3 Results from tensile tests

To investigate the maximum elongation of the film system before the formation of cracks occurs tensile tests have been performed. For this purpose a miniature mechanical test rig from Kammrath & Weiss was used for in-situ pulling and straining to failure of the film system in a scanning electron microscope of type Jeol JSM-840A. For the tensile tests, film systems consisting of DLC/a-Si:H are deposited on metal samples with a special shape (see figure 8.12).
Materials generally exhibit a very linear stress-strain relationship up to a well defined yield point (see figure 8.13). The linear portion of the curve is the elastic region and the slope is the modulus of elasticity or Young’s Modulus. In this region the strain follows Hook’s law and the deformation totally disappears when the stress is released. After the yield point the curve typically decreases slightly due to dislocations. As deformation continues the stress increases due to strain hardening until it reaches the ultimate strength. Until this point the cross-sectional area decreases uniformly due to Poisson contractions. Beyond this point a neck forms where the local cross-sectional area decreases more quickly than the rest of the sample resulting in an increase in the true stress. Eventually the neck becomes unstable and the specimen ruptures.

For the tensile test, the sample coated with the film system is placed into the test rig, which is then placed into the SEM. During pulling the sample can be watched in situ with the SEM, video sequences can be recorded simultaneously. Figure 8.14
Figure 8.14: Strain applied to the metal sample versus total elongation of the sample. Denoted are the local elongations in percent.

shows the strain applied to the metal sample versus the total elongation of the sample. First elastic and then plastic deformation of the substrate are clearly observable.

During expansion of the sample, the relative elongation is not constant all over the sample but may be higher in the thinner part of it. To determine the local elongation, two parallel lines (distance about 1 mm) have been "burned" into the sample perpendicular to the direction of traction with help of the electron beam of the SEM. During the tensile test the machine was stopped several times (vertical lines in figure 8.14) to measure the distance between the lines in order to determine the actual local elongation in between. The area between the lines was carefully watched to observe the occurrence of cracks. When the formation of cracks could be observed, the pulling was stopped and the actual local elongation in the area where the cracks occurred was measured.

In a first test with a DLC/a-Si:H film system deposited on stainless steel substrates
local elongations up to 4.4 % could be achieved until first cracks became visible (figure 8.15). In this case the a-Si:H film was 36 nm thick, the DLC film 126 nm. The second sample has been heated during deposition and the film thicknesses were 28 nm and 169 nm for a-Si:H and DLC, respectively. Here, the maximum elongation was only 2.4 %, may be due to the thinner amorphous silicon film.

An elongation of more than 4 % is a good result for the first test. But since elongations of up to 8 % can occur during the phase transition of NiTi, further tests have to be performed to find the optimal deposition parameters for maximal elongation.

It should be noted that under strain a uniform network of cracks develops in the film system instead of one big single crack at one particular position of the surface.

8.3 Summary

In this chapter it has been shown that the adhesion of DLC on different metals is strongly increased with the use of an intermediate layer of a-Si:H between DLC and metal. Without this layer adhesion of DLC on stainless steel is quite poor and on other metals like copper, nickel and NiTi not possible at all. A preliminary argon sputter-process for the removal of contamination of the surface and of the oxide layer is crucial for a good adhesion of the film system.

The growth of the a-Si:H and subsequent of the DLC film can be watched during growth by in situ ellipsometry. To deposit films with a designated thickness the plasma process can be stopped when certain values for $\Psi$ and $\Delta$ are reached.
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TOF-SIMS measurements reveal that contamination of materials from other samples lying in the reactor at the same time can be found on all samples. It should therefore be ensured that only samples made of one material are present in the plasma chamber. The TOF-SIMS results also show the presence of SiC at the interface DLC–silicon film and of different silicides at the interface silicon-metal, depending on the metal. These stable compounds ensure the strong adhesion of the films among themselves and to the substrate.

The use of an amorphous silicon intermediate layer does not only ensure good chemical bonding between DLC and metal but it also leads to a decrease of the internal stress of the film system. The stress of film systems with a DLC film in the range of several hundred nm could be decreased to half the stress of the pure DLC film. It seems that an a-Si:H film half as thick as the DLC film leads to best results.

Cavitation erosion measurements show that the failure mechanism of the DLC/a-Si:H film system under load is adhesive. That means that the film system does not fail cohesive (removal bit by bit) which could lead to wear debris and therefore inflammations of the surrounding tissue in the case of a biomedical application. The crucial point is to ensure good adhesion of the film system to the substrate.

When the film system is exposed to strain it shows the formation of a network of numerous small cracks. This is preferred to the formation of one big crack under strain because the wear resistance can be assured longer in this case. First formation of cracks can be observed after a local elongation of about 4%.
Chapter 9

Summary and Outlook

In this work the deposition of DLC films on different metals via plasma enhanced chemical vapour deposition (PECVD) has been investigated. The coating of various metals with a wear- and corrosion-resistant, and for some applications additionally biocompatible layer is desirable in different technical fields. Up to now the coating of various metals with DLC films has not been possible at all. Other metals such as stainless steel could only be coated with a DLC film of limited thickness because of the strong internal stresses emerging in the deposited films. Therefore, a new approach was necessary to enable the good adhesion of DLC to metals.

The low adhesion of a-C:H films on metals is due to poor chemical binding between most metals and carbon. To enable the coating of metals like stainless steel, copper, nickel or in particular the shape memory alloy NiTi with DLC films, the concept of an intermediate layer between substrate and DLC film has been applied in this work. A thin a-Si:H film has been used to improve chemical binding between metal and DLC and therefore to increase the adhesion. The investigations have shown that the adhesion of DLC on the metals under study has in fact been improved considerably by using an intermediate layer of a-Si:H. A thickness of several 10 nm is sufficient for the intermediation of the adhesion. The film system consisting of a-Si:H and DLC showed excellent adhesion on copper, stainless steel, nickel, and NiTi. The films have been systematically characterised and properties like hydrogen content, optical properties and chemical composition have been determined.

The a-Si:H and a-C:H films have been deposited in a capacitively coupled low temperature plasma with an excitation frequency of 13.56 MHz. This process enables the
coating of temperature sensitive materials as well. Silane (SiH\(_4\), diluted in argon) and acetylene (C\(_2\)H\(_2\)) have been used to deposit thin amorphous hydrogenated silicon and carbon films, respectively. The coating proceeds in three consecutive steps consisting of argon sputtering, deposition of a-Si:H and subsequent deposition of a-C:H, without removing the sample out of the vacuum reactor in the mean time. The argon sputtering serves to remove the native oxide layer and impurities present on the surface of the metals.

The formation of nanoparticles in both types of plasmas has been avoided to obtain homogeneous films. The deposited amorphous silicon (a-Si:H) and amorphous carbon (a-C:H) films have been characterised thoroughly before the deposition on metal substrates.

One decisive property of the films is their hardness. The hardness is mainly controlled by the hydrogen content of the film. Therefore, the hydrogen content of the a-Si:H films has been measured by FTIR. The refractive index is an empirical measure for the hydrogen content and therefore for the hardness of the film. Hence, the hardness of the DLC films has been determined via the refractive index measured by optical ellipsometry.

The growth rates of the a-Si:H films lie in the range from 5 to 14 nm/min, depending on applied power and substrate temperature. The growth rate of a-Si:H films decreases significantly with increasing substrate temperature mainly due to thermal desorption of growth precursors on the surface.

Via FTIR the hydrogen content C\(_H\) of a-Si:H films deposited at different substrate temperatures has been determined. Without substrate heating C\(_H\) lies in the range of 30 at. % and decreases down to about 15 at. % for samples heated at 320 °C. The hydrogen of films with a high C\(_H\) is mainly bonded in monohydrides whereas the ratio of mono- and dihydrides in films with lower hydrogen content is almost equal. With less hydrogen in the amorphous silicon film the refractive index \(n\) increases from about 3.85 to about 4.05 due to a higher film density. The bandgap decreases slightly with increasing \(n\) and lies in the range of 1.8 eV.

The hard a-C:H films (DLC) have been deposited from acetylene plasmas. The growth rate of the DLC films lies in the range from 5 to 20 nm/min, depending on
applied power. Higher substrate temperatures have no influence on the growth rate, but on optical constants of the DLC films. The refractive index of the deposited films lies in the range of 2.18 to 2.34, which is quite high for DLC films and an indicator for very hard films and a low hydrogen content. Refractive index and index of absorption increase significantly with heating due to a lower hydrogen content and a higher film density. The surface roughness of deposited DLC films is about 1 nm, for heated and unheated substrates, and is therefore suitable for applications with blood or tissue contact.

When acetylene and silane are used simultaneously in a plasma, films with new properties compared to films deposited from either pure acetylene (a-C:H) or silane (a-Si:H) are formed. The result is an amorphous network consisting of silicon, carbon, and hydrogen in the form a-Si$_{1-x}$C$_x$:H. Here, $x$ represents the carbon concentration present in the film, which varies between 0 and 1, depending on the gas mixture in the plasma. Via XPS the formation of SiC in the films has been evidenced, leading to an increase of the optical bandgap up to 2.6. The refractive index $n$ of the deposited a-Si:C:H films lies in the range from 2.05 to 3.97, depending on the gas mixture and therefore silicon concentration in the film.

After the characterisation of the individual films, film systems consisting of a-Si:H and DLC films have been deposited on different metal substrates. Cavitation erosion tests reveal that the film system suffers from adhesive but not from cohesive failure under load. The attractive forces inside the film system are high enough to avoid the occurrence of damage and wear debris. Therefore, the adhesion to the substrate is the critical point to be optimised for different metal substrates. Results from TOF-SIMS measurements show the presence of SiC at the interface DLC–silicon film and of different silicides at the interface silicon–metal, depending on the metal. These stable compounds ensure the strong adhesion of the films among themselves and to the substrate. The use of an amorphous silicon intermediate layer does not only ensure good chemical bonding between DLC and metal but it also lowers the internal stress of the film system. The stress of film systems with a DLC film in the range of several hundred nm could be decreased to half the stress of the pure DLC film. It seems that an a-Si:H film half as thick as the DLC film leads to best results.
Tensile tests reveal the formation of a uniform network of small cracks when the film system is exposed to strain. This is preferred to the formation of one big crack under strain because the wear resistance can be assured longer in this case. First formation of cracks can be observed after a local elongation of about 4 %.

For the first time a reliable DLC coating of metals has been accomplished via the use of an intermediate layer of a-Si:H between metal and DLC film. Best results ever in the realm of coating metals with wear-resistant coatings have been achieved regarding adhesion as well as wear of the film system. The outstanding performance of the film system under load promises usability for various applications. Therefore, continuative investigations on the optimisation of the film system are intended.

In future, further systematic investigations have to be performed to reveal the influence of parameters like film thickness, hydrogen content, and substrate temperature on the adhesion of the film system on metals. The adhesion is to measure quantitatively by a nano scratch-tester which is applicable especially for very thin films. Such a device has not been accessible up to now. The influence of the above mentioned parameters on the elasticity of the film system will also be investigated in more detail in the near future. In doing so, more tensile tests will be performed to find appropriate conditions under which the film system can be elongated as much as possible without showing the occurrence of cracks. To achieve a smooth transition from amorphous silicon film to amorphous carbon film the a-Si:C:H films presented in chapter 7 will be used in form of a gradient layer going from 100 % a-Si:H to 100 % a-C:H. It may be expected that the use of a single film instead of a film system with an interface between a-Si:H and DLC leads to an even better stability.

The results obtained in this work show that it is possible to coat various metals with DLC films. The findings are basis for subsequent activities in this field and present basic knowledge for further developments of the technique for coating metals with wear- and corrosion-resistant coatings.
Bibliography


Appendix A

Rutherford Backscattering Results

In this chapter the results from Rutherford Backscattering measurements for a-C:H, a-Si:H, and a-Si:C:H films are shown.

The broad peak around channel 150 denoted to carbon decreases and vanishes from pure a-C:H to pure a-Si:H films. In contrast, the shoulder around channel 300-400 (silicon in film) gets more pronounced with increasing silicon content in the films. The signal for argon around channel 450 is biggest for a pure a-Si:H film (figure A.11).

Figure A.1: Measured RBS spectrum of an a-C:H film.
Figure A.2: Measured RBS spectrum of an a-Si$_{1-x}$:C$_x$:H film with $x=0.85$.

Figure A.3: Measured RBS spectrum of an a-Si$_{1-x}$:C$_x$:H film with $x=0.76$. 
Figure A.4: Measured RBS spectrum of an a-Si$_{1-x}$:C$_x$:H film with x=0.72.

Figure A.5: Measured RBS spectrum of an a-Si$_{1-x}$:C$_x$:H film with x=0.73.
Figure A.6: Measured RBS spectrum of an a-Si$_{1-x}$:C$_x$:H film with $x=0.67$.

Figure A.7: Measured RBS spectrum of an a-Si$_{1-x}$:C$_x$:H film with $x=0.62$. 
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Figure A.8: Measured RBS spectrum of an a-Si$_{1-x}$C$_x$H film with $x=0.50$.

Figure A.9: Measured RBS spectrum of an a-Si$_{1-x}$C$_x$H film with $x=0.40$. 
Figure A.10: Measured RBS spectrum of an a-Si$_{1-x}$:C$_x$:H film with $x=0.31$.

Figure A.11: Measured RBS spectrum of an a-Si:H film.
Appendix B

TOF-SIMS Results

TOF-SIMS measurements of a-Si:H and DLC/a-Si:H films on different metal substrates are displayed in this chapter.

The results of figures B.7 and B.8 have been obtained from heated substrates. For the sake of lucidity some intensities are divided by a factor of 100 and are labelled in the legend with ”/100”.

Figure B.1: TOF-SIMS depth profile of a-Si:H on stainless steel.
Figure B.2: TOF-SIMS depth profile of DLC/a-Si:H on stainless steel.
Figure B.3: TOF-SIMS depth profile of a-Si:H on nickel.
Figure B.4: TOF-SIMS depth profile of DLC/a-Si:H on nickel.
Figure B.5: TOF-SIMS depth profile of a-Si:H on copper.
Figure B.6: TOF-SIMS depth profile of DLC/a-Si:H on copper.
Figure B.7: TOF-SIMS depth profile of DLC/a-Si:H on heated NiTi.
Figure B.8: TOF-SIMS depth profile of DLC/a-Si:H on heated stainless steel.
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