Growth and Characterization of Carbon-Metal-Nanocomposite- Thin-Films and Self-Organized Layer Growth

Dissertation

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Chapter 1.

Introduction

The extreme properties of diamond-like films makes them very interesting for various applications. The most well-known property is the high hardness in the sp^3 -bonded diamond form. Since diamond is also a wide band gap semiconductor material with excellent thermal conductivity, it has been utilized in high power and high frequency electronic components, heat sinks for integrated circuits as well as optical windows and other optical components [1, 2]. There is also a growing interest in using carbon-based materials as field emission devices and thin film transistors [3]. More recently, superconductivity was found in B-doped diamond below 2 K [4] and in W-doped amorphous carbon below 3.8 K [5].

The properties of a-C can vary between those of graphite and diamond depending on its ratio of sp^2 to sp^3 bonded carbon atoms. If the sp^3 bonding ratio is high, these films are known as tetrahedral amorphous carbon (ta-C). The nucleation and growth mechanisms are well understood [1] and the growth techniques are limited to ion beam based techniques and pulsed laser deposition. New and more exciting is to prepare materials combining the outstanding diamond-like properties of a-C with other special morphological, optical, electrical or magnetic properties, which will open new fields of application. For this purpose two different approaches can be used: The combination of carbon and e.g. a metal during the growth by co-deposition [6–16] or the incorporation of suitable impurities by ion implantation [17, 18]. In this thesis both methods are used, but the focus is on the co-deposition of carbon and metal with the aim to prepare carbon-metal nanocomposite thin films.

Amorphous carbon films can be used for different applications. The tribological properties as well as the biological compatibility turns them into possible coatings for medical implants [19–22]. Jing and co-workers demonstrated the improved cell adhesion and proliferation of human umbilical vein endothelial cells on micro-patterned a-C:H samples [23], while Popov et al. pointed out the bioproperties of nano-crystalline diamond/a-C composite films [24]. Pure a-C:H films can also be used as a gas diffusion barrier in PET bottles [25].

As reviewed by Grill, the diamond-like carbon films show low friction coefficients and low wear rates, which depend on the environment (humidity) [26]. The adhesion of these films can be optimized by introducing metals into these films, which results in carbon-metal nanocomposite films [16, 27]. A further optimization of the adhesion

and wear rate can be achieved by the creation of layered and gradient films. The effect of self-lubrication due to graphitization of the surface reduces the friction and is related to internal compressive stress in the films [28]. Additionally, the biological properties can be tuned by incorporation of certain metals e.g. silver [29–32].

Another interesting application of metal containing amorphous carbon films or carbon-metal nanocomposites originates from the great hardness of these films [33, 34]. The combination of diamond-like carbon (DLC) and a ceramic to a DLC-ceramic multilayer results in a film with a high hardness (23.8 Pa) and high adhesion (critical load higher than 20 N) for automotive applications [35].

The introduction of metals into the amorphous carbon matrix also modifies the optical absorption properties, e.g. a-C:Cr thin films can be used as coatings for solar absorbers as shown by Gampp and co-workers [36–39].

The simultaneous deposition of energetic species of two different elements (co-deposition) usually leads to homogeneously mixed films due to the energy of the atoms available for diffusion and rearrangement processes in subsurface and surface regions [40]. Using immiscible elements, a phase separation with precipitates (clusters) of one element within the other may occur. The deposition parameters (ion energy, provided stoichiometry, temperature) strongly influence the size and distribution of such clusters [14]. A number of studies have shown that this phase separation process can also result in the formation of a self-organized multilayer structure [15, 41–47].

Gerhards et al. presented a model which explains the formation of a multilayer structure by segregation of a fraction of metal atoms towards the film surface during ion deposition [15]. These atoms will form clusters on the surface. Due to the further impinging carbon and metal ions these clusters are subject to sputtering. The sputter coefficient S_M consisting of the sputter yield of the metal atoms sputtered by carbon ions and the sputter yield of metal atoms sputtered by metal ions can be calculated using SRIM simulations [48].

This sputter yield S_M turns out to be the key parameter of the transition from the growth mode of the homogeneous carbon-metal nanocomposites to the formation of a multilayer structure. If the sputter yield is $S_M > 1$, the clusters emerging on the surface cannot grow and after a short time a steady-state coverage of the carbon surface with metal clusters is reached. In case of $S_M < 1$, the clusters on the surface will grow and a layered structure of alternating carbon rich / metal deficient and carbon deficient / metal rich layers may form. The layer spacing depends on the sputtering coefficient S_M , which is a function of the ion energy E_{ion} , the fluence ratio r_f , and the fraction of metal atoms segregating to the surface f_{surf} [15]. The model is described in detail in Section 2.2 and some approximations in the model are discussed in Chapter 2.2.1.

There are various models for the evolution of the layered structure, each dedicated to special film preparation conditions. The different models are presented in detail in Chapter 2 as well as the growth model for the diamond-like carbon.

The techniques and setups used during this work are presented in Chapter 3. The focus is on the ion beam setups, which were the tools for the preparation of the amorphous carbon samples. The techniques utilized for the analysis of the films are described in Chapter 4.

Amorphous carbon films containing metal nano-particles can be prepared by magnetron sputter deposition. With this technique, amorphous carbon with copper or iron clusters has been prepared during former studies [49]. The results are summarized in Section 1.3. Recent studies pick up the results from Gerhards and co-workers, who prepared homogeneous a-C:Cu films by mass-selected ion beam deposition and explore the ion energy E_{ion} and fluence ratio r_f space with the aim of creating a multilayered morphology [14, 50]. The results are presented briefly in Chapter 5.

The carbon-metal nanocomposites were investigated in detail for the a-C:Ni system. The dependence of the film morphology on the deposition parameters ‘ion energy E_{ion} ’ and ‘fluence ratio r_f ’ is examined and compared to previous studies. These results for a-C:Ni films prepared by two different ion beam setups are discussed in detail in Chapter 6.

The metallic clusters in the amorphous carbon or any other matrix can have properties deviating from the bulk material. The properties are determined by the size and shape of these clusters. The optical absorption is, for instance, influenced by non-linear effects in small clusters [51–53]. A famous example are the gold nano-particles in the red windows seen in old churches. The interesting properties of small metal clusters and metal nano-particles in amorphous carbon are described briefly in Sections 1.1 and 1.2.

The magnetic properties of small clusters are interesting for the creation of media with a high recording density, since these require high coercive fields. This can be achieved by the introduction of small CoPt or FePt nano-particles in an amorphous carbon matrix [54–57].

In this work the magnetic and magneto-electronic properties of ta-C, doped with Gd via ion implantation were investigated. Gd is found to be always in a trivalent state, with a half-filled f electron shell ($J = S = 7/2$), which provides a large local moment. Gd-doped a-Si films have shown significant carrier-moment interactions, indicated by their spin-glass ground state, an unsaturated magnetization at high fields and enormous negative magneto resistance (MR) (10^4 at 1 K, in a 60 kOe field) [58, 59]. However, all interactions become smaller in Gd-doped a-Ge, which seems to be most likely due to a screening effect [60]. Therefore, one can speculate that the magneto resistance (MR) and characteristic temperature for moment-carrier interactions scales with the band gap. Since the band gap of a-C increases up to 2.5 eV with increasing sp^3 content [61], ta-C could be an ideal matrix. Previous studies show that Gd-doped a-C, which has been prepared via sputtering, is mostly sp^2 -bonded and thus exhibits only a small band gap. Nevertheless, a large negative magneto-resistance was found at low temperatures, comparable to that of a-Gd_xSi_{1-x} [62]. The results of this topic are summarized in Chapter 7.

Figure 1.1: Index of refraction n (top) and index of extinction k (bottom) depending on the photon energy for various gold cluster sizes (a: 2.0 nm, b: 2.3 nm, c: 2.6 nm, d: 3.7 nm). From [63].

Chapter 8 discusses a novel technique called surfactant-sputtering. This method utilizes the steady-state coverage of a surface with foreign atoms during ion beam erosion. The technique is described briefly together with the results on the a-C:Pt and a-C:W systems.

The thesis closes with a final conclusion and discussion and, additionally, an outlook on further research (Chapter 9).

1.1. Properties of Metal-Clusters

Agglomeration of atoms with sizes between 1 nm and 100 nm are called clusters in this thesis. These clusters show very different properties compared to bulk solids, e.g. regarding optical properties [53, 63–65]: Smaller clusters show a smaller index of refraction (Figure 1.1), or a deviating melting behavior [66] (larger clusters have a higher melting temperature than smaller clusters). These changes depend on the extreme surface-to-volume ratio of the systems. With decreasing cluster size this ratio increases. Additionally, the properties of free clusters deviate from clusters surrounded by a matrix or surrounded by other clusters.

During time-of-flight mass-spectroscopy of vaporized metal-clusters an increased intensity is found for so-called magic numbers of atoms [67]. These magic numbers can be explained by closed shells of certain elements in the *jellium model* [68–71]. The model neglects the charge distribution in the clusters and assumes a homogeneous charged background instead. The whole cluster is treated as a drop of liquid metal and the position of each single atom in the clusters is not taken into account. This model is suitable for silver clusters [67, 72] but not for copper and many other

Figure 1.2.: *The stability function for Ni clusters in dependence on the cluster size. The maxima indicate more stable cluster configurations. From [75].*

clusters. For copper an exclusive consideration of the electronic structure is not sufficient, but instead the geometric shape of the icosahedron copper clusters has to be taken into account [73]. An appropriately modified model then explains the magic numbers.

The mechanical stability of silver and copper clusters was examined by means of scanning tunneling microscopy (STM) [74]. The clusters were moved on a silicon (111)-(7×7)-surface by the tip of the STM. The silver clusters could be moved on the surface and create a ≈ 1.6 Å height track on the substrate, whereas the copper clusters do not move and break. The copper clusters exhibit a higher interaction with the substrate than the silver clusters due to stronger mixing of silicon and copper and formation of silicides at the interface. The silver clusters act like a liquid and wet the surface of the STM tip. This effect can be attributed to the low surface energy of silver.

Nickel clusters and their stability gained some interest in the past years [75–84]. The structure of small nickel clusters was investigated by Parks and co-workers by adsorption of molecular nitrogen [77]. In the size range from Ni_{49} to Ni_{71} the icosahedral packaging seemed to be the dominant structural configuration. These results are expanded with embedded-atom method (EAM) calculations by Grigoryan and co-workers [75, 81], explaining the stability of certain magic numbers (see Figure 1.2), which was already attributed to the closing of layers in the multilayered icosahedral packaging by Montejano-Carrizales and co-workers [78]. Grigoryan and co-workers also calculated the binding energy per nickel atom in clusters of the size N (Ni_N). The result is shown in Figure 1.3. The binding energy increases with increasing cluster size. This result is also approved by Zhou and co-workers, who calculated the stability of nickel clusters using particle swarm optimization and found a stability increase with the cluster size N .

Figure 1.3.: Binding energy per nickel atom as a function of size for the four energetically lowest isomers for N up to 150 (continuous curves) together with that of relaxed, spherical parts of the fcc crystal structure with an atom at the center (closed circles). The horizontal dashed lines mark the value for bulk Ni as obtained with the same method. From [75].

A dependency of the reaction cross-section for nickel clusters and carbon monoxide or methanol on the cluster size is found for small clusters, even the type of the reaction depends on the cluster size [85–87]. This dependence is attributed to the energy levels in the clusters and the HOMO-LUMO gap, which depends on the number of atoms in the cluster [87].

1.2. Metal Nano-Particles in Amorphous Carbon

In former studies of Gerhards and co-workers films of copper nano-clusters in an amorphous carbon (a-C) matrix (see Figure 1.4) were grown by mass-selected ion beam deposition (see Section 3.1). The copper ratio was varied between 0% and 50%. The copper clusters' sizes increase with the copper fraction while the sp^3 -bond ratio decreases. The mean clusters size was (3 - 4) nm for a copper fraction of 5% and increased up to 9 nm at 50% copper ratio. For other systems (a-C:(H,Co), a-C:(H,Cu)), the size distribution of clusters in amorphous hydrogen-containing carbon was investigated by Ivanov-Omskii et al. [88–90] and Kulikov et al. [91]. It was observed that the cluster size in the matrix increases with increasing metal content, which is also the case during annealing of the films. The optical density increases for copper doped a-C:H films with increasing copper content [92]. The non-linear optical $\chi^{(3)}$ susceptibility depends on the cluster size and the interaction of the clusters with the matrix (see e. g. Figure 1.5) [53, 93, 94].

Another interesting application of clusters in amorphous carbon results from magnetic clusters: The large coercive fields allows the use of small grains and therefore the production of media with high data densities [54, 55, 95]. Figure 1.6 shows the

Figure 1.4: High-resolution cross-section TEM images of an a-C:Cu film with 20% Cu grown at an ion energy of 40eV Cu^+ and 100eV C^+ by means of mass-selected ion beam deposition. From [14].

Figure 1.5.: Intrinsic non-linear optical susceptibility of third-order $\chi_m^{(3)}$ as function of the metal cluster diameter d . Closed circles: $\text{Cu}:\text{Al}_2\text{O}_3$ -film, open circles: $\text{Cu}:\text{SiO}_2$. The solid line represents a $1/d^3$ fit to the experimental data. From [93].

Figure 1.6.: Magnetization M of cobalt in carbon over temperature measured in a magnetic field of 100Oe. Different times (different symbols) correlate to different cluster sizes. Longer times correspond to larger clusters. From [95].

magnetization M of cobalt clusters depending on the temperature. The clusters were formed inside a cluster gun by a gas condensation process from dc magnetron sputtered cobalt in high pressure argon plasma. By varying the sputtering time before releasing the clusters from the source, the cluster size can be tuned. The indicated time in Figure 1.6 describes how long the clusters were deposited, therefore longer times correspond to larger clusters sizes (e. g. 25 s sputtering time results in a

Figure 1.7: *Fine structure of the temperature dependence on the resistance change in magnetron sputtered $(a-C:H)_{0.84}Cu_{0.16}$. From [97].*

cluster diameter of ≈ 9 nm). The blocking temperature decreases from $T_B = 325$ K over 250 K, to 130 K for cobalt clusters made with sputtering times of 25 s, 15 s, and 3 s, respectively.

Babonneau et al. studied the growth of iron and carbon by ion beam sputter co-deposition and found a columnar growth of iron-rich clusters. The magnetic investigation reveals an increasing coercive field strength with decreasing cluster size (and increasing cluster distances) [96].

The conduction mechanisms and their temperature dependence in the films depend on the size and form of the clusters and have been investigated for various systems ($(a-C:H)_{1-x}Cu_x$, $aC:Mo$, $Me-C:H$) [97, 98]. As an example the temperature dependence of the change of the electric resistance dR/RdT in magnetron sputtered $(a-C:H)_{0.84}Cu_{0.16}$ films was investigated by Lutsev and co-workers and is shown in Figure 1.7. They found a quasi-periodicity with $\Delta T = 5.8$ K for the resistance change with the temperature, which is explained by two different processes: There are either discrete levels in the energy spectrum of the potential well for the isolated metal clusters or reordering processes in the cluster structure take place [97], which leads to periodic changes of the resistance with temperature.

Nickel containing amorphous carbon films were investigated by Sylvestre and co-workers [99] and Kukićka and co-workers [100]. Sylvestre and co-workers deposited the films in a distributed electron cyclotron resonance (DECR) microwave plasma reactor by sputtering from a DC negatively polarized nickel target in an argon / methane atmosphere, while Kukićka and co-workers used an argon / acetylene plasma. Sylvestre et al. examined the film composition in dependence on the sputtering power and found an increase of the nickel content with the sputtering power. Additionally, the dielectric properties of the films was investigated and an increase

Figure 1.8.: Dielectric constant (ϵ') for Ni/a-C:H films deposited at different powers as function of the frequency at 25°. From [99].

Figure 1.9.: “Nanohardness and magnitude of residual stresses of Ni/a-C:H films as functions of the acetylene concentration in the gas phase.” From [100].

of the dielectric constant ϵ' with increasing nickel content in the Ni/a-C:H films up to 19% Ni was stated [99]. This phenomenon is induced by high polarizability of the conductive Ni clusters. Above 19% Ni dielectric instabilities appear which lead to a breakdown at frequencies below 100 Hz, due to a percolation of the clusters (see Figure 1.8).

Kukielka and co-workers investigated the Ni/a-C:H films in dependence on the acetylene (C_2H_2) concentration in the gas phase in the reactor and found a decrease of the relative nickel content of the films with increasing C_2H_2 concentration [100]. The nanohardness and residual stress of the films was examined: A maximum for the

Figure 1.10.: *The temperature dependence on the conductivity for some different Ni concentrations in the Ni:a-C:H films. From [101].*

nanohardness of 14 GPa and a minimum for the residual stress of -0.8 GPa was found for a composition of the films corresponding to the stoichiometry of Ni_3C . These values are an improvement relative to films grown in pure C_2H_2 (see Figure 1.9).

The electrical properties of Ni:a-C:H films were studied by Schultes and co-workers [101]. They deposited the films by low temperature r.f. diode sputtering in an argon/ethylen (C_2H_4) atmosphere. The films show an increase of the conductivity with the nickel content and a low temperature dependence on the conductivity for higher nickel contents as shown in Figure 1.10. Schultes and co-workers state that the temperature dependence on conductivity is normal metallic for high nickel concentrations and transfers to semi-conducting for low nickel concentrations. The aim was to prepare a film with a low temperature coefficient of the resistivity which is achieved for a (C_2H_4) concentration of 2.5% of the argon gas.

1.3. Review of Previous Work

In this section previous experiments to carbon-metal nanocomposite films are discussed which were done in the course of my diploma thesis. The final results of the experiments on the a-C:Cu and a-C:Fe systems mainly grown by reactive magnetron sputtering are summarized briefly.

1.3.1. Films Prepared by Magnetron Sputter Deposition

In the studies, mentioned above, metal containing amorphous carbon nanocomposite film have been grown by reactive magnetron sputtering using CH_4 as reactive gas and iron and copper as sputter targets [49]. The films were grown on p-type silicon which was mounted on a water-cooled sample holder to prevent heating during deposition. The composition of the films was varied by changing the target-substrate distance (3.5 cm - 7 cm), the rf-power (80 W - 120 W) and the gas volume ratio of argon to methane ($\text{Ar}/\text{CH}_4 = 15/1 - 1/1$).

Figure 1.11.: *Cross-section transmission electron microscopy overview of an a-C:Cu film. The glue originates from the preparation process. Several clusters are visible in an amorphous matrix. From [49].*

Figure 1.12.: *High-resolution cross-section transmission electron microscopic image of an a-C:Cu film. There are some crystalline clusters in an amorphous carbon matrix on top of the crystalline silicon substrate visible. The mean cluster diameter is about (5.7 ± 2.3) nm. From [49].*

The a-C:Cu system grown by Magnetron Sputter Deposition

For the a-C:Cu system the results are in good agreement with the results presented from Gerhards and co-workers for a-C:Cu grown by mass-selected ion beam deposition [14, 102]. A representative cross-section transmission electron microscopy of a film is shown in Figure 1.11 (overview) and Figure 1.12 (high-resolution). The film was grown at an argon/methane ratio of 9 sccm / 3 sccm, a target-substrate distance of 5.5 cm and a rf-power of 100W. In the images large clusters with up to 10 nm diameter and many smaller clusters are visible. The mean cluster diameter is about (5.7 ± 2.3) nm while the film is around 300 nm thick.

The films show a rising carbon fraction and decreasing copper fraction for an increasing methane concentration in the gas. The mean cluster diameter decreases from 8 nm (50 at% Cu) to 2.1 nm (>0.5 at% Cu) for decreasing copper concentration.

The a-C:Fe system grown by Magnetron Sputter Deposition

The second part of the diploma thesis deals with a-C:Fe nano-composite films. The films were grown under different conditions using the reactive magnetron sputter deposition. A typical a-C:Fe film is presented in the cross-section transmission electron microscopy images in Figures 1.13 and 1.14. The film was grown at a

Figure 1.13.: *Cross-section transmission electron microscopy image of an a-C:Fe film. The whole film is about 120 nm thick. From [49].*

Figure 1.14.: *High-resolution cross-section transmission electron microscopy image of an a-C:Fe film. The onset of a layered structure is visible above the silicon substrate. The mean cluster diameter is (3.7 ± 0.7) nm. From [49].*

gas ratio of argon/methane of 15/1, a target-substrate distance of 4 cm and a rf-power of 100 W. In the high resolution image (Figure 1.14) a weak onset of a layered structure is visible. The whole film is around 120 nm thick and the clusters in the amorphous matrix have a mean cluster diameter of (3.7 ± 0.7) nm.

The iron fraction of the samples increases with increasing gas ratio while the deposition rate decreases. The increase of the target-substrate distance has no strong effect on the iron concentration in the sample but the deposition rate decreases. The variation of the rf-power has also no strong effect on the composition but the deposition rate increases with increasing rf-power.

For all parameters metal-containing amorphous carbon nano-composite films emerge. The thickness and stoichiometry can be controlled within some limits by variation of the gas ratio, the target-substrate distance and the rf-power.

1.4. Diamond-Like-Carbon

The best known allotropes of carbon are graphite and diamond. Graphite is built of six-fold carbon-rings which are stacked in layers. Each carbon atom is surrounded by three neighbors and is therefore sp^2 hybridized. Graphite is a soft material due to weak van-der-Waals bonds between the layers. In the diamond phase each atom is surrounded by four neighbor atoms. The atoms are ordered in two combined face-

Figure 1.15.: Calculated atomic structure of amorphous carbon. Green atoms are sp^2 -bonded, while blue atoms are sp^3 -bonded. From [103].

Figure 1.16.: Ternary phase diagram of sp^2 -bonded, sp^3 -bonded amorphous carbon and hydrogen. From [104] and references therein.

Table 1.1.: Properties of ta-C films. Data taken from [104].

Hardness [GPa]	$\approx 60 - 80$
Density [g/cm ³]	≈ 3
sp^3 -bonding ratio [%]	≈ 80
Spec. resistance [Ωcm]	$\approx 10^{12}$
Optical bandgap [eV]	≈ 2.5
Index of refraction	≈ 2.4
Surface roughness [nm]	< 1
Transparency [cm ⁻¹]	4000-400
Compressive stress [GPa]	4 - 15

centered-cubic lattices resulting in a sp^3 hybridization. Besides the two crystalline allotropes graphite and diamond, the amorphous carbon exists, which contains sp^2 -bonded as well as sp^3 -bonded atoms (see Figure 1.15). At high sp^3 -bonding content, the material shows great hardness [105] and is called diamond-like-carbon (DLC). Another class of amorphous carbon structures are the hydrogen containing amorphous carbon films (see Figure 1.16). These films can be deposited using reactive magnetron sputter deposition (see Section 3.3). The metal containing amorphous carbon films deposited for this thesis by means of mass-selected ion beam deposition are hydrogen free.

Figure 1.17.: Phase diagram of the binary system Ni-Si. Various Ni_xSi_y phases exist. From [106].

The amorphous carbon is called tetrahedral amorphous carbon (ta-C) at sp^3 bonding ratios above 80%. It can be produced by various methods using energetic species including the mass-selected ion beam deposition (see Section 3.1). The important parameter for the formation of sp^3 -rich amorphous carbon is the deposition energy. The maximum sp^3 -bonding ratio of 80% is reached for 100 eV carbon atoms. The growth model is described in detail in Section 2.1. Due to the high sp^3 -bond content the films exhibit a high hardness (> 40 GPa), a mass density of ≈ 3 g/cm³ and other extreme properties summarized in Table 1.1.

1.5. Phase Diagrams

In this work films containing carbon, nickel or copper on silicon were grown and investigated. The solubility of one element in another is described by phase diagrams. The metals form various compounds with the silicon substrate (see e.g. Figure 1.17). This unwanted effect is prevented with a pure carbon coating of the substrate before growing the a-C:Me films (see Figure 1.18). For the binary system C-Cu no compounds exist (see Figure 1.19) while for the C-Ni systems at elevated temperatures a compound phase exists (see Figure 1.20). Therefore the co-deposition of carbon and copper should lead to completely phase separated films while the co-deposition of carbon and nickel may lead to the formation of a carbide phase.

Figure 1.18.: Phase diagram of the binary system C-Si. One compound CSi phase exists. From [106].

Figure 1.19.: Phase diagram of the binary system C-Cu. The C-Cu systems is a demixing system with no compound phase. From [106].

Figure 1.20.: Phase diagram of the binary system C-Ni. The C-Ni system is an almost demixing system with a compound phase existing at elevated temperatures. From [106].

Chapter 2.

Multilayer Structures of Metal-Nano-Clusters in a Host Matrix

Multilayer structures of metal nano-clusters are structures of metal-cluster-rich layers and metal-cluster-deficient layers in a host matrix of e.g. amorphous carbon or periodic variations of the concentration of one metal in another metal (e.g. in the Au-Ni system investigated by He and co-worker). The carbon based multilayer structures exhibit a higher wear resistance than pure amorphous carbon films [28]. There are two different ways of creating such structures: the alternating deposition of matrix material and metal clusters [27, 28, 47] or the simultaneous deposition of metal and matrix material under utilization of self-organizing effects in the system which lead to a demixing and an evolution of a multilayer structure [15, 41]. In References [15] and [41] amorphous carbon was used as matrix material. The films showed layer distance in the order of 10 nm.

In this chapter, first the growth of the pure matrix material amorphous carbon is described and then the various growth models for self-organized layer growth are discussed. Whereas the model of He and co-workers is the only one for a pure metal multilayer system, all others are carbon-metal nanocomposite multilayer systems.

2.1. Growth Model for Diamond Like Carbon

The matrix material for the metal cluster in this work is amorphous carbon. A specialty is tetrahedrally bonded amorphous carbon ta-C (see Section 1.4). The growth of ta-C is described by the cylindrical thermal spike model of Hofsäss et al. which considers each ion impact as a separated event [107]. Each impacting ion distributes its energy in a thermal spike. During the thermal spike the energy is partially transformed into lattice vibrations. These vibrations are generated in a small volume along the ion path and can cause local heating and melting. The energy distribution is not point-like but along the track of the ion through the material and a so-called cylindrical thermal spike forms. The part of the energy that is not transferred to lattice vibrations and rearrangements of the atoms in the

Figure 2.1: Schematic energy dependence of the length (a-c) and width (d) of a cylindrical thermal spike. For low energies (a): no collision. For mean energies (b): primary collision (m_p) and (c) for high energies: primary (m_p) and secondary collisions (m_s). $L_1 \leq L_2 \leq L_3$. From [107].

spike volume, is transferred to electronic excitations of the surrounding atoms. The radial distribution of the rearrangement processes is assumed to be Gaussian and longitudinal symmetric. These assumptions allow the calculation of the number of rearrangements n_t per incoming ion in relation to the number of atoms in the spike volume n_s :

$$\frac{n_t}{n_s} \approx \left(\frac{Q}{L}\right) \left(\frac{1}{E'}\right) \frac{ev_0}{4\pi ND} \exp(-\sigma^2/\sigma_c^2). \quad (2.1)$$

The needed values are: The energy Q transferred from the incoming ion to lattice vibrations, the length L and width σ of the spike, a characteristic width σ_c , the activation energy E' for one rearrangement process, the phonon frequency v_0 (in this case of the TO-phonons of diamond), the atomic density N and the thermal diffusion constant D .

The width of the thermal spike σ is determined by the width of the radial Gaussian. It is shown schematically in Figure 2.1 together with the spike length L and their energy dependence. Both values have a huge impact on the ratio of n_t to n_s . For low kinetic energies a spike sketched in Figure 2.1a will form without any collision. For this situation a minimal spike width of $\sigma_{\min} \approx 0.15$ nm is assumed (atomic distance in diamond-like carbon). For higher kinetic energies the situation in Figure 2.1b is reached: The ion creates primary displacements (m_P) and the width of the spike is nearly doubled. It is given that $L_2 \geq L_1$. A further increase of the kinetic energy results in primary (m_P) and secondary (m_S) displacements (see Figure 2.1c). The width of the spike σ depends on the ion energy and the ratio m_S/m_P . For the length

Figure 2.2.: n_t/n_s ratio calculated according to the “Cylindrical Thermal Spike” model and measured sp^3 -bonding ratios depending on the ion energy. From [107].

it is given $L_3 \geq L_2$. The Gaussian distributions for all three situations are sketched in Figure 2.1d. For a complete rearrangement of the spike volume $n_t/n_s \geq 1$ is required. In Figure 2.2 the n_t/n_s dependency on the ion energy is shown. Additionally the measured sp^3 -bonding ratio of amorphous carbon grown by mass-selected ion beam deposition at various energies is shown. A relation between the calculated n_t/n_s ratio and the experimentally determined value of the sp^3 -bonding ratio can easily be recognized.

The highest sp^3 -bonding ratio of around 80% can be reached with ion energies of $E_{\text{ion}} = (100 - 200)$ eV.

2.2. Growth Model for Multilayer Evolution During Mass-Selected Ion Beam Deposition

During the simultaneous deposition of carbon and various metals by means of mass-selected ion beam deposition of energetic particles (see Section 3.1) a self-organization effect resulting in a layered structure was found (see Figure 2.3) [15, 108]. Gerhards and co-workers proposed a model based on the interplay of subplantation, cluster formation, ion induced diffusion, inverse Ostwald ripening, surface segregation and sputtering [15]. The model will be described using the a-C:Au systems as a reference (see Figure 2.4).

During co-deposition of carbon and gold ions both ions will be implanted due to their kinetic energy just below the film surface ((1 - 3) nm) (Figure 2.4(1)). Since gold is immiscible in carbon it will diffuse toward the film surface with a fraction f_{surf} and will form small clusters (Figure 2.4(2)). The ion-induced diffusion is driven by the density gradient and the compressive stress in the film and is not

Figure 2.3.: Cross-section transmission electron microscopy image of an *a*-C:Au multilayer grown by means of mass-selected ion beam deposition with ion energies of (100-150) eV and a fluence ratio of C/Au = 80/20. There are four gold-rich layers visible in the EDX linescan (a) (marked by solid lines), which are marked by white arrows in the cross-section transmission electron microscopy image (b). The layers are separated by (9 - 13) nm. From [108].

Figure 2.4.: Sketch of the growth model for multilayer formation during deposition of energetic particles.

thermally activated. The clusters on the film surface can be removed (sputtered) by the incoming ions. The sputter yield S_M depends in the ion energy and the fluence ratio between carbon and gold ions $r_{\text{fluence}} = f_C/f_{\text{Au}}$. If the sputter yield is $S_M > 1$, the clusters cannot grow and instead a steady-state coverage of the film surface with gold atoms establishes.

If the sputter yield is $S_M < 1$ the clusters on the surface can grow due to the incoming gold ions and the gold atom segregating to the surface. The incoming carbon ions promote the film growth below the clusters and the carbon, which is implanted into the clusters (Figure 2.4(3)), will diffuse to the cluster's surface. There it will fill the gaps between the clusters (Figure 2.4(4)) and eventually overgrow the cluster layer (Figure 2.4(5)). The growth of the clusters will continue until the depth of the cluster below the surface is larger than the implantation depth r_I of the gold ions (Figure 2.4(6)). One layer is completed if neither carbon nor gold contribute to its growth (Figure 2.4(7)) and the process starts again at (Figure 2.4(2)). A layer periodicity in the order of 10 nm establishes.

The model allows the estimation of the layer period t based on the knowledge of following values:

- The width of the metal-cluster-rich layer d_M , which can be determined by means of cross-section transmission electron microscopy.
- The atom density of the metal n_M and of carbon n_C .
- The mean volume fraction of the surface covered with the metal clusters c .
- The fluence ratio of incoming carbon to metal ions during deposition $r_f = f_C/f_{Me}$.

- The total metal sputtering yield $S_M = r_f \cdot S_{CM} + S_{MM}$, which contains the sputter yield of the incoming carbon C^+ ions on the metal clusters S_{CM} and the sputter yield of the incoming metal $^+$ ions on the metal clusters S_{MM} .
- The sputter yield of the incoming carbon C^+ ions on the amorphous carbon S_{CC} .
- The fraction of metal atoms segregating to the film surface f_{surf} .

by using equation 2.2:

$$t = d_M \left[1 + \frac{n_{MC}}{(1 - S_M) f_{\text{surf}}} \times \left(\frac{1}{n_C} r_{\text{fluence}} (1 - S_{CC}) + \frac{1}{n_M} (1 - f_{\text{surf}}) \right) \right] . \quad (2.2)$$

The sputter yields can be determined by using SRIM simulations [48].

The simple model allows the estimations of the layer period and the prediction of the layer growth regime by calculation of the total metal sputtering yield S_M . For $S_M < 1$ a layer growth can be expected, while for $S_M > 1$ a layer growth is only possible if the surface segregation factor $f_{\text{surf}} \ll 1$, which is e. g. given for the carbide forming system a-C:Fe [15, 46].

2.2.1. Approximations in the Multilayer Growth Model of Gerhards and Co-workers

The model of Gerhards and Co-workers described in Section 2.2 is based on the interplay of subplantation, cluster formation, ion induced diffusion, inverse Ostwald ripening, surface segregation and sputtering [15]. The model neglects some effects that may become important for certain deposition conditions. These effects will be discussed in the following sections.

Backscattering of Atoms from the Film

The first effect, which was neglected is the backscattering or reflection of ions from the surface. This could happen especially at low ion energies and decreases the overall deposition of the reflected species. The backscattering can be determined by SRIM simulations and the results are shown in Figure 2.5 for the a-C:Ni system.

The backscattering of carbon on a carbon surface and nickel on a nickel surface is quite low and can be neglected. The backscattering of nickel on a carbon surface is not shown, since it is zero due to the mass difference. The most important result is the high backscattering rate of carbon on a nickel surface. Since the model assumes a segregation of nickel towards the surface due to the ion induced diffusion in the non mixing system, a metal rich surface layer can be expected. Therefore, a high carbon loss due to backscattering may occur. This may explain, together with the carbon sputtering, that the films contains around 60% of the deposited carbon according

Figure 2.5.: *The backscattering ratio for the deposition of carbon on carbon (C-C), carbon on nickel (C-Ni) and nickel on nickel (Ni-Ni) in dependence on the ion energy.*

to the charge measurement. A precise value of the backscattering ratio for each film cannot be given, since the backscattering ratio scales with the metal content of the surface and surface near regions of the films, which will change in during the deposition process (cluster layer formation and overgrowth).

Sputtering of Carbon by Metal Ions

The sputtering of carbon in the film and on the surface by incoming metal ions is neglected, since it is small compared to all other sputter yields in the system. This is shown for the a-C:Ni system in Figure 6.2. The assumption is valid even for energies of $E_{ion} = 1000$ eV, where the nickel-carbon sputter yield is $S_{NiC} = 0.24$ atoms/ion, which is less than the carbon self-sputtering of $S_{CC} = 0.30$ atoms/ion. It can be concluded, that the carbon sputtering by metal ions can be neglected for a pure carbon surface. If the surface is not pure carbon, but a mixture of carbon and metal (clusters), the carbon sputter yield may increase due to the so-called sputter yield amplification effect [109–111]. E. g. the irradiation of a surface consisting of 10 at.% carbon and 90 at.% nickel with 100 eV nickel ions result in a carbon sputter yield of $S_{NiC} = 0.005$ atoms/ion which is about three times higher than for a pure carbon film. The increase of the sputter yield is explained by the collision cascade of the incoming nickel ions, which may get reflected towards the film (or cluster) surface, where it may eject carbon atoms.

Since the films consist of metallic clusters surrounded and covered by carbon layers, at least at some stages of the film growth, this effect may have an impact on the film growth and the structure evolution. The carbon loss during the film growth gets dependent on the surface composition, which changes in time. Therefore, it can only be introduced into the model by dynamic simulation of the whole film growth process.

The TRIDYN program, mentioned already in the Section 8, uses a dynamic version of the static SRIM code, taking ballistic transport into account. The segregation towards the surface is included in a modified version of the code, but a layer growth on the surface is not covered correctly.

Steady-state Coverage of the Film Surface by Metal Atoms

For conditions of high total metal sputter yields ($S_M > 1$), a metal rich surface layer cannot evolve due to severe sputtering of the metal atoms. The continuously subplanted metal atoms, will segregate to the surface, where they can be sputtered, and form a steady-state coverage. This coverage can be estimated by following calculation [112]:

The change of the coverage $d\sigma(t)/dt$ is given in linear approximation by two terms: The growth of the coverage due to the atoms segregating to the surface and the sputtering of the existing layer by the incoming ions. The growth term is determined by the fraction of metal ions segregating to the surface f_{surf} and the flux of the metal ions j_{Me} : $j_{\text{Me}} \cdot f_{\text{surf}}$; and the sputtering term is given by the flux of sputtered atom $j_{\text{Me}} \cdot S_M$ and the time-dependend coverage $\sigma(t)$ of the surface scaled by a characteristic coverage σ_c . The resulting rate equation is given by:

$$\frac{d\sigma(t)}{dt} = j_{\text{Me}} \cdot f_{\text{surf}} - j_{\text{Me}} \cdot S_M \cdot \frac{\sigma(t)}{\sigma_c}$$

which can be solved with an exponential Ansatz with

$$\sigma(t) = \frac{\sigma_c}{S_M} \cdot f_{\text{surf}} (1 - e^{-t \cdot j_{\text{Me}} \cdot S_M / \sigma_c})$$

For long times this could be evaluated to the steady-state coverage:

$$\sigma(\infty) = \frac{\sigma_c}{S_M} \cdot f_{\text{surf}}$$

The steady-state coverage depends only on the total metal sputtering yield and the surface segregation factor. For a high sputter yield only a low coverage can establish. Additionally, for total metal sputtering yields of $S_M < 1$, this estimation is inapplicable, since the film will grow with time.

The steady-state coverage may effect the effective sputter yields for the carbon and metal atoms due to the already mentioned sputter yield amplification effect.

Melting of Clusters due to Deposited Energy

The last point in this collection is the melting of cluster on the surface or just below the surface due to the incoming ions.

The clusters in the films have sizes of some nm, which is enough to stop the incoming ions at low energies completely. Therefore, the complete energy of one ion is deposited in a nm-sized cluster. For example, a 100 eV nickel ion is stopped in a cluster of a diameter of 2 nm. The cluster volume consist of around 400 atoms, resulting in an energy transfer of $E_{\text{atom}} \approx 250 \text{ meV} / \text{atom}$. This can be converted to a temperature by division with the Boltzmann constant of $k_B = 8.617 \cdot 10^{-5} \text{ eV/K}$: $T = E_{\text{atom}}/k_B \approx 3000 \text{ K}$.

This estimated temperature is extremely high and can cause the cluster to melt. The melted cluster may have different properties concerning sputtering and diffusion as well as stability against ion impacts. This modifies the sputter yields and segregation factors used in the rate equation at certain stage of the film growth.

Summary

The mentioned effects, which are not covered by the simple approach of the rate equation may have an effect on the formation of the layered structure. The basic parameters of the rate equation become time and growth stage dependent, which can only be solved by dynamic simulation of the film growth. Since the processes during the film deposition cannot be described by simple equations, the rate equation is a good estimation of the underlying processes. For some situation, where one of the effects become important, the input parameters should be inspected and adjusted if necessary, e. g. the sputter yields for metal and carbon and the surface segregation factor.

To include all effects, a molecular dynamics simulations is necessary, which takes the dynamic evolution of the film and the film's surface into account.

2.3. Catalytic Growth Model for Multilayer Evolution

For the simultaneous deposition of carbon and various metals by means of reactive magnetron sputter deposition (see Section 3.3) also a self-organizing effect resulting in layered structures was found by Wu and Ting. The model proposed in Reference [41] is based on the characteristics of the reactive deposition: Carbon and metal (Me) are deposited simultaneously (see Figure 2.6). The carbon is deposited from the gas phase as CH_X -radicals which are formed in the plasma. For multilayer evolution it is required that the deposition rate of the metal, which is sputtered from a solid target, is higher than the deposition rate of carbon. This results in a growth of a metal-rich layer on the substrate surface. This layer acts as a catalyst for the carbon growth, since carbon has to be released from the CH_X -radicals before precipitation on the surface. Therefore, the deposition rate of carbon increases and

Figure 2.6.: Catalytic growth model for the evolution of a multilayer structure. Adapted from [42, 113].

Figure 2.7.: Cross-section transmission electron microscopy images of Ni-DLC, Cu-DLC and Pt-DLC multilayer films deposited by means of reactive magnetron sputter deposition with an Ar/CH₄-ratio of 3 and a rf-power of 100 W. From [41].

a carbon-rich, metal-deficient layer starts to grow. With increasing thickness of this layer, the catalytic effect of the underlying metal-rich layer decreases; and therefore, the carbon deposition rate decreases. Now the metal deposition rate is again higher than the carbon deposition rate and the process starts again.

The model explains the evolution of the layered structure for the applied metals nickel, copper and platinum (see Figure 2.7). For an argon/methane ratio of 3/1 for all used metals a layered structure evolves and is visible in the cross-section transmission electron microscopy images. For an argon/methane ratio of 1/1 the nickel containing film do not show a layered structure while the others do. This is explained by the deposition rate of the metals which is lowest for nickel. In this case the deposition rate of nickel is equal or lower than the deposition rate of carbon.

The deposition rate of nickel rises with respect to the carbon deposition rate if the argon/methane ratio is increased to 3/1 and a layered structure appears. The exact interpretation of the influence of the gas mixing ratio on the film growth is difficult, due to the complexity of the process. The argon does not contribute directly to the film growth but sputters the target and the film. The more argon is in the gas mixture, the more both are sputtered. Additionally the plasma itself changes: the plasma density depends on the composition of the gas due to the different ionization probabilities of argon and methane. Therefore, the influence of the gas mixing ratio and the rf-power on the film growth is not trivial.

2.4. Multilayer Evolution Found by He and Co-workers

He and co-workers found spontaneous multilayer formation in the system AuNi. This shows that the layer structure evolution is not limited to carbon/metal systems.

2.4.1. Experimental Results by He and Co-workers

In their studies He and co-workers deposited Au-Ni films on Si $\langle 100 \rangle$ substrates [114]. The deposition was carried out using e-beam evaporation of nickel and gold simultaneously with deposition rates of approximately 0.3 Å/s for gold and 0.9 Å/s for nickel, respectively. The films were irradiated during deposition with an assisting argon ion beam ((100 - 800) eV, 25 $\mu\text{A}/\text{cm}^2$ or 50 $\mu\text{A}/\text{cm}^2$). The film morphology was analyzed using specular x-ray reflectivity measurements (see Figure 2.8). The Bragg peaks visible in the spectra 2.8(a) correspond to different superlattice periodicities which are calculated in Figure 2.8(b) for the different assisting ion beam energies and currents. A clear increase with the ion energy is visible while for no assisting ion beam no periodicity evolves. The dent visible for ion energies around (300 - 400) eV in the data for the 50 $\mu\text{A}/\text{cm}^2$ beam current is attributed to “synergistic effects of several processes in the ion bombardment” [114].

2.4.2. Film Growth Model Based on Cahn-Hilliard Decomposition/Ion Beam Induced Segregation

He and co-workers derived an alternative model for the evolution of the multilayer structure found in the gold-nickel system. They considered two different driving forces in a nanoscale subsurface zone: One results from the strong radiation enhanced spinodal decomposition of the immiscible AuNi system, giving the mass flow J_A^{chem} for species A in direction of the concentration gradient. The second driving force results from the bombardment-induced segregation and gives the mass-flow J_A^{BIS} for

Figure 2.8.: Dependence of superlattice structures upon the bombarded ion energy and flux. (a) X-ray reflectivity spectra (b) multilayer periodicity calculated from the spectra depending on the ion energy and flux. From [114].

species A along the direction of the film growth. They used a modified Cahn-Hilliard equation

$$\frac{\partial \phi}{\partial t} = M \nabla^2 [-\phi + \phi^3 - \nabla^2 \phi + V(z)]$$

where they introduce a surface potential $V(z)$ which resembles the radiation-induced segregation [115].

At the beginning of the film growth the bombardment-induced segregation results in the depletion of one element (say A) in the surface and an enrichment in the subsurface region. The chemical decomposition flux J_A^{chem} is therefore in the same direction as the flux J_A^{BIS} by bombardment. Now a fresh surface layer is deposited and the composition of this layer is determined by the deposition flux. In fact it has a higher concentration of element A than the now buried surface layer. Therefore, the direction of J_A^{chem} changes and the total mass flow is calculated by $J_A^{tot} = J_A^{chem} + J_A^{BIS}$. If J_A^{BIS} dominates, species A is transported from the fresh layer toward the subsurface. Due to the moving active subsurface zone it reaches the depleted region and the J_A^{chem} becomes dominant. The total flux reverses towards the surface and A gets enriched in the surface. This feedback loop finally gives the observed formation of multilayers. The schematic sketch of the process is given in Figure 2.9.

Additionally He and co-workers demonstrated the mechanism using the ABV model for kinetic Monte-Carlo simulations. The ABV model deals with an AB binary alloy with nearest neighbor pair interactions where transports is only possible

Figure 2.9.: Schematic illustration of the concentration profile of species A (C_A) and mass flows at two different depths (dotted lines) in the nanoscale subsurface zone during the film growth. The two competing mass transports are the uphill chemical diffusion (J_A^{chem}) and the bombardment-induced segregation flux (J_A^{BIS}). Their interplay in the film growth can induce self-organization of compositional modulations along the growth direction. The inset shows a kinetic Monte Carlo configuration of $A_{0.075}B_{0.925}$ with the competing parameters $\beta J = -0.45$ and $\beta U = 0.3$. From [114].

by vacancies [116, 117]. They used the Hamiltonian

$$H = H_0 + J \sum_{\langle i,j \rangle} \sigma_i \sigma_j + U \sum_{\langle i,j \rangle} (\sigma_i^2 \sigma_j + \sigma_i \sigma_j^2) + K \sum_{\langle i,j \rangle} \sigma_i^2 \sigma_j^2$$

with the spin variable $\sigma_i(-1, 0, 1)$ representing the site i occupied by an A,B atom or a vacancy. The phase separation is given by the parameter $J < 0$ while the parameter U describes the segregation ($U \neq 0$). For the gold-nickel system both parameters are strong. Therefore, the inset in Figure 2.9 is calculated using strongly competing values for U and J . The resulting structure resembles the observed layered structure quite well.

2.5. Multilayer Evolution Found by Corbella and Co-workers

Corbella and co-workers studied the amorphous carbon system with introduced metal for enhanced mechanical properties. In their studies they used magnetron sputtering from two targets for creating multilayer structures. They showed that

Figure 2.10.: “Cross-section transmission electron micrographs of Ti-C films with: 60 at.% Ti (a), 25 at.% Ti (b), and 5 at.% Ti (c). The corresponding SAED patterns are located below each image.” From [43].

these films have lower compressive stress and an improved adherence to the substrate compared to single amorphous carbon layers [118]. In later studies they used reactive magnetron sputtering of a metal targets in an argon/methane atmosphere [119]. A transmission electron microscopy analysis of these films grown with a titanium target revealed a spontaneous self-organized layer formation [43].

2.5.1. Experimental Results by Corbella and Co-workers

The films were grown by means of pulsed-dc reactive magnetron sputter deposition [119]. Titanium was used as sputter target and the sample was a monocrystalline silicon (100) wafer at a holder biased by 13.56 MHz to -200 V. The magnetron was driven by 100 W, 100 kHz pulse frequency with 70% duty cycle. The atmosphere was an argon and methane (0 - 25%) flow of 40 sccm at a pressure of 5 Pa.

The transmission electron micrographs of samples containing 60 at%, 25 at% and 5 at% titanium reveals well separated layers with nearly periodical contrast variations (see Figure 2.10). This first layer after the substrate is for all three sample the thickest one, revealing the affinity of one element to the substrate. The contrast modulation is lost towards the surface of the films. Selected area electron diffraction (SAED) patterns (see Figure 2.10, lower part) show randomly oriented TiC crystals. An electron energy loss spectroscopy (EELS) mapping indicates that the darker areas are titanium rich while the brighter areas are carbon rich.

Figure 2.11.: *Simulation patterns of Ti-C multilayers generated with the Cahn-Hilliard model for phase separation. The concentration is (a) $u_0 = -0.2$, (b) $u_0 = 0$, (c) $u_0 = 0.4$, with a growth velocity $v_{fg} = 0.6$, and (d) $u_0 = 0$, with a slower growth velocity $v_{fg} = 0.3$. From [43].*

2.5.2. Film Growth Model Based on Cahn-Hilliard Spinodal Decomposition

The spontaneous evolution of the layered structure was explained by Corbella and co-workers by a model based on a modified Cahn-Hilliard mechanism for spinodal decomposition [120] further developed by Puri and Binder [115] similar to He et al. (see Section 2.4.2). During the film growth the diffusivity in the surface and subsurface region is strongly enhanced due to the energy deposition of the impinging atoms. This drives the decomposition into carbon and metal-carbide phases together with the affinity of one element to the substrate.

They introduce a new variable $u = (2c - c_\beta - c_\alpha)/(c_\beta - c_\alpha)$ where c is the integral carbon concentration and c_α and c_β are the carbon concentrations in the Ti-rich and C-rich metastable amorphous states, respectively. The films growth is described by the velocity v_{fg} and the affinity of one element to the substrate is introduced into the chemical potential of the Cahn-Hilliard model by addition of a potential $V(z)$: $V(z) = h_1$ for $z < z_0$ and $V(z) = h_1 z_0^2/z^2$ [115].

The wavelength λ_{sp} of the segregation pattern is determined by the curvature of the free energy at the given initial concentrations, and the interfacial gradient coefficient. The results of the simulations are shown in Figure 2.11 for different initial concentrations and growth velocities. Corbella and co-workers conclude that the initial segregation by the affinity of one element to the substrate is more effective for concentrations in the miscibility gap (Figure 2.11b). This segregation forms only a few layers for the given growth velocity since the time the enhanced diffusions is active is too short. For a lower velocity pronounced and nearly perfect layers are produced (see Figure 2.11d).

Figure 2.12.: *Cross-section transmission electron micrograph of C/Cr film deposited at bias voltage of $U_b = -95$ V and $T = 250^\circ$ C. From [10].*

Figure 2.13.: *Cross-section transmission electron micrograph of C/Cr film deposited at bias voltage of $U_b = -350$ V and $T = 450^\circ$ C. From [10].*

2.6. Multilayer Evolution Found by Hovsepian and Co-workers

Hovsepian and co-workers investigated carbon/chromium coatings deposited by a combined steered cathodic arc/unbalanced magnetron sputtering technique [121, 122]. The films structure and tribological features were analyzed with respect to the different deposition parameters like the bias voltage [9, 123].

2.6.1. Experimental Results by Hovsepian and Co-workers

The films grown by Hovsepian and co-workers show a multilayer structure with periodicities around 2 nm which results from the non-reactive deposition with three carbon and one chromium target and a rotating sample (see Figure 2.12). For a certain bias regime a multilayer structure in the cross-section images (Figure 2.13) appear, that cannot be explained by the expectations from growth rates and sample rotation [10]. These multilayer structures exhibit layer periodicities around 20 nm increasing with the bias voltage. They were attributed to segregation and self-organization triggered by high-energy ion irradiation during film growth.

2.6.2. Irradiation Induced Self-Organization Mechanism by Hovsepian and Co-workers

The formation of alternating carbon and metal layers or metal-carbide layers during reactive sputtering is already described and explained for titanium, tungsten or niobium with similar layer periodicities around 30 nm [124]. These periodicities clearly evolve due to sample rotation, which can be excluded for the 20 nm periodicity seen

Figure 2.14.: Sketch of the formation of a nanoscale multilayer structure in the carbon-metal system. Δ is the critical thickness of the carbon-metal layer and λ the bi-layer thickness. From [10].

in Figure 2.13. Hovsepian and co-workers therefore proposed a new model sketched in Figure 2.14.

First a metal-carbide+carbon layer is formed (see Figure 2.14a). This layer grows due to three parallel processes: The formation of a metal-carbide phase (Cr_3C_2 and/or Cr_7C_3), the segregation of the excess carbon not incorporated in the carbides and the re-sputtering of the free carbon. The light-bonded carbon ad-atoms will be preferentially re-sputtered due to the argon plasma. The loss of carbon increases the chromium content of the film which enhances the flux of backscattered argon and further increases the carbon sputtering (sputter yield amplification [109, 110]). The elevated temperature due to ion bombardment and heating increases the diffusivity of the free carbon and promotes the carbon segregation.

After reaching a certain thickness of the metal-carbide+carbon layer pure carbon clusters will spontaneously form on the surface (see Figure 2.14b). The clusters form a layer repeating the surface topography. These clusters have only a small sputtering yield due to the suppressed sputter yield amplification effect and will act as sink for carbon atoms - mobile surface atoms and segregation atoms from the metal-carbide matrix. If the excess carbon is depleted the carbon-rich layer will be overgrown by the metal-carbide+carbon layer and a new carbon segregation layer will form. The nucleation process of carbon clusters will repeat if a certain critical thickness λ is reached. This explains the increasing bi-layer thickness λ with the bias voltage (see Figure 2.14c), since the re-sputtering of carbon at higher bias voltages increases. The increased re-sputtering decreases the overall carbon content and therefore a larger volume (=higher thickness) of metal-carbide+carbon is required for carbon cluster nucleation on the surface.

Figure 2.15.: *Cross-section TEM image of a 90:10 STPLD film. A clear layered structure is visible. From [47].*

The layer formation is suppressed in areas of high local curvature due to the angular dependency of the sputtering yield. This multilayer formation process requires an element with long range diffusion like carbon, an ion-induced formation of a metal-carbide phase and the segregation of excess carbon.

2.7. Self-organized Structures in Carbon - Stainless Steel Films by Cusenza and Co-workers

Cusenza and co-workers used sequential target pulsed laser deposition (STPLD) for creation of multilayer films of carbon and stainless steel. The STPLD uses a standard pulsed layer deposition setup with a Brilliant Nd:YAG laser ($\lambda = 1064$ nm, pulse duration (5 - 6) ns, repetition rate 20 Hz). The films were deposited on amorphous SiO_2 substrates from commercial AISI 316 (X5Cr5NiMo17-12-2, 1.4401) target with stripes of carbon or boron in the desired ratio. During deposition the laser spot is scanned across the surface in a controlled way along a scan line. This gives the desired compositional variation. The target chamber is evacuated before deposition to 10^{-6} Pa and the laser energy is set to 5 mJcm^{-2} [47, 125].

2.7.1. Experimental Results by Cusenza and Co-workers

The cross-section TEM image in Figure 2.15 shows a layered structure. The film was grown using a segmented target of 90:10 stainless steel to carbon. The film was grown in 46:51 min at room temperature and has a thickness of $d = 495$ nm.

An EDX linescan was performed on the cross-section TEM image and afterwards correlated with a time to space diagram of the scan process and convoluted with the

Figure 2.16.: “EDX-time to space correlation diagram of the 90:10 STPLD film. The dashed line corresponds to the situation, in which the layer spot hits the graphite layer of the target.” From [47].

laser spot diameter of 2 mm. The result is shown in Figure 2.16. No correspondence of the layer thicknesses and the locality of the laser spot is seen by Cusenza only the maximum of the carbon layers correspond to the moment when the laser spot hits the graphite part of the target. A weak superstructure can be seen in the time to space correlation diagram, which is indicated by red semi-circles in Figure 2.16. This superstructure corresponds to the multilayer structure visible in the TEM images.

Cusenza and co-workers conclude that the multilayer phenomenon seen in the carbon - stainless steel samples is induced self-organization by induced long range diffusion due to the alternating scan process, which drives the segregation of carbon and metal atoms instead of forming carbides. The Mo atoms of the stainless steel can redistribute and induce long-range diffusion. The layered structure cannot be explained solely by the target scanning process since the carbon layer thicknesses then should be very small, which is not the case.

2.7.2. Nucleation Model of Carbon-Stainless Steel Multilayer Films

Cusenza and co-workers examined the ion distribution in the plasma by mapping the target voltage during deposition and taking the first derivative. For the 90:10 target the result is shown in Figure 2.17. The ad-atoms have barely enough energy to adsorbate. The energy low seems to promote the influence of the Mo atoms on the layer evolution relative to reactive sputtered films. No solidification of the metal matrix occurs in the film which benefits the carbon diffusion in the metal matrix.

Figure 2.17.: *Distribution of the plasma ions of the 90:10 target with respect to the energy. Derived from the mapping of the target voltage during film deposition. From [47].*

Due to the local carbon inhomogeneities induced by the target scan process local diffusion gradients were induced which promotes the decomposition of carbon and stainless steel and assists a multilayer formation.

A similar explanation is given for multilayer structures evolving when utilizing a modified target with not just 2 stripes (one stainless steel and one graphite) but a target with smaller stripes of carbon equally spaced in the stainless steel. These targets show considerably higher ion energies and the ion implantation has to be taken into account. The ion implantation hinders the carbon diffusion and therefore reduces the size of the superstructure.

The reduction of the multilayer thickness with increasing film thickness is explained by the cavitation of the target during ablation. The plasma plume shifts and the deposition rate drops during deposition. This non linear deposition rate can explain the observed thickness decrease.

Additionally the layered structure was observed for Al/C and Ti/C. For an understanding of the complete process, Cusenza states, that experiments with a varying laser energy are needed [47, Section 7.4.5].

2.8. Discussion of the Presented Models

The growth models presented in this Chapter are dedicated to specific growth conditions applicable to the investigated deposition techniques. The model of Ting and Wu is based on the preferential deposition of one element at different film growth stages due to catalytic reactions [41]. This results in varying deposition rate during the film growth for carbon and the investigated metal. This model is therefore not applicable to the mass-selected ion beam deposition, since this technique determines the deposition rates of the elements by the ion currents. Additionally, no reaction in the film influences the deposition rates. Nevertheless, the model successfully ex-

plains the gained results and is accordance with the cross-section TEM images that reveal a metal-rich layer on top of the substrate, as claimed by the model. On the other hand, the model does not allow any predictions concerning growth regime or layer periodicity, additionally the vanishing of the multilayer structure towards the films surface as seen by e.g. Corbella et al. cannot be explained.

The model of He and co-workers and Corbella and co-workers are both based on the spinodal-decomposition due to non equilibrium thermodynamics [43, 114]. They proposed the affinity of element to the substrate, but it remains unclear, if the element found close to the substrate is the one proposed to be from the thermodynamical point of view. He and co-workers expanded the model of Corbella and co-workers by the addition of an enhanced diffusion due to substrate heating during film deposition and the incoming energetic particles [114]. Their simulations are in agreement with their experimental results for the morphology, but it is not stated if the simulated transport directions are in accordance with their investigated films. These models are not applicable to the ion beam deposition, since the heating of the substrate due to the ion beam can be neglect at low ion currents.

The model proposed by Hovsepian and co-workers shows some similarities to the model of Gerhards and co-workers but is dedicated to the film growth in a reactive plasma [10]. The re-sputtering of free carbon ad-atoms due to the argon plasma is a crucial steps in the layer formation process as well as the elevated temperature which enhances the diffusivity of the carbon. Therefore, the model is not applicable to the films grown by mass-selected ion beam deposition due to the lack of substrate heating and argon sputtering.

The multilayers found by Cusenza and co-workers are slightly different from the layers described above, since the layered structure itself results from a sequential deposition process but the detailed film morphology is determined by enhanced diffusion due to local carbon inhomogeneities [47]. The sequential depositions of the layer do not happen in the mass-selected ion beam depositions or reactive sputter deposition of the a-C:Me films. Therefore, this model cannot be used to explain the layered structures as seen by the other groups.

The model proposed of Gerhards and co-workers may be applicable to some of the situations above, but some of the details seen in the developed morphologies cannot be explained: The origin of the metal-rich layer as seen by Wu and Ting or the vanishing of the layer structure towards the film surface as seen by Corbella and co-workers.

On the other hand, it allows predictions for the films grown by mass-selected ion beam deposition, if a few basic parameters are calculated or determined experimentally.

Chapter 3.

Film Growth

In the following chapter the different film growth methods used in this thesis will be described. The a-C:Metal films were grown using the mass-selected ion beam deposition (MSIBD) (see Section 3.1), ion implantation (see Section 3.2) and in former studies by means of reactive magnetron sputter deposition (see Section 3.3).

3.1. Mass-Selected Ion Beam Deposition - MSIBD

One part of the a-C:Ni samples prepared in this works, were deposited with the mass-selected ion beam deposition setup ‘Mr. Stringer’ (see Section 3.1.2). The setup is equipped with a penning ion gun providing carbon and metal ions at the same time. The other part of the samples is prepared using the setup ‘Adonis’ equipped with a Sidenius hot filament hollow cathode ion source with an enlarged oven (see Section 3.1.3).

3.1.1. The Penning-Ion Source

The Penning-Ion-Gun (PIG) (see Figure 3.1) consists of two cathodes and one anode cylinder surrounded by magnetic coils for a longitudinal magnetic field. The magnetic coils are driven by a maximum current of 3 A. The gas-plasma is ignited by a high tension of $U_d = (1 - 2.5)$ kV between the anode and the two cathodes. The supply gas is argon or CO_2 .

The additional sputter target (marked as cathode disk in the anode cylinder in Figure 3.1) allows the supply of metal ions by sputtering of atoms from the target, which get ionized in the plasma. The energy of the ions E_{Ion} shows an energy spread ΔE_{ion} of some ± 10 eV with ion energies up to some ± 100 eV [126].

For this thesis pure nickel targets (fabricated of a 99.5% pure nickel rod 0.5 inch diameter from Alfa Aesar) combined with CO_2 gas supply were used for film growth.

Figure 3.1.: Sketch of a Penning-Ion-Gun. From [126].

Figure 3.2.: Drawing of the MSIBD-setup 'Mr. Stringer'.

The source was operated in the high current discharge mode with a discharge current of (10 - 30) mA and a discharge voltage of around 1 kV [126]. This was achieved with a pressure of 10^{-5} mbar CO_2 and a source magnet coil current below 1 A. The resulting currents are above $20 \mu\text{A}$ for C^+ ions and above $1 \mu\text{A}$ for Ni^+ ions. The limiting factor is the extraction current of 10 mA at 30 kV.

3.1.2. The Ion Accelerator 'Mr. Stringer'

The ion accelerator 'Mr. Stringer' - sketched in Figure 3.2 - is equipped with a Penning Ion Source (see Section 3.1.1). The ion source is held on high potential of $U_{\text{HV}} = 30 \text{ kV}$. Therefore, the ions are extracted from the source and accelerated by the extraction dome in the beam pipe on ground potential. Directly after the extraction dome the ions pass an electrostatic einzel lens (around 20 kV), which focuses the beam. For mass-separation the ions fly into a 90° sector-field magnet which sorts out the desired isotope or more exactly the desired $\frac{q}{m}$ -ratio. The mass-selected beam crosses a pair of capacitor plates for steering and then passes a variable slit defining the exit of the mass-selection system. The beam quality can be monitored using a Faraday cup directly after the slit.

The ions are focused then, using another electrostatic einzel lens and a quadrupole lens system. For sweeping the beam across the substrate surface and ensuring a homogeneous deposition, the beam passes an electrostatic sweeping system and another

Figure 3.3.: *MSIBD: Cycles during Deposition.*

Figure 3.4.: *MSIBD: Overlapping implantation profile for carbon and metal.*

pair of steering capacitors. Before the beam arrives at the deposition chamber, it can be monitored using another Faraday cup.

In the deposition chamber the ion beam passes another electro-static lens at -3 kV preventing electrons from the beam pipe entering the chamber and an electrostatic lens for defocussing the ion beam to increase the deposition area. The deposition chamber is build up as box-in-chamber: the inner box is on high potential as the ion source; therefore the ion beam is decelerated. The substrate is on a variable potential relative to the box. The current between surrounding plate and the substrate is measured using a PC. The substrate bias potential is adjusted in a way that the ions get the desired deposition energy. The adjustment is taken out as follows: The maximum current is measured at maximum bias. Then the bias is reduced until the ion current decreases to the half of it's maximum. To that bias value the desired ion energy is added (see Reference [127]). Since the ion have an energy below eU_{HV} due to the polarity of the voltage applied to the ion source, the bias is always negative and at $U_{bias} = 0$ V almost no ions arrive at the substrate. The deposition process is computer controlled: The computer measures the charge which arrives at the substrate and can switch the beam on and off via the second steering capacitor. It also switches the separation magnet between different pre-defined isotopes and therefore can be used to deposit films of arbitrary stoichiometry.

Deposition of a-C:Me Films

For the a-C:Me samples grown for this thesis the following procedure was applied: The samples were cleaned from dust and dirt with acetone before inserting in the deposition chamber. The first layer of the substrate was removed using argon sputtering with a high energy beam of $E_{ion} > 1$ kV, $^{40}\text{Ar}^+$ ions. This ensures the removal of an oxide surface layer and the amorphization of the surface. This surface is

(a) Measured ion current vs. bias voltage. (b) Derivative of Measured ion current vs. bias voltage.

Figure 3.5.: (a) Measured ion current on the sample for the $^{12}\text{C}^+$ and nickel $^{58}\text{Ni}^+$ ions in dependence on the bias voltage applied to the sample. (b) Derivative of (a) with respect to the bias voltage applied to the sample.

coated with 0.1 C 100 eV $^{12}\text{C}^+$ ions for prevention of Metal-Si mixing. The resulting amorphous carbon layer has some 10 nm thickness.

Since the deposition of carbon and metal ions at the same time is impossible with this setup, the ions were deposited in cycles of 10^{15} ions divided according to the desired fluence ratio of carbon and metal (see Figure 3.3). Due to the ion energy the atoms are implanted just below the surface and the resulting implantation profiles of both species overlap ensuring a mixing of the film (see Figure 3.4). One film requires more than 1000 switching cycles and the whole deposition process takes up several days or weeks.

Characteristics of the Film Deposition Using ‘Mr. Stringer’

As stated above, the deposition energy has to be calibrated before and during deposition for the carbon $^{12}\text{C}^+$ and nickel $^{58}\text{Ni}^+$ ions. This calibration is done for the nickel ions only since the bias voltage U_{bias} cannot be controlled separately for each ion species. Therefore, the energy of the $^{12}\text{C}^+$ ions may not be exactly the same as for the nickel $^{58}\text{Ni}^+$ ions, if the ion energy distribution of both species is different. A difference can result from different ionization spots for both species in the ion source, which is quite reasonable since the nickel originates from the solid sputter target while the carbon comes directly from the gas phase CO_2 .

The energy distribution is measured by evaluating the current on the sample in dependence from the bias voltage U_{bias} . The ion current of the carbon $^{12}\text{C}^+$ and nickel $^{58}\text{Ni}^+$ ions is plotted in Figure 3.5a. The current axes are scaled in a way that

the data point for $U_{\text{bias}} = 3000$ V bias voltage overlap. No significant differences for both ion species above $U_{\text{bias}} = 500$ V can be seen. Below $U_{\text{bias}} = 500$ V the carbon ion current drops slightly faster than the nickel ion current.

To get an idea of the energy distribution the derivatives of the ions currents were taken with respect to the bias voltage U_{bias} . The results are presented in Figure 3.5b. The carbon ions seem to have a maximum energy distributed around 53 V with a broad profile extended towards higher bias voltages, while the nickel ions seem to have a maximum around 41 V with an extension towards lower bias voltages. Obviously there is only a small difference in the position of the maxima, but the energy distribution of the carbon is slightly broader, which may be attributed to a larger size of the ionization center. The ionization center for the nickel ions could be smaller than the one for the carbon ions, since the nickel can only originate from the localized sputter target.

The second point is the measurement of the charge collected on the sample. This measurement is done with a current integrator, which has a tested accuracy of some percent. On the other hand, the analysis of the area density of carbon and nickel measured by Rutherford Backscattering (RBS, see Section 4.1) and the comparison with the deposited area density of carbon and nickel show a serious mismatch. E. g. a film deposited with a bias voltage around $U_{\text{bias}} = 500$ V and a fluence ratio of carbon to metal $r_f = 50/50 = 1$ shows for the deposition of $0.2 \text{ C } ^{12}\text{C}^+$ (0.1 C a-C layer and $0.1 \text{ C a-C:Ni layer}$) and $0.1 \text{ C nickel } ^{58}\text{Ni}^+$ a measured area density of $9.7 \cdot 10^{17} \text{ cm}^{-2}$ carbon and $3.4 \cdot 10^{17} \text{ cm}^{-2}$ nickel while the deposited area density according to the charge and the size of the sample area is $5.6 \cdot 10^{17} \text{ cm}^{-2}$ for carbon and $2.8 \cdot 10^{17} \text{ cm}^{-2}$ for nickel. Therefore, the measured area density of both species is higher than the deposited area density. This leads to the conclusion that the charge measurement loses some charge during the deposition.

The missing charge can be explained by free negative charges (electrons) neutralizing some of the positive charges of the ions. The deposition chamber of ‘Mr. Stringer’ is sketched in Figure 3.6 with the applied voltages and possible source of free electrons. These source are discussed below in detail.

The free electrons could emerge from the sample itself by secondary electron emission due to the ion beam. These charges cannot escape from the biased sample, because of the potential well. Therefore, this possibility can be excluded.

Another source of electrons can be the surrounding target holder, from which electrons are also created by secondary electron emission. These electrons could reach the sample, if they are created directly at the border of the hole in the target holder plate and decrease the measured current on the sample, but this possibility is more theoretical since most of the secondary electrons will not reach the sample due to the potential gradient created by the suppressor lens.

The third source of electrons may be found in the space between sample and chamber: Since the vacuum is in the order of 10^{-6} mbar, the residual gas may get ionized and the free electrons can neutralize some of the ions in the beam. These

Figure 3.6.: Sketch of the deposition chamber of the ion accelerator ‘Mr. Stringer’. The possible sources of free electrons are marked by green arrows. Sputtered atoms are marked by a red arrow. The applied voltages are indicated.

ions will not count to the ion current and the measured ion current is lower than the deposited flux.

The last source of free electrons could be the defocussing lens installed in the deposition chamber. This lens is hit by sputtered atoms from the sample and the sample holder, which will trigger secondary electron emission. These electron will leave the proximity of the lens due to the potential well and hit sample, the target holder or the chamber. If they hit the later is does not matter, but if they hit the sample, they will reduce the measured current. Additionally and more likely these electron may neutralize again parts of the ion beam. This lens also exists in the setup ‘Adonis’, but is built as a small tube which is not extensively hit by sputtered atoms due to the small area facing the target.

Therefore, at least two sources of free electrons have been identified. These electrons should be prevented from reaching the substrate by the third einzel lens, the defocussing lens, in the chamber, but if they are generated close to the sample, this will not work properly. The neutralization of the ions in the beam may also happen in the beam pipe after the separation magnet. These neutral atoms will get to the substrate but will not be counted and will not be decelerated to the desired energy, resulting in a permanent low rate irradiation of the films with high energy atoms.

The inaccuracy in the charge measurement influences also the adjustment of the deposition energy, since it depends on the measured ion current. Additionally, at low voltages, the ions may get reflected due to defocussing issues, which also reduces the measured current and cannot be distinguished from an reduction due to deceleration.

Figure 3.7.: Sketch of the ion accelerator ‘Adonis’.

To conclude, the energy of the ions deposited with ‘Mr. Stringer’ depend on the bias voltage U_{bias} but cannot be exactly given as number. Therefore, in the following only the adjusted voltage U_{adjusted} is given for samples deposited with the setup ‘Mr. Stringer’, which is the voltage added to the voltage where the ion current is half of the ion current at maximum U_{bias} . Additionally, the charge may have an unknown margin of error, which renders an comparison with area densities calculated from RBS impossible. The fluence ratio determination during deposition also relies on the correct charge measurement and may be affected also, if the mismeasurement of the charge depends on the ion, nevertheless the fluence ratio r_f is given for the samples as preset value.

3.1.3. The Ion Accelerator ‘Adonis’

The ion accelerator ‘Adonis’ (Anlage zur DepOsition Niederenergetischer Ionen auf Substrate) is equipped with a sidenius hot filament hollow cathode ion source (see Section 3.1.4). The main difference between ‘Adonis’ and ‘Mr. Stringer’ is, beside the ion source, the electrostatic deflector for removing neutral particles from the beam (see Figure 3.7). The neutralized ions will distort the control of the film growth by measuring the collected charge and will not be decelerated to the desired energy and therefore will introduce defects in the existing film. Details of the setup can be found in [128].

The ion source ignites the plasma not by a high voltage as the Penning ion source does, but uses a hot tungsten filament providing free electrons. These electrons are

Figure 3.8: *Lateral cut through the enlarged oven source of the ion accelerator 'Adonis'. Adapted from [102].*

accelerated toward the discharge region of the source and ionize the gas. Since the source does not allow a sputter target, all desired isotopes have to be feed in gaseous form into the source or have to be evaporated in the source.

The film deposition follows the same procedure as described in Section 3.1.2.

3.1.4. Sidenius Ion Source With Enlarged Oven

For the deposition of metal ions, a large amount of source material should be present in the ion source. Therefore an altered ion source with an enlarged oven was used for this thesis (see Figure 3.8). The ion source allows the introduction of a hollow rod with the metal containing compound (mostly chlorides). The enlarged space enables the introduction of the rod after heating up of the filament, therefore, no source material is lost due to evaporation during start-up. The source is used with nickel chloride (NiCl_2) and fed with CO_2 for the samples prepared for this thesis. The source delivered up to $30 \mu\text{A C}^+$ and up to $20 \mu\text{A Ni}^+$ ions.

Figure 3.9.: *Schematic diagram of a magnetron-sputtering setup.*

3.2. Ion Implantation

The a-C:Gd samples were not grown by co-deposition but were prepared by Gd implantations into ta-C films. As substrate SiN_x coated Si (from the group of F. Hellmann, University of California, Berkley, California, USA) was used in this case. On these $10 \times 10 \text{ mm}^2$ substrates pure ta-C films with thickness around 50 nm were grown with the setup ‘Adonis’. The ta-C films were implanted after deposition with the same setup with gadolinium at 50 keV and partially at 30 keV ion energy and various fluences. The implantation depth is around 19 nm with a straggle of 3 nm as calculated by SRIM simulations for 50 keV Gd ions into ta-C [48]. Another set of samples was implanted with xenon instead for reference purpose. The ion fluence was up to $4.6 \cdot 10^{16} \text{ Gd ions/cm}^2$.

3.3. Reactive Magnetron-Sputter-Deposition

Another way to produce a-C:Me film is reactive magnetron sputtering. This method was used in former studies and is a much faster method than mass-selected ion beam deposition [41].

Sputtering usually describes the erosion of a surface by an ion beam or a plasma. The eroded atoms can be deposited on a substrate. At a magnetron the desired metal is used as sputter target. It is fixed on the cathode, while the substrate acts as anode (see Figure 3.9). The plasma is ignited and powered by a high voltage rf-generator connected to the anode and cathode. The metal atoms deposited on the substrate create secondary electrons which promote the plasma. To enlarge the free-path of the electrons a magnetic field with various geometries can be applied.

The reactive magnetron is a special case of the magnetron sputter deposition. A multi-atomic gas (e.g. CH_4) is introduced into the plasma and is dissociated into

radicals (CH_x) which react on the substrate surface. In this way it is possible to grow multi-component films like a-C:Metal.

The CH_x react on the film surface and form a layer while the metal atoms from the sputter-target are introduced into this layer. The purity of the films depends critically on the purity of the precursors (gases, sputter targets,...). The process can be controlled by the pressure and the amount of the reactive gas in relation to an inert gas (Ar), the rf-power and the substrate-target distance. A complete control over the stoichiometry of the growing film is not possible.

Chapter 4.

Characterization Techniques

4.1. Rutherford-Backscattering (RBS)

The sample's integral elemental composition and concentration depth profile is evaluated using Rutherford Backscattering Spectroscopy (RBS). This technique is based on the elastic backscattering. Figure 4.1 shows the basic principle of an RBS measurement. A beam of light ions (e.g. He^{++}) of energy E_0 is focused onto the sample. The ions are scattered by the target atoms due to elastic interactions based on coulomb repulsion. Therefore the energy transfer to the target atom E_P of the mass M_T from the projectile (mass M_P) depends on the scattering angle θ and can be described by the kinematic factor [129]:

Figure 4.1.: *Schematic diagram of Rutherford-Backscattering.*

$$K := \frac{E_P}{E_0} = \left[\frac{\sqrt{1 - [(M_P/M_T) \sin \theta]^2} + (M_P/M_T) \cos \theta}{1 + (M_P/M_T)} \right]^2. \quad (4.1)$$

The largest energy loss of the projectile - and minimal K -, is possible for (back)scattering ($M_P < M_T$) under a scattering angle of $\theta = 180^\circ$. For geometric reasons the minimal value is $\theta < 170^\circ$, because of the incoming ion beam under 180° . For a fixed combination of θ , M_P and M_T , K is a fixed value and allows the identification of M_T , for given M_P , θ , E_0 and E_P . If the projectile M_P is not scattered on the target surface, it will loss energy in the target due to electronic stopping. Therefore a projectile scattered in some depth has less energy than a particle scattered on the surface. A typical spectrum of a gold thin film deposited on a chromium coated silicon substrate is shown in Figure 4.2. The elements with higher atomic mass appear at higher backscattering energies (e.g. gold) while the lighter elements appear at low backscattering energies (chromium and silicon). If a film of a light element is on top of a substrate of heavier element, the signal of the projectiles scattered in the film overlap with the signal of projectiles scattered in the substrate.

Figure 4.2.: *Rutherford-backscattering spectrum of a Au thin film on a chromium coated silicon substrate. The counts of backscattered ions is plotted versus their energy. The gold, chromium and silicon edges are marked.*

The determination of the stoichiometry of the sample requires the calculation of the Rutherford-scattering cross-section $\frac{d\sigma}{d\Omega}$. This is done while assuming a resting target and $M_P \ll M_T$ in the center-of-mass system by:

$$\frac{d\sigma}{d\Omega} = \left(\frac{Z_P Z_T e^2}{16\pi\epsilon_0 E_0} \right)^2 \frac{1}{\sin^4(\theta/2)}. \quad (4.2)$$

Here, Z_P and Z_T are the atomic numbers of the projectile- and target atom, E_0 , θ as above, e electron charge and ϵ_0 is the dielectric constant. The areal density n of an element can be calculated for a given number of counts N in that signal by knowing the number of incoming ions Q and the detector opening angle $\Delta\Omega$ by:

$$n = \frac{N}{Q \frac{d\sigma}{d\Omega} \Delta\Omega} \quad (4.3)$$

This areal density can be compared to the expected areal density due to deposition conditions, which gives a hints for the sputtering yield during deposition.

The RBS-measurements were performed at the Göttinger heavy ion implanter *IONAS* using 900 keV He^{++} ions [130]. The backscattered ions were detected by a silicon surface barrier detector under 165° to the incoming beam with an opening angle of 3.4 msr. The calculation of concentration depth profiles was performed using the RUMP software package [131].

4.2. Transmissions-Electron-Microscopy (TEM)

The micro-structure of the films was analyzed in detail by cross-section transmission electron microscopy. The sample is irradiated by an energetic electron beam and the image is recorded in transmission geometry like in conventional light microscopy. The theoretical resolution is given by Abbe's law applied for high energy electrons. However, this resolution cannot be achieved in today's electron microscopy due to the poor quality of the electron lenses. Nevertheless, the transmission electron microscopy is a convenient tool for micro-structure analysis of the film. A detailed description of the applying contrast mechanisms and general aspects can be found in the textbook of Williams et al. [132].

The cross-section analysis requires the preparation of a thin and electron transparent lamella. This lamella can be analyzed with nearly atomic resolution and the spatial and size distribution of particles in an amorphous matrix can be determined in great detail.

4.2.1. Focused Ion Beam Preparation

Since the samples have to be very thin (a few nanometer), for not absorbing all electrons, they have to be thinned very extensively. This could be done either by grinding and ion milling ('the conventional way') described in detail in Reference [133], or by preparation using a focused ion beam. The textbook from Giannuzzi and Stevie gives a good overview over the possibilities of focused ion beams [134].

For this thesis all samples were prepared using the *Dual FIB Nova Nanolab 600* system from *FEI*. This system combines a scanning electron microscope with a focused gallium ion beam (FIB). Additionally, the system is equipped with different gas injection systems for e.g. platinum deposition from a Pt-organic gas. The sample can be tilted by up to 60° and rotated by 360°. The system is computer controlled and allows in combination with an image recognition system a semi-automatic preparation of the lamellas. The whole process takes about 3 hours time, which is much faster than the conventional way, which takes at least a few days [133].

The preparation using the FIB divides in the following steps:

- After bringing the sample to the eucentric height¹ (≈ 5 mm below the electron gun), a sufficient large and clean spot on the sample is covered with a thin $12 \times 3 \times 0.1 \mu\text{m}^3$ platinum layer by electron beam deposition (5 keV, 1.6 nA) from a Pt-organic gas $(\text{CH}_3)_3\text{Pt}(\text{C}_P\text{CH}_3)$. This layer protects the surface of the film against the ion beam sputtering. This protection layer is especially important for thin films where the surface layers should not be altered by the ion beam.

¹The eucentric height is characterized by being the height where the image of the sample acquired with the scanning electron microscope does not change laterally during sample tilting. This is achieved when the sample axis is on the same height as the rotation axis of the sample stage.

- The main preparation of the lamella and the pre-thinning is done by using an *Auto-TEM* script. This script uses a gallium ion beam (30 keV, beam currents up to 30 nA) and first sputters small crosses next to the lamella for image recognition. The lamella is then coated with another platinum protection layer by ion beam deposition using the Pt-organic gas. This layer is about (2-3) μm thick. Then automatically a cross-section is milled on each side of the lamella and the lamella is pre-thinned on each side. The depth of the lamella is about 8 μm per default, but it can be adjusted in the script (see Figure 4.3a).
- In the next step the sample is tilted to 7° relative to the electron beam and the lamella is cut by ion beam milling at three edges but with a little bridge preventing it from falling down. After that, the sample is tilted to 0° and lowered to at least 7 mm below the electron gun for protection during insertion of the omniprobe tip at the next step (see Figure 4.3a).
- The tungsten tip of the Omniprobe nanomanipulator is inserted and lowered to the eucentric height. Then the sample is raised until the tip is in contact with the platinum cover layer of the lamella. The process is monitored using the electron beam and the ion beam (30 keV, 10 pA) systems. Then the tip is connected by 1 μm ion beam platinum deposition. Before carefully removing the lamella with the tip, the remaining bridge is cut by ion beam sputtering.
- In the next step, the lamella is fixed to a copper grid, which fits into regular transmission electron microscope sample holders. Therefore, the lamella is brought in the center of the ion beam image and then the grid, which is mounted on a special holder, is raised and positioned carefully until the lamella is in contact with the grid. The lamella is fixed by 1 μm thick ion beam platinum deposition (30 keV, 0.1 nA, 5 pA/ μm^2). Then the tungsten tip is cut off by ion beam sputtering and the backside of the lamella also fixed by platinum deposition after rotation by 150° (see Figure 4.3b).
- After bringing the lamella into the eucentric height, the final thinning procedure starts. The front side of the lamella is thinned by milling a cleaning cross-section of 1 μm depth and 7 μm width under 1.2° relative to the ion beam with an ion current of 0.30 nA. After that the backside is milled under the same conditions. The next step is milling with an ion current of 0.10 nA and a width of 6 μm for both sides.
- The finally milling steps uses an ion current of 30 pA and a width of 5 μm for both sides at an angle of 0.5° , starting at the backside of the lamella. When milling the front-side, the process is stopped when the ion beam has decreased the thickness of the platinum cover layer to a minimum above the film interface (Figure 4.3c).

Figure 4.3.: (a): The pre-thinned, three edge cutted lamella is held by one bridge at the right side and covered with platinum. The crosses at the left and right sides were used for the image recognition. (b): Three finally thinned lamellas at the copper grid. (c): Finally thinned lamella with both platinum layers and film visible.

- The last step is a low energy polishing using 5 keV, 29 pA gallium ions. The lamella is milled with a rectangle of 4 μm under 7° for about 30 seconds each side. The result is an electron transparent lamella which is mechanically stable and can be easily handled due to the copper grid (see Figure 4.3c).

4.2.2. Philips CM-200-FEG-UT

The cross-section transmission electron microscope measurements were done at the *Philips CM200-FEG-UT* in the workgroup of Prof. Dr. Michael Seibt at the 4th Institute of Physics. The microscope is equipped with a field-emission electron source and uses 200 kV acceleration voltage. The high resolution lens allows a point resolution of 0.188 nm, images were recorded using a fiber-optic coupled CCD camera system from *Gatan* [135].

The microscope permits the focusing of the electron beam down to 0.5 nm and scanning the beam across the sample (*scanning transmission electron microscopy - STEM*). Additionally, the energy of the generated X-rays can be analyzed using a *Link ISIS* setup from *Oxford Instruments*, commonly called energy dispersive X-ray (EDX). Together with the scanning electron beam, this setup is capable of the space-resolved analysis of the elemental composition in the sample. The beam can be scanned along a line while recording the position and the X-ray-spectra. This gives the so-called linescan, showing the elemental composition along the scan path.

4.3. X-ray Diffraction (XRD)

X-ray diffraction (*XRD*) utilizes the diffraction of X-rays on crystal-planes. An electro-magnetic wave is diffracted by a lattice with lattice distances in the order of the wavelength. For constructive interference of two diffracted waves, the phase difference is an integer multiple of the wavelength λ . For parallel beams engaging

Figure 4.4.: Schematic diagram for Bragg-diffraction. From [136].

under an angle θ on a set of lattice planes with distances of d the Bragg-equation for constructive interference denotes as (see Figure 4.4):

$$2d \sin \theta = n\lambda . \quad (4.4)$$

This is only strict for an infinite crystal: For poly-crystalline materials or nano-crystallites in a non-crystalline matrix, analyzed in this thesis, the finite number of lattice planes results in an broadening B of the corresponding reflexes. For crystals with a size t one calculate for the beam broadening in the diffraction direction B :

$$t = \frac{0.9\lambda}{B \cos \theta} . \quad (4.5)$$

Equation 4.5 is called the Scherrer-formula. It allows the estimation of the mean particle size in a given sample [136]. An additional broadening of the reflexes takes place due to the finite energy sharpness of the incident X-ray beams. This broadening is about two orders of magnitude smaller than the broadening because of the particle size due to the small crystallite sizes in this thesis. The XRD-measurements were done at a D8 X-ray diffractometer of Bruker AXS. The copper-anode of the X-ray tube delivers radiation with a wavelength of $\lambda = 1.54 \text{ \AA}$. The optical path is shown in Figure 4.5. The X-ray beam starts in the X-ray tube (R) and is focused (F) through the aperture (AB) on the sample (P). After being diffracted according to the Bragg-equation 4.4, the beam is detected (D) through a scattered-light-aperture (SB), the K_{β} -filter (K_{β}) and the detector-aperture (DB). There are two different mode of measurement: The grazing incidence mode, where the angle of incidence is kept constant and detector is rotated around the sample and the $\theta - 2\theta$ -mode, where the angle of incidence changes constantly and the detector is rotated with twice angular velocity around the sample in a way that the angle between incoming and outgoing beam is kept constant at 2θ .

Figure 4.5: Optical path of the X-ray diffractometer D8 of Bruker AXS. From [137].

4.4. X-ray Induced Photo-electron Spectroscopy (XPS)

The X-ray induced photo electron spectroscopy (XPS) is used to analyze the sample's composition directly after growth. An intense X-ray beam is focused on the sample's surface and creates free electrons by the photo-effect [138].

The X-ray photons ejects electron from inner-shell orbits of the atoms in the surface. The kinetic energy E_K of these electrons is determined by the energy of the photons $h\nu$, the electron binding energy E_B and the work function of the solid E_W by:

$$E_K = h\nu - E_B - E_W$$

with h the Planck constant and ν the frequency of the X-ray radiation [139]. The binding energy depends on the energy level of the electron and on the atomic core (see Figure 4.6).

Therefore, XP-spectroscopy can be used to analyze the composition of the surface of the sample. The information is collected from depth of less than 100 Å and depends on the inelastic mean free path of the electron in the material [140]. A typical XP-spectra for Nickel is shown in Figure 4.7. The line for photo-electrons originating from different core levels are well resolved. Additionally the lines for the competing Auger process appear in the spectrum [139].

Since the required energy resolution is high, an electro-static analyzer is used. A sketch is shown in Figure 4.8. The cylinder shape capacitor allows in combination with a channel-plate detector an energy-independent resolution. The whole range from 0 to the maximum kinetic energy of the photo-electrons is accessible. For

Figure 4.6.: Energy scheme of XPS. The X-ray photons eject an electron from the core level with a kinetic energy of $E_K = h\nu - E_B - E_W$. From [139].

Figure 4.7.: XP-Spectrum of Nickel with MgK α radiation. From [139].

Figure 4.8.: Schematic diagram of a XPS detector setup. From [139].

best energy resolution the vacuum in the chamber has to be in the UHV range to minimize the scattering of the photo-electrons at residual gas atoms.

The samples were irradiated by an *Omnicon DAR400* X-ray source providing MgK α or AlK α at users choice. For this thesis MgK α ($E = 1253.6$ eV) with an emission current of 12mA was used. The photo electrons were detected by an *Omicron EA125* analyzer equipped with 7 *Channeltron* detectors attached to an *EAC 2000-125* power supply.

4.5. Raman Spectroscopy

Raman-scattering describes the inelastic scattering of photons by molecule or solid state bodies. This inelastic scattering creates phonons (*Stokes-scattering*) or annihilates phonons (*Anti-Stokes-scattering*) by transferring energy from or to the vibrations of the molecules. Anti-Stokes-scattering requires excited states in the molecule, which are only weakly populated at room-temperature. Therefore, the measurement of the Stokes-scattering is preferred in most cases.

A simple description of the Raman-scattering is given by the classical theory [141]: Molecules are treated as an ensemble of atoms conducting harmonic oscillations. The incident light can be described as a temporary oscillating electro-magnetic field: $E = E_0 \cos \omega_0 t$ with an oscillation amplitude of E_0 and an oscillation frequency of ω_0 . This field slides the electrons of the atoms in a way, that a dipole with a dipole moment

$$\mu = \alpha E \quad (4.6)$$

forms. Here α describes the polarizability. A molecule consisting of two atoms oscillates with a frequency ω_v ($x = x_0 \cos \omega_v t$) and changes polarizability during the oscillation. For small amplitudes this is given by:

$$\alpha = \alpha_0 + \left(\frac{\partial \alpha}{\partial x} \right)_0 x_0 \cos \omega_v t . \quad (4.7)$$

The interaction between the incident light and the molecule is described by combining equations (4.6) and (4.7):

$$\mu = \underbrace{\alpha_0 E_0 \cos \omega_0 t}_{\text{Rayleigh}} + \frac{1}{2} \left(\frac{\partial \alpha}{\partial x} \right)_0 x_0 E_0 \left[\underbrace{\cos (\omega_0 + \omega_v) t}_{\text{Anti-Stokes}} + \underbrace{\cos (\omega_0 - \omega_v) t}_{\text{Stokes}} \right] . \quad (4.8)$$

The first term describes the elastic Rayleigh-scattering while the second term describes the Anti-Stokes-scattering with an energy transfer from the oscillating molecule. The Stokes-scattering is described by the third term: Energy is transferred to the molecule. Therefore, the Stoke-line is ω_v below the frequency of the incoming light ω_0 , while the Anti-Stokes line is ω_v above.

The condition for Raman-scattering results from Equation 4.7: The polarizability change during one oscillation in a way that $(\partial \alpha / \partial x)_0 \neq 0$ applies. The quantum mechanical calculation takes the quantization of the oscillator states into account. In Figure 4.9 all possible transitions including additions from the quantum mechanical calculations are shown. The transitions from and to the ground states are Rayleigh scattering, the transitions from the ground to an excited state are Stokes-scattering and the transitions from an excited state to the ground state are Anti-Stokes scattering. As mentioned above, the low occupation of the excited state at room temperature makes the Stokes-scattering more likely than Anti-Stokes-scattering, therefore the corresponding line intensity is larger by one order of magnitude.

Figure 4.9.: Molecular energy states with possible Raman transitions. Adapted from [141].

Due to the strongly differing Raman spectra for diamond, micro-crystalline graphite and amorphous carbon, Raman spectroscopy is particularly interesting for carbon containing samples. The spectra are shown in Figure 4.10: diamond shows a sharp line at 1331 cm^{-1} which belongs to the transverse optical phonon, graphite (HOPG) has a line at 1581 cm^{-1} and sp^2 -bonded, amorphous carbon shows broadened lines at ca. 1580 cm^{-1} and 1350 cm^{-1} .

Figure 4.11 shows the possible oscillation modes of sp^2 bonded, unordered carbon. The oscillation sketch in Figure 4.11A in E_{2g} -Symmetrie (G-Mode) is not limited to a perfect six-fold geometry of the graphitic ring unlike the D-mode (Figure 4.11B). The D-mode is forbidden in a perfect graphitic lattice and can therefore be used as indicator for the fraction of unordered, sp^2 -bonded six-atom-rings.

For ta-C with up to 80% sp^3 -bonded carbon this line is indeed very weak. The line at ca. 1580 cm^{-1} can be fitted using a skewed Lorentian (Breit-Wigner-Fano (BWF)) function [144]:

$$I(\omega) = \frac{I_0 [1 + 2(\omega - \omega_0)/Q\Gamma]^2}{1 + [2(\omega - \omega_0)/\Gamma]^2} \quad (4.9)$$

Here $I(\omega)$ is the intensity depending on the frequency, I_0 the line intensity, ω_0 the line position and Γ the full width at half maximum. The BWF-coupling constant Q is negatively large for samples with high sp^3 -bonding ratios, corresponding to a symmetric line [144]. The coupling constant has no physical meaning for the amorphous carbon system. It describes the coupling of phonons to an electronic continuum which does not exist in this system (it allows e.g. the discrimination between metallic and semi-conducting carbon nanotubes [145]).

Figure 4.10.: Raman spectra of diamond, graphite and sp^2 -bonded amorphous carbon. From [142].

Figure 4.11.: Oscillations in graphitic carbon. From [143].

The measurements were taken out using μ UV-Raman at a *Ranishaw inVia Raman microscope* with a 244 nm laser in the Center of Superdiamond and Advanced Films (COSDAF) of the City University of Hong Kong. The taC:Gd samples were analyzed with a *SPEX 1877 0.6m Triple Spectrometer* with a 488 nm laser (visible Raman) by the group of F. Hellman, Department of Physics at the University of California, Berkley, California, USA.

4.6. DC Transport, Magnetization and Magneto-Electronic Properties

The dc transport in the ta-C:Gd films was measured using a standard four-point-probe setup with all contacts on top of the sample. This methods allows to get rid of the influence of the lead contact resistance, but it is still essential to get good ohmic contact to reduce parasitic capacitances. The sample resistance R can be evaluated

using:

$$R = \frac{V_+ - V_-}{2I} \quad (4.10)$$

where V_+ and V_- are the voltage measured for two different current polarities. The measurements are taken out at different temperatures. For a reliable dc conductivity σ_{dc} , the sample geometry (lateral dimensions, sample thickness) needs to be known and is the dominant error.

The magneto-transport measurements are performed with the same setup but in a dc magnetic field. This gives insight into the electric transport phenomena depending on an external magnetic field. The orientation of the H and E fields can be changed to distinguish different physical sources for the magnetic field depended resistance, the so-called magneto resistance (MR). The magneto resistance is defined as follows:

$$MR = \frac{\Delta R}{R_H} = \frac{\rho(H, T) - \rho(H = 0, T)}{\rho(H, T)} \quad (4.11)$$

where $\rho(H = 0, T)$ is the zero-field resistivity and $\rho(H, T)$ is the resistivity with applied magnetic field.

The magnetization measurements are done in a superconducting quantum interference device (SQUID) manufactured by Quantum Design. The magnetization $M(T)$ can be measured temperature dependent by cooling down with zero field (zero-field cooling, ZFC) and then measuring on heating up in a dc H field or on cooling down with field (FC). The third way is the thermoremanent moment (TRM) measurement where the sample is cooled down in a high field (70 kOe) and then heated up and measured in zero field. The field (H)- and temperature (T) dependency of the magnetization for free magnetic ions is described by the Brillouin function:

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{(2J+1)x}{2J}\right) - \frac{1}{2J} \coth\left(\frac{x}{2J}\right) \quad (4.12)$$

and is given by the Curie-Brillouin law:

$$M = ngJ\mu_B B_J(X), \quad (4.13)$$

where $x \equiv gJ\mu_B H/k_B T$, n is the number density of the magnetic ions, g is the g factor, J is the quantum number of the total angular momentum, μ_B is the Bohr magneton and k_B is the Boltzmann constant. Equation 4.13 can be reduced for $x \ll 1$ to the Curie law [146]:

$$\frac{M}{B} = \frac{C}{T}, \quad (4.14)$$

where C is the Curie constant.

More details to the measurement can be found in Reference [147]. All the measurement were done at the University of California, Berkley, California, USA in the group of F. Hellmann.

Chapter 5.

The a-C:Cu System Prepared by Mass-Selected Ion Beam Deposition

The a-C:Cu system was also investigated for films grown with mass-selected ion beam deposition. Previous studies of Gerhards et al. show a copper containing amorphous carbon nano-composite with small copper clusters in the an amorphous matrix (see e. g. Figure 1.4) [14]. The new studies of D. Lyzwa focused on the films with high copper concentration [50, 112]. These films show in a certain energy and fluence range a strong multilayer structure.

5.1. Fluence Ratio r_f Dependence of the Layer Periodicity and the Metal Layer Thickness

The layer periodicity and the metal layer thickness depend on the fluence ratio of carbon and copper and is shown in Figure 5.1. For this analysis a-C:Cu films were grown by means of mass-selected ion beam deposition using low energy (50 eV) carbon and copper ions with various fluence ratios $r_f = f_C/f_{Cu}$ using the ion beam setup ‘Mr. Stringer’ (see Section 3.1.2). The layer periodicity can be determined by direct measurements in the cross-section transmission electron microscopy images “ p_{TEM} ” or by measuring in the Fourier-transformed images “ p_{FFT} ”. The theoretical value “ p_{th} ” can be calculated using Equation 2.2 and the measured values for the volume coverage ratio c and the metal layer thickness d_m (see Figure 5.2). All films are described by the model in the margin of error.

5.2. Ion Energy E_{ion} Dependence of the Layer Periodicity and the Metal Layer Thickness

Another set of samples were grown with fixed fluence ratio r_f but varying ion energy E_{ion} using the ion beam setup ‘Adonis’. The film morphology depends on the ion energy since the sputter yields for carbon and copper on the film surface depend on the ion energy. As long as the total metal sputtering yield $S_M < 1$, layered

Figure 5.1.: Layer periodicity dependence on fluence ratio. The periodicity is determined by direct measurement in the cross-section transmission electron microscopy images p_{TEM} , from a fourier-transformed images p_{FFT} and calculated using empirical data p_{th} . From [50].

Figure 5.2.: Dependency of cluster diameter, copper layer thickness d_m and coverage ratio c on fluence ratio. Adapted from [50].

films are observed. For $S_M > 1$ no multilayer formation is visible in the cross-section transmission electron microscopy images. Typical cross-section transmission electron microscopy images and EDX linescans for both cases are shown in Figure 5.3 ($S_M < 1$) and Figure 5.4 ($S_M > 1$), respectively. For $S_M < 1$ ($E_{ion} = 50$ eV, $r_f = 1/9$) the cross-section transmission electron microscopy image shows a complicated layered structure which is also clearly visible in the EDX line scan. For $S_M > 1$ ($E_{ion} = 250$ eV, $r_f = 4$) the cross-section transmission electron microscopy image shows a clustered surface layer which is visible in the EDX linescan as an elevated

Figure 5.3.: Lower part: EDX linescan across an a-C:Cu film grown with a fluence ratio of $r_f = 1/9$ and an ion energy of 50 eV; Top: cross-section transmission electron microscopy image of the same film. A complex layered structure is visible. From [49].

Figure 5.4.: Lower part: EDX linescan across an a-C:Cu film grown with a fluence ratio of $r_f = 4$ and an ion energy of 250 eV; upper part: cross-section transmission electron microscopy image of the same film. Only a thin copper-containing surface layer is visible. From [49].

copper concentration towards the surface and no layer formation. The results are in good agreement with the prediction from the model of Gerhards et al. [15].

5.3. Summary of all Grown a-C:Cu Films

The samples of the a-C:Ni system are summarized in Figure 5.5 in fluence ratio r_f over adjusted voltage U_{adjusted} , or ion energy E_{ion} plots for film grown with the setups ‘Mr. Stringer’ and ‘Adonis’, respectively. The samples are marked with a red open circle. If the films shows a homogeneous film of amorphous carbon and copper, the circle is marked with a red X and if the films shows a layered structure,

(c) 'Mr. Stringer' grown films.

(d) 'Adonis' grown films.

Figure 5.5.: Copper samples: All samples in the fluence ratio r_f and adjusted voltage $U_{adjusted}$ space grown by 'Mr. Stringer' (c) and in the fluence ratio r_f over ion energy E_{ion} plot (d). The films revealing a layered structure are marked with a black dot, while the films showing a homogeneous a-C:Cu layers are marked with a red X. The green dashed area is the space where $S_M < 1$ is fulfilled.

the circle is marked with a black dot. The samples shown in Figure 5.5c are grown with 'Mr. Stringer' and are plot over the adjusted voltage $U_{adjusted}$ and not over the energy due to the issues mentioned in Section 3.1.2. The green dashed area describes the space where $S_M < 1$ is fulfilled under the assumption of $eU_{adjusted} = E_{ion}$. In Figure 5.5d the results for the 'Adonis' grown films is presented. The films show layers or homogeneous nanocomposites in the expected regions, predicted from the model of Gerhards et al. [15], for both systems.

Chapter 6.

Experimental Results on the a-C:Ni System

The model for multilayer evolution during mass-selected ion beam deposition of Gerhards and co-workers allows the prediction of certain regimes in the fluence ratio $r_f = f_C/f_{Ni}$ and energy E_{ion} space where an evolution of multilayers can be expected. This regime will be investigated in detail in this thesis for the weak carbide forming system a-C:Ni. In this system, the cluster stability for free clusters increases with the cluster size as mentioned in Section 1.1. Together with the result from the phase diagram that a compound only exists at an elevated temperature (see Figure 1.20), the formation of a nanocomposite consisting of clusters in an amorphous carbon matrix can be expected.

Various films with different parameters were grown by means of mass-selected ion beam deposition using the ion beam setups ‘Mr. Stringer’ (see Section 3.1.2) and ‘Adonis’ (see Section 3.1.3). The parameters of all samples are summarized in a fluence ratio r_f over adjusted voltage $U_{adjusted}$ plot for the films grown with the setup ‘Mr. Stringer’ (see Figure 6.1a) and in a fluence ratio r_f over ion energy E_{ion} plot for the films grown with the setup ‘Adonis’ (see Figure 6.1b).

The parameters of all samples are summarized in Table 6.1. The fluence ratio $r_f = f_C/f_{Ni}$ and the ion energy E_{ion} for both species (C^+ and Ni^+) are varied and determine the total metal sputter yield $S_M = r_f \cdot S_{C \rightarrow Ni} + S_{Ni \rightarrow Ni}$, which is calculated using simulated sputter yields from the SRIM 2006 program [48]. The charge is collected during deposition and gives the total number n of atoms contributed to the film growth: $n = \text{charge}/e$ with e being the elementary charge. This number is an indication of the film’s thickness.

The region where a self-organized layer evolution can be expected is given by the constraint:

$$S_M = r_f \cdot S_{C_{Ni}} + S_{Ni_{Ni}} < 1 \quad \Leftrightarrow \quad r_f < \frac{1 - S_{Ni_{Ni}}}{S_{C_{Ni}}} .$$

This is sketched in Figure 6.1b as green filled area. The sputter yields for carbon ions on nickel (C-Ni), nickel ions on nickel (Ni-Ni), carbon ions on carbon (C-C) and nickel ions on carbon (Ni-C) are calculated using the SRIM 2006 program [48]. The energy dependencies of these sputter yields are shown in Figure 6.2. The sputter yields increase with the ion energy and above a certain energy no evolution of a

Table 6.1.: Summary of all a-C:Ni samples grown for this thesis. The sample names beginning with Sxxx indicate samples grown in the setup ‘Mr. Stringer’ and the sample names beginning with #xxx indicate samples grown in the setup ‘Adonis’. The fluence ratio $r_f = f_C/f_{Ni}$, the adjusted voltage $U_{adjusted}$, and the ion energy E_{ion} indicate the values used for deposition. The total metal sputtering yield S_M is calculated using SRIM 2006 data [48]. The last column is the charge collected on the sample during deposition.

Sample	Fluence ratio $r_f = f_C/f_{Ni}$	Adjusted voltage $U_{adjusted}/V$	Total metal sputter yield S_M	Charge/C
S077	80/20	50	0,24	0,104
S078	90/10	50	0,38	0,112
S054	93/7	100	4,93	0,244
S053	90/10	100	3,45	0,185
S076	80/20	100	1,71	0,1
S075	70/30	100	1,13	0,122
S057	60/40	100	0,84	0,093
S102	50/50	100	0,67	0,118
S079	20/80	200	0,86	0,087
S080	60/40	200	1,71	0,112
S104	90/10	200	6,82	0,266
S081	50/50	300	1,95	0,102
S088	70/30	500	4,51	0,134
S082	50/50	500	2,85	0,073
S098	50/50	500	2,85	0,2
S099	50/50	1000	4,33	0,12

Sample	Fluence ratio $r_f = f_C/f_{Ni}$	Ion energy E_{ion}/eV	Total metal sputter yield S_M	Charge/C
#1182	90/10	50	0,38	0,100
#1227	90/10	100	3,45	0,19
#1177	80/20	100	1,71	0,105
#1224	60/40	100	0,84	0,22
#1164	50/50	100	0,67	0,096
#1212	60/40	200	1,71	0,16
#1230	60/40	200	1,71	0,350
#1204	50/50	300	1,95	0,15
#1233	50/50	300	1,95	0,29
#1195	50/50	500	2,85	0,113
#1207	70/30	500	4,51	0,185

Figure 6.1.: Summary of all samples in the fluence ratio r_f / adjusted voltage U_{adjusted} (a) and ion energy E_{ion} space (b). In the green dashed area the condition $S_M < 1$ is fulfilled. The symbols state, if the film shows a layered structure or one almost homogeneous layer.

metal rich surface layer is expected. This segregation layer is necessary for a non mixing system to develop a multilayer structure (see Section 2.2).

Two series of samples were systematically analyzed. A first set was grown using a fixed ion energy of $E_{\text{ion}} = 100$ eV and a varying fluence ratio r_f to investigate the layer and film evolution with respect to the nickel fluence offered during deposition. The other set was grown at a fixed fluence ratio of $r_f = 50/50 = 1$. A few samples were grown with other parameters to further explore the fluence ratio r_f / ion energy E_{ion} space.

6.1. The Dependence of the Film Growth on the Fluence Ratio r_f

The films for this analysis were grown with both ion beam systems for the evaluation of systematical differences. Therefore, samples with identical parameters were grown and analyzed with respect to the film morphology and composition with both systems and compared afterwards.

All samples will be described in detail in the following section with the corresponding TEM images to give an overview over the observed structures and film morphologies. In the following, the samples from both systems are evaluated separately and compared afterwards.

Figure 6.2.: The sputter yields of nickel ions on nickel, carbon ions on nickel, carbon ions on carbon, and nickel ions on carbon calculated using the SRIM 2006 program in dependence on the ion energy E_{ion} .

6.1.1. Films Prepared with the Setup ‘Mr. Stringer’

The films presented in this part were prepared with an adjusted voltage of $U_{adjusted} = 100$ V and a varying fluence ratio r_f with the setup ‘Mr. Stringer’.

TEM and EDX Analysis

For a high fluence ratio of $r_f = 90/10 = 9$ no layer growth is expected and high metal sputtering due to excess carbon during deposition takes place. In Figure 6.3 a representative cross-section TEM image of such a film is shown. On top of the crystalline silicon substrate the amorphous carbon layer (a-C), deposited prior to the a-C:Ni film, is visible ($d_{aC} \approx 30$ nm). This layer is followed by an amorphous nickel containing carbon layer of a thickness $d_{a-C:Ni} = (113.7 \pm 0.4)$ nm and the platinum protection layer from the focused ion beam preparation. The total layer thickness including the a-C layer on the substrate and the a-C:Ni layer is $d_{film} = (143.7 \pm 0.6)$ nm.

Reducing the fluence ratio to $r_f = 80/20 = 4$ significantly reduces the sputtering by carbon ions. A characteristic cross-section TEM image of a film grown by ‘Mr. Stringer’ is shown in Figure 6.4. The total film on the silicon substrate is $d_{film} = (67.6 \pm 0.3)$ nm thick and a relatively thick amorphous silicon layer shows up above the crystalline silicon substrate. This film shows a weak layered structure while the total metal sputtering yield is $S_M = 1.7 > 1$. This may be due to

Figure 6.3.: Cross-section TEM image of a film grown with a fluence ratio of $r_f = 90/10 = 9$ and an adjusted voltage of $U_{adjusted} = 100$ V. The film is grown in the setup ‘Mr. Stringer’ and shows an almost homogeneously mixed a-C:Ni layer on top of the a-C on the silicon substrate. The film’s thickness is: $d_{film} = (143.7 \pm 0.6)$ nm.

the energy issue described in Section 3.1.2 and will be discussed in detail in Section 6.6. The large margin of error of the layer periodicity results from the weak incisive layered structure. It is estimated by dividing the a-C:Ni film thickness by the number of layers and is $p_{TEM} = (16.0 \pm 10.7)$ nm with a mean metal layer thickness of $d_m = (8.2 \pm 5.7)$ nm. The layer periodicity can also be obtained from the Fourier-transformation of the image: $p_{FFT} = (14.1 \pm 14.4)$ nm.

Figure 6.5 shows a sample grown with a fluence ratio $r_f = 70/30 \approx 2.33$. On top of the silicon substrate an amorphous carbon layer is visible, which is followed by a layer consisting of alternating 6 ± 2 metal-rich/carbon-deficient and metal-deficient/carbon-rich layers. This film is covered by the platinum cover layer from the FIB preparation. The layered area shows no perfect periodicity, nevertheless it can be estimated by: $p_{TEM} = (13.9 \pm 4.6)$ nm and $p_{FFT} = (14.4 \pm 4.7)$ nm. The metal rich layers have a thickness of $d_m = (9.8 \pm 4.1)$ nm.

For a fluence ratio of $r_f = 60/40 = 1.5$, Figure 6.6 shows a typical cross-section TEM image of a film grown with ‘Mr. Stringer’, which shows a layered structure which is only weakly and not very regularly developed. The EDX linescan is shown as intensity over distance plot in Figure 6.6b. The signal is weak and noisy making an identification of the composition variations difficult. Nevertheless three more nickel rich layers can be identified which corresponds to the visual impression from the cross-section TEM images in Figure 6.6a.

A further reduction of the fluence ratio leads to $r_f = 50/50 = 1$. A typical cross-section image revealing a pronounced layered structure in the a-C:Ni film is shown

Figure 6.4.: Cross-section TEM image of a film grown with a fluence ratio of $r_f = 80/20 = 4$ and an adjusted voltage of $U_{adjusted} = 100$ V with the setup ‘Mr. Stringer’. The film shows a weak layered structure in the a-C:Ni layer on top of the a-C on the silicon substrate. The whole film is $d_{film} = (67.6 \pm 0.3)$ nm thick.

Figure 6.5.: Cross-section TEM image of a film grown with a fluence ratio of $r_f = 70/30 = 2.33$ and an adjusted voltage of $U_{adjusted} = 100$ V with the setup ‘Mr. Stringer’. The film shows a layered structure in the a-C:Ni layer on top of the a-C on the silicon substrate. The whole film is $d_{film} = (118.2 \pm 1.2)$ nm thick.

Figure 6.6.: (a) Cross-section TEM image of a film grown with a fluence ratio of $r_f = 60/40 = 1.5$ and an adjusted voltage of $U_{\text{adjusted}} = 100$ V. The film shows a pronounced layered structure in the a-C:Ni layer on top of the a-C on the silicon substrate. The film's thickness is: $d_{\text{film}} = (157.4 \pm 0.7)$ nm. (b) EDX linescan of the film shown in (a). The abscissa is the position in the film from the starting point of the scan and the ordinate is the recorded intensity of the given X-ray line. The layered structure is only weakly recognizable, due to the low intensity of the signals and the large noise. Nevertheless a pure carbon layer is visible and about three nickel rich layers can be identified.

in Figure 6.7. The sample has a total film thickness of $d_{\text{film}} = (124.7 \pm 0.9)$ nm with a layer periodicity of $p_{\text{TEM}} = (28.8 \pm 43.3)$ nm and from the Fourier transformed image $p_{\text{FFT}} = (10.1 \pm 6.4)$ nm. The large uncertainty results from the uncertainty of the number of layers visible in the cross-section TEM image. The metal layer's mean thickness is $d_m = (21.9 \pm 2.0)$ nm. The amorphous silicon region seen in the TEM image is again unexpectedly thick.

RBS Analysis

The Rutherford back-scattering spectroscopy (RBS) allows the analysis of the sample's concentration depth profile. The RBS spectrum of a film grown with an adjusted voltage $U_{\text{adjusted}} = 100$ V and a fluence ratio of $r_f = 60/40 = 1.5$ is shown in Figure 6.8. The number of counts is plotted versus the energy of the backscattered helium ions. The profile used for the Rump simulation (solid line in the spectrum) is sketched in Figure 6.8b [131, 148]. The vertical width of the layers in the profile corresponds to the area density of the layer and the nickel content is color coded: white = no nickel = 100 at% carbon and black = 100 at% nickel and no carbon. The

Figure 6.7.: Cross-section TEM image of a film grown with a fluence ratio of $r_f = 50/50 = 1$ and an adjusted voltage of $U_{\text{adjusted}} = 100$ V. The film is grown in the setup ‘Mr. Stringer’ and shows a pronounced layered structure in the a-C:Ni layer on top of the a-C on the silicon substrate. The film’s thickness is: $d_{\text{film}} = (124.7 \pm 0.9)$ nm.

area density cannot be converted directly to a film thickness due to the unknown atomic density of the nanocomposite. The density depends on the composition of the layers and can only roughly be extrapolated from the atomic densities of a pure carbon film ($\approx 110 \text{ nm}^{-3}$) and a pure nickel film ($\approx 91 \text{ nm}^{-3}$) and is therefore not given here. The profile is generated using the structure seen in the cross-section TEM images and the EDX analysis of the film (Figure 6.6) and varying the concentrations and area densities. The vertical solid lines are a guide for the eye at the energies where carbon and nickel at the surface and silicon in the depth of the sample appear.

The layered structure visible in the cross-section TEM image (Figure 6.6a) is reproduced by a layer profile used for Rump simulation (solid line in the spectrum in Figure 6.8a). The nickel content does not vary much in depth as seen in the spectrum. The layered structure may not be homogeneous over the whole spot analyzed by RBS (diameter $d = 1$ mm), which does not allow to resolve each visible cluster layer individually. Additionally, the depth resolution of RBS decreases in depth due to multiple straggling and depends on the energy resolution of the detector.

6.1.2. Films Prepared with the Setup ‘Adonis’

In this section the results for the films prepared by the setup ‘Adonis’ with an ion energy $E_{\text{ion}} = 100$ eV and a varying fluence ratio r_f are presented.

Figure 6.8.: RBS spectrum of a film grown with a fluence ratio of $r_f = 60/40 = 1.5$ and an adjusted voltage of $U_{\text{adjusted}} = 100$ V. The number of detected backscattered ions is plotted versus their energy. The C, Ni and Si edges describe the beginning of the corresponding signals and are marked by vertical lines. The solid line is the Rump simulation of the structure profile plotted in (b). The profile describes the layer composition. The vertical width of each layer corresponds to the area density of the layer and the brightness corresponds to the relative nickel content (black = pure nickel, white = pure carbon).

TEM and EDX Analysis

As seen for the ‘Mr. Stringer’ grown films, for a high fluence ratio of $r_f = 90/10 = 9$ no layer growth is expected. In Figure 6.9 a cross-section TEM image of a film grown with the setup ‘Adonis’ is shown. On top of the crystalline silicon substrate the amorphous carbon layer (a-C) with a thickness of $d_{\text{aC}} \approx 14$ nm, which was deposited prior to the a-C:Ni film, is visible. This layer is followed by an amorphous nickel containing carbon layer with a thickness of $d_{\text{a-C:Ni}} = (51.2 \pm 0.7)$ nm and the platinum protection layer from the focused ion beam preparation. Together with the a-C layer the total layer thickness is: $d_{\text{film}} = (65.1 \pm 0.5)$ nm.

Decreasing the fluence ratio to $r_f = 80/20 = 4$ at an ion energy of $E_{\text{ion}} = 100$ eV further reduces the total metal sputtering yield to $S_M = 1.7 > 1$. The cross-section TEM image of the film is presented in Figure 6.10 and does not show a layered structure. Additionally, no nickel rich layer is visible. The a-C:Ni layer shows only a weak contrast to the a-C layer on top of the substrate. The interface between the a-C and the a-C:Ni layer is indicated by the black line in Figure 6.10. The

Figure 6.9.: Cross-section TEM images of a film grown with a fluence ratio of $r_f = 90/10 = 9$ and an ion energy of $E_{ion} = 100$ eV. The film grown with the setup ‘Adonis’ shows an almost homogeneously mixed a-C:Ni layer on top of the a-C on the silicon substrate. The film’s thickness is: $d_{film} = (65.1 \pm 0.5)$ nm.

whole film is about $d_{film} = (52.8 \pm 0.6)$ nm thick while the nickel containing layer is about $d_{a-C:Ni} = (26.2 \pm 0.7)$ nm thick. The thickness of the nickel rich surface layer can only be estimated, since the surface layer is hidden in the platinum cover layer: $d_m = (6.7 \pm 3.8)$ nm.

At a fluence ratio of $r_f = 60/40 = 1.5$ the total metal sputtering drops to the region where multilayer growth with metal-rich/carbon-deficient and metal-deficient/carbon-rich layers can be expected according to the model of Gerhards and co-workers (see Section 2.2). Figure 6.11a shows a typical cross-section TEM image for a sample grown with the setup ‘Adonis’ at an ion energy of $E_{ion} = 100$ eV and a fluence ratio of $r_f = 60/40 = 1.5$. The sample shows 7 to 8 very well separated layers with a periodicity $p_{TEM} = (11.6 \pm 1.7)$ nm ($p_{FFT} = (13.3 \pm 4.6)$ nm) and a mean metal layer thickness of $d_m = (7.4 \pm 1.9)$ nm.

The EDX linescan is shown as intensity over distance plot in Figure 6.11b. It reveals 5 nickel rich layers. The maxima in the nickel Ni K_α signal correspond to local minima in the carbon C K_α signal. By a comparison to the cross-section TEM image of the film (Figure 6.11a), it can be concluded that the a-C:Ni film consists of nickel-rich / carbon-deficient (darker) and nickel-deficient / carbon-rich (brighter) layers. The linescan also reveals that the ‘Adonis’ film contains an iron rich layer (visible as Fe K_α peak). This layer directly follows the amorphous carbon a-C layer and was deposited due to a mistake in the adjustment of the mass-separation system at the beginning of the film growth.

A further reduction of the fluence ratio r_f leads to $S_M = 0.7 < 1$ for $r_f = 50/50 = 1$. The cross-section TEM image is presented in Figure 6.12 and shows a layered film

Figure 6.10.: Cross-section TEM image of a film grown with a fluence ratio of $r_f = 80/20 = 4$ and an ion energy of $E_{ion} = 100$ eV. This film is grown in the setup ‘Adonis’ and shows no layered structure. The a-C:Ni film is hard to distinguish from the a-C film on top of the silicon substrate. The black line indicates the interface between both layers. The whole film is $d_{film} = (52.8 \pm 0.6)$ nm thick.

with a total film thickness of $d_{film} = (69.4 \pm 0.8)$ nm. The layer periodicities are $p_{TEM} = (10.4 \pm 2.1)$ nm and $p_{FFT} = (11.4 \pm 2.2)$ nm), respectively. The mean metal layer thickness can be determined to be $d_m = (10.6 \pm 5.8)$ nm.

RBS Analysis

The concentration depth profile of the samples was analyzed by Rutherford back-scattering (RBS). An RBS spectrum of the film grown with an ion energy $E_{ion} = 100$ eV and a fluence ratio of $r_f = 60/40$ is shown in Figure 6.13. The number of counts is plotted versus the energy of the backscattered helium ions. The profile used for the Rump simulation (solid line in the spectrum) is sketched in Figure 6.13b [131, 148]. The vertical width of the layers in the profile corresponds to the area density of the layer and the nickel content is color coded: white = no nickel = 100 at% carbon and black = 100 at% nickel and no carbon. The profile is generated by using the structure evaluated from the cross-section TEM images and the EDX analysis of the films (Figure 6.11) and varying the stoichiometry and the area density of the sublayers. The vertical solid lines are a guide for the eye at the energies where carbon and nickel at the surface and silicon in the depth of the sample appear.

(a) Cross-section TEM image.

(b) EDX linescan.

Figure 6.11.: (a) Cross-section TEM images of a film grown with a fluence ratio of $r_f = 60/40 = 1.5$ and an ion energy of $E_{ion} = 100$ eV. The film shows a pronounced layered structure in the a-C:Ni layer on top of the a-C on the silicon substrate. The film's thickness is: $d_{film} = (99.5 \pm 1.5)$ nm. (b) EDX linescan of the film shown in (a). The abscissa is the position in the film from the starting point of the scan and the ordinate is the recorded intensity for the given X-ray line. The scan reveals a layered structure with 5 nickel rich and carbon deficient layers, while the 1st layer on top of the a-C film is iron containing due to an error in the adjustment of the mass-separation during film growth.

Figure 6.12.: Cross-section TEM image of a film grown with a fluence ratio of $r_f = 50/50 = 1$ and an ion energy of $E_{ion} = 100$ eV. The film is grown in the setup ‘Adonis’ and shows a pronounced layered structure in the a-C:Ni layer on top of the a-C on the silicon substrate. The film’s thickness is: $d_{film} = (69.4 \pm 0.8)$ nm.

The analysis shown in Figure 6.13 reveals that the first metal rich (dark) layer after the pure carbon layer contains iron which also contributes to the spectrum (as seen also in the EDX linescan, Figure 6.11b). Due to the small atomic mass difference between ^{56}Fe iron and ^{58}Ni nickel and the overlapping profile, both contributions are not separated in the spectrum but contribute to the signal starting at the nickel edge. Due to the depth resolution of this RBS measurement, the layers are not very well resolved in the spectrum, therefore, the simulation needs more information which is derived from the cross-section TEM image (Figure 6.11a). The cluster rich layers do not consist of 100 at% nickel, which is also visible in the cross-section TEM image where they appear as dark noncontinuous layers. The mean nickel volume fraction in a layer can be estimated by $c = (0.42 \pm 0.34)$.

The Rump simulation data allows the calculation of the nickel area density and the comparison with the area density deposited on the sample. The area density deposited on the sample is calculated from the fluence ratio, the collected charge and the size of the beam spot on the sample. This size of the beam spot is the largest source of error since it can only be measured for the final film. The size may vary slightly during deposition due to ion source and focusing issues and the beam spot is not necessarily a perfect circle. Therefore, an error of $\Delta A = 0.23 \text{ cm}^2$ is assumed. The results for the films grown with ‘Adonis’ at a fixed ion energy of $E_{ion} = 100$ eV are shown in Figure 6.14. The nickel area density is plotted in dependence on the deposited nickel fluence. The nickel percentage used for deposition are marked and no strong dependence of the deviation from the 1:1 line (dotted line in Figure 6.14)

Figure 6.13.: RBS spectrum of a film grown with a fluence ratio of $r_f = 60/40 = 1.5$ and an ion energy of $E_{ion} = 100$ eV. The number of detected backscattered ions is plotted versus their energy. The C, Ni and Si edges describe the beginning of the corresponding signals and are marked by vertical lines. The solid line is the Rump simulation of the structure profile plotted in (b). The profile describes the layer composition. The vertical width of each layer corresponds to the area density of the layer and the brightness corresponds to the relative nickel content (black = pure nickel, white = pure carbon).

is visible. For the samples with $S_M > 1$ the deviation indicates the sputter loss and yields the surface segregation factor f_{surf} (see page 107).

Comparison of ‘Mr. Stringer’ and ‘Adonis’ Grown Films

The experimental data for the mean metal layer thickness d_m is summarized in Figure 6.15. A minimum metal layer thickness around $d_m = 7$ nm seems to be reached for $2 < r_f < 9$ for the ‘Mr. Stringer’ grown samples. This minimum cannot be definitely seen for the ‘Adonis’ grown samples since the samples do not have a clearly distinguishable metal layer for $r_f \geq 4$. Therefore, the margin of error is huge for these samples. Additionally the ‘Mr. Stringer’ and ‘Adonis’ samples do not show the same layer thickness for the same deposition parameters. This difference may arise from the differences in the setups mentioned in Section 3.1.2 and will be discussed in detail in Section 6.6. Nevertheless the mean metal layer thicknesses d_m seem to follow the same trend for both setups.

Figure 6.14.: The measured area density of Ni is plotted in dependence on the deposited Ni fluence. The dotted line is a guide for the eye at measured area density = deposited area density. The deviation of the data points from this line is an indication for the sputter loss.

The fluence ratio r_f dependence of the layer periodicity (p_{TEM} , p_{FFT}) shows a weak minimum for $r_f = 70/30 = 2.33$ of $p_{TEM} = (13.9 \pm 4.6)$ nm (Figure 6.16). This minimum is not visible in the data for the ‘Adonis’ samples since these films do not show a layered structure above $r_f = 60/40 = 1.5$. This difference in the sample morphology will also be discussed in Section 6.6 and will be possible related to the differences between both ion beam setups.

6.2. Dependence of the Film Growth on the Ion Energy E_{ion}

To analyze the dependence of the structure evolution during the film growth on the ion energy E_{ion} , a set of samples were grown with a fix fluence ratio of $r_f = 50/50 = 1$ with the setup ‘Mr. Stringer’. Since the energy of the ions depend on the adjusted voltage $U_{adjusted}$ in case of the film grown with this setup, this value is used then.

6.2.1. Films Prepared with the Setup ‘Mr. Stringer’

The films presented in this part were prepared with fixed fluence ratio of $r_f = 50/50 = 1$ and a varying adjusted voltage $U_{adjusted}$ with the setup ‘Mr. Stringer’.

Figure 6.15.: The fluence ratio r_f dependence of the experimental mean metal layer thickness d_m from samples grown by 'Mr. Stringer' (black dots) and 'Adonis' (red, open circles). A slight minimum is visible for $2 < r_f < 9$.

Figure 6.16.: The fluence ratio r_f dependence of the experimental layer periodicity p_{TEM} for samples grown by 'Mr. Stringer' (black dots) and 'Adonis' (red open circles) and the experimental layer periodicity determined from Fourier-transformed images p_{FFT} for the 'Mr. Stringer' (green squares) and 'Adonis' (blue open squares) samples.

Figure 6.17.: Cross-section TEM image of a film grown with a fluence ratio of $r_f = 50/50 = 1$ and an adjusted voltage of $U_{adjusted} = 300$ V. The film have a thickness of: $d_{film} = (67.1 \pm 0.6)$ nm.

The total metal sputtering yields S_M are given here for information only. They are calculated by assuming $e \cdot U_{adjusted} = E_{ion}$.

TEM and EDX Analysis

The first sample of this set was grown with an adjusted voltage of $U_{adjusted} = 100$ eV. The results are already presented in Section 6.1.1 on page 69 and the TEM image is shown in Figure 6.7. The layer periodicities were measured to be $p_{TEM} = (28.8 \pm 43.3)$ nm and $p_{FFT} = (10.1 \pm 6.4)$ nm.

Increasing the adjusted voltage to $U_{adjusted} = 300$ V results in a changed morphology. The total metal sputtering yield is $S_M = 1.95$ causing severe sputtering of metal on the film surface. Figure 6.17 shows the cross-section TEM image, revealing a ≈ 40 nm thick amorphous silicon layer (a-Si) on top of the crystalline silicon substrate. This layer is covered with $d_{aC} \approx 29$ nm amorphous carbon (a-C) and the layered nickel containing amorphous carbon film (a-C:Ni). This film shows a structure of one dense layer followed by a less dense double layer showing some kind of columnar structure. Then again a dense layer follows, covered by the platinum film from the FIB preparation. The a-C:Ni film is $d_{a-C:Ni} = (37.9 \pm 0.3)$ nm thick and the total deposited film thickness is $d_{film} = (67.1 \pm 0.6)$ nm. The metal-rich layers have a mean thickness of $d_m = (8.5 \pm 2.2)$ nm, yielding a mean layer periodicity of $p_{TEM} = (9.5 \pm 4.7)$ nm and $p_{FFT} = (6.8 \pm 1.7)$ nm.

Increasing the adjusted voltage to $U_{adjusted} = 500$ V results in dramatically changed morphology. The total metal sputter yield increases and the carbon-carbon sputtering gets more significant. The cross-section TEM images for a film grown with the setup ‘Mr. Stringer’ is shown in Figure 6.18a. The film exhibit a strong pronounced layered structure with 6 to 7 well separated layer. The film has a total

Figure 6.18.: (a) Cross-section TEM image of a film grown with a fluence ratio of $r_f = 50/50 = 1$ and an adjusted voltage of $U_{adjusted} = 500$ V with the setup ‘Mr. Stringer’. The film’s thickness is: $d_{film} = (119.4 \pm 0.5)$ nm. (b) EDX linescan of the film shown in (a). The abscissa is the position in the film from the starting point of the scan and the ordinate is the recorded intensity for the given X-ray line. The scan for ‘Mr. Stringer’ grown sample reveals a strong modulation in the Ni K α signal which corresponds to an anti-cyclic modulation in the C K α signal. The amorphous carbon layer on top of the substrate is also clearly distinguishable.

thickness of $d_{film} = (119.4 \pm 0.5)$ nm. The crystalline silicon substrate is amorphized up to a thickness of ≈ 60 nm and followed by an amorphous carbon layer of $d_{aC} \approx 35$ nm. The a-C:Ni layer is $d_{aC:Ni} = (83.6 \pm 0.9)$ nm thick with mean metal layer thickness of $d_m = (8.7 \pm 4.9)$ nm. The layer periodicity can be calculated to be $p_{TEM} = (13.9 \pm 4.6)$ nm and using the Fourier transformed TEM image: $p_{FFT} = (11.6 \pm 2.0)$ nm.

Figure 6.18b shows the EDX analysis of this film. There are 6 well resolved maxima in the nickel Ni K α signal, which corresponds to 6 local minima in the carbon C K α signal. The amorphous carbon (a-C) layer is also well resolved after the a-C:Ni film. The total film is terminated by the platinum Pt M β signal from the platinum cover layer and the silicon Si K α signal from the silicon substrate. A comparison of the linescan and the cross-section TEM image (Figure 6.18a) leads to the conclusion that the darker stripes are nickel-rich and carbon-deficient while the brighter stripes are nickel-deficient and carbon-rich.

The highest adjusted voltage $U_{adjusted}$ used for film growth during this thesis is $U_{adjusted} = 1000$ eV. Figure 6.19 displays a cross-section TEM images of the film: The crystalline silicon substrate is covered with an amorphous silicon layer of ≈ 75 nm and an amorphous carbon film of $d_{aC} \approx 29$ nm. The a-C:Ni films

Figure 6.19.: Cross-section TEM image of a film grown with a fluence ratio of $r_f = 50/50 = 1$ and an adjusted voltage of $U_{adjusted} = 1000$ V. The film is grown in the setup ‘Mr. Stringer’ and the film’s thickness is: $d_{film} = (63.0 \pm 1.1)$ nm.

is $d_{a-C:Ni} = (34.0 \pm 0.7)$ nm thick and is divided into two layers with a mean metal layer thickness of $d_m = (9.6 \pm 2.7)$ nm. This yields a layer periodicity of $p_{TEM} = (17.0 \pm 8.5)$ nm, which is difficult to determine in the Fourier transformed image: $p_{FFT} = (14.3 \pm 15.0)$ nm. The whole film is (63.0 ± 1.1) nm thick.

RBS Analysis

All films of this series were analyzed by Rutherford backscattering spectroscopy in order to get information about the concentration depth profile of the films.

The measured spectrum is analyzed by simulating a given layer profile (from the TEM image) and fitting this profile to the data by varying the concentrations and area densities of carbon and nickel. A typical RBS spectrum for a film grown with ‘Mr. Stringer’ at $U_{adjusted} = 500$ V and $r_f = 50/50 = 1$ is shown in Figure 6.20 together with the layer profile used for simulation with the Rump code [131, 148]. The solid line represents the Rump simulation of the profile given in Figure 6.20b. The nickel concentrations are color coded (black = pure nickel, white = pure carbon) and the vertical width of the layers corresponds to the area density of the layer. An absolute thickness cannot be given due to the unknown atomic density of the composite layers. The comparison with the cross-section TEM image (see Figure 6.18a) and the EDX linescan (see Figure 6.18b) reveals that the layers closer to the substrate (deeper in the sample) are not so well resolved. Due to multiple-scattering of the ions in the depth of the sample and the resulting the energy straggle, the depth

Figure 6.20.: RBS spectrum of a film grown with a fluence ratio of $r_f = 50/50 = 1$ and an adjusted voltage of $U_{adjusted} = 500 \text{ V}$ with the setup ‘Mr. Stringer’. The number of detected backscattered ions is plotted versus their energy. The C, Ni and Si edges describe the beginning of the corresponding signals and are marked by vertical lines. The solid line is the Rump simulation of the structure profile, which describes the layer composition and is plotted in (b). The vertical width of each layer corresponds to the area density of the layer and the brightness corresponds to the relative nickel content (black = pure nickel, white = pure carbon).

resolution of RBS decreases. Therefore, the layered structure cannot be resolved in detail at larger depth.

6.2.2. Films Prepared with the Setup ‘Adonis’

After discussing the results for the films grown with the setup ‘Mr. Stringer’, the following part covers the results from the films prepared with the setup ‘Adonis’.

TEM and EDX Analysis

This set starts with a film already presented in Section 6.1.2 on page 74. The film was grown with an ion energy $E_{ion} = 100 \text{ eV}$ and a fluence ratio of $r_f = 50/50 = 1$. The TEM image is shown in Figure 6.12. The layer periodicities were measured to be $p_{TEM} = (10.4 \pm 2.1) \text{ nm}$ and $p_{FFT} = (11.4 \pm 2.2) \text{ nm}$.

Increasing the deposition energy to $E_{ion} = 300 \text{ eV}$ results in a strongly changed morphology. The total metal sputtering yield is $S_M = 1.95$ causing severe sputtering of metal on the film surface. Figure 6.21 displays the film grown with ‘Adonis’. This

Figure 6.21.: Cross-section TEM image of a film grown with a fluence ratio of $r_f = 50/50 = 1$ and an ion energy of $E_{ion} = 300$ eV. The film grown with the setup ‘Adonis’ has a film thickness of: $d_{film} = (66.3 \pm 0.2)$ nm.

film shows ≈ 32 nm amorphous silicon on top of the crystalline silicon. This substrate was sputtered with 30 mC $^{40}\text{Ar}^+$ at 1 keV instead of 15 mC before deposition of the amorphous carbon layer, but this cannot explain the thick amorphous silicon layer since the penetration depth of 1 keV $^{40}\text{Ar}^+$ into silicon is only (2 - 5) nm [48]. Maybe this is an artifact of the FIB preparation of the sample for the TEM since the intense gallium ion beam erodes and amorphizes the surface of the TEM lamella. This amorphous silicon layer is covered with the amorphous carbon layer ($d_{aC} \approx 14$ nm) deposited prior to the a-C:Ni film. This film is $d_{a-C:Ni} = (52.0 \pm 0.2)$ nm thick and seems to consist of one very thin nickel rich layer, which is not resolved in the EDX linescan (not shown), and two not well separated layers. This gives a layer periodicity of $p_{TEM} = (26.0 \pm 13.0)$ nm with a mean metal layer thickness $d_m = (15.5 \pm 9.9)$ nm. The surface of the film is covered with the (electron and ion beam deposited) platinum from the FIB preparation and the total film thickness is $d_{film} = (66.3 \pm 0.2)$ nm.

Increasing the deposition energy to $E_{ion} = 500$ eV results in an increase of the total metal sputter yield to $S_M = 2.85$ and the carbon-carbon sputtering gets more significant: $S_{C \rightarrow C} = 0.24$. The cross-section TEM image for a film grown with the setup ‘Adonis’ is presented in Figure 6.22a. The sample is quite thin and has a total film thickness of: $d_{film} = (29.4 \pm 0.2)$ nm. The a-C:Ni layer of $d_{a-C:Ni} = (8.4 \pm 0.3)$ nm could hardly be recognized between the amorphous carbon layer of ≈ 21 nm and the platinum cover layer. The amorphized silicon layer is only ≈ 6 nm thick, which is a sign that the amorphization thickness does not depend directly on the ion energy E_{ion} during film deposition (see the film grown with $E_{ion} = 300$ eV).

Figure 6.22.: (a) Cross-section TEM image of a film grown with a fluence ratio of $r_f = 50/50 = 1$ and an ion energy of $E_{ion} = 500$ eV. The film is grown with the setup ‘Adonis’ and has a thickness of (29.4 ± 0.2) nm. (b) EDX linescan of the film shown in (a). The abscissa is the position in the film from the starting point of the scan and the ordinate is the recorded intensity for the given X-ray line. The scan on the ‘Adonis’ sample shows the amorphous carbon layer and only a weak Ni K α signal on the film surface.

Figure 6.22b shows the EDX analysis of these films. The linescan does not show any modulation in the nickel Ni K α signal (Figure 6.18b). Instead the nickel Ni K α is very weak and shows only a slight increase towards the film surface in the platinum region. The carbon rich layer, deposited prior to the a-C:Ni film, is otherwise well resolved. This leads to the conclusion that the sample is indeed very nickel deficient and only a thin nickel rich surface layer exists, which is hard to resolve in the cross-section TEM image (Figure 6.22a) due to the inevitable platinum cover layer.

RBS Analysis

All films of this series were analyzed by Rutherford backscattering spectroscopy in order to get information about the concentration depth profiles of the films and the area densities of carbon and metal in the layers.

A measured spectrum for the film grown with ‘Adonis’ at an ion energy of $E_{ion} = 500$ eV and a fluence ratio of $r_f = 50/50 = 1$ is shown in Figure 6.23, together with the layer profile used for simulation with the Rump code [131, 148]. The spectrum shows very few nickel which can also be seen in the cross-section TEM image (see Figure 6.22a) and the EDX linescan (see Figure 6.22b). The simulation does not follow exactly the data at the silicon edge, due to the not included channeling effect. The channeling effect reduces the backscattering yield for the helium ions

Figure 6.23.: RBS spectrum of a film grown with a fluence ratio of $r_f = 50/50 = 1$ and an ion energy of $E_{ion} = 500$ eV. The number of detected backscattered ions is plotted versus their energy. The C, Ni and Si edges describe the beginning of the corresponding signals and are marked by vertical lines. The solid line is the Rump simulation of the structure profile, which describes the layer composition and is plotted in (b). The vertical width of each layer corresponds to the area density of the layer and the brightness corresponds to the relative nickel content (black = pure nickel, white = pure carbon).

along the lattices direction due to lattice guiding and therefore reduces the signal in channeling direction of the substrate.

The Rump analysis results in a determination of the area density of nickel in relation to the area density of nickel deposited during film growth. This allows the estimation of a sputter losses. The results are plotted in Figure 6.24. The films grown at higher ion energies show less nickel incorporated in the film than films at e. g. $E_{ion} = 100$ eV. This is expected due to the increasing sputtering yield of nickel with increasing ion energy (see Figure 6.2). On the other hand, the carbon content is around 57% of the deposited carbon in total film (a-C + a-C:Ni layer) and shows no significant dependence on the ion energy.

Comparison of ‘Mr. Stringer’ and ‘Adonis’ Grown Films

The energy dependence of the mean metal layer thickness d_m is summarized in Figure 6.25. There is a minimum mean metal layer thickness for the ‘Mr. Stringer’ grown samples observable. The minimum is $d_m = (8.5 \pm 2.2)$ for $U_{adjusted} = 300$ eV. The ‘Adonis’ grown samples show a maximum for d_m in the same energy regime: $d_m = (15.5 \pm 9.9)$ nm. For higher energies (≥ 500 eV) only a weak metal layer is

Figure 6.24.: The measured area density of Ni is plotted in dependence on the deposited Ni fluence. The dotted line is a guide for the eye at measured area density = deposited area density.

observed for the ‘Adonis’ grown samples, therefore it can be concluded that there is a decrease of the mean metal layer thickness to $d_m \approx 0$ for higher energies. The same should be expected for the ‘Mr. Stringer’ grown samples since the sputter yield for nickel by the incoming carbon and nickel ions increases with the ion energy (see Figure 6.2).

The ion energy E_{ion} dependence of the layer periodicity (p_{TEM} and p_{FFT}) is shown in Figure 6.26. The ‘Mr. Stringer’ grown samples show a minimum layer periodicity for $100 \text{ eV} < E_{ion} < 500 \text{ eV}$ of $p_{TEM} = (9.5 \pm 4.7) \text{ nm}$ and $p_{FFT} = (6.8 \pm 1.7) \text{ nm}$. The films grown with ‘Adonis’ do not show this behavior. Only an increase of the layer periodicity from 100 eV to 300 eV can be determined, for higher energies no multilayer evolution takes places. While the multilayer evolution continues even to high adjusted voltages $U_{adjusted}$ for the ‘Mr. Stringer’ grown samples, the evolution stops in case of the ‘Adonis’ grown sample above 300 eV. The onset of the multilayer formation for increasing ion energies is not expected according to the model of Gerhards and co-workers (Section 2.2) since the total metal sputtering yield S_M increases with the ion energy and is $S_M > 1$ at energies above 150 eV for $r_f = 50/50 = 1$. Possible reasons for this behavior are discussed in detail in Section 6.6.

Figure 6.25.: The ion energy E_{ion} dependence of the experimental mean metal layer thickness d_m from samples grown by 'Mr. Stringer' (black dots) and 'Adonis' (red, open circles). A slight minimum is visible for $100 < U_{adjusted} < 500$ for the 'Mr. Stringer' samples while the 'Adonis' samples show a maximum layer periodicity in this energy regime.

Figure 6.26.: The ion energy E_{ion} dependence of the experimental layer periodicity p_{TEM} for samples grown by 'Mr. Stringer' (black dots) and 'Adonis' (red open circles) and the experimental layer periodicity determined from Fourier-transformed images p_{FFT} for the 'Mr. Stringer' (green squares) and 'Adonis' (blue open squares) samples.

Figure 6.27.: XRD diffractogram of a pure nickel target. The diffracted intensity is plotted over the diffraction angle 2θ . The solid lines are fits to the peaks using a Voigt function. The Ni (111) and Ni (200) reflexes are clearly visible.

6.3. X-ray Diffraction Analysis of the Films

Some films were examined using X-ray diffraction (XRD) to get an estimation of the cluster sizes and phases present in the samples.

The first result is from a pure nickel sputter target used in the Penning ion source. Figure 6.27 shows the $\theta - 2\theta$ diffractogram for $2\theta = (40 - 55)^\circ$. The solid lines are plots of Voigt functions used for fitting the peaks [150]. The Lorentz half-width of the peaks can give an estimate for the crystallite size in the sample using equation 4.5. The results for the two peaks with the highest Bragg-intensity are summarized in the Table 6.2.

A weighted mean crystallite size (= grain size) of the sputter target can be calculated to be (94 ± 11) nm. Since the small peak width is strongly influenced by the peak broadening induced by the setup (approximately in the same order of magnitude), the grain size in the nickel target is underestimated by the Scherrer formula in this case. The reflexes were assigned to the lattice directions by using the PCPDFWIN 1.30 database [149].

The $\theta - 2\theta$ XRD analysis of the grown films is quite difficult due to the small total amount of nickel in the films, the small total film thickness and the very small cluster sizes in the samples (as seen in the cross-section TEM images). The sample with

Figure 6.28.: XRD diffractogram of the film grown with ‘Mr. Stringer’ using an adjusted voltage of $U_{\text{adjusted}} = 500 \text{ V}$ and a fluence ratio of $r_f = 50/50 = 1$. The diffracted intensity is plotted over the diffraction angle 2θ . The vertical lines are guides for the eye where the Ni (solid black), Ni₃C (dotted red) and NiC_x (dashed green) reflexes are expected. The height is the relative Bragg intensity of these peaks according to Reference [149].

the possibly largest total amount of nickel is the one grown with an adjusted voltage of $U_{\text{adjusted}} = 500 \text{ V}$ and a fluence ratio of $r_f = 50/50 = 1$ with ‘Mr. Stringer’. The sample was positioned in the XRD setup by measuring and maximizing the count rate for the Si (400) reflex of the crystalline silicon (100) substrate at $2\theta = 69.130^\circ$. This ensures a maximum measurable intensity for the peaks of the a-C:Ni film. The resulting diffractogram is shown in Figure 6.28. The XRD intensity is plotted over the diffraction angle 2θ and the vertical lines are guide for the eye at the expected positions of the nickel (Ni) and the nickel carbide (Ni₃C and NiC_x) reflexes according to the PCPDFWIN database [149]. The low intensity does not allow a definite identification of the phase nor the fitting of any peak. It can be estimated that the sample contains a mixture of small nickel and nickel carbide Ni₃C clusters since there are weak uprisings in the noise level at the expected position. Any further analysis is not possible with these data.

Table 6.2.: Diffraction lines of the pure nickel target. The position and Lorentz-width of the peaks fitted by Voigt functions are given together with the estimation of the crystallite size.

Line	Position 2θ [degrees]	w_{Lorentz} [degrees]	Crystallite size [nm]
Ni (111)	44.437 ± 0.006	0.06 ± 0.02	145 ± 52
Ni (200)	51.778 ± 0.002	0.10 ± 0.01	91 ± 11

Table 6.3.: Diffraction lines of the film grown at $E_{\text{ion}} = 300$ eV and $r_f = 50/50 = 1$ with the setup ‘Adonis’. The position and Lorentz-width of the peaks fitted by Voigt functions are given together with the estimation of the crystallite size.

Possible Line	Position 2θ [degrees]	w_{Lorentz} [degrees]	Crystallite size [nm]
Ni (111) or Ni ₃ C	44.00 ± 0.05	0.7 ± 1.1	13 ± 23
Ni ₃ C (006)	41.74 ± 0.06	1.3 ± 1.7	7 ± 9

Figure 6.29 display the diffractogram of the film grown with ‘Adonis’ at an ion energy $E_{\text{ion}} = 300$ eV and a fluence ratio $r_f = 50/50 = 1$. It is the only sample that shows some weak peaks that possibly could be attributed to Ni₃C. The solid lines show the Voigt-functions fits to this peaks. Since the peaks are very noisy the results has a quite huge margin of error. Nevertheless, it allows the estimation of a crystallite size. The results are given in Table 6.3. The weighted mean value of the crystallite size is (7.5 ± 8.2) nm, whereas the cross-section TEM images show an average cluster size of (5.4 ± 0.8) . It can be concluded that these results are consistent, but have a large margin of error due to the weak intensities.

Any further spectra taken from other sample show almost the same, just the overall noise level varies at bit. Even the increase of the measuring time does not result in acceptable spectra. An estimation of the expected peak width using the Scherrer formula (Equation 4.5) results: $w_{\text{Lorentz}} \approx (1 - 10)^\circ$ for nickel crystallites of a size of $10 - 1$ nm. As these size should be expected knowing the cross-section TEM images, the lines may be too broad to distinguish from the background. Therefore, it can be concluded that the size of the clusters is well below 10 nm for the thicker films. On the other hand the nickel cluster amount in the films may be too low due to the low film thickness or the distribution of the nickel in the amorphous carbon layer with even smaller clusters size.

Figure 6.29.: XRD diffractogram of the film grown with ‘Adonis’ using an ion energy of $E_{ion} = 300$ eV and a fluence ratio of $r_f = 50/50 = 1$. The diffracted intensity is plotted over the diffraction angle 2θ . The vertical lines are guides for the eye where the Ni (solid black), Ni_3C (dotted red) and NiC_x (dashed green) reflexes are expected. The height is relative Bragg intensity of these peaks according to Reference [149]. The solid lines are Voigt-functions fits to the peaks.

6.4. X-ray Induced Photo-electron Spectroscopy Analysis of the Films

All films grown with the setup ‘Adonis’ were analyzed in-situ by X-ray induced photo-electron spectroscopy (XPS). This surface sensitive technique allows the estimation of the sp^2/sp^3 -bonding ratio [107, 151] and additionally an estimation of the nickel cluster size evolution in the surface near layers [102, 152].

XPS Matrix and Cluster Analysis

The carbon C $1s_{1/2}$ peak as well as nickel Ni $2p_{1/2}$ and Ni $2p_{3/2}$ peaks were recorded and analyzed in detail. A typical XPS spectrum is shown in Figure 6.30. The XPS peaks are indexed using the database of the EIS software package [153] and the Auger

Figure 6.30.: XPS survey spectrum of a film deposited at $E_{ion} = 100$ eV and $r_f = 60/40 = 1.5$ with ‘Adonis’. The XPS intensity is plotted in dependence on the binding energy. The peaks are indexed to the corresponding carbon and nickel lines.

line are identified using the publication of G. C. Allen and co-workers [154]. There are no other lines and it can be concluded that the film is free of contaminations of other elements on the surface and in the surface near region. This is also true for all other films grown with the setup ‘Adonis’. For the films grown with the setup ‘Mr. Stringer’ the analysis was not carried out, since this required the ex-situ transfer between ‘Mr. Stringer’ and the XPS setup attached to ‘Adonis’, which will contaminate the film surface with adsorbates.

Figure 6.31 shows the detail spectra of the carbon C $1s_{1/2}$ line (see Figure 6.31a) and the nickel Ni $2p_{3/2}$ and Ni $2p_{1/2}$ lines (see Figure 6.31b). The carbon spectrum reveals beside the C $1s_{1/2}$ line also a line at a smaller binding energy. This peak results also from the C $1s_{1/2}$ line but excited by the $MgK\beta$ line which is not filtered in the X-ray source. The peak at a higher binding energy results from the plasmon resonance of the carbon. The energy difference between the C $1s_{1/2}$ line and the plasmon allows the estimation of the sp^2/sp^3 -bonding ratio f_{sp^3} in the surface near film region by using the formula:

$$f_{sp^3} \approx \frac{\omega_{pl} - \omega_{pl,G}}{\omega_{pl,D} - \omega_{pl,G}}$$

where $\hbar\omega_{pl}$ is the measured energy of the plasmon, $\hbar\omega_{pl,G} \approx 24$ eV the plasmon energy of graphite and $\hbar\omega_{pl,D} \approx 33$ eV of diamond [107].

(a) Carbon C 1s spectrum.

(b) Nickel Ni 2p_{3/2} and Ni 2p_{1/2} spectrum.

Figure 6.31.: XPS detail spectra of a film deposited at $E_{ion} = 100$ eV and $r_f = 60/40 = 1.5$ with ‘Adonis’. The XPS intensity is plotted in dependence on the binding energy. (a) shows the carbon C 1s line and (b) the Ni 2p_{3/2} and Ni 2p_{1/2} lines.

Table 6.4.: sp³ bonding fraction f_{sp^3} for films grown at $E_{ion} = 100$ eV and varied r_f with the setup ‘Adonis’.

Ion energy E_{ion} [eV]	Fluence ratio r_f	f_{sp^3}
100	90/10 = 9	0.56 ± 0.02
100	80/20 = 4	0.46 ± 0.03
100	60/40 = 1.5	0.63 ± 0.06
100	50/50 = 1	0.67 ± 0.06

The C 1s_{1/2} line and the plasmon position were fitted using two gaussian profiles and a linear background. From this data the plasmon energy is calculated as difference between both positions and the sp³ bonding ratio f_{sp^3} is estimated. For the samples grown with ‘Adonis’ and discussed in the Sections 6.1 and 6.2 the results are summarized in Table 6.4. For the samples grown with an ion energy $E_{ion} = 100$ eV no definite trend with respect to the nickel content can be observed for the f_{sp^3} ratio, a decrease would be expected since the addition of metal atoms to the carbon matrix could reduce the f_{sp^3} ratio, since the metal cluster are probably surrounded by sp² bonded atoms [102]. This behavior could not be observed, but the influence of the nickel atoms on the plasmon energy is not taken into account.

Table 6.5.: sp^3 bonding fraction f_{sp^3} for films grown at $r_f = 50/50 = 1$ and varied E_{ion} with the setup ‘Adonis’.

Ion energy E_{ion} [eV]	Fluence ratio r_f	f_{sp^3}
100	50/50 = 1	0.67 ± 0.06
300	50/50 = 1	0.22 ± 0.22
500	50/50 = 1	0.16 ± 0.03

(a) Carbon C 1s spectra for various nickel fractions. (b) Carbon C 1s line positions for various nickel fractions.

Figure 6.32.: XPS C 1s spectra of films deposited at $E_{ion} = 100$ eV and various r_f deposited with ‘Adonis’. (a) displays the spectrum as intensity of binding energy while (b) is the extracted C 1s position for the given nickel fractions. The line positions of the C 1s for graphite and ta-C are marked.

The ion energy E_{ion} dependence of the sp^3 bonding ratio f_{sp^3} shows a clearly observable decrease with increasing ion energy E_{ion} (see Table 6.5). This behavior is well known for pure amorphous carbon films, where the maximum $f_{sp^3} \approx 0.8$ is reached for a $^{12}C^+$ ion energy of $E_{ion} = 100$ eV [107]. The margin of error of the f_{sp^3} ratio for the film grown with an ion energy $E_{ion} = 300$ eV is huge due the weak visible plasmon, which can only be fitted with a huge margin of error for the position.

Additionally, another hint on the sp^3 content can be extracted from the peak shift of the C $1s_{1/2}$ line. The results are plotted for the fluence ratio r_f dependence in Figure 6.32. The spectra in Figure 6.32a are shifted vertically to gain a better overview over the evolution of the line positions. In Figure 6.32b the line positions are plotted for the nickel fraction offered during deposition. The positions for pure

(a) Nickel 2p spectra for various nickel fractions. (b) Ni 2p line positions for various nickel fractions.

Figure 6.33.: XPS Ni 2p spectra of films deposited at $E_{ion} = 100$ eV and various r_f deposited with ‘Adonis’. (a) displays the spectrum as intensity of binding energy while (b) is the extracted Ni 2p line positions for the given nickel fractions. The dotted lines give the Ni 2p_{3/2} and Ni 2p_{1/2} line positions according to the EIS database [153].

graphite and pure ta-C are marked with the dotted lines [155]. The peak shifts to lower binding energies for rising nickel fractions, meaning the matrix gets more sp² bonded and then at $r_f = 50/5 = 1$ the peak shifts to higher binding energies again. Therefore, no clear trend can be identified and no conclusion for the bonding ratio evolution can be drawn here. The evolution is also not in conformation with the results from the plasmon analysis, which is a hint that the peak position and the plasmon energy may be influenced by the nickel directly and not only by affecting the bonding ratio.

The evolution of the positions of the nickel Ni 2p lines can give a hint on the evolution of the cluster size in the surface near regions (see Figure 6.33). The small clusters cannot neutralize their charge fast enough in the non or only weakly conductive matrix and therefore influence the energy of the escaping photo electron. The line will shift to higher binding energies for smaller cluster sizes [102, 152]. The spectra are shown in Figure 6.33a and vertically offset for visual clarity and the extracted line positions are given in Figure 6.33b for the corresponding nickel fractions offered during deposition. No clear trend is observable with respect to the deposited nickel fraction but all measured lines show a shift towards higher binding energies and both Ni 2p lines shift in the same manner. It can be concluded that the films contains small nickel clusters and for low nickel concentration (10 at.%) these clusters are smaller than for higher nickel content.

(a) Carbon C1 line position for various deposition energies.

(b) Nickel 2p lines position for various deposition energies.

Figure 6.34.: XPS line positions of the (a) $C 1s_{1/2}$ and (b) $Ni 2p$ lines in dependence on the deposition energy E_{ion} . The films were grown with a fixed fluence ratio of $r_f = 50/50 = 1$ with the setup ‘Adonis’. The line positions of the $C 1s$ for graphite and ta-C as well as the Nickel $2p$ lines are marked.

The same analysis is carried out for the $C 1s_{1/2}$ and the $Ni 2p_{3/2}$ and $2p_{1/2}$ lines in dependence on the ion energy E_{ion} at a fixed fluence ratio $r_f = 50/50 = 1$ for films grown with ‘Adonis’. The line positions are plotted in Figure 6.34. The carbon $C 1s_{1/2}$ line show no trend with the ion energy, the line position seems to scatter without any energy dependence between the values for graphite and ta-C [155]. The observed decrease of the sp^3 -bonding ratio from the plasmon energy analysis is not visible here. Maybe the already mentioned unknown contribution of the nickel to the line position and plasmon energy is also visible here. The line positions of the nickel $Ni 2p_{3/2}$ and $2p_{1/2}$ line shift both to higher binding energies indicating the presents of small clusters which cannot discharge quick enough due to the surrounding matrix.

XPS Stoichiometry Analysis

The stoichiometry of the surface near region can be estimated by measuring the area below the $C 1s_{1/2}$ and the $Ni 2p_{3/2}$ lines. This area has to be scaled with the sensitivity factors of the lines (from the EIS software package [153]). The results for the energy E_{ion} and fluence ratio r_f dependence are plotted in Figure 6.35. The probed surface near region contains less nickel than offered during deposition. This is expected due to sputtering of segregated nickel at the film surface. On the other hand, the clusters in the film have a size large than the sampling depth of the XPS (2 - 10) nm [139]. Therefore, some nickel may not be seen by XPS. The energy dependence of the nickel concentration reveals a strong decrease towards ion energies

(a) Measured nickel concentration in dependence on the Ni⁺ ion supply for fixed $E_{ion} = 100$ eV .

(b) Measured nickel concentration in dependence on the deposition energies E_{ion} for fixed $r_f = 50/50 = 1$.

Figure 6.35.: The estimated nickel concentration from the peak area of the C 1s and the Ni 2p_{3/2} lines. (a) shows the dependence with respect to the offered Ni⁺ ions during growth for a fixed ion energy of $E_{ion} = 100$ eV and (b) with respect to the ion energy E_{ion} at fixed fluence ratio $r_f = 50/50 = 1$. The nickel contents fraction = nickel fluence ratio line is marked.

of $E_{ion} = 500$ eV , which is expected due to the increasing sputtering of nickel with increasing ion energy E_{ion} (see Figure 6.35b). On the other hand, the implantation depth increases and the nickel surface segregation may decrease, which also yields a decrease of nickel in the examined sample volume. Additionally the films at higher ion energies are thin and the substrate is covered with a pure amorphous carbon layer which also may shift the concentration towards the carbon rich regime.

It can be concluded that the surface near region is always depleted from nickel with respect to the offered nickel during deposition. A nickel rich surface layer cannot be excluded due to the sampling depth of (2 - 10) nm [139].

6.5. UV-Raman Analysis of the Films

Some films were investigate using μ UV-Raman at the Center of Superdiamond and Advanced Films (COSDAF) of the City University of Hong Kong. The films are positioned using a light microscope which also allow the investigation of surface changes after measurement.

Figure 6.36.: (a) The Raman spectra of a film grown with ‘Mr. Stringer’ with an adjusted Voltage of $U_{\text{adjusted}} = 100$ V and a fluence ratio of $r_f = 90/10 = 9$. The solid line is a fit using three Gauss functions for the D- and G- band and the oxygen peak. (b) A microscopy image of the investigated position. The film is clearly damaged in the marked region.

Figure 6.36a displays the Raman measurement of a film grown with ‘Mr. Stringer’ at an adjusted voltage of $U_{\text{adjusted}} = 100$ V and a fluence ratio of $r_f = 90/10 = 9$. The D- and G-band and the sharp oxygen peak are fitted using three Gauss functions. The positions are 1488 cm^{-1} (D-band), 1580 cm^{-1} G-band and 1556 cm^{-1} oxygen, respectively. The microscopy image shown in Figure 6.36b was taken directly after acquisition of the spectrum. The darker region in the center marked by the circle is the region irradiated by the laser during the measurement. The color change is a clear hint that the laser changed the sample irreversibly in this spot due to a too high energy deposition. Therefore, the intensity was decreased and the sample was measured in 441 spots in a 21×21 raster with a measuring time of 6 second per spot. The resulting spectra were summed up afterwards. A typical spectrum is shown in Figure 6.37a. The spectrum is dominated by an extremely sharp (1 channel) peak at 1486 cm^{-1} and the oxygen peak at $\approx 1552 \text{ cm}^{-1}$. The D- and G-band cannot be identified due to the weak overall signal to noise ratio (noise ≈ 3000 counts, signal ≈ 600 counts), therefore no reasonable fitting can be done.

Another typical spectrum is shown in Figure 6.37b. This spectrum is completely dominated by the oxygen line and no carbon signal can be recognized in the noise level. All other spectra taken during the research stay in Hong Kong look similar to the shown examples: The spectra show a low signal-to-noise ratio due to the low laser intensity and the short measuring time of each spot. This results in a too low statistic, but the increase of measuring time or laser power damages the film. The

(a) Film grown with a fluence ratio of $r_f = 90/10 = 9$. (b) Film grown with a fluence ratio of $r_f = 60/40 = 1.5$.

Figure 6.37.: The Raman sum-spectra of 441 single spectra of a film grown with ‘Mr. Stringer’ with an adjusted Voltage of 100 eV and a fluence ratio of $r_f = 90/10 = 9$ (a) and $r_f = 60/40 = 1.5$ (b). The spectra are dominated by a 1 channel wide line at 1486 cm^{-1} (a) and the oxygen line (a+b).

low intensity of the carbon signal could be a hint for a low transparent matrix due to a high sp^2 bonding ratio or an optical dense matrix due to the incorporated nickel clusters. The absorption of the laser energy by the film changes the morphology and bonding structure of the film, which makes the investigated area visible to naked eye as darker spot. The low intensity of the Raman signal for the metal containing amorphous carbon films have also been reported in previous studies [49, 102]. It can be concluded that the absorption of the laser energy in the films is strong and results in a change of the film and in a low Raman intensity. This could possibly be attributed to the densely distributed nickel clusters in the films.

6.6. The Impact of the Characteristics of ‘Mr. Stringer’ on the Film Deposition

The main points have already been discussed in Section 3.1.2 and only are summarized here:

- The ion currents are lower than for the setup ‘Adonis’, resulting in a longer deposition time.
- The Penning ion source delivers an ion beam with a broad energy distribution.
 - The distribution depends slightly on the extracted isotope.

- The energy have to be adjusted using the bias voltage.
- The charge measurement is influenced by free electrons.
 - These free electrons originate from from sputtering and residual gas ionizing.
- The setup does not have an neutral trap, which could prevent ion which will get neutralized to arrive at the substrate.

The different aspects will be discussed in the following with respect to the impact on the film deposition.

6.6.1. Influence of the Deposition Duration on the Film Evolution

One difference between the setups ‘Mr. Stringer’ and ‘Adonis’ shows up in the possible ion currents. The ion currents on the substrate are in the case of ‘Adonis’ with the Sidenius hot filament hollow-cathode source up to $20 \mu\text{A } ^{12}\text{C}^+$ and $10 \mu\text{A } ^{58}\text{Ni}^+$, which allows the deposition of one film in a few days. On the other hand the ion currents with the Penning ion source of ‘Mr. Stringer’ are around $10 \mu\text{A}$ for $^{12}\text{C}^+$ and $(0.3 - 0.5) \mu\text{A } ^{58}\text{Ni}^+$. This needs much more time for deposition of the films, e. g. the deposition of the film with an ion energy of $E_{ion} = 500 \text{ eV}$ and a fluence ratio of $r_f = 50/50 = 1$ took about 1 month. Together with a less good vacuum in the deposition chamber of ‘Mr. Stringer’ ($< 1 \cdot 10^{-6} \text{ mbar}$) compared with ‘Adonis’ ($< 1 \cdot 10^{-7} \text{ mbar}$) a deposition induced structure could arise and could be different for both setups.

To test the influence of the deposition timespan on the film evolution, the charge deposited per day is plotted and compared with the cross-section TEM images. The first set was the films grown with an adjusted voltage of $U_{adjusted} = 100 \text{ V}$ or an ion energy of $E_{ion} = 100 \text{ eV}$ and a fluence ratio $r_f = 50/50 = 1$. The results are shown in Figure 6.38: The cross-section TEM images are always a detail of the images printed in Sections 6.1.1, 6.1.2 and 6.2.1, 6.2.2, respectively. The charge per day is extracted from the deposition protocols and does not correlated directly with the ion current on the sample, e. g. a short time with a high current may have the same height as a longer time with a smaller ion current. For the ‘Mr. Stringer’ grown film (see Figure 6.38a) almost no correlation between deposition and breaks time and the layered structure can be seen. Even if a correlation for the first layer on top of the a-C may be seen, this correlation drops for the next two dark layers, which then should have a distance correlated to the breaks time, which cannot be seen. In the case of the ‘Adonis’ grown sample (see Figure 6.38b) no correlation between days of deposition and days with no deposition on the film structure is visible at all.

The second test is done with the set of samples grown at $U_{adjusted} = 500 \text{ V}$ or at $E_{ion} = 500 \text{ eV}$ and $r_f = 50/50 = 1$. Figure 6.39a shows the result for the ‘Mr.

Figure 6.38.: Charge per day of deposition for the samples grown with an ion energy of $E_{ion} = 100$ eV and a fluence ratio of $r_f = 50/50 = 1$. (a) displays the ‘Mr. Stringer’ grown film while (b) display the ‘Adonis’ grown film. On top of both pictures the details of the a-C:Ni film of the cross-section TEM images are shown. No correlation between dark and bright layers and deposition days or breaks can be seen.

Stringer’ grown sample. The cross-section TEM image above the deposition diagram shows a clear layered structure, which cannot be linked to the deposited charge per day diagram. The first layer following the amorphous carbon a-C may be attributed to the growth of day 1 to day 5 but the following layers do not correspond to the deposition day and breaks structure. The second layer is much thicker than the third one, but the deposition on day 9 is followed by a break of one day and then 2 days of deposition which should lead to an reversed thickness distribution if a correlation exist.

For the ‘Adonis’ grown film the result is shown in Figure 6.39b. The film is very thin and the cross-section TEM image does not allow a clear identification of an a-C:Ni layer (see Figure 6.22a). Therefore, the deposition profile cannot be linked to any layers in the a-C:Ni film.

Figure 6.39.: Charge per day of deposition for the sample grown by ‘Mr. Stringer’ with an ion energy of $E_{ion} = 500$ eV and a fluence ratio of $r_f = 50/50 = 1$. (a) displays the ‘Mr. Stringer’ grown film while (b) display the ‘Adonis’ grown film. On top of (a) the detail of the a-C:Ni film of the cross-section TEM images is shown. No correlation between dark and bright layers and deposition days or breaks can be seen. For the (b) film the a-C:Ni layer is very thin an cannot be identified clearly in the cross-section TEM image.

The stated results allows to conclude that the sequence of deposition days and breaks do not have a significant influence on the evolution of the nanocomposite a-C:Ni film and on the layer formation process for both setups.

6.6.2. Influence of the Energy Distribution and the Charge Measurement on the Film Evolution

The charge measurement in the setup ‘Mr. Stringer’ is influenced by free electrons, which results in a charge measurement, which is to low. Therefore, the films are thicker than expected and contain more carbon and nickel than calculated from the measured charge, as stated in Section 3.1.2 and proven by an RBS analysis.

The cross-section TEM images for the films grown at higher adjusted voltages (> 200 V), show a pronounced layered structure (see Section 6.2.1), which is not expected from the model of Gerhards et al. and is not seen in the cross-section TEM images for films grown with ‘Adonis’ (see Section 6.2.2). Due to the high total metal sputtering yield for e. g. $E_{ion} = 500$ eV and $r_f = 50/50 = 1$ of $S_M = 2.85$, no metal rich surface layer could evolve. Therefore, it can be concluded that the adjusted

voltage U_{adjusted} is not equal E_{ion}/e , which was assumed for deposition. Actually the energy must be lower than $U_{\text{adjusted}} \cdot e$.

This could possibly explained by the following scenario: The adjusted voltage U_{adjusted} is determined by decreasing the bias voltage U_{bias} until the ion current reaches $I_{1/2} = \frac{1}{2} \cdot I(U_{\text{bias}} = \text{max}) = \frac{1}{2} \cdot I_{\text{max}}$. This voltage is $U_{\text{adjusted}} = 0$ V. If the actual energy of the ions is lower than the adjusted energy, it can be concluded that the determined voltage $U_{\text{adjusted}} = 0$ V is too low. This is possible, if the measured ion current decreases slower than the real ion current ion dependence on bias voltage U_{bias} .

The ion current is affected by free electrons resulting from sputtering and ionization of the residual gas. Since the ions are deflected and defocused by the substrate if the bias voltage U_{bias} is low, these processes may play an increasing role. The reflected ions will hit the chamber and the surrounding of the target holder, where they eject free electrons. These electrons will increase the measured current, if they arrive at the sample or neutralize the ions in the beam. Therefore, the measured current will not decrease as slow as the ion current and the $U_{\text{adjusted},0}$ is improperly determined too low.

6.6.3. Influence of the Neutral Atoms on the Film Evolution

The neutral atoms will contribute to the films growth without being counted for the charge and, since they are not decelerated, they will deposit energy in the film and get implanted in the depth of the film or the substrate. The implantation depth of 30 keV $^{12}\text{C}^+$ into carbon is about 71 nm and of $^{58}\text{Ni}^+$ into carbon is about 24 nm [48].

To get an estimation of the amount of metal ions contributing to the film growth, a pure silicon substrate was irradiated in former studies at $U_{\text{bias}} = 0$ V with copper atoms. Therefore, the source was prepared with a pure copper target and the separation magnet was tuned to the desired mass. Due to the bias voltage, no current was measured at the sample and the irradiation was stopped after a few hours. The sample was analyzed afterwards with RBS to determine the copper area density. The area density seems to be too low to measure, since no signal except the silicon one appears in the spectrum. Therefore, it can be concluded that the amount of metal atoms contributing to the films growth can be neglected. On the other hand, the influence of the energy deposition remains unclear and has to be kept in mind, when discussing the results.

6.7. Discussion and Conclusion

The results of the films grown with ‘Mr. Stringer’ show that the current measurement is important to get the right energy calibration. Since the films show a well defined layered structure for a deposition voltage of $U_{\text{adjusted}} = 500$ eV, the deposition energy has to be lower than 140 eV for the fluence ratio $r_f = 50/50 = 1$, which could be

estimated from the green dashed area in Figure 6.1b. With a 3rd order polynomial fit to energy dependence of the sputter yields $S_{C\text{Ni}}$ and S_{NiNi} an approximation function for $S_M(E_{\text{ion}})$ could be created. With this function and estimated c and f_{surf} from RBS, TEM and EDX the deposition energy could be roughly estimated to be $E_{\text{ion}} = (30 - 100)$ eV for the adjusted voltage of $U_{\text{adjusted}} = (50 - 1000)$ nm.

For the samples grown with the setup ‘Adonis’, the films showing a layered structure, are summarized in Table 6.6, together with the number of layers, the thickness of the metal layer d_m extracted from gaussian fits to an EDX linescan, and the cluster sizes, extracted from the cross-section TEM image.

Table 6.6.: Number of layers, mean metal layer thickness and the cluster size of a-C:Ni films grown with the setup ‘Adonis’.

r_f	E_{ion} [eV]	S_M	# of layers	d_m [nm]	Cluster size [nm]
9	50	0.38	3 ± 1	10 ± 7	3.5 ± 0.1
1	100	0.67	5 ± 1	9 ± 2	8 ± 2
1.5	100	0.84	7 ± 2	8 ± 2	8 ± 3

With this data and the RBS results, the metal volume fraction c and the surface segregation fraction can be estimated. The metal volume fraction c of a layer can be calculated from the difference in the EDX signal height for the nickel line in the maximum of a layer and the minimum between two nickel rich layers. The surface segregation fractions f_{surf} results directly from the sputter loss for films grown in the $S_M > 1$ regime or can be estimated from the sputter loss of nickel in the $S_M < 1$ regime and the total metal sputtering coefficient S_M . The data is summarized in Table 6.7.

Table 6.7.: Mean metal volume fraction c , and surface segregation factor f_{surf} of a-C:Ni films grown with the setup ‘Adonis’.

r_f	E_{ion} [eV]	S_M	c	f_{surf}
9	50	0.38	0.11 ± 0.09	1.0 ± 0.2
1	100	0.67	0.6 ± 0.2	0.9 ± 0.2
1.5	100	0.84	0.4 ± 0.3	0.9 ± 0.2

With this data, the layer periodicity p_{th} can be calculated using the rate Equation 2.2. The results are given in Table 6.8.

Table 6.8.: Measured and calculated layer periodicities of a-C:Ni films grown with the setup ‘Adonis’.

r_f	E_{ion}	S_M	p_{TEM}	p_{FFT}	p_{th}
9	50	0.38	19 ± 13	15 ± 5	23 ± 16
1	100	0.67	10 ± 2	11 ± 2	24 ± 10
1.5	100	0.84	12 ± 2	13 ± 5	38 ± 14

The results are almost in the margin of error of the experimental results extracted from the TEM images p_{TEM} and the Fourier transformed images p_{FFT} . The result for the film with $r_f = 60/40 = 1.5$ shows the largest deviation. This could be attributed to the distorted layered structure also visible in the cross-section TEM image (see Figure 6.11a), which may lead to an over estimation of the mean metal volume fraction in a layer c in the EDX linescan. An estimation of $c \approx 0.1$ leads to a layer periodicity of $p_{th} = 15$ nm. This value for c seem to be low but since the cross-section TEM image is just a small cut-out of the film and the layers are obviously not closed but more like a loose line of clusters, this value could be reasonable.

The surface segregation factor f_{surf} could be estimated for the films grown with the setup ‘Adonis’ from the RBS analysis by

$$f_{surf} = 1 - \frac{n_{RBS}}{n_{Dep}}$$

for the films grown in the $S_M > 1$ regime. The energy evolution is summarized in Table 6.9. The surface segregation fraction f_{surf} decrease with increasing energy,

Table 6.9.: Energy dependence of the surface segregation factor f_{surf} of a-C:Ni films grown with the setup ‘Adonis’.

E_{ion} [eV]	50	100	200	300	500
f_{surf}	1 ± 0.2	0.9 ± 0.2	0.9 ± 0.1	0.5 ± 0.1	0.9 ± 0.1

but it increases again at energies above $E_{ion} = 300$ eV. This is reasonable since the overall sputtering of metal and surrounding carbon matrix gets more and more severe with increasing energy. Therefore, the complete film is sputtered and no layer can form which is equal to a complete nickel loss.

The results of this chapter demonstrate the successful growth of nickel cluster containing amorphous carbon films. The morphology and composition of the films were investigated by various methods and the model developed by Gerhards and co-workers have been applied successfully to predict the regimes of multilayer formation.

Additionally, the ion energies of ‘Mr. Stringer’ could be roughly matched to the adjusted voltage U_{adjusted} .

Chapter 7.

Synthesis and Properties of a-C:Gd Prepared by Ion Implantation

The a-C:Gd system was investigated in collaboration with the group of F. Hellmann at the University of California, Berkley, California, USA [17, 156].

The properties of a-C can be emerged by special electrical and magnetical properties. For this purpose, doping by incorporation of suitable impurities of certain levels is the most promising approach. One recent study shows that *ta*-C can be indeed doped by low concentrations of rare earth elements (between 10^{17} to 10^{19} cm^{-3}) [157]. This work focuses on the intra-4*f* luminescence of the lanthanides, and the material shows sharp luminescence lines over the whole UV-visible-infrared range; thus, this feature together with the high hardness make such a system very interesting for optoelectronic devices. On the other hand, rare earth elements exhibit also exciting magnetic properties, if incorporated with high concentrations into suitable matrices.

This chapter focuses on the magnetic and magneto-electronic properties of *ta*-C, which was doped with Gd via ion implantation. Previous studies show that Gd-doped a-C, which has been prepared via sputtering, is mostly sp^2 -bonded and thus exhibit only a small band gap. Nevertheless, a large negative magneto-resistance was found at low temperatures, comparable to that of a-Gd_{*x*}Si_{1-*x*} [62].

7.1. Experimental

The *ta*-C:Gd films were prepared as described in Section 3.2.

Details of the parameters and samples are listed in Table 7.1.

Annealing studies were performed up to 550 °C in a rapid thermal annealer with forming gas (5% H₂ in N₂) to avoid oxidation. A typical temperature profile for annealing consists of three stages: a two-minute temperature rise, an one-minute temperature soak and an exponential temperature decay back to room temperature.

A set of Xe-implanted *ta*-C films (*ta*-C_{1-*x*}:Xe_{*x*}) were prepared under the identical implantation and annealing conditions. These samples were used as control samples for all measurements monitoring the implantation damage. Xe and Gd ions have almost the identical radii and similar masses; therefore, the radiation damage created

Table 7.1.: Sample Informations of $ta\text{-C}_{1-x}\text{:Gd}_x$ prepared by ion-implantation of Gd into *ta*-C thin films.

x^a	$ta\text{-C}$ total thickness (nm)	$^{155}\text{Gd}^{3+}$ dose (10^{15} atm/cm 2)	Gd energy (keV)	p_{eff}^b (μ_B)
0.040	42	5.0	50	8.54
0.070	42	9.5	50	9.35
0.200	42	40	50	8.80
0.022	43	2.5+3.25	30+50	9.02
0.088	61	10+13	30+50	8.88
0.176	43	20+26	30+50	8.12

^aBased on RUMP [131] simulation of RBS data^b p_{eff} per Gd obtained from CW constant $A = n_{\text{Gd}} p_{\text{eff}}^2 \mu_B^2 / 3k_B$

in the *ta*-C matrix is similar for both sets of samples (see table 7.1). However, the difference is that Xe has a stable closed-shell electron structure, is chemically inert and does not form any bonds. Most likely, it even diffuse out of the amorphous matrix after implantation. Thus, any structural, electrical or magnetic differences between $ta\text{-C}_{1-x}\text{:Gd}_x$ and $ta\text{-C}_{1-x}\text{:Xe}_x$ are due to the incorporated Gd atoms.

All sample information is displayed in Table 7.1, and more experimental details are available in Reference [62].

7.2. Experimental Results

7.2.1. Structural Characterization

Figure 7.1 shows a TRIM simulation of 50 keV Gd-ions implanted into *ta*-C reflecting the Gaussian-type distribution of the implanted ions, together with a representative RBS spectrum of a *ta*-C film, which was implanted with this energy and 5×10^{15} Gd ions/cm 2 . The calculated ion range is about ~ 19 nm with a straggling of ~ 3 nm, thus, an undoped surface layer in the order of ~ 10 nm is expected (see Figure 7.1a). The analysis of the RBS spectrum confirmed the simulation both in depth and expected concentration including the undoped surface layer not only for this particular sample displayed in Figure 7.1b, but also in general for all samples. For high ion fluence implantations, sputtering of the surface must be considered and results into a reduction of the undoped surface layer down to ~ 5 nm, which was also confirmed by our RBS analysis. Furthermore, it was corroborated that the double-energy (30 and 50 keV) Gd-implantations resulted into the expected more homogeneous and broader doping profile. The measured stoichiometry and Gd concentrations were used throughout this study and, for simplicity, one single homogeneous buried doped

Figure 7.1.: (a) TRIM simulation of 50 keV Gd ions implanted into *ta*-C with a density of 3 g/cm³ revealing the Gaussian-type implantation profile; (b) RBS data and RUMP simulation for a single-energy implanted sample with an ion fluence of $5 \cdot 10^{15} \text{ cm}^{-2}$. The best fit was obtained using a simple layered structure: undoped *ta*-C (10 nm)/*ta*-C_{0.94}Gd_{0.04} (8 nm)/*ta*-C (35 nm).

layer with an average Gd concentration and a thickness of ~ 9 nm and ~ 20 nm for the single-energy and the double-energy implanted samples is defined, respectively.

High resolution transmission electron microscopy (HR-TEM) was performed on several samples in order to check whether $\text{C}_{X-1}\text{Gd}_X$ -crystallites are formed upon the implantation process or the *ta*-C:Gd structure remains amorphous. Figure 7.2(left) shows the cross-section of the sample with the highest Gd concentration (*ta*-C_{0.8}:Gd_{0.2}), and the right micrograph is a high resolution picture of the respective center region. The overview picture again confirms the implantation range as well as the presence of the undoped surface layer. Furthermore, no crystalline clusters are visible in this sample, even not in the HR-TEM picture Figure 7.2(right). This allows us to conclude that the samples remain amorphous within the resolution of our transmission electron microscopy setup, and if crystalline clusters are present, they are well below 2 nm in size. In addition, no cluster formation of Gd or $\text{C}_{X-1}\text{Gd}_X$ -crystallites was observed in those samples, which were annealed up to 550 °C, where the respective HR-TEM images also revealed only an amorphous structure.

Raman spectroscopy was used to obtain information on the carbon bonding before and after Gd/Xe implantation, as well as after thermal annealing. There are two major Raman active modes corresponding to the breathing mode of disordered graphitic 6-member rings (the *D* peak, $\sim 1350 \text{ cm}^{-1}$) and the stretching mode of C-C pairs (the *G* peak, $\sim 1580 \text{ cm}^{-1}$), respectively. Using the integrated peak intensity ratio I_D/I_G (both peaks are fitted with Gaussian functions) according to the three-stage model for a-C's Raman spectroscopy [143], one can draw conclusions on the sp^2/sp^3 ratio.

Figure 7.2.: Three representative cross-section TEM images for the Gd implanted *ta*-C sample, which was implanted with the highest ion fluence. The left picture shows an overview of the whole film. The Pt top layer originates from the FIB preparation process. The middle shows an magnification of the implanted film - note, the SiN substrate is in the left upper part and the surface of the *ta*-C-film in the right bottom part of the micrograph. The Gd containing layer is clearly visible by the strong contrast change induced by the heavy mass of Gd. The right picture is a HR-TEM zoom out image of the center Gd layer: No crystalline clusters are visible.

The Raman spectra of undoped as-grown *ta*-C films with high sp^3 fraction show a predominant *G* peak due to the lack of graphitic ring sites; thus, a very small I_D/I_G ratio. Annealing up to 550 °C in reducing environment does not change the Raman spectra significantly (not shown), consistent with literature [1, 158]. The strong sp^3 covalent bonds, once formed, are very stable under thermal treatments, since the energy barrier for converting sp^3 to sp^2 is large (oxygen can act as a catalyst to lower this barrier, thus annealing in vacuum or a reducing environment is essential). Diamond can be annealed in vacuum at a temperature as high as 1800 K (~ 155 meV) without graphitization (see chapter 13.3 of Reference [159]). There is, however, a small increase of the I_D/I_G for annealed *ta*-C films. This is presumably due to the graphitization of the $<20\%$ sp^2 -bonded carbon chains in as-grown *ta*-C films.

Figure 7.3 shows the normalized Raman spectra of all Xe-implanted *ta*-C thin films with increasing irradiation fluence. As it can be clearly seen, the change of the shape is small and only a slight increase of the I_D/I_G ratio is observable for x above 0.04. The values are small (~ 2.3) and almost constant for increasing ion fluence up to $x = 0.20$. However, the total Raman intensity increases monotonically after an initial drop from undoped *ta*-C film, which is due to an overall increase of the absorption coefficient of the implanted layer. Therefore, it can be concluded from these reference samples that the change of the matrix caused by the energetic

Figure 7.3.: Raman spectra of $ta-C$ and $ta-C_{1-x}:Xe_x$ thin films. Solid lines represent spectra of single-energy implanted samples; whereas, dash dotted lines are spectra of double-energy implanted samples. The dotted line shows for comparison a Raman spectrum of an annealed sample with $x = 0.07$.

implantation process is small, but observable. A fraction of sp^3 bonds have been converted to sp^2 bonds. These results are in agreement with a study on radiation-induced transformation of diamond [160].

Figure 7.4 shows the Raman spectra of all Gd-implanted $ta-C$ samples, where the peak height was also normalized in order to show the effects on the line shape. In contrast to the $ta-C_{1-x}:Xe_x$ samples, there is a more pronounced effect for high Gd concentrations (see also direct comparison spectra in Figure 7.4). For $x = 0.20$ a broad band is observable with a maximum shifted to lower wavenumbers (towards the D-position) compared to the reference samples. This holds for both the single- and double-energy implanted $ta-C_{1-x}:Gd_x$ samples. Here, it can be concluded that the introduced Gd atoms enhance local sp^2 -bonding. Additionally, it is observed, that the intensity of the Raman spectra decreases for increasing Gd concentration. Figure 7.5 shows the raw Raman spectra of the $ta-C_{1-x}:Gd_x$ films together with an plot (inset) of the Raman intensities of both the Gd- and Xe-implanted samples. After a strong decrease, the Raman intensity of the $ta-C_{1-x}:Xe_x$ films remain almost stable with increasing Xe dose. However, the Raman intensity of the $ta-C_{1-x}:Gd_x$ films decrease monotonically and dramatically with Gd dose. This again accounts for the influence of the incorporated Gd atoms on their surrounding yielding into non-Raman active bonds in this energy range. Furthermore, this supports the conclusion

Figure 7.4.: Raman spectra of $ta-C_{1-x}:Gd_x$ thin films, which were prepared by (a) single-energy implantation or (b) double-energy implantation. Compare with Table 7.1. The two dashed lines are comparison spectra of samples implanted with high fluences of Xe. Note the apparent difference between the $ta-C_{1-x}:Gd_x$ and $ta-C_{1-x}:Xe_x$ Raman spectra.

that Gd atoms are randomly distributed within the carbon matrix and do not form clusters; otherwise, a much more Raman-active carbon matrix should be visible.

After post-implantation rapid thermal annealing, the I_D/I_G -ratio increases up to 8 for both Xe- and Gd-implanted films (see e.g. Figure 7.3, dotted line), which was not the case for the unimplanted sample. This can be understood by graphitization of the radiation-induced damage centers, which include vacancies, interstitials, dangling bonds or defect clusters. Although there is some initial graphitization upon room temperature implantation, most of the damage centers are "frozen" and bond rearrangement is unlikely at this low temperature. However, during annealing at sufficiently high temperatures, vacancies and interstitials become mobile, and local bond rearrangement is possible. This results in the formation of more stable sp^2 -bonded graphitic sites which gives rise to a more intense Raman D line and thus much larger I_D/I_G ratios after annealing.

Raman line shapes and I_D/I_G values indicate that the matrix of $ta-C_{1-x}:Gd_x$ films is less graphitic than in co-sputtered a- Gd_xC_{1-x} films [62]. For a- Gd_xC_{1-x} films, the

Figure 7.5.: Raw Raman spectra of single-energy Gd-implanted $ta-C$ thin films with increasing concentration. The inset shows the observed peak intensity ($I_D + I_G$) vs x for both $ta-C_{1-x}:Xe_x$ and $ta-C_{1-x}:Gd_x$ samples.

I_D/I_G ratio can be as high as 12 and the Raman spectra show a distinct D peak corresponding to the disordered sp^2 -bonded graphitic rings with increasing Gd x .

7.2.2. d.c. Conductivity

The temperature dependent d. c. conductivity $\sigma(T)$ of the $ta-C_{1-x}:Gd_x$ films increases with the Gd concentration, suggesting effective Gd doping. Figure 7.6 plots two $ta-C_{1-x}:Gd_x$ samples together with sputtered a- Gd_xC and a-C samples. The room temperature (RT) conductivity of $ta-C:Gd_x$ is much higher than any other co-deposited Gd doped amorphous semiconductors with similar x , namely a- Gd_xSi (prepared by e-beam co-evaporation or co-sputtering), a- Gd_xGe (co-evaporation), or a- $GdC(:H)$ (co-sputtering). However, $\sigma(T)$ decreases rapidly with decreasing temperature and shows insulating behavior. (In metal-insulator transition physics, an insulator is defined as having zero conductivity, while a metal has finite conductivity in the limit T goes to 0 K). The high RT conductivity could arise from the graphitization of the sp^3 matrix during the Gd implantation process, and/or a graphitic top layer (thickness around 15 nm). The $\sigma(T)$ of an a-C film is strongly depending on the sp^2 fraction.

7.2.3. Magnetization

The M vs. T fits the Curie-Weiss law very well, with a very small θ . The M vs. H dependence fits the Brillouin function for $S = 7/2$ with a small excess of the

Figure 7.6.: Temperature dependence of the d.c. conductivity of Gd doped a-C samples, prepared by different methods. From [17].

saturation value. The data show that the implanted Gd atoms behave like free moments. This is in sharp contrast to any other co-deposited Gd doped amorphous semiconductors, whose magnetic ground state is a spin-glass with strong competing ferromagnetic and antiferromagnetic interactions. The antiferromagnetic interaction in a-Gd_xSi is very strong, even for a 4 at.% a-Gd-Si which does not show spin glass freezing down to $T = 2\text{K}$ [161]. Its M vs. H curve is greatly suppressed below the Brillouin function. The origin of this strong interaction is believed to be the carrier mediated RKKY interaction. However, these samples are insulating below the critical concentration x_c ($x_c = 14$ at.% for a-Gd_xSi). The argument is that the localization length of the carriers is very large, greater than the Gd-Gd spacing in a-Gd_xSi. In the Gd implanted ta-C samples, despite a much higher $\sigma(T)$, there is no carrier mediated interactions between the Gd moments. Fitting the data to Curie-Weiss and Brillouin functions yields Gd moment slightly larger than a free Gd moment, presumably due to induced polarization of the local environment.

7.2.4. Magnetoresistance

Large negative magnetoresistance (MR) was found in these samples as shown in Figure 7.7. The magnetoresistance (MR) drops sharply with increasing temperature, passing through zero at a characteristic crossover temperature. This temperature is defined as T' . T' increases with the Gd concentration, unlike T^* , which is defined in earlier studies as the temperature when $\sigma(T)$ deviates from the nonmagnetic analog a-Y-Si [162]. The highest measured T' is 23 K for the 7 at.% sample, which is lower than T^* found for an insulating a-Gd_{0.13}Si samples ($T^* \approx 70\text{K}$). Above T' , an approximately 1% positive MR at $H = 7\text{ T}$ is found with a small temperature

Figure 7.7.: *ta-C:Gd_x* samples have a large negative magnetoresistance (MR) below a characteristic crossover temperature T' . T' decreases with the annealing temperature. (a) Magnetic field dependence of $\sigma(T)$; at $H = 0$ T, $\sigma(T)$ is thermally activated and goes to zero as T approaches 0, while in $H = 7$ T, $\sigma(T)$ is much larger and instead fits a power law dependence with finite value as T goes to zero, hence showing a field-induced insulator to metal transition, (b) Temperature dependence of the magnetoresistance (MR). From [17].

dependence and becoming immeasurably small around 100 K. The sharp increase of the magnetoresistance below T' leads to a magnetic field induced insulator to metal transition for this 7 at.% sample. Similar magnetoresistance and T' behaviors are found for co-sputtered a-Gd_xC(:H) samples.

7.3. Conclusions

In summary, *ta-C* thin films provide a new type of *a-C* matrix to study the moment-carrier interactions when magnetically doped. Radiation-induced damage alone can not account for the largely increased conductivity, and the electrical doping effect of Gd is obvious. Only after the thermal annealing treatment, the radiation-induced damage centers are converted into sp²-bonded graphitic sites, providing a metallic matrix. The as-implanted samples are insulators. Gd ions act as non-interacting large local f moments in the paramagnetic states with no sign of clustering. There is strong evidence of moment-carrier interactions. p_{eff} of Gd is higher than the $7.9 \mu_B$ in the paramagnetic state likely due to s electron polarization. Strong Gd moment-moment interactions through carriers (RKKY-like) gradually developed with Gd doping, leading to spin-glass freezing for higher doses, similar to other Gd-doped amorphous semiconductors. However, the x -dependence of the freezing temperature is not exactly the same due to detailed difference in electronic structures of the carbon matrices. An enormous negative MR is found in all *ta-C*_{1- x} :Gd _{x} films below a crossover temperature T' , which is found to be increased with Gd concentration.

Chapter 8.

Nanostructured Metal Carbide Surfaces Prepared by Surfactant Sputtering

Surfactant sputtering is a novel ion beam erosion technique, which uses a steady-state coverage of a substrate surface with foreign atoms by simultaneous sputter erosion of the substrate and a target. The foreign atoms act as surface active agents (surfactants) and modify the sputter yield of the substrate. This could be used for smoothing the surface or the generation of novel surface patterns and nanostructures [163, 164].

In this work the formation and the structural properties of thin metal carbide layers formed on the surface of ta-C thin films by surfactant sputtering are investigated. The following results were extracted from the publication by Hofsäss, Zhang and Zutz published in the proceedings to the Ion Beam Modification of Materials Conference 2008 [165].

In the study a surface coverage of typically $< 10^{16}$ cm² W or Ti atoms is achieved by low rate sputter deposition of W or Ti onto the ta-C film during erosion. The deposited atoms act as surfactants and modify the sputtering yield of the substrate atoms. In earlier studies similar erosion conditions lead to cone formation on metal and silicon targets [166, 167] and sputtering yield amplification [111].

8.1. Experimental

Ta-C thin films of about 100 nm thickness were grown on silicon (100) substrates by mass-selected ion beam deposition of 100 eV ¹²C⁺ ions (see Section 3.1 and Reference [128]). The films were afterwards sputter eroded by a mass-selected 5 keV Xenon ion beam under simultaneous deposition of W and Ti surfactant atoms. The ion flux was about 2 μ A/cm² and the ion fluences were up to $1.2 \cdot 10^{17}$ cm⁻². The erosion ion beam system is described in detail in Reference [168]. The surfactant sputtering is made possible with a special geometric arrangement of the ta-C film and the sputter target which were both exposed to the ion beam [163] (see Figure 8.1). This arrangement delivers the surfactant atoms by sputtering a thin W or Ti foil

Figure 8.1.: “Geometrical arrangement of ta-C substrate and target with respect to the ion beam. The W or Ti target is the source of the surfactant atoms deposited onto the ta-C film with steady-state coverage increasing from $d = 0$ mm to $d = 7$ mm.” From [165].

placed behind the ta-C film with a certain angle to the ta-C film and the incoming ion beam. The angle between surface normal of the sputter target and the ion beam direction was 30° , while the angle between ta-C film surface normal and ion beam direction was varied between 30° and 70° .

8.2. Results and Discussion

The erosion of a ta-C thin film creates a ripple pattern and the influence of the W surfactant on the ripple formation is shown in Figure 8.2. The Xe beam was at an incident angle of 70° . The as-deposited ta-C has an rms roughness of just < 0.8 nm and the erosion leads to surface ripples with a wavelength of $\lambda \approx 40$ nm [169]. The increasing W coverage coarsens the ripple pattern and eventually converts it to a dot like one. A similar behavior is observed for the Ti surfactant. At incidence angles below 50° the surface gets unstructured and rather smooth with W or Ti area densities of $(10^{15} - 10^{16}) \text{ cm}^{-2}$.

Cross-section TEM measurements show a thin layer of W+C and Ti+C, respectively (see Figure 8.3). The W+C layer is about 10 nm thick and has no crystalline features while the Ti+C layer shows crystals with a lattice spacing of 0.21 nm, which is in accordance with the spacing in TiC (200) planes. The effective carbon sputter yield is measured as a function of the surfactant area density and is plotted in Figures 8.4 and 8.5, for the W and Ti surfactant, respectively. For the W surfactant the sputter yield is almost independent of the W coverage and is about 50% reduced relative to the pure ta-C surface. These results cannot be explained by SRIM or TRIDYN simulations taking ballistic mixing into account and the calculated sputter yields for a WC layer on ta-C are lower than the experimental values. The W+C layer visible in the cross-section TEM images can therefore be described as W_xC with x just smaller than 1. The formation of a stoichiometric WC steady-state surface layer requires ion-induced diffusion processes and ballistic mixing. This ion-induced mixing was also observed for erosion of silicon with a gold surfactant [170].

Figure 8.2.: “AFM images of as-deposited ta-C and ta-C films irradiated with $5 \cdot 10^{16} \text{ cm}^{-2}$ 5 keV Xe ions at incidence angel of 70° and co-deposition of W surfactant atoms. The steady-state area density of W as measured by RBS is indicated. The arrow indicates the projected ion beam direction. Upper right diagram: rms roughness and ripple wavelength as function of steady state W coverage.” From [165].

Figure 8.3.: “TEM images of ta-C films irradiated with $5 \cdot 10^{16} \text{ cm}^{-2}$ 5 keV Xe ions at incidence angel of 70° and co-deposition of W (left column) and Ti (right column) surfactant atoms. The steady-state area density of W and Ti as measured by RBS is indicated. The upper left image shows a cross-section parallel to the ripple orientation. The W+C layer shows no crystalline structure, whereas the Ti+C layer consists of nano-crystals with planar spacing corresponding to TiC (200) planes.” From [165].

Figure 8.4.: “Comparison of measured sputter yield as function of W steady state surfactant area density with SRIM simulations for W/a-C and WC/a-C bi-layer systems and TRIDYN simulations for ballistic mixing. The measured sputter yield is in accordance with the formation of a WC surface layer.” From [165].

Figure 8.5.: “Comparison of measured sputter yield as function of Ti steady state surfactant area density with SRIM simulations for a TiC/a-C bi-layer system and TRIDYN simulations for ballistic mixing. The measured sputter yield is in accordance with the formation of a TiC/a-C nanocomposite layer with composition determined ballistic mixing.” From [165].

The lower sputter yield for Ti relative to W results in a lower flux of Ti onto the ta-C sample during erosion. Therefore, the area density of Ti is lower than for W. The effective carbon sputter yield decreases with the Ti coverage, which cannot be explained by a Ti-C/ta-C bilayer system but with TRIDYN simulations taking ballistic mixing into account. Together with the nano-crystals visible in the cross-section TEM images it is concluded that a TiC/a-C nanocomposite is formed with a composition gradient determined by ballistic mixing.

8.3. Conclusion

Surfactant sputtering was applied for the modification of the surface region of ta-C thin films during Xe beam erosion with W and Ti surfactant atoms. A steady-state surface near carbide layer was formed and results in a few nm thick frozen-in surfactant layer after deposition. The surfactants influence the ripple formation

and lead to the transformation to dot like patterns for increasing coverage. W surfactants lead to an W_xC surface layer, while Ti forms a nano-crystalline TiC/a-C composite thin film. SRIM and TRIDYN simulations are useful tools for analyzing and interpreting the measured sputter yields.

Chapter 9.

Conclusion and Discussion

The films grown during this thesis show that the model of Gerhards and co-workers (see Section 2.2) allows the successful prediction of the regimes of homogeneous nanocomposite and multilayered nanocomposite growth for the mass-selected ion beam deposition technique. The model was successfully applied to the a-C:Cu and a-C:Ni systems.

The model of Gerhards and co-worker was originally developed on the a-C:Cu, a-C:Ag and a-C:Au systems. In the first studies it was demonstrated that it is possible to grow copper containing amorphous carbon nanocomposite films with small copper clusters distributed homogeneously in the matrix by co-deposition of mass-selected carbon and copper ions [14]. In later studies a self-organized multilayer structure was found in the a-C:Au system. No layer growth is found for the a-C:Ag system, which was attributed to the high surface segregation factor $f_{\text{surf}} \approx 1$ and the total metal sputtering yield S_M close to 1 in their studies, which results in a large sputtering loss of silver and a layer structure could not evolve in the examined film thickness.

In this work, it could be shown that the model is suitable for the prediction of the layer formation regime in the a-C:Ni system and a layer growth in the a-C:Cu system could be shown. It was shown that the surface segregation factor f_{surf} depends on the ion energy E_{ion} , as well as the mean metal volume fraction c depends on the fluence ratio r_f . Together with the studies of Gerhards and co-workers it can be concluded that the morphology depends on the total metal sputtering yield S_M and is strongly influenced by the surface segregation factor f_{surf} . The importance of f_{surf} became obvious for highly segregating systems like a-C:Ag: Layer growth is expected for large film thickness and $S_M < 1$ only and the formation of a nanocomposite containing homogeneously distributed clusters is rather difficult. For the gold, copper, or nickel containing amorphous carbon films a layered structure can emerge more easily, if $S_M < 1$ is fulfilled, or a homogeneous nanocomposite with small metal clusters in the amorphous carbon matrix can be formed for $S_M > 1$.

To summarize the results, all films for the non-carbide forming systems a-C:Au [46, 133], a-C:Cu [50, 112] and a-C:Ni are plotted in Figure 9.1. The region where a multilayer growth can be expected is marked by the green dashed area. In this fluence ratio r_f / ion energy E_{ion} region the constraint $S_M < 1$ is fulfilled. The prepared samples are marked by red circles and a black dot indicates the forma-

Figure 9.1.: Summary of the samples in the fluence ratio r_f / ion energy E_{ion} space for (a) the a-C:Au system [46, 133], (b) the a-C:Cu system [50, 112], and (c) the a-C:Ni (‘Adonis’ samples only) system. In the green dashed area the condition $S_M < 1$ is fulfilled. The symbols state, if the film shows a layered structure or one almost homogeneous layer.

tion of a multilayer structure in the sample, while a red X indicates a homogeneous nanocomposite. These results allow the conscious choice of deposition parameters for the growth of homogeneous nanocomposites and the suppression of the layer formation. On the other hand, deposition parameters for the selective growth of multilayer films can be chosen, but the multilayer films can possibly be deposited more easily by alternating deposition of the precursors, while a homogeneous nanocomposite is more difficult especially in the low energy regime.

The results on the a-C:Ni system could be used to further optimize the layer structure of the films and the growth of thick films with an optimized structure. Thicker films containing more nickel allow the investigation concerning magnetic properties, which probably depend on the film morphology and the cluster size distribution.

For a further understanding of the mechanisms and dependencies of the multilayer, formation molecular dynamic simulations are necessary. These simulations could give hints to estimate the layer periodicity ab-initio. The current model is based on empirical values for the mean metal layer thickness d_m and the mean metal volume fraction in a metal rich layer c , as well as the surface segregation factor f_{surf} . These values could possibly estimated from molecular dynamic simulation taking all sputtering, diffusion and, segregation processes as well as the chemical properties of the involved elements into account.

The magnetic and magneto-resistance properties of gadolinium doped ta-C film show interesting features. A field-induced insulator to metal transition could be demonstrated. The next steps could be the co-deposition of carbon and gadolinium and the preparation of a-C:Gd nanocomposite film containing gadolinium clusters and possibly layered structures.

Amorphous carbon films containing metal nano-clusters are prepared by various groups with different aims. Most of the groups do not investigate the micro-structure of their films further. Transmission electron microscopy analysis is often limited to plane-view imaging, leaving the depth profile unexplored. Therefore, the multilayer growth could be found in various other systems and being responsible for some of the outstanding properties of the layers, like hardness or wear-resistance (see Section 1.2).

Since the results of He and co-workers demonstrate that the self-organized layer growth is not limited to the metal-containing amorphous carbon system, new experiments using the mass-selected ion beam deposition on pure metal systems are imaginable. The great advantage of the mass-selected ion beam deposition, as is the independent control of all crucial parameters, can help in understanding the details of the mechanisms leading to self-organized layered structures.

The analysis of the films grown with the setups ‘Mr. Stringer’ and ‘Adonis’ show that the evolving structures apparently depend on the ion energy E_{ion} and the fluence ratio r_f . The difference in the morphologies in the films between the setups ‘Mr. Stringer’ and ‘Adonis’ could be solved by a careful analysis of the setup and the deposition procedure. It could be attributed to inadequacies of the charge measurement of Mr. Stringer which results in deposition energies of $E_{ion} < 140$ eV.

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Appendix A.

List of Publications

Publication contributing to This Thesis

- H. Zutz, D. Lyzwa, C. Ronning, M. Seibt and H. Hofsäss: “*Self-organized formation of carbon/copper layered thin films*”; Nuclear Instruments & Methods B (2008), in press, doi:10.1016/j.nimb.2009.01.046
- H. Zutz , I. Gerhards , C. Ronning , H. Hofsäss , W.Y. Wu , J.M. Ting: “*Self-organized nanoscale multilayer growth during the deposition of hyperthermal species*”; Reviews on Advanced Materials Science 15 (2007) 241-246
- W.Y. Wu , J.M. Ting , H. Zutz , D. Lyzwa , I. Gerhards , C. Ronning , H. Hofsäss: “*Comparative study of self-assembling of multilayers using reactive sputter deposition and mass selective ion beam deposition*”; Diamond and Related Materials 17 (2008) 1494
- H. Hofsäss, K. Zhang and H. Zutz: “*Nanostructured carbide surface prepared by surfactant sputtering*”; Nuclear Instruments & Methods B (2008), in press, doi:10.1016/j.nimb.2009.01.053
- L. Zheng , E. Helgren , H. Zutz , C. Ronning , F. Hellman: “*Magnetic rare earth (Gd) implanted tetrahedral amorphous carbon (ta-C)*”; “*Magnetic thin films, heterostructures, and device materials*”, T. Ambrose, W. Bailey, D. Keaveny, Y.D. Park (eds.), Mater. Res. Soc. Proc. Vol. 941 (2006) 8-22
- Zutz, H. and Zeng, L. and Hellman, F. and Helgren, E. and Ager III, J. W. and Ronning, C.: “*Magneto-electronic properties of Gd-implanted tetrahedral amorphous carbon*”; in preparation

Other Publications

- M. Schumm , M. Koerdel , S. Müller , H. Zutz , C. Ronning , J. Stehr , D.M. Hofmann , J. Geurts: “*Structural impact of Mn implantation on ZnO*”; New Journal of Physics 10 (2008) 043004

- D. Höche, H. Schikora, H. Zutz, R. Queitsch, A. Emmel, P. Schaaf: “*Microstructure of TiN coatings synthesized by direct pulsed Nd:YAG laser nitriding of titanium: Development of grain size, microstrain, and grain orientation*”; Applied Physics A: Materials Science & Processing 91(2008) 305-314
- D. Höche, H. Schikora, H. Zutz, A. Emmel, R. Queitsch and P. Schaaf: “*TiN-coating formation by pulsed Nd:YAG laser irradiation of titanium in nitrogen*”; Journal of Coatings Technology and Research 5 (2008) 505-512
- Cusenza, S. and Zutz, H. and Schaaf, P.: “*Control of magnetic properties and self organized structures in carbon - stainless steel multilayer films*”; in preparation

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