Chapter 9
Summary and Outlook

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

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

The a-Si:H and a-C:H films have been deposited in a capacitively coupled low temperature plasma with an excitation frequency of 13.56 MHz. This process enables the
coating of temperature sensitive materials as well. Silane (SiH₄, diluted in argon) and acetylene (C₂H₂) have been used to deposit thin amorphous hydrogenated silicon and carbon films, respectively. The coating proceeds in three consecutive steps consisting of argon sputtering, deposition of a-Si:H and subsequent deposition of a-C:H, without removing the sample out of the vacuum reactor in the mean time. The argon sputtering serves to remove the native oxide layer and impurities present on the surface of the metals.

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

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

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

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

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

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

After the characterisation of the individual films, film systems consisting of a-Si:H and DLC films have been deposited on different metal substrates. Cavitation erosion tests reveal that the film system suffers from adhesive but not from cohesive failure under load. The attractive forces inside the film system are high enough to avoid the occurrence of damage and wear debris. Therefore, the adhesion to the substrate is the critical point to be optimised for different metal substrates. Results from TOF-SIMS measurements show the presence of SiC at the interface DLC–silicon film and of different silicides at the interface silicon–metal, depending on the metal. These stable compounds ensure the strong adhesion of the films among themselves and to the substrate.

The use of an amorphous silicon intermediate layer does not only ensure good chemical bonding between DLC and metal but it also lowers the internal stress of the film system. The stress of film systems with a DLC film in the range of several hundred nm could be decreased to half the stress of the pure DLC film. It seems that an a-Si:H film half as thick as the DLC film leads to best results.
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Tensile tests reveal the formation of a uniform network of small cracks when the film system is exposed to strain. This is preferred to the formation of one big crack under strain because the wear resistance can be assured longer in this case. First formation of cracks can be observed after a local elongation of about 4 %.

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

In future, further systematic investigations have to be performed to reveal the influence of parameters like film thickness, hydrogen content, and substrate temperature on the adhesion of the film system on metals. The adhesion is to measure quantitatively by a nano scratch-tester which is applicable especially for very thin films. Such a device has not been accessible up to now. The influence of the above mentioned parameters on the elasticity of the film system will also be investigated in more detail in the near future. In doing so, more tensile tests will be performed to find appropriate conditions under which the film system can be elongated as much as possible without showing the occurrence of cracks.

To achieve a smooth transition from amorphous silicon film to amorphous carbon film the a-Si:C:H films presented in chapter 7 will be used in form of a gradient layer going from 100 % a-Si:H to 100 % a-C:H. It may be expected that the use of a single film instead of a film system with an interface between a-Si:H and DLC leads to an even better stability.

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