Thin Functional Plasma Polymer and Metal/Plasma Polymer Nanocomposite Films

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Abstract

Various thin plasma polymer films were developed to achieve different functionalities by plasma polymerization and electron beam evaporation. The thin plasma polymer films are single fluorocarbon or organosilicon plasma polymer films, thin fluorocarbon and organosilicon bilayer plasma polymer films, and fluorocarbon plasma polymer-supported silver nanoparticles, as well as silver/fluorocarbon plasma polymer nanocomposite films, respectively. The synthesis and characterization of thin fluorocarbon and organosilicon plasma polymer films are reported in detail. The obtained fluorocarbon plasma polymer films exhibit very low surface energy, high chemical inertness and high barrier properties. The Ar-plasma etching was performed to tailor the chemical structure, morphology and the wettability of the thin fluorocarbon plasma polymer films. A novel patterning process of thin organosilicon and fluorocarbon bilayer plasma polymer films was presented, which could achieve substrate independence and simplify the patterning process of polymers. Well-defined silver nanoparticles were successfully prepared by means of electron beam evaporation of silver on ultra-thin fluorocarbon plasma polymer films. The growth of the silver nanoparticles on ultra-thin plasma polymer films and on fluorinated self-assembled monolayers (SAMs) was intensively studied, which demonstrated a higher stability of the ultra-thin cross-linked fluorocarbon plasma polymer films against the penetration of silver through the film during the silver deposition in comparison to the SAMs. In particular, the micro-structural, barrier and the optical properties of the thin Ag/fluorocarbon plasma polymer nanocomposite films were studied by means of high-resolution transmission electron microscopy (HR-TEM), electrochemical impedance spectroscopy and UV-Vis spectroscopy during the ageing process in water-based electrolytes. It was found that the annealing treatment leads to the increase of the silver nanoparticle size and the shape factor, broadening of the size distribution as well as the increase of the interparticle distance. The optical properties of the thin Ag/fluorocarbon plasma polymer nanocomposite films changed with the annealing treatment correspondingly. Moreover, it was found that the microstructure of silver nanoparticles changed during the ageing process in water. A mechanism was proposed based on the combination of the atomic metal diffusion, coalescence between particles and the electrochemical Oswald ripening driven by the size dependence of the work function and standard electrode potential according to the HR-TEM results.
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Chapter 1: Preface

1.1 Motivation

Over the past few decades plasma polymerizations and plasma modifications have been proved to be very useful and effective techniques for both the preparation and the surface modification of a large variety of thin functional films. By appropriate choice of monomers and deposition parameters, the physical and chemical properties of thin plasma polymer films, as well as their surface properties, can be well tailored to acquire necessary functionalities. The corresponding properties of thin plasma polymer films, such as excellent adhesion to substrates, chemical inertness, thermal stability, high hydrophobicity, good barrier and mechanical properties make them very attractive for applications such as corrosion resistant coatings, anti-fouling films and diffusion barriers.

Thin Teflon-like plasma polymer films are of great interest for microelectronic and optical applications, but are also considered as long-term stable corrosion resistant and aesthetic thin films for their low dielectric constant, extremely low surface energy, high chemical inertness, low friction coefficient and the tunable chemical composition and degree of cross-linking. Moreover, increasing interest has been devoted to the modification of the fluoropolymer surfaces to obtain improved adhesion, wettability and other functionalities. Yet, little has been published on the detailed structure of thin Teflon-like plasma polymer films and their behavior etched in inert plasmas to tailor the chemical structure, the surface roughness and thereby the wettability.

The ability to actively induce features on polymer surfaces has been of high interest for many potential applications, including stretchable electronics, micro-electro-mechanical systems, tunable surface adhesion and friction. One widely adopted simple and effective approach is based on the internal buckling force equilibrium within materials by deposition of a hard thin layer on top of a pre-strained bulk substrate, followed by release of the pre-strain. Plasma polymerization provides the possibility to design patterned thin films by depositing a hard layer on top of a soft film adhering to a solid substrate, which is based on the buckling theory to release the compressive stress in plasma polymer films. The aim was to achieve patterned plasma polymer films, which could possess novel mechanical properties. Moreover, by the deposition of bilayer plasma polymer films, patterning independent of the substrate material can be achieved and the whole patterning process can
Chapter 1: Preface

be simplified.

Metal nanoparticles show many interesting characteristics, such as optical, electrical, and catalytic properties, which depend on the size, size distribution and shape of the nanoparticles. The growth and arrangement of metal nanoparticles on various substrates are therefore key issues in all fields of modern science and technology related to nanoelectronics, photonics, catalysis and sensors. In particular, silver metal nanoparticles are most widely studied due to their strong surface plasmon resonances in the UV-Vis range and their antibacterial properties. A method combining deposition of fluorocarbon plasma polymer films and electron beam evaporation of silver allows synthesis of well-defined silver nanoparticles with narrow size distribution. Moreover, self-assembled monolayers (SAMs) are quite widely used to fabricate a substrate/organic thin film/metal “sandwich” structure, which can be used in the field of the nanoscale electronics. Therefore, interactions between SAMs and deposited metal overlayers are of great importance. A comparison between the growth of silver nanoparticles on ultra-thin plasma polymers and on well-defined SAMs would be interesting for the potential use of ultra-thin plasma polymer films in this field.

Thin polymer films are especially suitable as host materials for nanoparticles in order to stabilize the particle size and the growth of nanoparticles. By alternating deposition of fluorocarbon plasma polymers and silver nanoparticles, model multilayer silver nanocomposite films with well-defined vertical distribution of nanoparticles can be achieved. While numerous reports demonstrated the interesting structural, optical, electrical, release and antibacterial properties of thin silver-based nanocomposite films, only very little is known about the ageing mechanisms of silver nanocomposite films during the immersion in water-based electrolytes. The ageing behaviour of silver nanocomposite films in water-based electrolytes may provide some reference for their long-term applications in industrial field.

1.2 Scope of the Thesis

The thesis is divided into ten chapters. Chapter 2 contains a brief introduction to plasma polymerization and plasma etching, as well as an overview of preparation, characterization and applications of metal nanoparticles and thin metal/polymer nanocomposite films. The overview of literature shows that plasma polymerization combined with physical vapor
deposition (PVD) is a quite promising technique to prepare thin metal/polymer nanocomposite films. In chapter 3, the basic theories and principles of the main analytical methods used to characterize thin plasma polymer and metal/plasma polymer nanocomposite films, such as atomic force microscopy (AFM), electron microscopy, X-ray photoelectron spectroscopy (XPS), UV-Vis spectroscopy and ellipsometry, are described. The synthesis and characterization of thin fluorocarbon and organosilicon plasma polymer films are discussed in chapter 4. In chapter 5 the Ar-plasma etching of thin fluorocarbon plasma polymer films is investigated to tailor the chemical structure, morphology and the wettability of the thin fluorocarbon plasma polymer films. A novel patterning process of thin organosilicon and fluorocarbon bilayer plasma polymer films is reported in chapter 6, which could achieve substrate independence and simplify the patterning process of polymers. In chapter 7 the deposition of well-defined silver nanoparticles by combining plasma polymerization and electron beam evaporation is presented and the growth of PVD silver nanoparticles on ultra-thin fluorocarbon plasma polymer films and on fluorinated SAMs is compared. It is indicated that during the silver deposition process ultra-thin cross-linked fluorocarbon plasma polymer films are more stable against the penetration of silver than the fluorinated SAMs. In chapter 8, the ageing behaviour of thin silver/fluorocarbon plasma polymer nanocomposite films exposed to water-based electrolytes is investigated by means of UV-Vis spectroscopy, electrochemical impedance spectroscopy (EIS) and high-resolution transmission electron microscopy (HR-TEM). The mechanisms of silver nanoparticles’ morphological changes during the annealing and ageing processes in water-based electrolytes are discussed at length. The thesis is concluded in chapter 9 and the further work in the future is indicated. The abbreviations and symbols used in the thesis are listed in chapter 10.

As a whole, this work is based on the functionalities of the thin plasma polymer and metal/plasma polymer nanocomposite films. Different thin film systems were developed to achieve different functionalities, such as pure fluorocarbon or organosilicon plasma polymer films, thin fluorocarbon and organosilicon bilayer plasma polymer films, fluorocarbon plasma polymer-supported silver nanoparticles, and silver/fluorocarbon plasma polymer nanocomposite films. Various surface-sensitive analytical methods, such as fourier transform infrared spectroscopy (FT-IR), UV-Vis spectroscopy, XPS, time of flight secondary ion mass spectroscopy (ToF-SIMS), scanning electron microscopy (SEM), AFM and EIS etc., were intensively applied to characterize the above-mentioned thin films. HR-
TEM was frequently used to clarify the morphology of silver nanoparticles in order to elucidate the mechanisms of their morphological changes during the annealing process and the ageing process of silver/fluorocarbon plasma polymer nanocomposite films in water-based electrolytes.
Chapter 2: Theory

2.1 Plasma Deposition and Plasma Etching

2.1.1 Introduction to Plasma and Plasma Polymerization

2.1.1.1 Plasma state

Plasmas are ionized gases, which consist of positive and negative ions, atoms and electrons, as well as neutral species. The ionization degree can vary from 100% (fully ionized gases) to very low values (e.g. $10^{-4}$-$10^{-6}$, partially ionized gases). The plasma state is often referred to as the fourth state of matter with respect to solids, liquids and gases [1, 2].

In general, a subdivision can be made between plasmas, which are in thermal equilibrium and not in thermal equilibrium. Thermal equilibrium implies that the temperatures of all species (electrons, ions, and neutral species) are the same. These equilibrium plasmas, which are typically characterized by rather high temperatures ranging from 4000 $K$ (for easy-to-ionize elements, such as cesium) to 20000 $K$ (for hard-to-ionize elements, like helium), are typically used for applications where heat is required, such as for cutting, spraying, welding or in the analytical inductively coupled plasma, for the evaporation of an analyte. On the other hand, in nonequilibrium plasmas the temperatures of the different plasma species are not the same. More precisely, the electrons are characterized by much higher temperatures than the heavy particles (ions, atoms and molecules). The high electron temperature gives rise to inelastic electron collisions, which, on the one hand, sustain the plasma (e.g. electron impact ionization) and on the other hand, result in a ‘chemically-rich’ environment. The electrons are, therefore, considered to be the ‘primary agents’ in the plasma. Nonequilibrium plasmas are typically used for applications where heat is not desirable, such as for etching or deposition of thin layers [3, 4].

2.1.1.2 Plasma polymerization

Thin polymer films can be deposited by so-called ‘plasma polymerization’ [5-7]. It refers to the deposition of polymer films through plasma dissociation, the excitation of an organic monomer gas and subsequent deposition and polymerization of the excited species on the surface of a substrate. Plasma polymerization is used to deposit films with thicknesses from several tens to several thousands of Angstroms. The deposited films are called plasma polymers, which are generally chemically and physically different from conventional
polymers. Whereas conventional polymerization is based on molecular processes during which rearrangements of the atoms within the monomer seldom occur, plasma polymerization is essentially an atomic process. Plasma polymers are, in most cases, highly branched and highly cross-linked [5].

Plasma polymerization is characterized by several features [7]:

1. Plasma polymers are not characterized by repeating units, as is typical for conventional polymers.
2. The properties of the plasma polymer are not determined by the monomer being used but rather by the plasma parameters. For example, an ethylene plasma does not simply give rise to polyethylene, but to a variety of products (including unsaturated groups, aromatic groups and side branches), depending on the plasma conditions.
3. The monomer used for plasma polymerization does not have to contain a functional group, such as a double bond.

The structure of plasma polymer films is highly complex and depends on many factors, including reactor design [8], power level [9], substrate temperature [10], frequency [11] and structure, pressure and flow rate of monomer [12-14].

2.1.2 Fluorocarbon Plasma Polymers

The reasons for the wide utilization of fluorocarbon plasma polymer films are the good adhesion to many organic and inorganic substrates, relatively inert surfaces with extremely low free energy, the biocompatibility, the low friction coefficient and the tunable chemical composition and degree of cross-linking to produce tailored films for the protection of a variety of plastics, fibers and metals [7, 15-17].

The chemical structure of the fluorocarbon plasma polymer films can be adjusted by varying the feed composition, the sample location and the power input. When different gas monomers are used some differences are expected as a function of the instauration degree. A shift to the higher binding energy side will appear as the F/C ratio of inlet monomer increases. Increasing the hydrogen percentage in the feed gas can increase the degree of cross-linking and the C/F ratio [1]. The chemical structure of fluorocarbon plasma polymer film is markedly affected by the location of the film position with respect to the glow region. The farther the sample is located from the glow region, i.e. where there are no ions bombarding the samples, the higher the CF$_2$/C-CF ratio in the films [18]. Both the positive
ion bombardment and the electron irradiation produce fluorine deficiency and cross-linking [19].

2.1.3 Organosilicon Plasma Polymers

Plasma polymers obtained from organosilicon monomers have demonstrated excellent thermal and chemical resistance and outstanding electrical, optical and biomedical properties. Therefore, they may find uses in many branches of modern technology, for example, as dielectric coatings or encapsulations in microelectronics, and as antireflection coatings in conventional optics [20].

Bieg and Wishmann applied thin plasma polymer films from different organosilicone monomers to Al and Ag front surfaces, which were employed in various solar applications, and provided good protection against weathering, abrasion and buildup of static charge [21]. Templier et al. reported the application of organosilicone plasma polymer films in interlayer dielectrics [22] and Fracassi et al. found that the deposition of organosilicone plasma polymers is a promising approach for the corrosion protection of metals [23].

2.1.4 Plasma Etching of Organic Polymers

Plasma treatments have become important processes in modifying polymer surfaces and been used extensively for altering the adhesion of substances to organic surfaces by changing their wettability or by roughing them [24, 25].

A lot of gases can be used for plasma etching such as helium, argon, oxygen-containing gases and nitrogen-containing gases. Inert gases such as argon can be used to physically modify the polymer surfaces or to pre-treat the substrates for cleaning purpose. For improving the adhesive characteristics of polymers, the exposure of polymers to inert gas plasmas is sufficient to abstract hydrogen and to form free radicals at or near the surface which then interact to form crosslinks and unsaturated groups. The plasma also removes low-molecular-weight materials or converts them to high-molecular-weight by cross-linking reactions. As a result, the weak boundary layer formed by the low-molecular-weight materials is removed; consequently, greater adhesive joint strengths are observed [20]. Oxygen and oxygen-containing plasmas are most commonly employed to produce a variety of oxygen functional groups, including C-O, C=O, C-O-O groups at the surface. Two processes occur competitively in an oxygen plasma: etching of the polymer surface through
the reactions of atomic oxygen with the surface carbon atoms, giving volatile reaction products; and the formation of oxygen functional groups at the polymer surface through the reactions between the active species of the plasma and the surface atoms [26]. Nitrogen-containing plasmas are widely used to improve wettability, bondability and biocompatibility of polymer surfaces. For example, to improve the interfacial strength between polyethylene fibers and epoxy resins, which are cured by amine cross-linking, amino groups (-NH₂) were introduced on the fiber surface to promote covalent binding between the -NH₂ groups on the fiber surface and the R-NH-CH₂-CH(OH)- groups in the epoxy resins [27].

2.2 Preparation and Characteristics of Metallic Nanoparticles

2.2.1 Introduction to Metallic Nanoparticles

The first syntheses of metal nanoparticles most probably date back to the 5th or 4th century BC where gold specimens were reported in China and Egypt [28]. Since then they have been used but not understood throughout Europe in stained glass windows of cathedrals and by the Chinese in coloring vases and other ornaments [29]. One of the most fascinating examples is probably the famous Lycurgus cup stored in the British museum in London [30]. This object, crafted by the Romans in the 4th century AD, features an amazing property of changing color depending on the light shed on it. Reflected light makes it appear green, whereas in transmission a bright red color can be seen. It was first reported by Faraday in 1857 that the synthesized colloidal solutions of gold exhibit colors ranging from ruby red to amethyst depending on the size of particles in the colloidal solutions [31].

A nanoparticle has dimensions in the nanometer range, i.e. between 1 and 100 nm. Many novel properties such as electronic [32], optical [33] and catalytic [34] properties are readily observed at the nanometer length scale, which are neither those of the individual constituents nor those of the bulk. Equally important, these properties change with the size and shape of nanoparticles [35]. The change in the properties at this length scale is not a result of scaling factors. It results from different causes in different materials. In semiconductors, it results from the further confinement of the electronic motion to a length scale characterizing the electronic motion in bulk semiconducting material (called the electron Bohr radius, which is usually a few nanometers). In transition metals, the decrease in the particle size to the nanometer length scale increases the surface-to-volume ratio. This,
together with the possibility to prepare them in different sizes and shapes, makes them potentially useful in the field of catalysis. As noble metals are reduced in size to tens of nanometers, a very strong absorption is observed resulting from the collective coherent oscillation of the electrons in the conduction band. This is called surface plasmon resonance (SPR) [36]. In this work, only the noble metallic nanoparticles will be addressed due to the space limitations.

When a small spherical metallic nanoparticle is irradiated by light, the oscillating electric field causes the conduction electrons to oscillate coherently as represented in figure 2-1 [37]. The displacement of the electron cloud relative to the nuclei due to an electric field gives rise to polarization charges at the surface of the metal sphere and hence to a restoring force resulting from Coulomb attraction between electrons and nuclei. This results in oscillation of the electron cloud relative to the nuclear framework. When the oscillating electrons resonantly couple with the light because of the frequency match, strong light scattering will occur in the appearance of intense surface plasmon resonance bands together with an enhancement of the local electromagnetic fields [38, 39]. The position, shape and the intensity of the SPR band strongly depend on various factors: the size, size distribution and shape of the nanoparticles, as well as the environments which surround them [40].

![Figure 2-1: Schematic representation of plasmon oscillation for a sphere, showing the displacement of the conduction electron charge cloud relative to the nuclei [37].](image)

### 2.2.2 Determination of the Resonance Conditions

#### 2.2.2.1 Free-electron-like spherical metallic nanoparticles

The idea is to determine the conditions for which the electron cloud will resonate. The positive charges in the clusters are assumed to be immobile and the negative charges, i.e. the conduction electrons, are allowed to move under the influence of external fields. Therefore, a displacement of the negative charges from the positive ones occurs if a metal
cluster is placed in an electric field. Using the boundary conditions at the sphere surface, one can calculate the resulting polarization of the sphere as a whole due to the external field. The internal field $E_i$ is

$$E_i = E_0 \frac{3\varepsilon_m}{\varepsilon(\omega) + 2\varepsilon_m} \quad (2-1),$$

where $E_0$ is the external field, $\varepsilon_m$ and $\varepsilon(\omega)$ represent the dielectric constant of the embedding medium and the embedded metal particles [33]. This gives a condition of resonance, which occurs when $E_i$ reaches maximum, hence whenever

$$|\varepsilon(\omega) + 2\varepsilon_m| = \text{Minimum} \quad (2-2),$$

i.e.

$$[\varepsilon_1(\omega) + 2\varepsilon_m]^2 + [\varepsilon_2(\omega)]^2 = \text{Minimum} \quad (2-3),$$

where $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ are the real and imaginary part of the dielectric constant of the embedded metal particles $\varepsilon(\omega)$.

The resonance frequency, amplitude and the full width at half maximum (FWHM) can be determined as follows:

If the particle is a free-electron-like metallic nanosphere like Na, its dielectric permittivity is described by the Drude formula,

$$\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\gamma \omega} \quad (2-4),$$

where $\omega_p$ is the plasma frequency of the conduction electrons in the particle and $\gamma$ represents the rate of electron collisions. Substituting the dielectric permittivity equation 2-4 into the expression for the dipolar polarizability $\alpha(\omega)$ of the spherical particle with a radius, $R$,

$$\alpha(\omega) = 4\pi R^3 \frac{\varepsilon(\omega) - \varepsilon_m}{\varepsilon(\omega) + 2\varepsilon_m} \quad (2-5),$$

the absorption cross section of the spherical metallic particle can be obtained [41],

$$C_{\text{abs}}(\omega) = \frac{\Omega V}{c} \left( \frac{\varepsilon_m^{3/2}}{1 + 2\varepsilon_m} \right)^{3/2} \left( \frac{\Omega^2}{\Omega^2 - \omega^2 - i\gamma \omega} \right) \quad (2-6),$$

where $\mathcal{J}$ stands for the imaginary part of the polarizability of the particle, $V = (4\pi/3)R^3$ is the volume of the particle, $c$ represents the speed of light and $\Omega$ is defined by

$$\Omega = \frac{\omega_p}{\sqrt{1 + 2\varepsilon_m}} \quad (2-7).$$
Taking the imaginary part in equation 2-6, we obtain the formula
\[
C_{abs}(\omega) = \frac{9V}{c} \frac{\varepsilon_m^{3/2}}{(1 + 2\varepsilon_m)} \left[ \frac{\omega^2 \Omega^2 \gamma}{(\Omega^2 - \omega^2)^2 + (\gamma\omega)^2} \right]
\] (2-8).

The maximum of the absorption cross section, \( C_{abs,max}(\Omega) \), which defines the resonance frequency \( \omega_{res} = \Omega \), is given by
\[
C_{abs,max}(\Omega) = \frac{9V}{c} \frac{\varepsilon_m^{3/2}}{(1 + 2\varepsilon_m)} \frac{\Omega^2}{\gamma}
\] (2-9)
assuming \( \varepsilon_m \) and \( \gamma \) are independent of \( \omega \). Comparing the expression for the half maximum, \( \frac{1}{2} C_{abs,max}(\Omega) \), of the absorption cross section with equation 2-8, we obtain the expressions for the frequencies \( \omega_1, \omega_2 \) that define the FWHM of the resonant curve, \( \Gamma \) [42]. The positions of the half maximum of the absorption cross section are
\[
\omega_1 = \frac{1}{2} \left( \sqrt{\gamma^2 + 4\Omega^2} - \gamma \right)
\] (2-10)
\[
\omega_2 = \frac{1}{2} \left( \sqrt{\gamma^2 + 4\Omega^2} + \gamma \right)
\] (2-11). The homogeneous line width (FWHM) is defined as
\[
\Gamma = \omega_2 - \omega_1 = \gamma
\] (2-12).

Thus, the resonance frequency, equation 2-7, the maximum of the absorption cross section, equation 2-9, and the bandwidth of the SPR band, equation 2-12, completely characterize the spectral features of the SPR band in free-electron-like metallic nanoparticles.

2.2.2.2 Noble metal nanoparticles

The optical response of noble metals, as well as many transition metals, is characterized by an additional contribution to the dielectric permittivity caused by interband electronic transitions. The complex valued interband susceptibility,
\[
\chi^{ib}(\omega) = \chi_1^{ib}(\omega) + i\chi_2^{ib}(\omega)
\] (2-13)
contributes to the total dielectric permittivity above a certain threshold frequency (interband transition edge \( \omega_i \)) as follows,
\[
\varepsilon(\omega) = 1 - \frac{\omega_i^2}{\omega^2 + i\gamma\omega} + \chi^{ib}(\omega)
\] (2-14).

A small \( \chi_2^{ib} \) is typical, e.g. for silver in the optical range \( h\omega_i \approx 3.8 \text{ eV} \) [43]. For \( \omega < \omega_i \) we consider just the influence of the real interband susceptibility \( \chi_1^{ib} \), and neglect the imaginary
part, $\chi_{2}^{ib} \rightarrow 0$. Substituting equation 2-14 into equation 2-5 the polarizability of the sphere can be obtained as follows:

$$\alpha(\omega) = 4\pi R^3 \frac{(1 + \chi_{1}^{ib} - \varepsilon_m)}{(1 + \chi_{1}^{ib} + 2\varepsilon_m)} + \frac{12\pi R^3\varepsilon_m}{(1 + \chi_{1}^{ib} + 2\varepsilon_m)(\Omega^2 - \omega^2 - i\gamma\omega)} \quad (2-15),$$

where we introduced the frequency

$$\Omega = \frac{\omega_p}{\sqrt{1 + \chi_{1}^{ib} + 2\varepsilon_m}} \quad (2-16).$$

Following the same procedure as for equation 2-6 to equation 2-12, at the resonance frequency, $\omega_{res} = \Omega$ (equation 2-16), the maximum of the absorption can be obtained as

$$C_{abs,\text{max}}(\Omega) = \frac{9V}{c} \frac{\varepsilon_m^{3/2}}{(1 + \chi_{1}^{ib} + 2\varepsilon_m)\gamma} \frac{\Omega^2}{\gamma} \quad (2-17),$$

and the frequency bandwidth can be determined to be $\Gamma = \gamma$.

When both the real and the imaginary parts of the interband susceptibility need to be taken into account, for example, in the case of gold nanoparticles in the frequency range of $\hbar\omega < 2.5$ eV, the situation becomes more complicated, more details can be found in the literature [41].

### 2.2.3 Different Factors Influencing the SPR Band

Following the above-described mathematical discussion to determine the resonance conditions, several various factors influencing the SPR band, such as the size, size distribution, shape and the charge of nanoparticles, as well as the dielectric constant of the matrix will be discussed as follows [44].

#### 2.2.3.1 Effect of size and shape of nanoparticles

As the radius $R$ of the nanoparticles appears in equation 2-9, the intensity of the SPR band is dependent on the size of the nanoparticles. Position and bandwidth are also affected by $R$, but through intrinsic effects (only when the particle size is smaller than 10 nm), which means that $R$ modifies the expression of the dielectric constant of the metal and thus alters the resonance condition expressed in equation 2-2 and 2-3. Many theories have been reported to correlate the size to the SPR position, but there are quite a lot conflicting results concerning even the direction of the SPR band shift as reviewed by Kreibig [33]. In fact, experimental results finally evidenced a blue shift of the SPR band on decreasing the
nanoparticle size [45, 46] and Liebsch rationalized the results subsequently [47]. For alkali metal nanoparticles, the SPR band red shifts while decreasing the mean diameter. This can be explained by the fact that the electrons spill out of the cationic frame of the nanoparticles and that thus the centroid of the fluctuating charge is located outside the metallic surface. On decreasing the size of the nanoparticles, spilling out electrons will have a bigger relative weight than the inner ones and the SPR will be less energetic [48]. In the case of noble metal, the existence of d electrons induces a mutual s-d polarization. This mechanism is important enough to justify an inversion of the trend between simple and noble metals.

The impact of the nanoparticle shape on the SPR band has been far less studied, because of both the intrinsic complexity of the problem and the synthesis limitations. Gans provided a theory to study the SPR band of oblate or prolate spheroidal nanoparticles based on Mie theory [49]. Link et al. reported that two SPR bands existed for the arbitrarily oriented nanorods, one corresponding to the longitudinal mode and the other to the transverse mode [50]. For more complicated shapes, various numerical methods have been developed. Among them discrete dipole approximation (DDA) appeared to be an ideal tool. As an example, Schatz et al. evidenced recently that the SPR band of three-tip-star-like nanoparticle red shifted (from 130 to 190 nm) compared to the spherical equivalents [51].

2.2.3.2 Effect of dielectric environment

It is obvious from equations 2-7 and 2-9 that the dielectric constant of the surrounding medium plays a predominant role in determining both the SPR band position and its intensity. For instance, strong SPR shifts are induced by transferring nanoparticles from water or ethanol to a transparent oxide matrix [52]. Moreover, the shell thickness and the dielectric constant of the shell material would induce a shift of the SPR band [53, 54].

All the considerations are relevant only if the particles are sufficiently far apart from each other to consider that they are not interacting. Ung et al. managed to synthesize composite layers with a fine tuning of the interparticle distances, which were directly controlled through the silica shell thickness [55]. The colors of those layers vary strongly with the interparticle distance as can be seen in figure 2-2 (the shorter the interparticle distance, the larger the wavelength of the resonance band).
2.2.3.3 Electronic effects

According to equation 2-7, the position of the SPR band depends on $\omega_p$, which itself varies as the square root of $n$, the electron density inside the nanoparticle. As a consequence, the SPR band shifts upon adding or subtracting electrons to the overall metallic core. The increase (decrease) in electron density resulted in the blue shift (red shift) [56, 57].

Stabilizing molecules, such as amines, thiols and phosphine are usually used to cover the nanoparticles, which prevent the agglomeration and the further growth of the nanoparticles due to the affinity for the metal surface [28]. Theses molecules are usually called ligands, which strongly impact the plasmon behaviour of the nanoparticles. First reason is that it modifies the dielectric constant of the surrounding medium, and the other one is that as these ligands interact electronically with the metal nanoparticles, they also partially reduce or oxidize the nanoparticles [40]. Moores et al. reported that the use of phosphinine, the phosphorus equivalent of pyridine, which is well known for its strong $\pi$-accepting properties, resulted in a strong red shift of the SPR band [58]. Yu et al. showed that the association of a metal oxide nanoparticle and a noble metal nanoparticle results in a red shift of the SPR band of the latter, because the oxide part deprives the noble metal nanoparticle from a part of it electron density [59].

2.2.4 Preparation Methods of Metallic Nanoparticles

Different methods can be applied to prepare metallic nanoparticles such as laser ablation [60], thermal decomposition of organometallic compounds [61], and electrochemical
reduction [62]. Furthermore, sol process can be used to synthesize monodisperse nanoparticles by adjusting the reaction parameters, such as the reaction time, temperature, concentration and the selection of reagents and surfactants [63-64]. Metal nanoparticles can be produced by micelles as well [65-66]. Another traditional synthetic route of metal nanoparticles is sol-gel method based on inorganic polymerization reactions, which includes four steps: hydrolysis of the metal alkoxide precursors, polycondensation, drying and thermal decomposition of organic precursor [67-68]. Chemical precipitation and pyrolysis are also applied to prepare different kinds of nanoparticles [69-70]. In addition, nanosphere lithography is another modern bottom-up technique to generate metal nanoparticles [71].

Complementary to the above-mentioned techniques, vapor deposition has been widely used to fabricate nanostructures. Vapor deposition processes can be generally classified as chemical vapor deposition (CVD) and physical vapor deposition (PVD). In CVD, the vaporized precursors are introduced into CVD reactor and adsorb onto a substance held at an elevated temperature. These adsorbed molecules will either thermally decompose or react with other gases to form crystals. Various nanoparticles, carbon nanotubes and different nanowires have been successfully synthesized by CVD [72-74]. The PVD process is composed of three main steps: (a) generating a vapor phase by evaporation or sublimation of a material, (b) transporting the material from the source to the substrate, and (c) formation of the particle and film by nucleation and growth. Different techniques have been used to evaporate the source such as electron beam, thermal energy, sputtering, cathodic arc plasma and pulsed laser [75]. Figure 2-3 shows one example of palladium-fluoropolymer nanocomposite film deposited by simultaneous sputtering of bulk Teflon and palladium targets in a vacuum chamber [76].

Applications that benefit from nano-properties require particles with well-defined size, shape and surface properties. However, metal nanoparticles are not stable or have a tendency to agglomerate because of their high surface energy, and therefore, it is necessary to protect those nanoparticles using surfactants, monolayers or polymers. Nanocomposite films provide a very promising possibility to acquire stable nanostructures even for long-term use.
Figure 2-3: Cross-sectional TEM image of a Pd–CF$_x$ nanocomposite film (metal volume fraction $\phi = 0.15$) deposited on a wax substrate (Histograms on the left and right side of the figure report the nanoparticle diameter distribution measured over the lower and upper part of the section, respectively; Circles mark the zones where size distribution has been calculated.) [76].

2.3 Thin Metal/Polymer Nanocomposite Films

2.3.1 Introduction to Thin Metal/Polymer Nanocomposite Films

Nanocomposite represents a two phase material in which one phase appears in the form of nanometer sized clusters or particles. Amongst these nanostructured materials, insulating materials with embedded metal nanoparticles are under focus because of their special structural properties and the extraordinary optical and electrical properties [77, 78]. Especially, thin insulating layers with embedded nanoparticles have raised special interest, because polymer thin films are especially suitable as host materials for nanoparticles in order to stabilize the particle size and the growth of nanoparticles, whilst their chemical and physical properties can be very different. Further, extensive management of the nanostructure is possible during the preparation process of polymer films with embedded nanoparticles. This can be done, for example, by self-organization of colloidal metal particles in polymer solutions or by combination of various vacuum deposition techniques [77].

2.3.2 Preparation Methods of Metal/Polymer Nanocomposite Films

Several of most frequently used preparation methods of metal/polymer nanocomposite films are reviewed as follows.

2.3.2.1 Layer-by-layer assembly

Layer-by-layer (LBL) assembly is a low-cost approach based on the alternating adsorption
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of materials containing complementary charged or functional groups to form integrated thin films. Liu et al. prepared multilayer silver nanocomposite films through the sequential electrostatic deposition of negatively charged poly(styrenesulfonate) (PSS) and poly(acrylic acid) (PAA) polyelectrolytes and positively charged third-generation poly(amidoamine) dendrimer (PAMAM). The silver ions were preorganized in LBL films composed of PAMAM dendrimers and subsequently reduced with hydrogen to prepare the silver nanoparticles as shown in figure 2-4 [79].

![Diagram of silver nanocomposite LBL films and structures of polyelectrolytes](image)

**Figure. 2-4:** Schematic representation of preparation of multilayer silver nanocomposite LBL films and structures of polyelectrolytes [79].

Another example is to construct the polymer-colloid multilayer nanocomposite films by the exploitation of electrostatic interaction. The basic colloid layer has a negative charge, so facilitates the assembly of a thin film of polycationic polymer. In turn, the polymer layer leaves a surface with positive charge, on which a second colloid layer is assembled. Subsequent layers are built like wise as shown in figure 2-5. Nanoparticle arrays can be constructed from any charged nanoparticle and an oppositely charged “crosslinker” in an analogous way to the construction of colloid-polymer architectures. Moreover, covalently linked colloid superstructure can be built analogously to electrostatically linked architecture. This has been accomplished by the use of bisthiol “crosslinker” for gold [80].
2.3.2.2 Ion implantation

In this technique, a selected host material (frequently an insulating ceramic or polymer) is injected with energetic ions that are accelerated from a few tens to a few thousand kilovolts. High-dose implantation can create a solid state supersaturation of the implanted ions in a layer extending from the specimen surface to a depth of several tens to hundreds of nanometers (see figure 2-6). Subsequent thermal processing or further ion (or electron) irradiation can, depending on the specific host/nanoparticle solid state chemistry, induce the implanted material to precipitate as discrete nanoparticles.

The versatility of the implantation technique arises from the fact that essentially any element in the periodic table can be implanted into virtually any selected host material. This versatility and the various possible combinations of implanted ions allow for an extremely large range of potential nanoparticle-host combinations. Useful properties of two or more precipitated phases can be combined into one well-defined, integrated structure; and the important physical properties of the nanocomposite can be optimized for a particular application by controlling the concentration and average size of the precipitates [81]. However, the energy of ions implanted is transferred to the matrix through the excitation of electronic shells (ionization) and nuclear collisions. This causes radiation-induced defects, which, in turn, may reversibly or irreversibly modify the material structure. Various types of polymer structure damage have been observed: breaking of covalent bonds in macromolecules, generation of free radicals, cross linkage, oxidation and carbonization of layers irradiated, as well as formation of new chemical bonds between atoms of the
insulator or between ions implanted, etc. In addition, ion implantation may be accompanied by the intense sputtering of the surface exposed or, sometimes, by the swelling of the polymer [82].

Figure 2-6: 1) Schematic representation of the ion implantation technique for producing embedded nanoparticles: a) the host specimen is implanted with energetic ions (arrows), b) a supersaturated solid solution is formed in the near surface region, c) implanted material is precipitated into a layer of discrete, isolated nanoparticles of varying size; 2) TEM image of silver nanoparticles produced by Ag⁺ implantation into Poly(methyl methacrylate) (PMMA) at a dose of $5 \times 10^{16}$ cm$^{-2}$ [82].

2.3.2.3 Alkaline surface modification combined with an ion exchange reaction

Polyimide is known to be a high-performance organic material that has been widely used in microelectronics device fabrication and packaging applications. In particular, the metallization of polyimide has been the subject of intense study aiming to develop metallic circuits on the polyimide substrate. However conventional ion implantation applied to polyimide substrates causes significant surface damage due to irradiation-induced carbonization. Akamatsu et al. [83, 84] reported a simple process for the preparation of polyimide-based nanocomposites containing monodispersed copper or nickel nanoparticles. The polyimide resin surface is chemically modified using potassium hydroxide (KOH) to form carboxylic acid groups in the modified layer through imide ring-cleavage reactions. The subsequent copper ion (or nickel ion) complexation achieved by ion exchange with the bound potassium ions is followed by reduction in a hydrogen atmosphere, yielding metallic nanoparticles (see figure 2-7).
Figure 2-7: 1) Schematic diagram of the synthesis process for composite polyimide layers containing monodispersed copper nanoparticles; 2) cross-sectional TEM image of Ni adsorbed surface modified polyimide film after heat treatment at 300 °C for 30 min in H₂ atmosphere in (a), (b) enlarged image of (a), inset: selected area electron diffraction pattern of the film [83, 84].

This methodology enabled the preparation of copper (or nickel) nanoparticle-based polyimide nanocomposites, by which the film morphology, for example, the particle size, volume fraction and the film thickness can be systematically controlled.

2.3.2.4 Vapor phase co-deposition

Vapor phase co-deposition is a single-step or straightforward method to produce metal/polymer functional nanocomposites films. Biswas et al. [85] reported that vapor phase co-deposition is an effective technique to generate an extremely narrow particle size distribution, which also allows easy tuning of particle plasmon resonance over a wide wavelength range. Deposition rates of polymer and metal were power controlled to prepare different metal volume filling in the polymer matrix. Relatively low rate of metal evaporation was chosen in order to control nanoparticle growth process in a better way (see figure 2-8). Vapor phase deposition of polymers has a range of advantageous features.
Some of these are excellent conformality over complex topography, the possibility of good film uniformity on large diameter wafers, and environmentally safe processing due to the absence of solvents.

Figure 2-8: a) TEM planar view of Ag nanoparticles 3D distributed in Teflon AF matrix (nanoparticle volume filling: ~ 10%) along with SAED pattern on the generated nanoparticles showing fcc nature, in the inset; b) size distribution profile of the generated Ag nanoparticles distributed in Teflon AF matrix showing almost 80% particles in the size range of 5-7 nm [85].

2.3.2.5 Co-sputtering

Another technique to prepare metal/polymer nanocomposite is PVD-based co-sputtering. Schuermann et al. successfully synthesized the Ag/polytetrafluoroethylene (PTFE) nanocomposite films by magnetron co-sputtering and produced Bragg reflectors using multilayer systems of composites and pure sputtered PTFE as shown in figure 2-9 [86]. By magnetron co-sputtering high deposition rates and good uniformity on a relatively large substrate can be achieved.
Figure 2-9: Cross-sectional TEM image of a multilayer system with four double layers: (a) composite layer with silver clusters, (b) sputtered PTFE and (c) polymer substrate [86].

Farella et al. employed the ion beam co-sputtering technique to deposit palladium-fluoropolymer nanocomposite films with good in-plane and in-depth morphological uniformity showing potential application in sensor technology [87].

2.3.2.6 Plasma polymerization combined with metal evaporation or sputtering

Plasma deposition is an established, low pollutant method, which is compatible with other thin film technologies in microelectronics. Metal/polymer nanocomposite films can be fabricated by combining the plasma polymerization and the metal evaporation or sputtering alternatively or simultaneously [88-91]. Heilmann gave a comprehensive overview of the preparation of metal/polymer nanocomposite combining plasma polymerization and metal evaporation and sputtering [77]. In the simultaneous deposition of metal/polymer nanocomposite film, the growth of embedded metal particles is substantially influenced by the coincidental growth of the polymer, whereas in the alternating deposition of metal/polymer nanocomposite film, it is easier to prepare multilayer systems with well-defined vertical distribution of nanoparticles.
Moreover, gamma and ultraviolet irradiation have also been used to prepare nanoparticles of Ag in poly(vinyl alcohol), PbS in poly(vinyl acetate), CdS in poly(acrylamide), Au in poly(acrylamide) and Ag in poly(acrylonitrile) [92-95]. Nanocomposite films have also been formed by reducing metal salts in various types of polymers, including epoxy, block copolymers and dendrimers [96-97].

2.3.3 Current State of the Art and Applications

Currently metal/polymer nanocomposite materials stimulate considerable interest in various research fields, due to their intriguing chemico-physical characteristics and their potential applications in catalysis, microelectronics, sensing, magnetism, photonics and energetics [36, 98-100]. By incorporating semiconductor nanoparticles into polymer matrix materials, many interesting optical properties including absorption, fluorescence, luminescence and nonlinearity can be utilized in more technologically important forms such as films and fibers [101]. Another attracting group of nanocomposite materials is carbon nanotube polymer composite due to their conductivity at very low loading levels and their mechanical properties, which could derive new and advanced engineering materials [102, 103]. Yu et al. [104] has found that gold nanoparticles stabilized with the ligand 4-(dimethylamino) pyridine (DMAP) can be absorbed into the interior of preexisting polyelectrolyte multilayers simply by soaking the film in a dispersion of nanoparticles. The presence of the gold nanoparticles in the multilayer greatly boosted the electron transfer in the film and exhibited electrocatalytic behavior in response to nitric oxide, which can be used in detecting the biological byproduct. Novel functional application of metal/polymer nanocomposite film in magnetics for data storage was reported by Ouyang et al [105]. Moreover, the sensitivity of the surface plasmon resonance frequency to the small variations of metal nanoparticle and the surrounding dielectric medium can be used in various applications such as absorption elements of solar cells [106], Bragg reflectors [107] and Raman spectroscopy [108]. In special case of silver nanocomposite films related to this thesis, many applications of them in household or medical field were reported because of their antibacterial properties [109-111].

In chapter 2, a short introduction to the plasma polymerization and plasma etching was given at the beginning of this chapter. The origin of the SPR band in noble metal nanoparticles and the factors influencing the SPR band were discussed. In addition, the preparation methods and applications of metal nanoparticles and metal/polymer
nanocomposite films were reviewed.

References


Chapter 2: Theory

Chapter 2: Theory

Chapter 2: Theory

Chapter 3: Analytical Methods

In this chapter, the basic theories and principles of the main analytical methods, such as atomic force microscopy, electron microscopy, X-ray photoelectron spectroscopy, UV-Vis spectroscopy and ellipsometry, are discussed.

3.1 Atomic Force Microscopy

3.1.1 Principle of Atomic Force Microscopy

Atomic force microscopy (AFM) together with scanning tunneling microscopy (STM) belongs to scanning probe microscopy (SPM) used to image and measure properties of material, chemical and biological surfaces. SPM images are obtained by scanning a sharp probe across a surface while monitoring and compiling the tip-sample interactions to provide an image. The advantage of AFM over scanning tunneling microscopy is that AFM is able to image insulating surfaces. AFM provides a number of advantages over conventional microscopy techniques. AFM can make measurements in three dimensions and requires neither a vacuum environment nor any special sample preparation. AFM can be used in either an ambient or liquid environment. With these advantages AFM has significantly impacted the fields of materials science, chemistry, biology, physics and the specialized field of semiconductors.

The principle behind the operation of an AFM is shown in figure 3-1. A typical AFM consists of a piezoelectric scanner, a probe, an optical head, and a base, which supports the scanner with the head and includes a circuit for measuring the deflection signal. The probe used in an AFM is a sharp tip, typically less than 5 µm tall and often less than 10 nm in diameter at the apex. The tip is located at the free end of a cantilever that is usually 100-500 µm long. It operates by scanning across the surface with a sharp tip mounted on a soft cantilever spring. Forces between the tip and the sample surface cause the cantilever to bend, or deflect. A detector measures the cantilever deflections as the tip is scanned over the sample, or the sample is scanned under the tip. An optical system is used to sense the position of the tip relative to the sample. The laser beam bounces off the back of the cantilever and onto a position-sensitive photodiode detector. As the cantilever bends, the position of the laser beam on the detector changes. As a result, the system can detect sub-Angstrom vertical movement at the free end of the cantilever, where the tip is located. The measured cantilever deflections allow a computer to generate a map of surface topography.
with the Z feedback turned on or off. With Z feedback off (constant-height mode), the spatial variation of the cantilever deflection is used to generate the topographic data set. With Z feedback on (constant-force mode), the image is based on the Z motion of the scanner as it moves in the Z direction to maintain a constant cantilever deflection.

![Figure 3-1: A schematic drawing of an atomic force microscope.](image)

### 3.1.2 Primary AFM Imaging Modes

There are three most commonly used primary imaging modes, which are contact mode, non-contact mode and Tapping Mode. We can differentiate the different imaging modes by means of the empirical force and distance curve between sample and AFM tip shown in figure 3-2 [1].

In contact mode the AFM tip and sample are so close together, so that their electron clouds begin to repel each other. In addition to the repulsive force, a capillary force exerted by the thin liquid layer often presents on the sample surface in an ambient (non-vacuum) environment (typically, this layer is mostly water), and the force exerted by the cantilever itself are present.

In non-contact mode the inter-atomic force between the cantilever and sample in this regime is attractive (largely a result of van der Waals interactions). As indicated in figure 3-2. The spacing between the tip and the sample for non-contact mode is on the order of tens to hundreds of Angstrom. The system detects changes in the cantilever’s resonance frequency or vibration amplitude. The attractive non-contact force between tip and sample is typically smaller and more difficult to maintain than the repulsive contact force.
Figure 3-2: Empirical force vs distance curve that reflects the type of interaction between the scanning tip and sample during AFM measurements using specific imaging modes [1].

In TappingMode an oscillating probe tip maps topography by lightly tapping the surface and the cantilever's oscillation amplitude changes with sample surface topography. The topography image is obtained by monitoring these changes and closing the Z feedback loop to minimize them. By using TappingMode damage to samples can be reduced. Another major advantage of TappingMode is that the amplitude of the cantilever oscillation in TappingMode is typically on the order of a few tens of nanometers, which ensures that the tip does not get stuck in the liquid layer on the sample surface in the ambient environment. The amplitude used in non-contact AFM is much smaller. As a result, the non-contact tip often gets stuck in the liquid layer unless the scan is performed at a very slow speed.

3.2 Electron Microscopy

Electron microscopes are scientific instruments that use a beam of highly energetic electrons to examine objects on a very fine scale. This examination can yield the following information, such as topography, morphology, composition and crystallographic information.
3.2.1 Scanning Electron Microscopy

3.2.1.1 Principles of scanning electron microscopy

The scanning electron microscope (SEM) is one of the most versatile and widely used tools of modern science, as it allows the study of topography, morphology, composition and crystallography of biological and physical materials. It has much higher resolution than optical microscopy due to the very small wavelength of the electron, and the sample preparation is not complex. It is faster than scanning probe microscopy as the beam can be scanned with electromagnetic fields rather than mechanical actuators. However, it requires a conductive sample (or a metallized surface of a non-conductive sample) and must be carried out in a vacuum.

An SEM operates by scanning an electron probe across a specimen, which enables high resolution images of the morphology or topography of a specimen, with great depth of field, at very low or very high magnifications to be obtained. Compositional analysis of such a specimen may be obtained by analysing the X-rays produced by the electron-specimen interactions. This enables detailed mapping of the elemental distribution to be produced from multi-phase materials.

In standard electron microscopes electrons are mostly generated by heating a tungsten filament by means of a current to a temperature of about 2800 °C (electron gun). The measurements in the scope of the thesis are performed using a field emission scanning electron microscope (FE-SEM). In field emission scanning electron microscope no heating but a so-called "cold" source is employed. An extremely thin and sharp tungsten needle (tip diameter 10^{-7}-10^{-8} m) functions as a cathode in front of a primary and secondary anode. The electrons are accelerated in the direction of the column by a voltage gradient. The voltage between cathode and anode is in the order of magnitude of 0.5 to 30 kV. Because the electron beam produced by the FE source is about 1000 times smaller than in a standard microscope, the image quality is markedly better. In contrast to a conventional tungsten filament, a FE tip lasts theoretically for a lifetime provided the vacuum is maintained stable. The electron beam, which typically has an energy ranging from a few hundred eV to 100 keV, is focused by one or two condenser lenses into a beam with a very fine focal spot sized 1 to 5 nm. The beam passes through pairs of scanning coils in the objective lens, which deflect the beam horizontally and vertically, so that it scans in a raster fashion over a rectangular area of the sample surface. The stigmator coils are utilized to correct
irregularities in the x and y deflection of the beam and thus to obtain a perfectly round-shaped beam. When the beam is not circular but ellipsoidal, the image looks blurred and stretched (see figure 3-3) [2].

![Figure 3-3: Schematic representation of a scanning electron microscope [3].](image)

3.2.1.2 Electron-specimen interactions

The primary electron beam effectively spreads and fills a teardrop-shaped volume, known as the interaction volume, extending from less than 100 nm to around 5 μm into the surface, from which the signals including secondary electrons, back-scattered electrons and X-rays are generated (see figure 3-4).

![Figure 3-4: Schematic representation of the electron beam-specimen interactions [4].](image)

The secondary electrons are collected to form the standard topography image and the back-scattered electrons provide an image with atomic number contrast. X-rays are produced by
the interaction of the electron beam with atoms in the specimen. These X-rays are characteristic of the elements present and they may be separated out in an energy spectrum to allow the identification of the elemental composition of the specimen and mapping of the distribution of the elements in the sample.

3.2.1.3 Properties of secondary electrons

Secondary electrons are predominantly produced by the interactions (inelastically scattering) between energetic beam electrons and weakly bonded conduction-band electrons in metals or the valence electrons of insulators and semiconductors. The ejected electrons typically have very small kinetic energy (5 eV) and 50 eV is an arbitrary cut-off below which they are called secondary electrons. Due to their low energy, only secondary electrons which are very near the surface (< 10 nm) can exit the sample and be detected, so secondary electrons are very topography related. Many electrons escape from areas with sharp edges or peaks to be deflected by the Faraday Cage (see figure 3-5 B). Some electrons escape from areas without sharp edges (see figure 3-5 A and C). Few secondary electrons are detected when generated secondary electrons are only deflected partially by the Faraday Cage due to the shadow location on the sample where they are generated (see figure 3-5 A). The phenomenon is called edge effect, which is the main origin of the topography contrast of secondary electrons.

Figure 3-5: Emission of secondary electrons from the sample surface (the sample-edge effect) [5].
3.2.2  Transmission Electron Microscopy

3.2.2.1  Principles of transmission electron microscopy

Transmission electron microscope (TEM) is in principle similar as a scanning electron microscope. The significant difference is that the electron beam is transmitted through the very thin specimen (see figure 3-6) [6]. As the electron beam passes through the specimen, it is affected by the structures and materials of specimen. The transmitted beam is then projected onto a phosphor viewing screen or to be detected by a CCD camera. TEM gives sub-nanometer resolution but it requires extensive sample preparation for high resolution imaging. The electron beam has very small interaction volume because of its high energy (several hundreds of kV), so it allows high spatial resolution (~ 1 nm) for energy-dispersive X-ray (EDX) analysis.

![Figure 3-6: Two basic operation modes of a transmission electron microscope [6].](image)

The electron beam is focused to a small, thin, coherent beam by the use of condenser lenses and restricted by the condenser aperture, knocking out high angle electrons. The beam then strikes the specimen and parts of it are transmitted. This transmitted portion is focused by the objective lens into an image. Optional objective and selected area metal apertures can restrict the beam; the objective aperture enhancing contrast by blocking out high-angle diffracted electrons, the selected area aperture enabling the user to examine the periodic diffraction of electrons by ordered arrangements of atoms in the sample. The image is passed down the column through the intermediate and projector lenses, being enlarged all
the way. The image strikes the phosphor image screen and light is generated, allowing the user to see the image. In the scope of the thesis, the bright field TEM image was applied to study the microstructure of the silver nanoparticles on plasma polymer films or in plasma polymer nanocomposite films. The selected area electron diffraction (SAED) was used to study the crystalline structure of the silver nanoparticles and EDX measurements were performed for the compositional analysis as well.

3.2.2.2 Contrast mechanisms

There are several contrast mechanisms in TEM measurements, which are scattering contrast, diffraction contrast and phase contrast, respectively. The most important contrast mechanism for the case study of metal nanoparticles in nanocomposite films is the different densities and atomic masses of the materials exhibiting different powers of scattering, so that the scattering contrast is measured. In addition, the thickness of the film has a large influence on the scattering, whereby the thicker the sample, the worse the resolution. Diffraction contrast is produced due to a local distortion in the orientation of the crystal (by defects, for example), so that the diffracted intensity of the incident electron beam is perturbed, leads to contrast observed in the Bright field image. Phase contrast is produced by the phase modulation of the incident electron wave which transmits through a crystal potential. This type of contrast is sensitive to the atom distribution in the specimen and is the basis of high-resolution TEM [7].

3.3 X-ray Photoelectron Spectroscopy

3.3.1 Introduction to X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS), also called electron spectroscopy for chemical analysis (ESCA), is one of the most powerful and valuable methods of surface analysis currently available. In XPS, the primary excitation is accomplished by irradiating the specimen by a source of monochromatic X-rays. The X-rays cause photoionisation of atoms in the specimen and the response of the specimen (photoemission) is observed by measuring the energy spectrum of the emitted photoelectrons. XPS can be used to study the chemical environment and the film composition quantitatively and it can provide depth profiles and the mapping of samples based on either elemental or chemical information.
3.3.2 *The Photoelectric Effect*

Normally MgK\(_\alpha\) (1253.6 eV) and AlK\(_\alpha\) (1486.6 eV) radiations are used as the X-ray sources, which are normally able to penetrate 1-10 \(\mu\)m depending on the materials. In the XPS experiment, the sample surface is irradiated by a source of low-energy X-rays under ultra high vacuum (UHV) conditions. Photoionisation then takes place on the sample surface, the resultant photoelectrons having a kinetic energy \(E_k\), which is related to the X-ray energy \(h\nu\) and binding energy \(E_b\) by the equation:

\[
E_k = h\nu - E_b \tag{3-1}
\]

If the photoelectrons have sufficient kinetic energy, they are able to escape from the surface by overcoming the specimen work function, and photoemission is said to occur as shown in figure 3-7 [8]. When an electron is ejected from an inner shell of an atom, the resultant vacancy is soon filled by an electron from one of the outer shells. The energy released may appear as X-ray photon or be transferred to another electron which is ejected from the atom with an energy, \(E_A\), determined by the three energy levels concerned,

\[
E_A = E_1 - E_2 - E_3^* \tag{3-2}
\]

where \(E_1\) and \(E_2\) are the binding energies of the atom in the singly ionized state and \(E_3^*\) is that for the doubly ionized state.

![Figure 3-7: Generation of photoelectrons and Auger electrons [8].](image)

Considering the emission of the photonelectron as excitation of particles and assuming the other electrons in the sample are not influenced by the excitation and emission of the photoelectron [9], the kinetic energy of an emitted electron without losing energy due to inelastic scattering can be calculated as follows:
\[ E_k = h\nu - E_h - \phi_{\text{spec}} \]  \hspace{1cm} (3-3)

Figure 3-8 illustrates the correlation shown in equation 3-3. \( E_k \) is the value to be measured and the work function of the spectrometer, \( \phi_{\text{spec}} \) has to be determined using some known samples beforehand, which is dependent on both the sample and the spectrometer.

**Figure 3-8**: Schematic representation of energy levels during the XPS measurements [10].

### 3.3.3 Inelastic Scattering and Sampling Depth

Following photoionization, the photoelectron of \( E_k \) must travel through the solid and escape into the vacuum, without energy loss, before it can be energetically analyzed and detected as a characteristic photoelectron. However, the stopping power of solids for electrons is several orders of magnitude higher than that for X-rays, with the net result that electrons in the energy range 50-1000 eV will typically travel only 1-3 nm before they lose energy through inelastic scattering.

The probability of an inelastic scattering is described by the standard exponential decay law [9]:

\[ I(x) = I_0 \exp(-x / \lambda(E_h, Z) \cdot \cos \theta) \]  \hspace{1cm} (3-4)

Where \( I_0 \) is the original photoelectron intensity, \( I(x) \) is the intensity remaining after
traveling through material of thickness $x$, $\theta$ is the angle of emission with respect to the surface normal, and $\lambda(E_k, Z)$ is a material and energy-dependent constant, termed the inelastic mean free path. Sampling Depth is normally defined as the depth from which 95% of all photoelectrons are scattered by the time they reach the surface ($3\lambda$). Most $\lambda$’s are in the range of 1-3.5 nm for AlK$_\alpha$ radiation, so the sampling depth ($3\lambda$) for XPS under these conditions is 3-10 nm.

### 3.3.4 Data Interpretation

Using XPS both qualitative and quantitative surface analyses can be achieved. Qualitative analysis is used to determine the elemental and chemical identification of sample constituents by combining the information in the survey spectra with the characteristic binding energy tables of electrons in atoms [11]. More importantly is to determine the relative concentrations of the various constituents. The method using peak area sensitivity factors for quantifying the XPS measurements is discussed below:

$$I = n \cdot f \cdot \sigma \cdot \theta \cdot y \cdot \lambda \cdot A \cdot T$$

(3-5)

$I$ The number of photoelectrons per second in a specific spectra peak,

$n$ The number of atoms of the element per cm$^3$ of the sample,

$f$ The X-ray flux in photons/cm$^2$-sec,

$\sigma$ The photoelectric cross-section for the atomic orbital of interest in cm$^2$,

$\theta$ An angular efficiency factor for the instrumental arrangement based on the angle, between the photon path and detected electron,

$y$ The efficiency in the photoelectric process for formation of photoelectrons of the normal photoelectron energy,

$\lambda$ The mean free path of the photoelectrons in the sample,

$A$ The area of the sample from which photoelectrons are detected,

$T$ The detection efficiency for electrons emitted from the sample.

From equation 3-5

$$n = I / f \cdot \sigma \cdot \theta \cdot y \cdot \lambda \cdot A \cdot T$$

(3-6)

can be obtained. The denominator in equation 3-6 can be defined as atomic sensitivity factor, $S$. Therefore, the expression

$$\frac{n_1}{n_2} = \frac{I_1 / S_1}{I_2 / S_2}$$

(3-7)

may be used for determining the atom fraction of any constituent in a sample, where a set of
relative values of $S$ for all of the elements are developed for the instrument with certain X-ray sources.

### 3.4 UV-Vis Spectroscopy

Just like IR spectroscopy the absorption of electromagnetic radiation by the sample is recorded by UV-Vis spectroscopy, only ultraviolet and visible light will be used for UV-Vis spectroscopy. The absorption of UV or visible radiation is not induced by the molecular vibrations like in the IR spectroscopy but by the electronic transitions. At nanometer scales, electron cloud can oscillate on the nanoparticle surface and adsorb electromagnetic radiation at a particular energy. This is so-called surface plasmon resonance. In the scope of the thesis, UV-Vis spectroscopy in transmission mode is used to observe the surface plasmon resonance of metal nanoparticles, thereby to relate surface plasmon resonance to the morphology and the surrounding matrix of metal nanoparticles.

Absorbance $A(\lambda)$ is directly proportional to the film thickness $d$, the concentration of materials $c$ and the molar absorptivity of the absorbing species $\varepsilon(\lambda)$ according to the Beer's Law states that

$$A(\lambda) = \log \frac{I_0}{I} = \varepsilon(\lambda) \cdot d \cdot c \quad (3-8),$$

where $I_0$ is the intensity of the incident light at a given wavelength and $I$ represents the transmitted intensity. Although light scattering and reflectance could also influence the the UV-Vis data, in our case study absorption should be dominant, because the nanoparticle size is relatively very small in comparison to the wavelength of the incident light [12].

### 3.5 Ellipsometry

Ellipsometry is currently being used extensively to measure the thickness and the optical properties of thin films. Linearly polarized light reflects from a surface under certain conditions and elliptically polarized light is generated. In fact this is the reason for the name ellipsometry (see figure 3-8). The amount of the induced ellipticity, which depends on the thickness, refractive indices and the morphology of the film, can be described and experimentally measured by $\Psi$ ( \( \tan \Psi = \left| \frac{R^s}{R^p} \right| \), where $R^p$ and $R^s$ are the total reflection coefficients, i.e. the ratio of the amplitude of the outgoing resultant wave to the amplitude of the incoming wave for p-waves and s-waves) and $\Delta$ ( \( \Delta = \delta_1 - \delta_2 \)), where $\delta_1$ and $\delta_2$
represent the phase difference between the p-wave and the s-wave before and after the reflection). The measured data will be then fitted by a certain model with the help of proper starting value of different parameters, which can describe the film system at the best. From the fitting results, the thickness and the complex refractive indices can be determined [13].

**Figure 3-9: Schematic diagram of an ellipsometer and its components in reflection mode.**

The ellipsometry measurements of different plasma polymer films and metal/polymer nanocomposite films were performed by using UV-Vis spectroscopic ellipsometry (Sentech SE800), which allows measurements within the wavelength ranging from 300 to 800 nm at different incident angles.

**References**


Chapter 4: Synthesis and Characterization of Thin Fluorocarbon and Organosilicon Plasma Polymer Films

4.1 Introduction

Recently considerable work has been undertaken to fabricate polymeric and dielectric thin films using plasma deposition due to its room temperature, solvent-free and versatile operation. Many organic precursors even not polymerizable by conventional means can be selected to prepare thin plasma polymer films with a wide range of compositions and chemical functionalities. The surface morphology, wettability and the mechanical properties can be tailored by varying the deposition process parameters. Moreover, plasma polymer films have some advantages over normal polymer films, i.e. plasma polymer films are generally chemically inert, insoluble, mechanically tough, and thermally stable [1, 2].

In particular, Teflon-like thin films are of high interest for microelectronic and optical applications but are also considered as long-term stable corrosion resistant and aesthetic thin films for their low dielectric constant, high hydrophobicity, high chemical inertness and low friction coefficient [3-5]. Haidopoulos et al. reported a plasma deposition process aiming to eliminate the corrosion of medical devices in biological environment by a thin, cohesive and strongly adherent coating of a fluorocarbon plasma polymer [6]. More recently Valentini et al. reported to use fluorinated amorphous carbon films prepared by plasma enhanced chemical vapor deposition as photovoltaic materials in solar cell applications [7].

In addition, organosilicon films (SiO$_x$C$_y$H$_z$) have found a lot of applications in different fields, especially in the ophthalmic and automotive industries as protective coatings, selective gas permeation membranes, low-k dielectric or biocompatible films. Rats et al. investigated the mechanical properties of the silicon oxide films used as protective coatings in order to improve the surface mechanical properties of polymers [8]. Grill et al. studied the dielectric properties and the thermal stability of the organosilicon films as a candidate for low dielectric constant films in microelectronics [9]. In addition, Hilton et al. reported the synthesis of the hexamethylocyclohexiloxane plasma polymer films for use as insulating biomaterials [10].

In all the above-mentioned applications of plasma polymer films, their chemical structures,
morphology, wettablity, and dielectric properties are of great importance. Therefore, while the syntheses of the fluorocarbon and organosilicon plasma polymer films are described, the obtained plasma polymer films are characterized by various techniques. The chemical structures of the plasma polymer films are investigated by means of FT-IR spectroscopy and XPS. The morphology and surface roughness of the plasma polymer films are studied by AFM. Contact angle measurements are performed to analyze the wettabiliy of the plasma polymer films. Ellipsometry is applied to investigate the optical properties of the plasma polymer films and to determine the thickness of the deposited plasma polymer films.

4.2 Experimental Section

4.2.1 Materials

Argon 99.998%, oxygen 99.995% and nitrogen 99.99% (Messer Griesheim GmbH Germany) were used as gases for the plasma deposition processes. Heptadecafluoro-1-decene (HDFD, CF$_3$(CF$_2$)$_7$CHCH$_2$, purity > 97%, Fluka) and hexamethyldisiloxane (HMDSO, (CH$_3$)$_6$Si$_2$O purity > 98%, Fluka) were used as liquid monomers without further purification for the deposition of plasma polymer films. Polished Si (100) wafers (Si-Mat, Germany) and gold coated quartz crystals were used as substrates.

4.2.2 Plasma Deposition

One custom made bell-jar type reactor with parallel capacitive electrodes was used to perform plasma deposition as shown in figure 4-1 [11]. The Si-wafer substrates and a gold coated quartz crystal of 20 mm diameter used for in-situ quartz crystal microbalance measurements (QCM) were fixed in the grounded electrode during the plasma deposition process. The details of the set-up have been published elsewhere by Wang and Grundmeier [12]. Prior to the plasma deposition process, the reactor was evacuated down to $5 \times 10^{-4}$ mbar by means of a turbo pump (Pfeiffer Vacuum). A liquid nitrogen trap was installed between the vacuum pump and the reactor to avoid the diffusion of oil from the pump into the vacuum chamber. The process pressure was adjusted by a down stream by-pass system and controlled by means of a gas independent capacitive pressure gauge (MKS). A mass flow controller (MKS) was used to adjust the overall flow rate by means of a pure argon flow, and the partial pressures of the monomers and oxygen were adjusted by needle valves.
Chapter 4: Synthesis and Characterization of Thin Plasma Polymer Films

Figure 4-1: Schematic representation of the audio-frequency (af) plasma polymer deposition set-up [11].

An audio-frequency voltage source supplying about 400 V to the electrodes was used to initiate the plasma. The overall flow rate was adjusted to 1.5 sccm for each treatment step. Prior to the deposition of the plasma polymers, all substrates were pre-treated with oxygen plasma for 5 minutes to clean the surfaces of substrates. The flow rate and the partial pressures for the plasma deposition are given in table 4-1. Films prepared using the same conditions on different dates showed good reproducibility in all of the tests used.

Table 4-1: Flow rate and partial pressures of HDFD and HMDSO plasma polymer deposition processes

<table>
<thead>
<tr>
<th>Plasma polymer</th>
<th>P_Ar (mbar)</th>
<th>P_HDFD (mbar)</th>
<th>P_O2 (mbar)</th>
<th>P_HMDSO (mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDFD</td>
<td>0.2</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HMDSO</td>
<td>0.2</td>
<td></td>
<td>0.05</td>
<td>0.05</td>
</tr>
</tbody>
</table>

4.2.3 Surface Analysis

The chemical compositions of the plasma polymer films were investigated by using FT-IR spectroscopy and XPS. The FT-IR spectra were measured by means of a Digilab FTS 3000 spectrometer with a liquid N2 cooled MCT detector and the XPS spectra were measured by means of XPS spectrometer (Quantum 2000, Physical Electronics, U.S.A.). XPS spectra were measured using a monochromated Al Kα source at pass energy of 23.5 eV. Calibration of the spectra was performed by using the F1s peak (Binding Energy, BE = 689 eV for -CF₂- groups) and C1s peak (BE = 284.5 eV for -C-C- groups) as internal references for
HDFD plasma polymers and HMDSO plasma polymers, respectively. During the fitting procedure, the line width (full width at half-maximum, FWHM) for the peaks was kept constant for all respective element spectrum components in a particular spectrum.

AFM measurements were carried out using a Dimension 3100 (Digital Instruments) in TappingMode with a tetrahedral silicon tip from Olympus company. For all the scans the images were measured in air typically at 1 Hz and 512 points per line. Plasma polymer films were deposited on Si (100) wafers, having an extremely flat surface, so that only the roughness of the plasma polymer films was evident.

The contact angles of different liquids such as water, ethylene glycol and diiodomethane on the surfaces of the obtained plasma polymer films were measured by the sessile-drop method using a goniometer (OCA 20, Dataphysics, Germany). The average value of ten measurements was taken as the contact angle for each liquid.

The thicknesses and the refractive indices of the plasma polymer films were measured by means of UV–Vis spectroscopic ellipsometry in the wavelength ranging from 300 to 800 nm (SE 800, Sentech, Germany).

4.3 Results and Discussion

4.3.1 Deposition Kinetics

In order to control the thickness of the deposited plasma polymer film, in-situ quartz crystal microbalance measurements were performed during the plasma deposition process. The thickness values of the HDFD and HMDSO plasma polymer films determined by means of ellipsometry were found to be linearly dependent on the measured shifts in the resonant frequencies of quartz crystals, \( \Delta f \), as shown in figure 4-2. The mass increment corresponding to the frequency shift, \( \Delta f \), was computed according to the Sauerbrey equation [13]:

\[
\Delta f = -\left(\frac{f_0^2}{N \cdot \rho_q}\right) \Delta m = -c_f \Delta m \tag{4-1}
\]

where \( \Delta f \) is the mean delta frequency observed, \( f_0 \) represents the resonance frequency of the quartz crystal (10 MHz), \( L_q \) is the thickness of the bare quartz disk (0.167 mm), \( N \) is the frequency constant (\( N = 1.668 \times 10^5 \text{ Hz} \cdot \text{cm})\), \( \rho_q \) is the density of quartz (2.468 g⋅cm\(^{-3}\)) respectively, and \( \Delta m \) is the change in mass per unit area. From the Sauerbrey equation it can
be calculated that \( c_f \) is equal to \( 2.426 \times 10^8 \) Hz·g\(^{-1}\)·cm\(^2\). The resulting density of the HDFD plasma polymer film obtained from the slope of the curve (\( \Delta f / h = 59.7 \) Hz·nm\(^{-1}\)) in figure 4-2 a) is about 2.46 g·cm\(^{-3}\). In the same way, the density of the HMDSO plasma polymer can be calculated from the slope of the curve (\( \Delta f / h = 35.5 \) Hz·nm\(^{-1}\)) in figure 4-2 b), which is 1.46 g·cm\(^{-3}\). Thus, the thickness changes of HDFD and HMDSO plasma polymer films can be controlled by in-situ observing the frequency changes of quartz crystal during the deposition process.

**Figure 4-2:** The correlations between measured frequency shifts and the film thickness values of plasma polymer films on Si-wafer substrates determined by ellipsometry: a) HDFD plasma polymer films; b) HMDSO plasma polymer films, respectively.

### 4.3.2 Chemical Structure of HDFD and HMDSO Plasma Polymer Films

#### 4.3.2.1 HDFD plasma polymer films

The FT-IRRAS spectra of the HDFD plasma polymer films are shown in figure 4-3 a) in the high wavenumber range and figure 4-3 b) in the fingerprint region according to the literature [14-16]. The assignments of the functional groups measured by FT-IRRAS were confirmed by the XPS results presented in figure 4-4. The composition of the HDFD plasma polymer films summarized in table 4-2 is C\(_{10}\)F\(_{11.4}\)H\(_x\) in comparison to C\(_{10}\)F\(_{17}\)H\(_3\) of the monomer. It demonstrates that some fluorine atoms are split off from carbon during plasma deposition. From the XPS C1s spectra shown in figure 4-4 and the evaluated peaks in table 4-3, it can be deduced that the C1s spectrum is composed of five peaks, namely -CH\(_2\)CFH\(_2\), -CH\(_2\)CFH\(_2\), -CH\(_2\)CF\(_2\)CF\(_2\), -CF\(_2\)CF\(_2\)CF\(_2\) and -CF\(_3\) [14, 17-19]. The largest contribution (41.3\%) corresponds to -CF\(_2\)CF\(_2\)CF\(_2\) groups, which are the principal groups in the HDFD monomer. It shows that the degree of the fragmentation in the plasma is...
moderate, so that the -CF$_2$CF$_2$CF$_2$- groups in the monomer can be mostly preserved.

**Figure 4-3**: FT-IR reflection absorption spectra (FT-IRRAS) of HDFD plasma polymer films: a) in the high wavenumber range; b) in the fingerprint region.

<table>
<thead>
<tr>
<th>Table 4-2: Atomic composition of the HDFD plasma polymer films</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Element</strong></td>
</tr>
<tr>
<td>F1s</td>
</tr>
<tr>
<td>C1s</td>
</tr>
</tbody>
</table>

**Figure 4-4**: XPS C1s spectrum of HDFD plasma polymer films (the correspondent data are summarized in table 4-2 and table 4-3).
Chapter 4: Synthesis and Characterization of Thin Plasma Polymer Films

Table 4-3: Fitting data of XPS C1s spectrum of HDFD plasma polymer films

<table>
<thead>
<tr>
<th>Element</th>
<th>Binding Energy (eV)</th>
<th>Assignment</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1s</td>
<td>689.0</td>
<td>-CF₂⁻⁴</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>286.0 ± 0.2</td>
<td>-CH₂-CFH⁻²⁸</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>288.0 ± 0.2</td>
<td>-CH₂-CFH⁻²⁸</td>
<td>17.3</td>
</tr>
<tr>
<td>C1s</td>
<td>290.6 ± 0.3</td>
<td>-CH₂-CF₂⁻²⁸</td>
<td>26.8</td>
</tr>
<tr>
<td></td>
<td>292.7 ± 0.3</td>
<td>-CF₂-CF₂⁻CF₂⁻²⁸</td>
<td>41.3</td>
</tr>
<tr>
<td></td>
<td>295.1 ± 0.2</td>
<td>-CF₃⁻²⁸</td>
<td>5.5</td>
</tr>
</tbody>
</table>

4.3.2.2 HMDSO plasma polymer films

The FT-IR transmission absorption spectrum of HMDSO plasma polymer film is shown in figure 4-5. The assignments of the absorbance peaks were done according to the literature [18]. The HDMSO plasma polymer films show the characteristic anti-symmetric stretching and symmetric stretching absorption vibrations of the Si-O-Si groups at wavenumbers of 1095 and 1043 cm⁻¹, respectively. Moreover, the bending vibration of Si(CH₃)ₓ groups at 1265 cm⁻¹ is observed as well in figure 4-5. The composition of HMDSO plasma polymer films is SiO₀.₈C₀.₈Hₓ as summarized in table 4-4 in comparison to SiO₀.₅C₃H₉ of the monomer. Moreover, the XPS C1s spectrum in figure 4-6 a) and the fitted data in table 4-5 show that the C1s spectrum of the HMDSO plasma polymer film is mainly composed of one component, which can be assigned to the -Si-CH₃ groups. In addition, the Si2p peak can be fitted with two components at 103 eV (CH₃-Si(OSi)₃) and 102 eV ((CH₃)₂Si(OSi)₂) as shown in figure 4-6 b).

Figure 4-5: FT-IR transmission absorption spectrum of HMDSO plasma polymer films.
Table 4-4: Atomic compositions of HMDSO plasma polymer films

<table>
<thead>
<tr>
<th>Element</th>
<th>At. Conc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>31.1</td>
</tr>
<tr>
<td>O 1s</td>
<td>30.3</td>
</tr>
<tr>
<td>Si 2p</td>
<td>38.6</td>
</tr>
</tbody>
</table>

Table 4-5: Fitting data of XPS C1s, O1s and Si2p spectra of HDMSO plasma polymer films

<table>
<thead>
<tr>
<th>Element</th>
<th>Binding Energy (eV)</th>
<th>Assignment</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>284.5 ± 0.1</td>
<td>-Si-CH₃</td>
<td>100</td>
</tr>
<tr>
<td>O 1s</td>
<td>532.5 ± 0.2</td>
<td>Si-O-Si</td>
<td>100</td>
</tr>
<tr>
<td>Si 2p</td>
<td>103.0 ± 0.2</td>
<td>CHₓ-Si(OSi)₃</td>
<td>63.8</td>
</tr>
<tr>
<td></td>
<td>102.0 ± 0.2</td>
<td>(CHₓ)₂-Si(OSi)₂</td>
<td>36.2</td>
</tr>
</tbody>
</table>

Figure 4-6: XPS C1s and Si2p spectra of HMDSO plasma polymer films (the corresponding data are summarized in table 4-4 and table 4-5).

4.3.3 Film Morphology

To investigate the morphologies of the obtained plasma polymer films, AFM measurements were performed on the 100 nm thick HDFD and HMDSO plasma polymer films on Si-wafer substrates (see figure 4-7). It has been shown that both surfaces are very smooth with RMS values of only 0.4 nm in comparison to 0.2 nm of the Si-wafer’s RMS value.
Chapter 4: Synthesis and Characterization of Thin Plasma Polymer Films

4.3.4 Wettability of HDFD Plasma Polymer Films

The static contact angles of different liquids on HDFD plasma polymer films were measured to calculate the surface energy of the HDFD plasma polymer surfaces as shown in table 4-6.

Table 4-6: The contact angles of different liquids on the fluorinated surfaces

<table>
<thead>
<tr>
<th>Liquids</th>
<th>Contact angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>108.2° ± 0.7°</td>
</tr>
<tr>
<td>diiodomethane</td>
<td>97.6° ± 0.7°</td>
</tr>
<tr>
<td>ethylene glycol</td>
<td>93.7° ± 0.4°</td>
</tr>
</tbody>
</table>

The surface energies were calculated according to the extended Fowkes’ method:

\[ \gamma_1(1 + \cos \theta) = 2(\gamma_1^d \gamma_2^d)^{1/2} + 2(\gamma_1^p \gamma_2^p)^{1/2} \]  

(4-2)
where $\gamma_1$, $\gamma_2$ are the surface energies of the respective liquid and the solid surface; $\gamma_i^d$, $\gamma_i^p$ ($i = 1, 2$) are the dispersion part and the polar part of the surface energy respectively as shown in table 4-7.

**Table 4-7: Surface energy of each fluorinated film calculated by the contact angle measurement**

<table>
<thead>
<tr>
<th>Energy (mJ/m²)</th>
<th>HDFD plasma polymers films</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\gamma^d$</td>
<td>7.90 ± 0.002</td>
</tr>
<tr>
<td>$\gamma^p$</td>
<td>2.79 ± 0.002</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>10.69 ± 0.004</td>
</tr>
</tbody>
</table>

The measured contact angle is related to the combined effects of surface chemistry and surface topography as described by Wenzel [20]. In this case study HDFD plasma polymer films are extremely smooth (RMS < 1 nm), so that the effect of roughness can be neglected. For the HDFD plasma polymer films, the main factors influencing the surface energy are the concentration of fluorine and the surface density of the perfluorinated surface functional groups (especially -CF₂-).

### 4.3.5 Optical Properties of HDFD and HMDSO Plasma Polymer Films

UV-Vis spectroscopic ellipsometry was used to study the optical properties of the thin HDFD and HMDSO plasma polymer films. Figure 4-8 shows the experimental $\Psi$ and $\Delta$ curves for the HDFD and HMDSO plasma polymer films on Si-wafers.

In order to determine the film thickness ($d$), refractive index ($n$) from ellipsometry spectroscopic analysis, the ellipsometry results of HDFD and HMDSO plasma polymer films, which can be considered to be homogeneous and described as dielectrics, are fitted using the Cauchy layer model [21]. The refractive indices ($n$) of HDFD and HMDSO plasma polymer films and the corresponding film thicknesses are shown in figure 4-8 c). The refractive indices decrease slightly, as the wavelength increases in the wavelength ranging from 300 to 800 nm.
Figure 4-8: Variations of $\Psi$, $\Psi$, and $\Delta$, with wavelength at the incident angle of 50, 60 and 70 degrees for different films: a) HDFD plasma polymer on Si-wafer; b) HMDSO plasma polymer on Si-wafer; c) the change of the refractive indices ($n$) of the HDFD and HMDSO plasma polymer films with wavelength.

For comparison purposes, the refractive indices of HDFD and HMDSO plasma polymers of different thicknesses are shown in figure 4-9.

Figure 4-9: a)-b) Change of refractive indices ($n$) of HDFD and HMDSO plasma polymer films with the film thicknesses.

It can be observed that with increasing film thickness, the refractive index, $n$, increases slightly. This could result from the inhomogeneity of the plasma polymer films. Another
reason could be the difference in the densification and the cross-linking density in different plasma polymer films of different thicknesses.

4.4 Conclusions

The HDFD and HMDSO plasma polymer films were synthesized by plasma polymerization, and the deposition kinetics was measured by combining in-situ quartz crystal microbalance measurements and ex-situ ellipsometry measurements. The thickness of the HDFD and HMDSO plasma polymer films were found to be linearly dependent on the frequency shifts of the quartz crystals. The densities of the HDFD and HMDSO plasma polymer films were determined to be 2.46 and 1.46 g·cm\(^{-3}\) respectively. FT-IR results showed the existence of CF, CF\(_2\), CF\(_3\) and CH\(_x\) functional groups in the HDFD plasma polymers and the Si(CH\(_3\))\(_x\) and Si-O-Si functional groups are main components of the HMDSO plasma polymers. The chemical compositions of HDFD and HMDSO plasma polymer films were determined to be C\(_{10}\)F\(_{11.4}\)H\(_x\) and SiO\(_{0.8}\)C\(_{0.8}\)H\(_x\) by means of XPS, respectively. AFM results demonstrated very smooth surfaces of HDFD and HMDSO plasma polymer films with RMS < 1 nm. The surface energy of HDFD plasma polymer films was calculated to be 10.69 mJ/m\(^2\) by measuring the contact angles of different liquids on HDFD plasma polymer films. Moreover, refractive indices of the HDFD and HMDSO plasma polymer films were determined to be in the range between 1.3 and 1.5 in the wavelength ranging from 300 to 800 nm. The refractive indices decrease slightly, as the wavelength increases in the above-mentioned wavelength range.

References

Chapter 5: Surface Analytical Studies of Ar-plasma Etching of Thin Heptadecafluoro-1-decene Plasma Polymer Films

5.1 Introduction

Teflon-like thin films are of high interest for microelectronic and optical applications as well as used as long-term stable corrosion resistant thin films for their low dielectric constant, high hydrophobicity, high chemical inertness and low friction coefficient [1-3]. At the same time, increasing interest has been devoted to the modification of the fluoropolymer surface characteristics to obtain improved adhesion, wettability and other functionalities [4-6].

Yet, little has been published on the detailed structure of thin Teflon-like plasma polymer films and their behavior etched in inert plasmas [7, 8]. The latter treatment can be used to tailor the chemical structure, the surface roughness of the functional films, the optical and mechanical properties as well as the wettability of thin plasma polymer films. In chapter 4 heptadecafluoro-1-decene (HDFD) plasma polymer films were successfully synthesized in an audio frequency discharge. In this chapter, the chemical structure and surface morphology of HDFD plasma polymer films were studied after thin film deposition and after an additional Ar-plasma treatment by combining in-situ FT-IRRAS, XPS, ToF-SIMS and AFM. The surface chemistry and surface morphology were correlated with the surface energy as calculated by contact angle measurements.

5.2 Experimental Section

5.2.1 Ar-plasma Etching of HDFD Plasma Polymer Films

HDFD plasma polymer films of 100 nm thickness were deposited on Si-wafer substrates for investigations. The corresponding information about the set-up and the deposition process has been shown in section 4.2.2 in detail. The exact plasma polymerization and Ar-plasma etching conditions are summarized in table 5-1. The Ar-plasma etching was performed directly after plasma polymerization with different gas atmospheres shown in table 5-1. Films prepared using the same conditions on different dates showed good reproducibility in all of the tests used.
Table 5-1: Process parameters of HDFD plasma polymerization and the following Ar-plasma etching of thin HDFD plasma polymer films

<table>
<thead>
<tr>
<th>Condition</th>
<th>( P_{\text{Ar}} ) (mbar)</th>
<th>( P_{\text{HDFD}} ) (mbar)</th>
<th>Voltage (( V_{\text{eff}} ))</th>
<th>Current (mA)</th>
<th>Frequency (kHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma polymerization</td>
<td>0.2</td>
<td>0.1</td>
<td>( \approx 400 )</td>
<td>1</td>
<td>4</td>
</tr>
<tr>
<td>Ar-plasma etching</td>
<td>0.3</td>
<td></td>
<td>( \approx 400 )</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

5.2.2 Surface Analysis

The parameters for the XPS measurements of the HDFD plasma polymer films before and after Ar-plasma treatment are the same as shown in section 4.2.3.

In-situ FT-IR reflection absorbance spectroscopy (FT-IRRAS) spectra were measured using a Digilab FTS 3000 spectrometer with a liquid N\(_2\) cooled MCT detector by means of an in-situ plasma cell. The corresponding set-up and method for the in-situ FT-IRRAS measurement were described by Raacke et al. [9]. The set-up consists of a vacuum chamber with moveable sample holder inside, so that the sample can be moved with defined velocities between 0.1 and 30 mm/s through the plasma region to the diagnostic position. The infrared beam of spectrometer is transmitted through ZnSe windows and reflected on the sample at an incidence angle of 80°. The absorbance spectra in parallel and vertical polarization were measured as \( A_p \) and \( A_s \), and then the ratio of \( A_p \) to \( A_s \) was calculated to eliminate the influence of the ambient medium on the spectra.

The mass spectrometry measurements were performed using a ToF-SIMS TRIFT II System (Physical Electronics). The primary \( \text{Ga}^+ \) ion beam was accelerated by a 15 kV voltage and had an intensity of 600 pA.

The parameters for the AFM and ellipsometry measurements of the HDFD plasma polymer films before and after Ar-plasma treatment are the same as shown in section 4.2.3.

The water contact angles were measured by the sessile-drop method using a goniometer (OCA 20, Dataphysics, Germany). Moreover, advancing and receding water contact angles on the test surfaces were measured by continuously adding or removing liquid at an
advancing or receding rate of 5 μl/min.

5.3 Results and Discussion

5.3.1 In-situ FT-IRRAS Measurements

The chemical structure of the HDFD plasma polymer films has been described in section 4.3.2. The effect of Ar-plasma etching on the chemical structure of the HDFD plasma polymer films was investigated by means of in-situ FT-IR reflection absorbance spectroscopy. The spectra of the HDFD plasma polymer films after being etched in the Ar-plasma (I - IV) were compared with the spectrum of that prior to the Ar-plasma etching in figure 5-1 a). It was found that during Ar-plasma etching the absorbance peak positions do not change, but the absorbance values of characteristic peaks such as CF, CF₂ and CF₃ decrease linearly with the Ar-plasma etching time as shown in figure 5-1 b).

![Figure 5-1](image)

**Figure 5-1:** a) In-situ FT-IRRAS difference spectra of Ar-plasma etched thin HDFD plasma polymer films on gold substrate: (I) difference after 10 s Ar-plasma etching; (II) after 30 s; (III) after 60 s; (IV) after 120 s; (b) the change in peak area of absorbance with the time of Ar-plasma etching.

5.3.2 XPS Measurements

To investigate the change of the atomic composition and the relative concentration of the functional groups in HDFD plasma polymer films due to the Ar-plasma etching, XPS measurements were performed on the as-deposited and the Ar-plasma treated HDFD plasma polymer films on Si-wafer substrates. After Ar-plasma etching for 30 and 60 s, the composition of the HDFD plasma polymer film changes from C₁₀F₁₁.₄Hₓ to C₁₀F₇.₉O₀.₆Hₓ and C₁₀F₆.₅O₀.₅Hₓ, respectively. The concentration of fluorine decreases from 53.2% to
42.7% and finally to 38.3% as shown in table 5-2.

**Table 5-2**: Atomic composition of the HDFD plasma polymer films before and after Ar-plasma etching (Condition I: HDFD plasma polymer films; II, III: HDFD plasma polymer films after Ar-plasma etching for 30 and 60 s, respectively)

<table>
<thead>
<tr>
<th>Element</th>
<th>At. Conc. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
</tr>
<tr>
<td>F1s</td>
<td>53.2</td>
</tr>
<tr>
<td>C1s</td>
<td>46.8</td>
</tr>
<tr>
<td>O1s</td>
<td>0</td>
</tr>
</tbody>
</table>

Moreover, the spectra in figure 5-2 and the fitted data in table 5-3 show that the concentration of -CH2-CFH- and -CH2-CF2H- functional groups increase at the expense of the -CF2-CF2-CF2- and -CF3 groups. This could be due to the cross-linking process induced by the Ar-plasma etching. In addition, a small amount of oxygen was detected in the surface spectrum after Ar-plasma etching, which could be due to the reaction between the dangling bonds on the surface induced by the Ar-plasma etching and the oxygen in the laboratory atmosphere during the transport of the sample from the plasma reaction chamber to the XPS analysis chamber (Transfer time about 15 min).

**Table 5-3**: Fitting data of C1s spectra from XPS analysis (Condition I: HDFD plasma polymer films; II, III: HDFD plasma polymer films after Ar-plasma etching for 30 and 60 s, respectively)

<table>
<thead>
<tr>
<th>Element</th>
<th>Binding Energy (eV)</th>
<th>Assignment</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>F1s</td>
<td>689.0</td>
<td>-CF2-</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>286.0 ± 0.2</td>
<td>-CH2-CFH-</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>288.0 ± 0.2</td>
<td>-CH2-CF2H-</td>
<td>17.3</td>
</tr>
<tr>
<td>C1s</td>
<td>290.6 ± 0.3</td>
<td>-CH2-CF2-</td>
<td>26.8</td>
</tr>
<tr>
<td></td>
<td>292.7 ± 0.3</td>
<td>-CF2-CF2-CF2-</td>
<td>41.3</td>
</tr>
<tr>
<td></td>
<td>295.1 ± 0.2</td>
<td>-CF3</td>
<td>5.5</td>
</tr>
<tr>
<td>O1s</td>
<td>534.5 ± 0.2</td>
<td>-CO-</td>
<td>0</td>
</tr>
</tbody>
</table>
5.3.3 ToF-SIMS Measurements

The effect of the Ar-plasma etching on the chemical structure of HDFD plasma polymer films was investigated by means of ToF-SIMS measurements parallel to in-situ FT-IRRAS and XPS measurements. Figure 5-3 a) and c) show the positive ion ToF-SIMS data of the HDFD plasma polymer films before and after a 60 s Ar-plasma etching. Figure 5-3 b) and d) represent the negative ion ToF-SIMS data for the above mentioned two films.

The corresponding assignments are given in table 5-4 according to the literature [7, 10]. The most intense peaks of the positive ion mass spectra of HDFD plasma polymer films appear at m/z 12 (C⁺) and at m/z 31 (CF⁺), followed by other intense CₓFᵧ⁺ ion peaks. CₓHᵧ⁺ ions are also observed at a much lower intensity. The Ar-plasma etching leads to an increased concentration of CₓHᵧ⁺ fragments and the intensity of the long chain CₓFᵧ⁺ ions (m/z ≥ 69) decreases, which hints again at the cross-linking and the defluorination during Ar-plasma etching. In the negative-ion mass spectra before and after Ar-plasma etching, the most intense peak is at m/z 19 (F⁻). O⁻ ions (m/z = 16) were also observed at low intensity for Ar-plasma treated HDFD samples, which agrees with the XPS results in section 5.3.2.
### Table 5-4: Assignments of the ToF-SIMS data (positive and negative ions) of the HDFD plasma polymer before and after Ar-plasma etching

<table>
<thead>
<tr>
<th>m/z</th>
<th>HDFD plasma polymer films</th>
<th>HDFD plasma polymer films after 60 s Ar-plasma etching</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>C⁺</td>
<td>C⁺</td>
</tr>
<tr>
<td>13</td>
<td>CH⁺</td>
<td>CH⁺</td>
</tr>
<tr>
<td>14</td>
<td>CH₂⁺</td>
<td>CH₃⁺</td>
</tr>
<tr>
<td>15</td>
<td>CH₃⁺</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>O⁻</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>F⁻</td>
<td>F⁻</td>
</tr>
<tr>
<td>27</td>
<td></td>
<td>C₂H₃⁺</td>
</tr>
<tr>
<td>29</td>
<td></td>
<td>C₂H₅⁺</td>
</tr>
<tr>
<td>30</td>
<td></td>
<td>C₂H₆⁺</td>
</tr>
<tr>
<td>31</td>
<td>CF⁺</td>
<td>CF⁺</td>
</tr>
<tr>
<td>39</td>
<td>CF₂⁺</td>
<td>CF₂⁺</td>
</tr>
<tr>
<td>41</td>
<td></td>
<td>C₃H₅⁺</td>
</tr>
<tr>
<td>43</td>
<td></td>
<td>C₃H₇⁺</td>
</tr>
<tr>
<td>50</td>
<td>CF₂⁺</td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>C₄H₃⁺</td>
<td></td>
</tr>
<tr>
<td>69</td>
<td>CF₃⁺</td>
<td>CF₃⁺</td>
</tr>
<tr>
<td>100</td>
<td>C₂F₄⁺</td>
<td></td>
</tr>
<tr>
<td>119</td>
<td>C₂F₅⁺</td>
<td></td>
</tr>
<tr>
<td>131</td>
<td>C₃F₅⁺</td>
<td>C₃F₅⁺</td>
</tr>
<tr>
<td>169</td>
<td>C₃F₇⁺</td>
<td></td>
</tr>
</tbody>
</table>
Figure 5-3: ToF-SIMS data of Si-supported HDFD plasma polymers: a) HDFD plasma film (positive ion spectra); b) HDFD plasma film (negative ion spectra); c) after 60 s Ar-plasma etching (positive ion spectra); d) after 60 s Ar-plasma etching (negative ion spectra).

5.3.4 Morphology of the HDFD Plasma Polymer Films

AFM measurements were used to study the morphology of the as-deposited and Ar-plasma treated HDFD plasma polymer films. As shown in figure 5-4, the roughness of the films increases with the time of Ar-plasma etching. The root mean square (RMS) value of the HDFD plasma polymer film increases from 0.44 to 4.32 nm after 120 s Ar-plasma etching. The generated morphology is mostly irregular and island-like structure. However, at the lower left corner of figure 5-4 c) a localised patterning can be observed as three small worm-like structures are aligned which have a diameter of about 200 nm and a length of about one micrometer.
5.3.5 Wettability of Ar-plasma Etched HDFD Plasma Polymer Films

To investigate the wettability of the HDFD plasma polymer films, the water contact angle measurements were performed on the as-deposited and Ar-plasma treated HDFD plasma polymer films. The static and dynamic water contact angles are related to the combined effects of surface chemistry and surface topography as described by Wenzel [11]. In this case study of the HDFD plasma polymer films, there are two main factors influencing the water contact angles. One of them is the concentration of the perfluorinated surface functional groups (especially -CF$_2$-) and the second factor is the surface roughness. Table 5-5 and figure 5-5 a) illustrate the advancing and receding water contact angles on HDFD plasma polymer film surfaces before and after Ar-plasma etching. Both of the advancing and receding contact angles decrease with the time of Ar-plasma etching while the contact angle hysteresis increases.
Table 5-5: Comparison of the advancing and receding water contact angles on HDFD plasma polymer films before and after Ar-plasma etching

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface film</th>
<th>RMS (nm)</th>
<th>Advancing $\theta_a$ (°)</th>
<th>Receding $\theta_r$ (°)</th>
<th>Hysteresis (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>HDFD plasma polymer film</td>
<td>0.4</td>
<td>115.9</td>
<td>78.7</td>
<td>37.2</td>
</tr>
<tr>
<td>B</td>
<td>HDFD-film + Ar-plasma (30 s)</td>
<td>0.8</td>
<td>97.2</td>
<td>57.0</td>
<td>40.2</td>
</tr>
<tr>
<td>C</td>
<td>HDFD-film + Ar-plasma (60 s)</td>
<td>1.6</td>
<td>95.0</td>
<td>53.3</td>
<td>41.7</td>
</tr>
<tr>
<td>D</td>
<td>HDFD-film + Ar-plasma (120 s)</td>
<td>4.3</td>
<td>92.6</td>
<td>41.9</td>
<td>50.7</td>
</tr>
</tbody>
</table>

Figure 5-5: a) Change of advancing and receding water contact angle with the Ar-Plasma etching time; b) change of RMS and hysteresis of water contact angle with the time of Ar-plasma etching.

The decrease in the contact angle is mainly due to the decrease in the concentration of -CF$_2$- functional groups resulting from the Ar-plasma etching effect (see XPS and ToF-SIMS results in section 5.3.2 and section 5.3.3). The increase in the hysteresis as shown in figure 5-5 b) reflects the increase in the nano-scope roughness of the films with Ar-plasma etching time (see figure 5-4) [11, 12].

5.4 Conclusions

The etching effect of Ar-plasma on the chemical structure, the induced morphology
modification and the wettability of Teflon-like plasma polymer films was investigated. An etching rate of about 7 nm/min for the Ar-plasma was calculated by the slope of the curve of frequency shift vs. deposition time in situ recorded by QCM. During the Ar-plasma etching cross-linking takes place at the expense of the -CF₂- and -CF₃ functional groups. The roughness of the Teflon-like film increases as the function of the etching time and the initially very smooth surface morphology changes to an island-like structure. Further Ar-plasma etching leads to more elongated worm-like structures. The values of the advancing and receding contact angles decrease with the increasing time of Ar-plasma etching due to the loss of -CF₂- and -CF₃ functional groups while the hysteresis increases with the generated roughness during the etching process.

References

Chapter 6: Morphology and Patterning Processes of Thin Organosilicon and Fluorocarbon Bilayer Plasma Polymer Films

6.1 Introduction

Bilayer or composite plasma polymer films offer the possibility to combine the properties of two different polymer structures in one coating system. Using plasma polymer deposition many investigations focused on the development of metal/polymer nano-composites [1, 2]. Recently, ceramic/polymer plasma polymers have also found increasing interest [3, 4]. Biederman et al. studied composite films consisting of SiOₓ/PTFE, which were deposited by means of co-sputtering. The authors showed that the hardness of the composite films is significantly increased when compared with the pure PTFE films [3]. Moreover, bilayer films of organosilicon and fluorinated monomers were synthesised in a microwave discharge to achieve functional films with defined morphology and wettability [5]. To pattern surfaces of bulk materials, Bowden et al. made use of an oxygen plasma treatment to introduce compressive stress to a poly(dimethylsiloxane) (PDMS) substrate. This leads to the formation of patterns of waves with wavelengths from 0.5 to 10 μm [6].

The buckling phenomenon of thin films due to compressive forces was widely studied and interesting results were published considering this topic [6-9]. The buckling instability is a result of the balance between the energy required to bend the stiff upper film and the energy required to deform the soft underlying substrate. There exists a critical wavelength that minimizes the total strain energy in the system, and the wavelength is dependent on the material properties of both the film and substrate [6-7]. Assuming a sinusoidal waveform of the buckling instability, the critical wavelength \( d \) can be expressed by

\[
d = 2\pi h \left[ \frac{(1 - \nu_s^2)E_f}{3(1 - \nu_f^2)E_s} \right]^{\frac{1}{3}}
\]  

(6-1),

where \( h \) is the thickness of the upper film, \( \nu \) represents Poisson’s ratio, and \( E \) is the Young’s modulus (subscripts \( f \) and \( s \) denote the film and substrate, respectively).

The aim of this work was to design patterned thin films based on the deposition of a hard top-layer on top of a soft film which adheres to a solid substrate and thereby to become independent of the substrate material. An audio frequency plasma polymerization set-up
with a planar plasma source was used to deposit thin plasma polymer films using heptadecafluoro-1-decene (HDFD) and hexamethyldisiloxane (HMDSO) as monomers. The former monomer was chosen to deposit a soft plasma polymer film with low surface energy and the HMDSO monomer could lead to films of increased hardness based on the dominating three dimensional cross-linking as reported in the literature [10-12]. The film thickness during deposition was controlled by QCM and correlated by the results of spectroscopic ellipsometry. The chemical structure of the plasma polymer films was measured by means of FT-IR transmission absorbance spectroscopy and XPS. The information about the surface morphology was provided by AFM measurements.

6.2 Experimental Section

6.2.1 Materials and Plasma Deposition

The information about the used fluorocarbon and organosilicon monomers and the process parameters for the plasma deposition are shown previously in section 4.2.2. The bilayer plasma polymer was deposited in two consecutive steps with different gas atmospheres in table 6-1.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Overall flow rate (1.5 sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_{Ar}$ (mbar)</td>
</tr>
<tr>
<td>Step 1</td>
<td>0.2</td>
</tr>
<tr>
<td>Step 2</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Films prepared using the same conditions on different dates showed good reproducibility in all of the tests used.

6.2.2 Surface Analysis

The chemical composition of the films was investigated by using FT-IR transmission spectroscopy and XPS. The FT-IR spectra were measured by using a Nicolet 870 spectrometer.

The parameters for XPS, AFM and ellipsometry measurements can be found in section 4.2.3.
To expose the underside of the bilayer plasma polymer films, they were deposited on Si-wafers. The backside of the Si-wafer and the film surface were glued to an epoxy resin block and a polished metal substrate using an epoxy resin adhesive respectively. After cooling down the bilayer system in liquid nitrogen, the plasma polymer film and the Si-wafer substrate were mechanically separated by peeling off the film from the Si-wafer.

6.3 Results and Discussion

6.3.1 Deposition Kinetics

The ellipsometrically determined thickness values of the HMDSO plasma polymer films were found to be linearly dependent on the measured shifts in the resonant frequencies i.e. $\Delta f$ as shown in figure 6-1.

![Figure 6-1](image)

**Figure 6-1**: a) Correlation between measured frequency shifts and the film thickness values of HMDSO plasma polymer films on Si-wafer substrates determined by ellipsometry; b) frequency shifts with time during the deposition of HMDSO plasma polymer film on top of HDFD plasma polymer film and on Au coated quartz, respectively.

As discussed in section 4.3.1 the resulting density of the HMDSO plasma polymer film obtained from the slope of the curve in figure 6-1 a) is 1.46 g·cm$^{-3}$ and the density of the HDFD plasma polymer film is about 2.46 g·cm$^{-3}$. Figure 6-1 b) shows the change in frequency shift $\Delta f$ during the deposition of HMDSO both on top of the HDFD plasma polymer film and on the bare gold coated quartz crystal as a function of deposition time. It can be observed that the deposition rates of HMDSO both on HDFD plasma polymer and on bare gold were nearly the same. Thus, the thickness change of HMDSO plasma polymer film on the top of HDFD plasma polymer film can be calculated with the frequency data of...
HMDSO plasma polymer film deposition using the slope of the curve in figure 6-1 a).

6.3.2 Film Chemistry

6.3.2.1 FT-IR transmission absorption spectroscopy measurements

The FT-IR transmission absorption spectrum of the bilayer CₓFᵧHz and SiCₓOᵧHz plasma polymer film is shown in figure 6-2 and the assignments of peaks are listed in table 6-2 according to the literature [5, 13-16]. The resulting spectrum of the bilayer plasma polymer film is an almost perfect superposition of the two spectra of the pure component plasma polymer layers. Thus no significant intermixing of the two plasma polymer films leading to new functional groups in the films could be detected during the HMDSO plasma polymer deposition.

![Figure 6-2: FT-IR transmission absorption spectra of a bilayer plasma polymer film (30 nm HMDSO plasma polymer film on top of 100 nm HFD plasma polymer film) in comparison to the spectra of the single films on Si-wafers.](image)
Table 6-2: Assignments of the absorbance peaks of the bilayer plasma polymer films in the FT-IR spectra

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Wavenumber (cm(^{-1}))</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-F</td>
<td>1370</td>
<td>(\nu_s) (C-F)</td>
</tr>
<tr>
<td>Si(CH(_3))(_x)</td>
<td>1265</td>
<td>(\delta_s) (CH(_3))</td>
</tr>
<tr>
<td>CF(_x), CF(_2), CF(_3)</td>
<td>1255</td>
<td>Overlap of vibrations</td>
</tr>
<tr>
<td>CF(_2)</td>
<td>1224</td>
<td>(\nu_s) (C-F)</td>
</tr>
<tr>
<td>CF(_2)</td>
<td>1155</td>
<td>(\nu_{as}) (C-F)</td>
</tr>
<tr>
<td>Si-O-Si</td>
<td>1095</td>
<td>(\nu_{as}) (Si-O-Si)</td>
</tr>
<tr>
<td>Si-O-Si</td>
<td>1043</td>
<td>(\nu_s) (Si-O-Si)</td>
</tr>
</tbody>
</table>

6.3.2.2 X-ray photoelectron spectroscopy measurements

The compositions of the HDFD, HMDSO and bilayer plasma polymer films are C\(_{10}\)F\(_{11.4}\)H\(_x\), SiO\(_{0.8}\)C\(_{0.8}\)H\(_x\) and SiO\(_{0.7}\)C\(_{0.7}\)F\(_{0.1}\)H\(_x\) respectively as shown in table 6-3. Moreover, the spectra in figure 6-3 and the fitted data in table 6-4 show that the C1s peak in HDFD plasma polymer film is composed of five peaks, namely \(-\text{CH}_2-\text{CFH}_2-, -\text{CH}_2-\text{CFH}_2-, -\text{CH}_2-\text{CF}_2-, -\text{CF}_2-\text{CF}_2-\text{CF}_2-\) and \(-\text{CF}_3\) [5, 13, 17]. The C1s spectrum of the HMDSO plasma polymer film is mainly composed of one component, which is assigned to the -Si-CH\(_3\) groups. In addition, the Si2p peak can be fitted with two components at 103 eV (CH\(_x\)-Si(OSi)\(_3\)) and 102 eV ((CH\(_x\))\(_2\)-Si(OSi)\(_2\)). For the bilayer plasma polymer film with a 5 nm thin HMDSO plasma polymer film on 100 nm HDFD plasma polymer film, a small amount of fluorine was detected in the surface spectrum. However, the C1s peak and the Si2p peak can be clearly assigned to the HMDSO plasma polymer. Therefore, the HMDSO film chemistry is not significantly changed due to the underlying Teflon-like film.
Table 6-3: Atomic compositions of the HDFD, HMDSO and bilayer plasma polymer films (Condition I: 100 nm HDFD plasma polymer films; II: 100 nm HDMSO plasma polymer films; III: 5 nm HMDSO film on 100 nm HDFD plasma polymer films; IV: residual material on Si-wafer after the plasma polymer film (30 nm HMDSO film on 100 nm HDFD plasma polymer film) being peeled off from Si-wafer, respectively)

<table>
<thead>
<tr>
<th>Element</th>
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<td>O1s</td>
<td>-</td>
<td>30.3</td>
<td>28.7</td>
<td>-</td>
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<tr>
<td>F1s</td>
<td>53.2</td>
<td>-</td>
<td>5.2</td>
<td>50.5</td>
</tr>
<tr>
<td>Si2p</td>
<td>-</td>
<td>38.6</td>
<td>38.7</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 6-3: XPS C1s spectra of the plasma polymer films: a) 100 nm HDFD film; b) 100 nm HMDSO film; c) 5 nm HMDSO film on 100 nm HDFD film (The corresponding data are shown in table 6-3 and table 6-4).
Table 6-4: Fitting data of C1s, O1s, F1s and Si2p spectra from XPS analysis (Condition I: 100 nm HDFD plasma polymer films; II: 100 nm HDMSO plasma polymer films; III: 5 nm HMDSO plasma polymer film on 100 nm HDFD plasma polymer films, respectively)

<table>
<thead>
<tr>
<th>Element</th>
<th>Binding Energy (eV)</th>
<th>Assignment</th>
<th>Percentage (%)</th>
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</thead>
<tbody>
<tr>
<td>C1s</td>
<td></td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>284.5 ± 0.1</td>
<td>-Si-CH₃</td>
<td>-</td>
<td>100</td>
</tr>
<tr>
<td>286.0 ± 0.2</td>
<td>-CH₂-CFH-</td>
<td>9.1</td>
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<td>288.0 ± 0.2</td>
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<td>290.6 ± 0.3</td>
<td>-CH₂-CF₂-</td>
<td>26.8</td>
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<tr>
<td>292.7 ± 0.3</td>
<td>-CF₂-CF₂-CF₂</td>
<td>41.3</td>
<td>-</td>
</tr>
<tr>
<td>295.1 ± 0.2</td>
<td>-CF₃</td>
<td>5.5</td>
<td>-</td>
</tr>
<tr>
<td>O1s</td>
<td>532.5 ± 0.2</td>
<td>Si-O-Si</td>
<td>-</td>
</tr>
<tr>
<td>F1s</td>
<td>689.0</td>
<td>p-(CF₂=CF₂)</td>
<td>100</td>
</tr>
<tr>
<td>687.0 ± 0.2</td>
<td>Fluoride</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Si2p</td>
<td>103 ± 0.2</td>
<td>CH₃-Si(OSi)₃</td>
<td>-</td>
</tr>
<tr>
<td>102 ± 0.2</td>
<td>(CH₃)₂-Si(OSi)₂</td>
<td>-</td>
<td>36.2</td>
</tr>
</tbody>
</table>

6.3.3 Morphology and Patterning Processes during the Growth of HMDSO Plasma Polymer Films on HDFD Plasma Polymer Films

The initial HMDSO film formation on the HDFD plasma polymer surface leads to an island-like film growth due to the low surface energy of the substrate HDFD plasma polymer film surface. In figure 6-4 a)-d) the surface topography of a 3 nm thin HMDSO plasma polymer film grown on a polished oxide covered Si-wafer surface and on a 100 nm thick HDFD plasma polymer surface as measured by means of AFM are compared. While the HMDSO plasma polymer film is continuous and smooth on the Si-wafer surface in figure 6-4 b), it shows an island-like character for the low surface energy of HDFD plasma polymer film in figure 6-4 d). The island-like initial growth can be explained with a high surface mobility of adsorbed molecular fragments from the HMDSO plasma on the perfluorinated surface of HDFD plasma polymer film.
Chapter 6: Morphology and Patterning Processes of Thin Bilayer Plasma Polymer Films

Figure 6-4: AFM images (3 × 3 µm) of different surfaces: a) Si-wafer; b) 3 nm HMDSO plasma polymer film; c) 100 nm HDFD plasma polymer film; d) 3 nm HMDSO film on 100 nm HDFD plasma polymer film, respectively.

The situation for increasing film thickness of the HMDSO plasma polymer is illustrated in figure 6-5. The corresponding thicknesses, deposition time of each layer in the film and the RMS value of the film measured by AFM are shown in table 6-5. The AFM images of the bilayer plasma polymer films as a function of the thickness of the HMDSO plasma polymer layer are shown in figures 6-5 a)-e).

At 10 nm HMDSO plasma polymer film thickness no island-like structures but elongated worm-like features are observed (see figure 6-5 a). The size of the worm-like pattern in lateral and vertical dimensions increases with the thickness of the HMDSO plasma polymer film up to a limiting film thickness. Figure 6-5 d) shows that when the thickness of the HMDSO plasma polymer is about 100 nm, the large sinusoidal patterns diminish, but the
surface is still composed of submicroscopic small worm-like structures. Contrary to the worm-like patterns of bilayer plasma polymer films, the pure HMDSO plasma polymer film of 100 nm film thickness (see figure 6-5 e) is very smooth with RMS value of only 0.4 nm.

**Table 6-5:** Thickness and deposition time of each layer and its RMS value measured by AFM

<table>
<thead>
<tr>
<th>Layer</th>
<th>HDFD Thickness (nm)</th>
<th>Deposition time (s)</th>
<th>HMDSO Thickness (nm)</th>
<th>Deposition time (s)</th>
<th>RMS Value (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bilayer a</td>
<td>100</td>
<td>242</td>
<td>3</td>
<td>21</td>
<td>1.6</td>
</tr>
<tr>
<td>Bilayer b</td>
<td>100</td>
<td>215</td>
<td>10</td>
<td>35</td>
<td>6.9</td>
</tr>
<tr>
<td>Bilayer c</td>
<td>100</td>
<td>224</td>
<td>30</td>
<td>100</td>
<td>36.6</td>
</tr>
<tr>
<td>Bilayer d</td>
<td>100</td>
<td>224</td>
<td>50</td>
<td>159</td>
<td>38.9</td>
</tr>
<tr>
<td>Bilayer e</td>
<td>100</td>
<td>209</td>
<td>100</td>
<td>320</td>
<td>7.6</td>
</tr>
<tr>
<td>HMDSO</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>315</td>
<td>0.4</td>
</tr>
</tbody>
</table>

It can be assumed that the isotropic patterning occurs due to the increasing compressive stress in the HMDSO plasma polymer film with increasing film thickness and the strain relieves by the underlying less cross-linked HDFD plasma polymer film. The buckling can only be induced by a compressive stress of the surface layer. Tensile stress would lead to cracking phenomena as reported in [18-19].

In figure 6-6 the characteristic wavelength of the patterns is plotted as a function of the film thickness of HMDSO plasma polymer layer. According to Whitesides et al. the wavelength of the microscopic pattern is proportional to the thickness of the top film [7]. For the samples in figure 6-5 a)-c), the wavelength increases first proportionally with the thickness of the HMDSO plasma polymer film. The measured wavelengths are about 30 times larger than the HMDSO film thickness and lie in the range between 100 and 1000 nm. However, already at 50 nm HMDSO plasma polymer film thickness the proportionality factor decreases and at 100 nm no large buckling induced patterning is observed anymore.
Figure 6-5: AFM images (10 × 10 µm) of bilayer plasma polymer films (HMDSO films on top of 100 nm HDFD films) on Si-wafers, for five different HMDSO thickness values: a) 10 nm; b) 30 nm; c) 50 nm and d) 100 nm respectively; e) 100 nm HMDSO plasma polymer film on Si-wafer [20].
Figure 6-6: Change in the characteristic wavelengths of the patterns in bilayer plasma polymer films as a function of the thickness of the HMDSO plasma polymer layer on top of a 100 nm HDFD plasma polymer layer.

Figure 6-7 shows the sinusoidal large patterning in higher spatial resolution (figure 6-7 a)) and the smaller worm-like structures for the 100 nm thick HMDSO plasma polymer film on the perfluorinated surface (figure 6-7 b)). On top of the large waves in figure 6-7 a) an additional roughness is observed, which might be due to the inherent roughness of the HMDSO plasma polymer film during its growth on the surface with low surface energy. These smaller structures might be again due to the compressive stress of the HMDSO plasma polymer film. The change in the size of worm-like structure could be explained by loss of adhesion at the HMDSO/HDFD plasma polymer film interface, which would then lead to a buckling just within the HMDSO plasma polymer film.

Figure 6-7: AFM images (3×3 µm) of bilayer plasma polymer films: a) 30 nm HMDSO film on top of 100 nm HDFD film; b) 100 nm HMDSO film on top of 100 nm HDFD film.
The wave-like patterns undergo a transition from disordered (figure 6-5) to ordered (figure 6-8) when located near defects, because the point defect leads to an anisotropic stress field. There is a strong orientation to the stress in the vicinity of the defects, with an associated maximum principal compressive stress direction at each point [7].

**Figure 6-8:** AFM image (50 × 50 µm) of anisotropic patterning of bilayer plasma polymer film (30 nm HMDSO plasma polymer film on top of 100 nm HDFD plasma polymer film) on Si-wafer at a point defect (dust particle).

### 6.3.4 AFM Investigations of the Underside of Bilayer Plasma Polymer Films

In figure 6-9 the topographs of the underside of the bilayer plasma polymer film and the surface of the Si-wafer after peeling off the bilayer plasma polymer film from the Si-wafer at the same location are presented as measured by means of AFM. While the underside of the bilayer plasma polymer film shows the typical height distribution of the bilayer plasma polymer film surface, only residuals of the plasma polymer film still adhere to the Si-wafer. The underside of the plasma polymer bilayer film does not show the submicroscopic small worm-like structures in comparison to the outer surface of the bilayer plasma polymer film (compare figure 6-9 a) and figure 6-5 b)).

In addition, XPS analysis of the residual surface layer on Si-wafer after the bilayer plasma polymer film being peeled off from the Si-wafer showed the typical composition of the HDFD plasma polymer layer (see table 6-3). It can be concluded that due to the transfer of the compressive stress from the HMDSO plasma polymer to the underlying HDFD plasma...
polymer film, adhesion was lost in the interphase region between the HDFD plasma polymer and the silicon substrate within the polymer film during the peeling process.

![AFM images (10 × 10 µm) of the underside of bilayer plasma polymer films (30 nm HMDSO film on top of 100 nm HDFD film) after the removal of the Si-wafer substrate: a) underside of the bilayer plasma polymer film; b) surface of the residual material after the bilayer plasma polymer film being peeled off from the Si-wafer respectively.](image)

**Figure 6-9:** AFM images (10 × 10 µm) of the underside of bilayer plasma polymer films (30 nm HMDSO film on top of 100 nm HDFD film) after the removal of the Si-wafer substrate: a) underside of the bilayer plasma polymer film; b) surface of the residual material after the bilayer plasma polymer film being peeled off from the Si-wafer respectively.

### 6.4 Conclusions

The formation of the island-like HMDSO plasma polymer morphology during the initial film formation can be explained by the inhomogeneous distribution of HMDSO plasma polymer layer on the low energy surface of HDFD plasma polymer films. In the second stage of film growth the formation of a laterally continuous HMDSO plasma polymer film leads to the increase of the compressive stress which is transferred to the underlying low cross-linked HDFD plasma polymer. However, as the top HMDSO plasma polymer layer forms a continuous film with certain film thickness and therefore the stress reaches a certain value, buckling will occur, in order to minimize the total strain energy in the system. This leads to the formation of worm-like structures during the deposition of the HMDSO plasma polymer layer.

The observed patterning and the formed interfacial voids can only be explained by a compressive stress of the HMDSO plasma polymer film. At high HMDSO plasma polymer film thickness (> 100 nm) no sinusoidal patterning is observed. This different behavior may be due to the loss of adhesion between the HDFD and the HMDSO plasma polymer films,
which would cause stress relief just within the HMDSO plasma polymer film.

The patterned thin plasma polymer films could show interesting mechanical properties by tailoring the composition and patterning structure of the plasma polymer films. Alternatively, they could be used as the basis for methods of mechanical properties analysis in materials science [21].

References

Chapter 6: Morphology and Patterning Processes of Thin Bilayer Plasma Polymer Films


Chapter 7: Growth of PVD Silver Nanoparticles on Ultra-thin Fluorocarbon Plasma Polymer Films

7.1 Introduction

Metal nanoparticles show many interesting characteristics, such as optical, electrical, and catalytic properties, which depend on the size, size distribution, shape and the interparticle distance of the nanoparticles. The growth and arrangement of metal nanoparticles on various substrates are therefore key issues in all fields of modern science and technology relating to nanoelectronics [1, 2], photonics [3], catalysis [4, 5] and sensors [6, 7]. In particular, noble metal nanoparticles (i.e. Ag, Au, etc.) with strong surface plasmon resonances in the UV-Vis range are most widely studied [8].

In the specific case of silver deposition on Si(100), detailed studies of the nucleation and growth of vapour-deposited silver at sub-monolayer coverage on the reconstructed Si(100)-2×1 surfaces have been reported [9, 10]. The film growth takes place according to a Volmer-Weber (V-W) mechanism (i.e. prompt three-dimensional growth of metal nuclei), and results in the formation of very small particles with a rather broad and often not a well-characterized size distribution. Pászti et al. tried to control the size and size distribution of silver islands by depositing the island-like silver film on Si substrates and diminishing the island sizes by low energy ion bombardment [11]. Shyjumon et al. reported on the size-selected silver cluster deposition by means of magnetron sputtering by varying the cluster forming chamber (aggregation tube) length and applying a QMF 200 mass filter [12]. Malynych and Chumanov studied the effect of the surface modification of Indium Tin Oxide with thiols and fluorocarbons on the structure and optical properties of evaporated silver island films. They found that the structures of the island-like silver films on different surfaces were rationalized in terms of different chemical affinity of the surfaces to the silver metal [13]. The nucleation and growth of noble metal clusters on metal/polymer depend on the particular metal/polymer combination and the deposition parameters as shown by Zaporojtchenko et al [14].

One aim of this chapter was to synthesize well-defined silver nanoparticles with narrow size distribution. A method to immobilize well-defined silver nanoparticles on ultra-thin fluorinated films by means of electron beam evaporation is described. The fluorinated films
are plasma polymer films which are synthesized by plasma polymerization of heptadecafluoro-1-decene (HDFD) and fluoroalkyl silane self-assembled monolayers (SAMs) prepared by means of chemical vapour surface modification of hydroxylated substrates. SAMs are quite widely used to fabricate a substrate/organic thin film/metal “sandwich” structure, which can be used in the field of the nanoscale electronics. Therefore, interactions between SAMs and deposited metal overlayers are of great importance [15, 16]. Another goal of this chapter is to compare the growth of silver nanoparticles on ultra-thin cross-linked plasma polymers and on well-defined SAMs. The key point is how the interactions between silver and the ultra-thin fluorinated films affect the growth of silver nanoparticles. Furthermore, the growth of silver nanoparticles on ultra-thin fluorinated films and their effect on the optical properties of the obtained films were investigated by means of FE-SEM and spectroscopic ellipsometry.

7.2 Experimental Section

Ultra-thin fluorocarbon films were synthesized by means of low temperature plasma polymerization of heptadecafluoro-1-decene (HDFD) and heptadecafluorodecyl-trimethoxysilane (FAS-17) monolayers were formed by means of chemical vapour surface modification of the substrates. Silver island films were generated by physical vapour deposition (PVD) of silver on the respective ultra-thin fluorinated films.

7.2.1 Deposition of Ultra-thin HDFD Plasma Polymer Films

Polished p-type Si (100) wafers (Si-Mat, Germany) and indium tin oxide (ITO) glass (R ≤ 20 Ohm/sq., 100 nm ITO coating on float glass substrates, Praezisions Glas & Optik GmbH, Iserlohn, Germany) were used as substrates. Argon (99.998%), oxygen (99.995%) and nitrogen (99.99%) (Messer Griesheim GmbH, Germany) were used as gases in the plasma processes, and HDFD (CF₃(CF₂)₇CHCH₂, purity > 97%, Fluka, Germany) was used as liquid monomer without further purification for the deposition of HDFD plasma polymer films. A bell-jar type reactor with internal parallel capacitive electrodes was used to carry out plasma polymer deposition [17]. The Si-wafer or ITO glass substrates and a gold-coated 10 MHz-AT-cut quartz crystal of 20 mm diameter used for in-situ quartz crystal microbalance (QCM) measurements were fixed in the grounded electrode. The film thickness was controlled by QCM and calibrated afterwards by spectroscopic ellipsometry. The exact process parameters of plasma polymerization are given in table 7-1. Prior to the
deposition of HDFD plasma polymer films, Si-wafer substrates were cleaned in oxygen plasma for 5 minutes to remove any kind of residual organic contamination layer.

Table 7-1: Process parameters of deposition of thin HDFD plasma polymer films

<table>
<thead>
<tr>
<th>Condition</th>
<th>Overall flow rate (1.5 sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_{Ar}$ (mbar)</td>
</tr>
<tr>
<td>Plasma deposition</td>
<td>0.2</td>
</tr>
</tbody>
</table>

7.2.2 Chemical Vapour Surface Modification Method

The following method was successfully established by Hozumi et al. [18]. The above mentioned Si-wafers and ITO glass substrates were cleaned with hydrogen peroxide and ammonia solution (1:1) at 80 °C for an hour, then rinsed by deionized water and dried with pure nitrogen. The cleaned substrates were placed in a 45 ml vessel together with a glass container filled with 0.1 mL of FAS-17 ($\text{CF}_3(\text{CF}_2)_7\text{CH}_2\text{CH}_2\text{Si(OCH}_3)_3$) liquid, then the vessel was sealed with a cap and heated at 150 °C for 3 hours. Afterwards the samples were taken out, rinsed with ethanol carefully and blown dry with nitrogen.

7.2.3 Deposition of Silver Nanoparticles on the Fluorinated Surfaces

Silver was deposited on the obtained smooth fluorinated surfaces by means of electron beam evaporation in a vacuum chamber under base pressure of $10^{-6}$ mbar (Univex 450, Leybold Technologies, INC, U.S.A.). The so-called mass thickness of deposited silver was controlled by QCM during the evaporation process. The mass increments ($\Delta m$) corresponding to the delta frequency, $\Delta f$, were calculated according to the Sauerbrey equation [19],

$$\Delta f = \left( \frac{f_0^2}{N \rho_q} \right) \Delta m = -c_f \Delta m$$

(7-1),

where $\Delta f$ is the mean delta frequency observed, $f_0$ the resonance frequency of the quartz crystal 6 MHz, $L_q$ is the thickness of the bare quartz disk 0.02 cm, $N$ is the frequency constant ($N = f_0 L_q$ is equal to $1.20 \times 10^5$ Hz·cm), $\rho_q$ is the density for quartz 2.468 g·cm$^{-3}$ respectively, and $\Delta m$ is the change in mass per unit area. From the Sauerbrey equation it can be calculated that $c_f$ is equal to $1.216 \times 10^8$ Hz·g$^{-1}$·cm$^2$. The silver deposited on
fluorinated surfaces is not a continuous film, so the thickness of the silver film cannot be accurately measured by QCM. In the following text m is used to denote the amount of the deposited silver, which is the change in mass corresponding to 5 nm continuous silver film per unit area. The silver deposition rate was maintained at $1.05 \times 10^{-8}$ g·cm$^{-2}$·s$^{-1}$ in this case study.

### 7.2.4 Surface Analysis

The parameters for the XPS and the contact angle measurements of the HDFD plasma polymer films and the FAS-17 SAMs are the same as shown in section 4.2.3.

The parameters for the ToF-SIMS measurements of the HDFD plasma polymer films and the FAS-17 SAMs are the same as shown in section 5.2.2.

Field emission scanning electron microscopy (FE-SEM) investigations were carried out at 15 kV accelerating voltage by means of a Zeiss 1550VP field emission scanning electron microscope.

Transmission electron microscopy (TEM), selected area electron diffraction (SAED) and energy-dispersive X-ray spectroscopic (EDX) measurements were performed at a 200 kV accelerating voltage on a Philips EM430 microscope. The data were acquired by depositing HDFD plasma polymers and silver nanoparticles on the carbon-coated copper TEM grids. Diffraction patterns were obtained at a camera length of 620 mm.

UV-Vis spectra were measured in transmission mode in the wavelength ranging from 300 to 900 nm by a Lambda 800 spectrometer (PerkinElmer™ Instruments GmbH, Germany). A cleaned ITO-covered glass was used as background to obtain UV-Vis spectra of the bare silver films and fluorinated films-supported silver films deposited on ITO-covered glass substrates.

The optical properties of the films were measured by means of UV-Vis spectroscopic ellipsometry (SE 800, Sentech, Germany) in the wavelength range between 300 to 800 nm at three different incident angles of 50°, 60° and 70°. In order to obtain information about the optical properties, film thicknesses and the particle sizes, a nucleus model in combination with a Cauchy layer model for the sub layer and Drude-Lorentz oscillator model for silver was applied to fit the experimental results [20].
7.3 Results and Discussion

7.3.1 Chemical Structure

7.3.1.1 X-ray photoelectron spectroscopy measurements

XPS surface analysis of the respective ultra-thin films showed that the composition of Si-supported HDFD plasma polymer films (shown in table 7-2) was $\text{C}_{10}\text{F}_{14.9}\text{H}_x$ in comparison to that of the monomers $\text{C}_{10}\text{F}_{17}\text{H}_3$. The XPS C1s spectra and the corresponding evaluated peaks are shown in figure 7-1 and table 7-3, respectively.

Table 7-2: Atomic composition of Si-supported HDFD plasma polymer films and FAS-17 SAMs (Condition I: HDFD plasma polymer films; II: FAS-17 SAMs; III: 2m silver deposited on Si-supported 4 nm HDFD plasma polymer etched by 0.1 M HNO$_3$ for 6 hours; IV: 2m silver deposited on Si-supported FAS-17 SAMs etched by 0.1 M HNO$_3$ for 6 hours.)

<table>
<thead>
<tr>
<th>Element</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cls</td>
<td>38.3</td>
<td>18.3</td>
<td>42.7</td>
<td>22.8</td>
</tr>
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<td>F1s</td>
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<td>Si2p</td>
<td>2.6</td>
<td>27.8</td>
<td>2.4</td>
<td>27.7</td>
</tr>
<tr>
<td>Ag3d</td>
<td>-</td>
<td>-</td>
<td>6.3</td>
<td>7.6</td>
</tr>
</tbody>
</table>

The composition of the HDFD plasma polymer films illustrates that fluorine atoms are split off from the carbon chain and it can be deduced that the C1s spectrum is composed of five peaks, namely, -$\text{CH}_2$-$\text{CFH}$-, -$\text{CH}_2$-$\text{CFH}$-, -$\text{CFH}$-$\text{CF}_2$-, -$\text{CF}_2$-$\text{CF}_2$-$\text{CF}_2$- and -$\text{CF}_3$ [21, 22]. The largest contribution (50.6%) corresponds to -$\text{CF}_2$-$\text{CF}_2$-$\text{CF}_2$- groups, which are the principal groups in the HDFD monomer. It shows that the degree of the fragmentation in the plasma is moderate, so that the -$\text{CF}_2$-$\text{CF}_2$-$\text{CF}_2$-groups in the monomer can be mostly preserved. In the case of Si-supported FAS-17 SAMs, deconvolution divides the C1s spectrum into six peaks which are identified as -$\text{C-C}$-, -$\text{CH}_2$-$\text{CFH}$-, -$\text{CH}_2$-$\text{CFH}$-, -$\text{CH}_2$-$\text{CF}_2$-, -$\text{CF}_2$-$\text{CF}_2$-$\text{CF}_2$- and -$\text{CF}_3$ groups as shown in figure 7-1 and table 7-3, respectively. The $\text{CF}_3$/CF$_2$ ratio in the FAS-17 SAMs increases compared with that of the monomer. This indicates that FAS-17 molecules are oriented in a way that their CF$_3$ head groups are aligned toward the outer surfaces. The ratio between F and C is around 17:10 (see table 7-2), so it can be concluded that the three methyl groups in the monomer react with the hydroxyl groups on the surface.
of Si-wafer, consequently the FAS-17 monomer is immobilized on the surface.

**Table 7-3**: Fitting data of C1s spectra from XPS surface analysis (Condition I: HDFD plasma polymer films; II: FAS-17 SAMs)

<table>
<thead>
<tr>
<th>Elem.</th>
<th>BE (eV)</th>
<th>Assignment</th>
<th>Perc (%)</th>
<th>BE (eV)</th>
<th>Assignment</th>
<th>Perc (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>I</td>
<td></td>
<td>II</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F1s</td>
<td>689.0</td>
<td>-CF₂⁻</td>
<td>100</td>
<td>689.0</td>
<td>-CF₂⁻</td>
<td>100</td>
</tr>
<tr>
<td>286.0 ± 0.2</td>
<td>-CH₂-CFH⁻</td>
<td>18.8</td>
<td></td>
<td>286.0 ± 0.2</td>
<td>-CH₂-CFH⁻</td>
<td>14.1</td>
</tr>
<tr>
<td>288.0 ± 0.2</td>
<td>-CH₂-CFH⁻</td>
<td>8.7</td>
<td></td>
<td>288.0 ± 0.2</td>
<td>-CH₂-CFH⁻</td>
<td>5.4</td>
</tr>
<tr>
<td>C1s</td>
<td>289.0 ± 0.2</td>
<td>-CFH-CF₂⁻</td>
<td>10.8</td>
<td>290.0 ± 0.3</td>
<td>-CH₂-CF₂⁻</td>
<td>7.1</td>
</tr>
<tr>
<td>292.0 ± 0.3</td>
<td>-CF₂-CF₂⁻</td>
<td>50.6</td>
<td></td>
<td>292.0 ± 0.3</td>
<td>-CF₂-CF₂⁻</td>
<td>49.9</td>
</tr>
<tr>
<td>294.0 ± 0.2</td>
<td>-CF₃</td>
<td>11.1</td>
<td></td>
<td>294.0 ± 0.2</td>
<td>-CF₃</td>
<td>11.5</td>
</tr>
<tr>
<td>O1s</td>
<td>533.6 ± 0.2</td>
<td>-CO⁻</td>
<td>100</td>
<td>532.4 ± 0.2</td>
<td>Si-O-Si</td>
<td>100</td>
</tr>
<tr>
<td>99.5 ± 0.2</td>
<td>Si</td>
<td>57.1</td>
<td></td>
<td>99.5 ± 0.2</td>
<td>Si</td>
<td>67.2</td>
</tr>
<tr>
<td>Si2p</td>
<td>103.5 ± 0.3</td>
<td>SiO₄</td>
<td>42.9</td>
<td>103.5 ± 0.3</td>
<td>SiO₄</td>
<td>32.8</td>
</tr>
</tbody>
</table>

At the same time it can be observed that the concentrations of Si and O distinctly increase compared with those in the monomer. This may arise from the native SiO₂ top layer on the Si-wafer substrates. The FAS-17 SAM is quite thin compared to the sampling depth of XPS, which is about several nanometres, so SiO₂ information on Si-wafer substrates can be detected during the measurement.
Figure 7-1: XPS C1s spectra of different Si-supported films: a) HDFD plasma polymer films; b) FAS-17 SAMs; c) 2m silver deposited on 4 nm HDFD plasma polymer etched by 0.1 M HNO₃ for 6 hours; d) 2m silver on FAS-17 SAM etched by 0.1 M HNO₃ for 6 hours (The corresponding data are shown in table 7-2 and table 7-3); e)-f) HDFD plasma polymer films and FAS-17 SAM etched by 0.1 M HNO₃ for 6 hours, respectively.
7.3.1.2 ToF-SIMS measurements

Figure 7-2 a) and c) show the positive ion ToF-SIMS data of HDFD plasma polymer films and FAS-17 SAMs. Figure 7-2 b) and d) represent the negative ion ToF-SIMS data of the two above-mentioned films. According to the literature [23, 24] the corresponding assignments are given in figure 7-2 as well.

![ToF-SIMS data of HDFD plasma polymer films and FAS-17 SAMs](image)

The most intense peaks of the positive ion mass spectra of HDFD plasma polymer films appear at $m/z$ 12 (C$^+$) and at $m/z$ 31 (CF$^+$), followed by other intense C$_x$F$_y^+$ ion peaks. C$_x$H$_y^+$ ions are also observed at a much lower intensity. In the case of FAS-17 SAMs, the positive ion ToF-SIMS data show similar peaks as for HDFD plasma polymer films. The presence of additional fragments at $m/z$ 28 and 47, which can be assigned to Si$^+$ and FSi$^+$, are attributed to the artefacts based on ion bombardment during the measurement process. The
negative ion mass spectra show a very intense peak at \( m/z \) 19 (F) for both HDFD plasma polymer films and FAS-17 SAMs. Oxygen ions at \( m/z \) 16 are also present at low intensity for FAS-17 SAMs in agreement with the XPS results shown in section 7.3.1.1.

### 7.3.2 Wettability of HDFD Plasma Polymer Films and FAS-17 SAMs

The static contact angles of different liquids on HDFD plasma polymer films and FAS-17 SAMs were measured as a basis for the calculation of the surface energy of the respective fluorinated surface as shown in table 7-4. The surface energies were calculated according to the extended Fowkes method:

\[
\frac{1}{2} \left( \frac{1}{\gamma_1} + \frac{1}{\gamma_2} \right) \frac{1}{1 - \cos \theta} = \frac{1}{2} \left( \frac{\gamma_1^d}{\gamma_1^d} + \frac{\gamma_2^d}{\gamma_2^d} \right) + \frac{1}{2} \left( \frac{\gamma_1^p}{\gamma_1^p} + \frac{\gamma_2^p}{\gamma_2^p} \right)
\]

(7-2),

where \( \gamma_1, \gamma_2 \) are the surface energies of the respective liquid and the solid surface; \( \gamma_1^d, \gamma_1^p \) \((i = 1, 2)\) are the dispersion and the polar part (see table 7-5), respectively.

#### Table 7-4: The contact angles of different liquids on the fluorinated surfaces

<table>
<thead>
<tr>
<th>Liquid</th>
<th>HDFD plasma polymers</th>
<th>FAS-17 SAMs</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>108.2 ± 0.7 °</td>
<td>111.5 ± 2.0 °</td>
</tr>
<tr>
<td>diiodomethane</td>
<td>97.6 ± 0.7 °</td>
<td>96.0 ± 1.8 °</td>
</tr>
<tr>
<td>ethylene glycol</td>
<td>93.7 ± 0.4 °</td>
<td>92.6 ± 0.5 °</td>
</tr>
</tbody>
</table>

#### Table 7-5: Surface energy of each film calculated by the contact angle measurements

<table>
<thead>
<tr>
<th>Energy (mJ/m²)</th>
<th>HDFD plasma polymers</th>
<th>FAS-17 SAMs</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \gamma^d )</td>
<td>7.90 ± 0.002</td>
<td>9.09 ± 0.010</td>
</tr>
<tr>
<td>( \gamma^p )</td>
<td>2.79 ± 0.002</td>
<td>2.31 ± 0.020</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>10.69 ± 0.004</td>
<td>11.40 ± 0.030</td>
</tr>
</tbody>
</table>

The contact angle is related to the combined effects of surface chemistry and surface topography as described by Wenzel [25]. In this case study both HDFD plasma polymer films and FAS-17 SAMs are extremely smooth (RMS < 1 nm), so that the effect of roughness can be neglected. In the case of the investigated HDFD plasma polymer films, the main factors influencing the surface energy are the concentration of fluorine and the surface density of perfluorinated surface functional groups (especially -CF₂⁻). In the case of FAS-17 SAMs, -CF₃ groups are the most prominent surface termination. However, the formed FAS-17 SAMs show similar surface energies as HDFD plasma polymer films. This
is very likely due to the high degree of ordering of the FAS-17 molecules in the monolayer as shown by Hozumi et al. [18].

7.3.3 Growth of PVD Silver Islands on the Fluorinated Surfaces

To investigate the growth of the PVD deposited silver on the fluorinated surfaces, FE-SEM studies were carried out on the samples with silver deposited on Si-wafers and Si-supported fluorinated films. In comparison to the randomly oriented coalesced islands of silver on top of Si-wafers (see figure 7-3 a)), isolated silver nanoparticles appear on top of the Si-supported fluorinated surfaces as shown in figure 7-3 b)-f). This is attributed to the low surface energy of the fluorinated surfaces, due to perfluorinated surface functional groups -CF₂-CF₂-CF₂- of the HDFD plasma polymer films or by -CF₃ groups and the high order orientation in FAS-17 SAMs. Moreover, the weak chemical affinity between silver and the fluorocarbon films contributes to island formation. Additionally, the presence of a fluorocarbon sub layer with a large number of vibration modes compared to the bare oxide surface facilitates the cooling of the adsorbing silver atoms and thereby promotes the formation of nucleation sites rather than the growth of pre-existing nuclei [13]. As a consequence, smaller nanoparticles with narrower size distribution can be achieved by using a thin HDFD plasma polymer or FAS-17 SAM to modify the Si-wafer substrates.

The morphology of the nanoparticles is mainly dependent on the deposition rate, the condensation coefficient C, which is defined as the ratio of the number of atoms actually deposited onto the surface to the total number of atoms arriving at the surface, and the substrate temperature [26, 27]. Silver atoms evaporated at higher rates reach the surface with a larger mean kinetic energy and require a longer cooling-down period. Consequently, they are more likely to collide with pre-existing nuclei rather than form other nucleation sites. Thus, the formation of larger particles with broader size distribution is expected at higher evaporation rates [13, 28]. Some conflicting results were reported, which showed no dependence of the morphology on the evaporation rate. Faupel et al. observed this lower and non-dependence of cluster densities on the deposition rate when they deposited Ag, Al, Ni on Teflon AF and polystyrene [26]. In addition they discovered that the silver evaporation deposition on Teflon AF showed an extremely low condensation coefficient C of only 0.002 [29]. This leads to many silver atoms undergoing non-sticking collisions with the surface or quickly desorbing during the evaporation process. In this case study, the silver deposition rate was maintained at 1.05-3.15 × 10⁻⁸ g·cm⁻²·s⁻¹.
Figure 7-3: FE-SEM images of a) 2m silver on Si-wafer substrates; b)-e) m, 2m, 3m and 4m silver on Si-supported 4 nm HDFD plasma polymer films, respectively; f) 2m silver on Si-supported FAS-17 SAMs (m is the change in mass corresponding to 5 nm continuous silver film per unit area during silver evaporation).
When taking a closer look at the morphology of silver nanoparticles deposited on Si-supported HDFD plasma polymer films in figure 7-3 b)-e), it can be observed that the particle size increases with the amount of the deposited silver. The shape of the nanoparticles changes from near-spherical form shown in figure 7-3 b) and c) to irregular ellipsoidal form in figure 7-3 d) and e) with the increasing deposited silver mass. The size distributions and width histograms with Maxwellian fitting for different films are shown in detail in figure 7-4 and table 7-6.

**Figure 7-4**: Size distribution profile of the generated Ag nanoparticles in figure 7-3: a)-d) m, 2m, 3m and 4m silver on top of Si-supported 4 nm HDFD plasma polymer films, respectively; e) 2m silver deposited on Si-supported FAS-17 SAMs.
Table 7-6: Size distributions and width histograms with Maxwellian fitting for different films

<table>
<thead>
<tr>
<th>Mass of silver/Film</th>
<th>Mean Value (nm)</th>
<th>Variance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 7-4 a)</td>
<td>m/HDFD</td>
<td>4.2</td>
</tr>
<tr>
<td>Figure 7-4 b)</td>
<td>2m/HDFD</td>
<td>5.4</td>
</tr>
<tr>
<td>Figure 7-4 c)</td>
<td>3m/HDFD</td>
<td>7.4</td>
</tr>
<tr>
<td>Figure 7-4 d)</td>
<td>4m/HDFD</td>
<td>15.8</td>
</tr>
<tr>
<td>Figure 7-4 e)</td>
<td>2m/FAS-17</td>
<td>25.0</td>
</tr>
</tbody>
</table>

With increasing mass of the deposited silver from m to 4m as shown in figure 7-4 a) to figure 7-4 d), the size of nanoparticles increases from 4.2 to 15.8 nm and size distribution expands from 3.6 to 13.4 nm. This fact may be regarded as a consequence of the size evolution of small Ag nanoparticles during the ongoing deposition process. More interestingly, the size of silver nanoparticles on Si-supported FAS-17 SAMs (see figure 7-4 e), diameter: 25.0 nm) is much larger than that of silver nanoparticles formed on Si-supported HDFD plasma polymer films (see figure 7-4 b), diameter: 5.4 nm), although the mass of the deposited silver is the same and the surface energies of both fluorinated sub layers are quite similar. At the same time the size distribution of silver nanoparticles 21.2 nm in figure 7-4 e) is much broader than that in figure 7-4 b) 4.6 nm.

This can be explained by a disordering process of the FAS-17 SAMs caused by the impinging silver atoms during evaporation and by the partial penetration of silver atoms through the FAS-17 SAMs [15]. It is very likely that the silver atoms penetrate the film through monolayer defective sites, because penetration through ordered monolayer domains seems energetically unfavourable. It would involve the concerted movement of many fluorocarbon chains to allow for the penetration of the silver atoms [30]. In comparison to FAS-17 SAMs, HDFD plasma polymers possess a strong cross-linked structure, and should be more stable and less easily penetrated by the adsorbed silver atoms. According to the literature [31] the chemical interaction between silver and the fluorinated films can be excluded. To prove this assumption, the silver nanoparticles were removed by chemical etching in 0.1 M HNO₃ for 6 hours and the samples were characterized again by means of XPS [32]. The corresponding results are already shown in table 7-2 and figure 7-1. The chemical composition in table 7-2 indicates the presence of a small amount of residual silver on the surface. The components of the C1s spectra for HDFD plasma polymer films
shown in figure 7-1 c) are quite similar to those before silver deposition, only a slight increase of \(-\text{CH}_2\text{-CFH}\)- component is observed. However, C1s spectra of FAS-17 SAMs shown in figure 7-1 d) exhibit an increased intensity of the C1s-peak at 285 eV but a decreased intensity of contributions assigned to \(-\text{CF}_2\text{-CF}_2\text{-CF}_2\)- and \(-\text{CF}_3\) groups. This supports the assumption that the high order orientation of the SAM was partially destroyed during silver deposition. The increased aliphatic contributions could be due to atmospheric contamination of the exposed polar SiO\(_2\)-surface.

For comparison purposes 4 nm Si-supported HDFD plasma polymers and FAS-17 SAMs were also treated in 0.1 M HNO\(_3\) using the same procedure as that for treating silver nanoparticle-covered samples and then analyzed by means of XPS as shown in figure 7-1 e) and f). No change in the chemical composition of these films and the relative proportions of the C1s components were observed, indicating that no damage of the films occurred as a result of the exposure to the HNO\(_3\) solution.

### 7.3.4 TEM and SAED Measurements

The chemical state of the deposited silver nanoparticles was determined using SAED in conjunction with TEM and EDX. It is more apparent in the TEM image in figure 7-5 a) that most of the nanoparticles are completely isolated but very few of them are agglomerated to each other because of the surface diffusion. It was observed that the crystal structure of the nanoparticles produced this way was of face centred cubic (fcc) structure, as analyzed by SAED pattern in figure 7-5 b) and the corresponding d-spacings of the diffraction rings shown in table 7-7. These values are consistent with diffraction data of fcc silver metal.

**Table 7-7**: Comparison of experimentally measured d-spacings of the diffraction rings for silver nanoparticles with expected ones for fcc silver

<table>
<thead>
<tr>
<th>hkl</th>
<th>111</th>
<th>200</th>
<th>220</th>
<th>311</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>d-spacing (Å)</td>
<td>2.35</td>
<td>2.01</td>
<td>1.44</td>
<td>1.23</td>
</tr>
</tbody>
</table>

|  d-spacing (Å) | 2.359 | 2.043 | 1.445 | 1.232 |
Figure 7-5: a) Bright field TEM image of 2m silver nanoparticles on top of 4 nm HDFD plasma polymer film; b) SAED pattern showing diffraction rings of the silver nanoparticles.

7.3.5 Annealing Induced Ostwald Ripening

7.3.5.1 Microstructural change of silver nanoparticles due to annealing treatment

To investigate the effect of annealing on the morphology of silver nanoparticles on fluorinated films, the ITO-supported bare silver films and silver nanoparticles deposited on fluorinated films were annealed at 120 °C in vacuum for one hour. FE-SEM and UV-Vis spectroscopy studies were performed on the as-deposited and annealed silver films on ITO-covered glass substrates. FE-SEM images of silver films deposited on ITO-covered glass substrates, on ITO-supported HDFD plasma polymer film and FAS-17 SAMs are presented in figure 7-6 a), c) and e). The corresponding FE-SEM images after annealing at 120 °C for one hour are shown in figure 7-6 b), d) and f). Comparing the FE-SEM images of silver films deposited on ITO-covered glass substrates before and after annealing in figure 7-6 a) and b), it can be observed that after annealing the randomly oriented coalesced islands of silver nanoparticles changed into isolated silver nanoparticles and the interparticle distance increased due to annealing. The comparison of the silver nanoparticles deposited on ITO-supported HDFD plasma polymer films in figure 7-6 c) and d) showed that particle size of silver nanoparticles and the interparticle distance between silver nanoparticles increased after annealing. The similar results can be observed comparing the silver nanoparticles on FAS-17 SAMs in figure 7-6 e) and f). Moreover, silver nanoparticles in figure 7-6 f) became more spherical after the annealing process.
Figure 7-6: FE-SEM images of different surfaces: a) 2m silver on ITO-covered glass substrates; c) 2m silver on ITO-supported 4 nm HDFD plasma polymer film; e) 2m silver deposited on ITO-supported FAS-17 SAMs; b), d) and f) are samples in a), c) and e) annealed at 120 °C for one hour, respectively (m is the change in mass corresponding to 5 nm continuous silver film per unit area during silver evaporation).
It shows that the annealing treatment is also responsible for the changes in the shape of the silver particles, which accompany the size changes. This should be induced by the Ostwald ripening during annealing process. In the Ostwald ripening process a few particles grow larger at the expense of small particles, because surface energy decreases with the increase of the particle size. This is also the reason why the numbers of silver particles in figure 7-6 d) and f) decrease and the interparticle distance increases in comparison to those in figure 7-6 c) and e). Moreover, diffusion of metal atoms along the particle surface should also contribute to the increase of the particle size and the interparticle distance in case of coalesced silver nanoparticles as shown in figure 7-6 a).

7.3.5.2 Annealing induced change in optical properties of silver nanoparticles

To study the change in the optical properties of the above-mentioned silver films on ITO-supported fluorinated polymer films and its relation to the microstructural change of silver nanoparticles due to annealing, UV-Vis spectroscopic measurements were performed on the as-deposited and annealed ITO-supported silver films as shown in figure 7-7. It is obvious that 2m silver deposited on ITO substrate showed typical absorption behavior of bulk silver, but it exhibited a pronounced surface plasmon resonance band indicating well-separated isolated silver nanoparticles after annealing. However, because of the polydispersity of the particles and the non-spherical particle shape, the quadrupole oscillation became clearly visible at 362.5 nm in figure 7-7 with dipole oscillation appearing at 497 nm. This agrees with the morphological change of silver nanoparticles due to annealing as shown in figure 7-6 a) and b). The samples with silver nanoparticles on ITO-supported HDFD plasma polymer film presented in figure 7-6 c) and d) showed pronounced surface plasmon resonance bands, and the annealing treatment induced changes in the position and form of the SPR bands. Changes in the optical properties of silver films are mainly due to changes in the microstructure of silver nanoparticles such as the size, size distribution, interparticle distance and the shape of the nanoparticles. SPR band of the sample with 2m silver deposited on ITO-supported HDFD plasma polymer film blue shifted from 445 to 424 nm after annealing at 120 °C for 1 hour. The mean half-width (FWHM) of the SPR band didn’t change significantly. It is supposed that both intrinsic cluster-size effects (R < 10 nm) and extrinsic cluster-size effects (R > 10 nm) have an effect on the the change of SPR band [8]. Concerning the change in SPR band there are two effects included in this case study. On the one hand the slight increase in nanoparticle size induces the red shift and the broadening of the SPR band. On the other hand the blue shift and the decrease of FWHW of the SPR band
result from the change of the nanoparticles’ shape from less spherical to more spherical [33]. The shift of the SPR band position and the change of FWHM after annealing can be understood as the results of the competition between the two effects. In this case study, the latter is more prominent than the former. Therefore, SPR band blue shifts and FWHM narrows. For the sample with 2m silver on ITO-supported FAS-SAMs, its SPR band showed a very large apparent FWHW. It is very likely due to the polydispersity of the particle size. All the various multipole oscillations are smeared out. Thus it seems as if only one single SPR band dominates the spectrum. The SPR band blue shifted from 450 to 402 nm after annealing at 120 °C for 1 hour and the FWHM of SPR band narrowed due to annealing treatment. More detailed analysis about the morphological changes of the silver nanoparticles due to annealing treatment and thereby induced changes in optical properties will be discussed in the next chapter.

![Figure 7-7: UV-Vis absorption spectra of different silver films deposited on ITO-covered glass substrate and on different ITO-supported fluorinated films before and after annealing treatment.](image)

7.3.6 Optical Properties of the Silver Nanoparticle-covered Thin HDFD Plasma Polymer Films by Ellipsometry

UV-Vis spectroscopic ellipsometry was used to study the optical properties of the silver nanoparticle-covered thin HDFD plasma polymer films. Figure 7-8 shows the experimental \( \Psi (\tan \Psi = |R^p|/|R^s|) \), where \( R^p \) and \( R^s \) are the total reflection coefficients, i.e. the ratio of the amplitude of the outgoing resultant wave to the amplitude of the incoming wave for p-
waves and s-waves) and $\Delta$ ($\Delta = \delta_1 - \delta_2$, where $\delta_1$ and $\delta_2$ represent the phase difference between the p-wave and the s-wave before and after the reflection) curves for the following different films:

- Si-wafer substrate,
- 4 nm Si-supported HDFD plasma polymer,
- m-4m silver on 4 nm Si-supported HDFD plasma polymer films and
- 2m silver on Si-wafers.

Due to the very large size distribution of silver nanoparticles formed on FAS-17 SAMs it became impossible to fit the corresponding data adequately. In the following, only the fitting data for silver nanoparticle-covered Si-supported HDFD plasma polymer films are discussed.

The type of film and mass of deposited silver (see figure 7-8) evidently illustrate a pronounced effect on the variation of the relative amplitude and phase of the reflected light with wavelength. Both the sample with m silver on 4 nm Si-supported HDFD plasma polymer film and the sample with just 4 nm Si-supported HDFD plasma polymer film show similar variations of $\Psi$ and $\Delta$ with wavelength as Si-wafer substrates. With an increasing mass of the deposited silver, variations of both $\Psi$ and $\Delta$ with wavelength deviated significantly.

![Figure 7-8: Variation of Psi ($\Psi$) and Delta ($\Delta$) with wavelength at the incident angle of 60 degree for different films: a) Psi ($\Psi$); b) Delta ($\Delta$) [35].](image)

For the sample with 2m silver on 4 nm Si-supported HDFD plasma polymer film, the relative amplitude $\Psi$ reaches a local minimum at 352 nm. With an additional increase in the
amount of silver the local minimum of $\Psi$ shifts to a lower wavelength. The samples with 3m, 4m silver on 4 nm Si-supported HDFD plasma polymer films show local minima at 345 and 327 nm, respectively. The local $\Psi$ minimum appears at 321 nm for the sample with 4m silver on Si-wafers. The spectral location of $\Psi$ minimum depends on the thickness and optical constants of the film as well as the substrate. However, for the above-mentioned films when the relative amplitude $\Psi$ shows a local minimum, the $\Delta$ spectrum goes abruptly from its local maximum to its local minimum. The turning point of the transition is exactly at the local minimum of the corresponding $\Psi$ spectrum.

The results can be explained on the basis of the variation of refractive index ($n$) and extinction coefficient ($k$) with wavelength as obtained from the measured $\Psi$ and $\Delta$ values. Figure 7-9 a) and b) show the $n$ and $k$ values for the silver nanoparticle-covered Si-supported HDFD plasma polymer films, 4m silver and 4 nm HDFD plasma polymer film on oxide covered Si-wafers, respectively. The refractive index $n$ of 4 nm HDFD plasma polymer decreases slightly, as the wavelength increases in the wavelength range between 300 and 800 nm. However, the $n$ values of the silver nanoparticles covered 4 nm Si-supported HDFD plasma polymers show anomalous dispersions where the extinction coefficient $k$ values reach the maxima (see figure 7-9 a)). This can be expected, because $n$ and $k$ values are determined by a Kramers-Kronig relation [34]. The extinction maximum is assigned to the surface plasmon resonance (SPR) band of the island-like films.

![Diagram](image)

**Figure 7-9:** Variation of a) refractive index ($n$) and b) extinction coefficient ($k$) with wavelength for different films.

For the film with m silver on 4 nm Si-supported HDFD plasma polymer film, only very
weak absorption at 400.4 nm is observed, which is due to the very small size of the silver nanoparticles in the film and the very small amount of deposited silver. This correlates with the fact that the sample with m silver on 4 nm Si-supported HDFD plasma polymer film and the sample with 4 nm Si-supported HDFD plasma polymer film show similar variations of $\Psi$ and $\Delta$ with the wavelength (see figure 7-8). Moreover, the SPR band shows a read shift with the increase in silver amount deposited on 4 nm HDFD plasma polymer films. The samples with 2m, 3m and 4m silver on 4 nm Si-supported HDFD plasma polymer films show SPR bands at 430.0, 460.2 and 519.2 nm, respectively. Additionally, the broadening of the SPR band with an increasing amount of silver deposited on 4 nm HDFD plasma polymer films can be observed in figure 7-9 b). This can be considered as the consequence of the effect of the increase in the size of nanoparticles and the broadening of the size distribution as discussed in section 7.3.3.

### 7.4 Conclusions

Well-defined silver nanoparticles with narrow size distribution were generated by means of electron beam evaporation of silver on ultra-thin Si-supported HDFD plasma polymer films. The size of nanoparticles increased from 4.2 to 15.8 nm and the size distribution broadened from 3.6 to 13.4 nm with increasing amount of deposited silver from m to 4m.

The growth of silver nanoparticles on ultra-thin Si-supported HDFD plasma polymers was compared with that on Si-supported FAS-17 SAMs since the latter show a similar surface energy but no internal cross-linking. Indeed, surface energy measurements showed similar small values of 10.69 (HDFD plasma polymer films) and 11.40 mJ/m$^2$ (FAS-17 SAMs) for both surfaces and the XPS analysis revealed high densities of -CF$_2$- groups for both films. It became obvious that the size of silver nanoparticles deposited on FAS-17 SAMs (25.0 nm) was larger than the size of those deposited on ultra-thin HDFD plasma polymer films (5.4 nm). Additionally, the size distribution of silver nanoparticles in the case of FAS-17 SAMs (21.2 nm) was much larger than that in the case of HDFD plasma polymers (4.6 nm). The corresponding XPS results indicate that during the silver deposition process ultra-thin cross-linked HDFD plasma polymer films are more stable against the penetration of silver than FAS-17 SAMs. Most probably, the disordering process of FAS-17 SAMs takes place when silver atoms are impinging on the monolayer surface and adsorbed Ag-atoms are penetrating the SAM. Both effects can explain the formation of larger nanoparticles.
FE-SEM results demonstrated that annealing treatment leads to the morphological change of silver nanoparticles such as the increase of silver nanoparticle size and the interparticle distance as well as the change of the particle shape. This results from the Ostwald ripening process and the diffusion of metal atoms along the particle surface. UV-Vis spectra showed that the optical properties of silver films change due to the microstructural change of silver nanoparticles resulting from the annealing treatment.

Spectroscopic ellipsometry was used to investigate the impact of the silver morphology on the optical properties of silver nanoparticle-covered thin HDFD plasma polymer films. The refractive indices of silver nanoparticle-covered HDFD plasma polymer films are quite different from those of the pure HDFD plasma polymer film and those of continuous silver films. For the silver nanoparticle-covered HDFD plasma polymer films, an SPR band appears in the extinction coefficient curve and the real part of the refractive index $n$ shows an anomalous dispersion at the SPR peak maximum. The SPR band red shifts and broadens with increasing amount of the deposited silver. This correlates to an increase in the size of silver nanoparticles and the broadening of the size distribution.

References

Chapter 7: Growth of PVD Silver Nanoparticles on Ultra-thin Fluorinated Films

Chapter 8: Combined Spectroscopic, Microscopic and Electrochemical Analysis of the Ageing Properties of Thin Ag/Fluorocarbon Plasma Polymer Nanocomposite Films

8.1 Introduction

Plasma polymer nanocomposite films consisting of finely dispersed metal nanoparticles and insulating polymers as matrix are under considerable focus because of their special microstructural, optical and electrical properties as well as a variety of technological applications [1-3]. In general, plasma polymer films are chemically inert, insoluble, mechanically and thermally stable. They can therefore be used as membranes or protective coatings [4]. Noble metals such as Ag, Au, etc are most widely used as embedded metal nanoparticles because of their strong surface plasmon resonances in the UV-Vis range [5, 6]. The microstructural and optical properties of nanocomposite films are determined by the morphology of the embedded metal nanoparticles characterized by the size, size distribution, interparticle distance and the shape of nanoparticles. Furthermore, the plasma polymer matrix has an influence on the microstructural and optical properties of nanocomposite films as well. The morphology of the embedded metal nanoparticles can be artificially modified by thermal annealing [7], laser irradiation [8] or electron beam irradiation [2] to acquire necessary structured nanomaterials.

In the special case of silver nanocomposites, detailed studies on the microstructural, optical, electrical and release properties have been reported. Heilmann et al. studied the depth profile and optical properties of benzene or styrene multilayer plasma polymers with embedded silver nanoparticles and concluded that the multilayer systems were not destroyed by thermal annealing up to 480 K or by appropriate laser annealing [9]. Kiesow et al. reported on the electronic switching behavior of hexamethyldisilazane or benzene plasma polymer films containing silver nanoparticles in percolation structures [10]. Radhesh et al. investigated the release and antimicrobial properties of silver/polyamide nanocomposite films [11]. Zaporojchenko et al. reported on the physical-chemical and antimicrobial properties of co-sputtered Ag-Au/PTFE nanocomposite coatings [12]. While numerous reports demonstrated the interesting structural, optical, electrical, release and antibacterial properties of silver-based coatings, only very little is known about the ageing mechanisms of thin metal nanocomposite films during the immersion in water-based
electrolytes.

In this chapter, a method combining consecutive plasma polymerization of heptadecafluoro-1-decene (HDFD) with electron beam evaporation of silver is described to synthesize the sandwich-like Ag/HDFD-plasma polymer nanocomposite films. The Ag/HDFD-plasma polymer nanocomposite films were characterized by XPS and high resolution transmission electron microscopy (HR-TEM). Furthermore, the effect of annealing on the microstructure of silver nanoparticles and the optical properties of the Ag/HDFD-plasma polymer nanocomposite films were investigated by HR-TEM and UV-Vis spectroscopy. In particular, the barrier and optical properties of the Ag/HDFD-plasma polymer nanocomposite films and the microstructural change of silver nanoparticles during the ageing process in water-based electrolytes were studied by using electrochemical impedance spectroscopy (EIS), UV-Vis spectroscopy and HR-TEM.

8.2 Experimental Section

8.2.1 Deposition of Thin Sandwich-like Ag/HDFD-Plasma Polymer Nanocomposite Films

The matrix of the thin sandwich-like Ag/HDFD-plasma polymer nanocomposite films was deposited by means of low temperature plasma polymerization of HDFD (CF$_3$(CF$_2$)$_7$CHCH$_2$, purity > 97%, Fluka, Germany, 0.3 mbar, 10 s, substrate at room temperature). Argon (99.998%), oxygen (99.995%) and nitrogen (99.990%) (Messer Griesheim GmbH, Germany) were used as gases in the plasma deposition processes. The embedded silver nanoparticles were deposited by means of electron beam evaporation of silver (10$^{-6}$ mbar, Univex 450, Leybold Technologies, INC, U.S.A.). The silver deposition rate was maintained at 1.05-3.15 × 10$^{-8}$ g·cm$^{-2}$·s$^{-1}$. Polished p-type Si (100) wafers (Si-Mat, Germany), indium tin oxide (ITO) glass (R ≤ 20 Ohm/sq., 100 nm ITO coating on float glass substrates, Praezisions Glas & Optik GmbH, Iserlohn, Germany) and TEM copper and gold grids (Formvar/carbon film, 200 mesh, 3.05 mm, Plano, Germany) were used as substrates for the respective measurements. The schematic representation of the thin sandwich-like Ag/HDFD-plasma polymer nanocomposite films and the field emission scanning electron microscopy (FE-SEM) image of the silver nanoparticles in the sandwich-like Ag/HDFD-plasma polymer nanocomposite films are shown in figure 8-1.
8.2.2 Annealing and Immersion of Thin Ag/HDFD-Plasma Polymer Nanocomposite Films

To reduce the residual stress in the HDFD plasma polymer film and to increase the adhesion between the thin Ag/HDFD-plasma polymer nanocomposite film and the substrate, the as-deposited Ag/HDFD-plasma polymer nanocomposite films were annealed at 120 °C in vacuum for different durations depending on the film thickness [13]. After annealing the samples were slowly cooled down to room temperature and taken out from the oven for investigations.

The as-deposited and annealed thin Ag/HDFD-plasma polymer nanocomposite films were immersed into pure deionized water or phosphate buffered saline (PBS) solution by placing the samples in a sealed Teflon container with 10 ml liquid and stored under ambient conditions. After immersion the samples were blown dry in a stream of pure nitrogen carefully.

8.2.3 Surface Analysis

The parameters for the XPS measurements of the HDFD plasma polymer films before and after immersion in PBS solution are the same as shown in section 4.2.3.

The FT-IRRAS measurements were performed on the HDFD plasma polymer films
deposited on 100 nm gold-covered Si-wafers using a Nicolet 870 spectrometer.

HR-TEM and selected area electron diffraction (SAED) measurements were performed at 200 kV accelerating voltage on a Tecnai F20 microscope (FEI company, U.S.A.). Energy-dispersive X-ray (EDX) measurements on the Tecnai F20 microscope were carried out to study the elemental composition of the embedded silver nanoparticles in the HDFD plasma polymer films.

Ex-situ UV–Vis spectra were measured in transmission mode in the wavelength ranging from 300 to 900 nm by a Lambda 800 spectrometer (PerkinElmer™ Instruments GmbH, Germany). A cleaned ITO-covered glass was used as background to obtain ex-situ UV-Vis spectra of the thin Ag/HDFD-plasma polymer nanocomposite films deposited on ITO-covered glass substrates.

8.2.4 Electrochemical Impedance Spectroscopy Measurements

Electrochemical impedance spectroscopy (EIS) measurements were performed on two coating systems by using two different electrochemical cells, respectively. EIS measurements of the HDFD plasma polymer films were performed by means of a Zahner IM6d potentiostat in the frequency range from 100 kHz to 0.1 Hz. The amplitude of the sinusoidal voltage signal applied to the system was 10 mV. The impedance spectra were obtained over a time range of 5 minutes. A three-electrode electrochemical cell was used: the working electrode with a reproducible exposed area of 0.785 cm², the saturated Ag/AgCl reference electrode (+ 198 mV versus SHE) and a platinum counter electrode. The electrochemical tests were carried out in a quiescent aerated borate buffer solution (pH = 8.4: 0.2 M H₃BO₃ (Merck, p.a.), 0.05 M Na₂SO₄ (Merck, p.a.), 0.05 M Na₂B₄O₇·10H₂O (Merck, p.a.)) prepared from distilled water at room temperature. EIS measurements of the thin Ag/HDFD-plasma polymer nanocomposite films were performed in a phosphate buffered saline solution (PBS, pH = 7.5: 0.137 M NaCl (Merck, p.a.), 2.68 mM KCl (Merck, p.a.), 8.1 mM Na₂HPO₄ (Fluka, p.a.) and 1.47 mM KH₂PO₄ (Fluka, TraceSelect)) at room temperature by using a Gamry FAS 2 Femtostat. PBS electrolyte was chosen due to its relevance for antibacterial tests. A three-electrode capillary electrochemical cell was applied, in which a thin Ag/HDFD-plasma polymer nanocomposite film on ITO-covered glass functioned as working electrode; a gold wire and a silver wire were used as the counter electrode and the reference electrode, respectively. The impedance spectra were
obtained in the frequency range from 100 kHz to 0.1 Hz. The electrode potential of the Ag wire was calibrated to be -0.12 V relative to the saturated Ag/AgCl reference electrode (+198 mV versus SHE).

The absorption of water modifies the dielectric constant of the polymer coating and thereby changes the capacitance of the polymer coating. If the substrate-supported coating is treated as a parallel plate capacitor, then its capacitance \( C \) is related to the relative dielectric constant \( \varepsilon \) by

\[
C = \varepsilon \cdot \varepsilon_0 \cdot \frac{A}{d} \tag{8-1},
\]

where \( \varepsilon_0 \) is the dielectric constant of free space \((8.854 \times 10^{-14} \text{ F cm}^{-1})\), \( A \) represents the surface area of the coating under immersion and \( d \) is the coating thickness, respectively. Since the relative dielectric constant of polymers is typically in the range between 3 and 5, and it is 78.4 for pure water at 25 °C [14], the water uptake leads to a rise in the dielectric constant of the coating, resulting in a higher coating capacitance. The coating capacitance is generally considered to provide information on the degree of water penetration through the coatings, and in principle its value is expected to increase with immersion time. In this case study, the frequency and the impedance modulus, where the phase shifts of the bold plots are 90° \((f = 20400 \text{ Hz})\), were used to calculate the coating capacitance according to the equation:

\[
C = \frac{1}{2\pi \cdot f \cdot |Z|} \tag{8-2},
\]

where \( C \) represents the capacitance, \( f \) is the frequency and \( |Z| \) is the magnitude of the impedance. By using the capacitance values obtained from equation 8-2 and the Brasher-Kingsbury equation [15], the water uptake \( \phi \) can be calculated according to the equation:

\[
\phi = \frac{\log(C_p / C_{p0})}{\log \varepsilon_w} \tag{8-3},
\]

where \( C_{p0} \) is the coating capacitance extrapolated for \( t = 0 \) (i.e. the dry film capacitance) and \( \varepsilon_w \) is the dielectric constant of water.

Using the theory of Fickian diffusion for immersed supported coatings, the water uptake \( \phi \) can be analytically expressed as a function of time \( \phi(t) \). If the process of water diffusion through the films follows Fick’s second law, the relation between the coating capacitance
(\(C_p\)), diffusion coefficient (\(D\)), film thickness (\(d\)) and immersion time (\(t\)) is as follows [16,17]:

\[
\log\left(\frac{C_p}{C_0}\right) = \left[ \frac{4D}{d^2 \cdot \pi} \right]^{1/2} t^{1/2}
\]

where \(C_0\) and \(C_s\) are the film capacitances at the beginning and saturation stage of the immersion, respectively. The solution of Fick’s law indicates a linear dependence of \(C(t)\) versus \(t^{1/2}\). For \(t \to 0\), \(C_0\) may be calculated from the extrapolation of this plot at \(t = 0\). \(C_s\) may be determined from the capacitance values at long immersion time, provided that no swelling of the coating takes place, i.e. \(C(t)\) is constant for \(t \to \infty\).

8.2.5 In-situ UV-Vis Spectroscopy Measurements of Thin Ag/HDFD-Plasma Polymer Nanocomposite Films in PBS Solution

In-situ UV–Vis spectroscopy measurements were performed in an in-situ cell in transmission mode in the wavelength ranging from 300 to 900 nm by a Lambda 800 spectrometer (PerkinElmer™ Instruments GmbH, Germany). The schematic representation of the in-situ cell is shown in figure 8-2. The in-situ cell consists of two sample holders for fixing the sample, a centre part and two O-rings with a diameter of 1 cm for sealing the cell. For the in-situ UV-Vis spectroscopy measurements the background is composed of two bare ITO-covered glass substrates, PBS solution filled in the in-situ cell. The sample consists of one bare ITO-covered glass substrate, PBS solution filled in the in-situ cell and one ITO-covered glass-supported thin Ag/HDFD-plasma polymer nanocomposite film.

![Figure 8-2: Schematic representation of the in-situ UV-Vis spectroscopy cell in transmission mode (built by Keil not published yet).](image)
8.3 Results and Discussion

8.3.1 Chemical Structure and Crystal Structure

XPS surface analysis was performed to investigate the chemical structure of the HDFD plasma polymer films. XPS C1s spectra and the corresponding deconvolution are shown in figure 8-3 a) and table 8-1, respectively. The C1s spectrum is composed of five peaks, namely, -CH2-CFH-, -CH2-CFH-, -CFH-CF2-, -CF2-CF2-CF2- and -CF3 [18, 19], as discussed previously in section 7.3.1. The EDX elemental analysis of the single silver nanoparticle in combination with HR-TEM measurements showed the embedded silver nanoparticles in the thin sandwich-like Ag/HDFD-plasma polymer nanocomposite films to be pure silver metal.

The HR-TEM results reveal the formation of nanoparticles as shown in figure 8-4 a). The silver nanoparticles demonstrate a narrow size distribution with a mean particle diameter of 12.0 nm (see figure 8-4 a)). The HR-TEM image of a single silver nanoparticle (see figure 8-4 b)) illustrates the crystalline structure with a spacing of 0.285 nm between adjacent lattice planes, which corresponds to the distance between two (110) crystal planes. By means of the further SAED measurements from a large amount of particles shown in figure 8-4 c), the d-spacings of the diffraction rings are determined to be 0.242, 0.207, 0.147 and 0.125 nm and can be indexed as (111), (200), (220) and (311) reflections, respectively. This confirms the fcc structure of the silver particles with a lattice constant of \( a = 0.416 \pm 0.008 \) nm, which is in acceptable agreement with the lattice constant of \( a = 0.40857 \) nm reported in literature [20].

In addition, the silver nanoparticles show a multiply twinned structure, as shown in figure 8-4 d) and e). In figure 8-4 d) a lamellar twinned structure is visible and in figure 8-4 e) a nanoparticle with cyclic twins can be observed. Twinning can be due to the faults in the attachment of atoms to growth sites and the chance forming such faults are greater at higher deposition rates [21]. In general, the formation of twinning is supposed to depend on twin-boundary energy and the deposition conditions of the films and it is frequently observed for fcc structured metallic nanocrystals [22, 23].
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Figure 8-3: XPS C1s spectra of the HDFD plasma polymers in the Ag/HDFD-plasma polymer nanocomposite films: (a) as-deposited HDFD plasma polymer film; (b) HDFD plasma polymer film immersed in PBS solution for 10 days.

Table 8-1: Fitting data of C1s spectra of HDFD plasma polymer films from XPS surface analysis (I: as-deposited HDFD plasma polymer film; II: HDFD plasma polymer film immersed in PBS for 10 days)

<table>
<thead>
<tr>
<th>Element</th>
<th>Binding energy (eV)</th>
<th>Assignment</th>
<th>Percentage (%) I</th>
<th>Percentage (%) II</th>
</tr>
</thead>
<tbody>
<tr>
<td>F1s</td>
<td>689.0</td>
<td>-CF_2^-</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>286.0 ± 0.2</td>
<td>-CH_2-CF_2^-</td>
<td>18.6</td>
<td>19.7</td>
</tr>
<tr>
<td></td>
<td>288.0 ± 0.2</td>
<td>-CH_2-CFH^-</td>
<td>9.6</td>
<td>11.1</td>
</tr>
<tr>
<td></td>
<td>289.0 ± 0.2</td>
<td>-CFH-CF_2^-</td>
<td>10.8</td>
<td>10.6</td>
</tr>
<tr>
<td></td>
<td>292.0 ± 0.3</td>
<td>-CF_2-CF_2-CF_2^-</td>
<td>50.6</td>
<td>47.4</td>
</tr>
<tr>
<td></td>
<td>294.0 ± 0.2</td>
<td>-CF_3</td>
<td>10.4</td>
<td>11.2</td>
</tr>
</tbody>
</table>
8.3.2 Annealing Induced Ostwald Ripening

To investigate the effect of annealing on the microstructure of the silver nanoparticles embedded in the Ag/HDFD-plasma polymer nanocomposite films, HR-TEM and UV-Vis spectroscopy studies were performed on the as-deposited and annealed Ag/HDFD-plasma
polymer nanocomposite samples.

8.3.2.1 Annealing induced microstructural change of silver nanoparticles

In figure 8-5 a) isolated silver nanoparticles are observed, although some nanoparticles coalesce together (selected coalesced nanoparticles as marked in circles). Coalescence is based on minimization of the surface energy of pairs of contacting particles [2]. The embedded silver nanoparticles after annealing at 120 °C for one hour shown in figure 8-5 b) are larger than those in the as-deposited nanocomposite films shown in figure 8-5 a). Moreover, it is observed that the interparticle distance between the silver nanoparticles in figure 8-5 b) is larger than in figure 8-5 a).

The particle size and size distribution were quantitatively analyzed in figure 8-5 c) and d). As a result, the particle size distribution follows neither a Gaussian distribution nor a logarithmic normal distribution. The reason can be that some particles were agglomerated during the deposition and annealing process. However, the arithmetic mean value of the particles increases from 12.0 ± 4.0 to 14.4 ± 4.9 nm after annealing. On comparing the size distribution histograms, it is observed that the number of particles with sizes D < 15 nm decreased and the number of particles with sizes 15 nm < D < 30 nm increased after the annealing treatment. This was induced by Ostwald ripening during annealing process. In this process a few particles grow larger at the expense of small particles, because the surface energy increases with decreasing particle size. This is the reason why the number of silver particles in figure 8-5 b) decreased and the interparticle distance increased in comparison to figure 8-5 a). Moreover, diffusion of metal atoms along the particle surface should also contribute to an increase of particle sizes in case of coalesced silver nanoparticles, which are marked in circles and shown in figure 8-5 a).
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Figure 8-5: Bright field TEM images of Ag/HDFD-plasma polymer nanocomposite films: a) Ag/HDFD-plasma polymer nanocomposite films as-deposited; b) samples in a) annealed at 120 °C for one hour; c) size distribution profile of the generated silver nanoparticles in a); d) size distribution profile of the generated silver nanoparticles in b); e) shape factor profile of the silver nanoparticles in a); f) shape factor profile of the silver nanoparticles in b).
In addition, silver nanoparticles become more spherical after the annealing process. The shape factor ($S$) of silver nanoparticles was determined by

$$ S = \frac{4\pi A}{U^2} $$

(8-5),

where $A$ is the particle area and $U$ represents the particle perimeter [2]. The value for the particle shape factor $S$ lies in the range of $0 \leq S \leq 1$, where $S = 1$ corresponds to a circular object. The shape factor profiles of silver nanoparticles are shown in figure 8-5 e) and f). The mean value of the shape factor increased from $0.89 \pm 0.09$ to $0.93 \pm 0.05$. Clearly after annealing treatment, silver particles with shape factors $S < 0.6$ no longer existed and the number of silver particles with shape factors $0.6 < S < 0.9$ decreased, whereas the number of silver particles with shape factors $S > 0.9$ increased. Figure 8-5 e) and f) present that the annealing treatment was also responsible for the changes in the shape of the embedded silver particles, which accompany the size changes.

8.3.2.2 Annealing induced change in optical properties of thin Ag/HDFD-plasma polymer nanocomposite films

To study the change in the optical properties of thin Ag/HDFD-plasma polymer nanocomposite films and its relation to the microstructural change of silver nanoparticles due to annealing, UV-Vis spectroscopic measurements were performed on the as-deposited and annealed ITO-covered glass-supported Ag/HDFD-nanocomposite films as shown in figure 8-6. To remove any base line offset and any linear slope, second-derivatives of UV-Vis absorption spectra were used to study the change in optical properties. Second-derivative spectra display sharp minimum values where maximum values are located in the original spectra, hence the minimum values can be used to identify the surface plasmon resonance (SPR) positions.

Both films in figure 8-6 a) exhibit a pronounced surface plasmon resonance band indicating well-separated isolated silver nanoparticles. However, the annealing treatment caused some changes in the form and position of the SPR band. It has to be mentioned that the film thickness as well as optical properties of the HDFD plasma polymer films were not substantially changed after annealing. FT-IRRAS spectra of HDFD plasma polymer film before annealing and the difference spectrum after annealing in figure 8-6 c) indicate that the peak positions do not change and the absorbance values of characteristic peaks such as CF, CF$_2$ and CF$_3$ have slightly decreased after annealing treatment. Therefore, changes in
the optical properties of Ag/HDFD-plasma polymer nanocomposite films are mainly due to changes in the microstructure of the silver nanoparticles e.g. size, size distribution, interparticle distance and the shape of the silver nanoparticles.

Figure 8-6: a) As-measured UV-Vis absorption spectra of as-deposited and annealed Ag/HDFD-plasma polymer nanocomposite films; b) second-derivative of UV-Vis spectra in a); c) FT-IRRAS spectrum of as-deposit ed 4 nm HDFD plasma polymer film and difference spectrum after annealing at 120 °C for 1 hour.

The position of the SPR band was determined by the second-derivative of absorption spectra in figure 8-6 b). SPR band of the as-deposited sample blue shifted from 465 to 452 nm after annealing at 120 °C for 1 hour. The mean half-width (FWHM) of the SPR band in the second-derivative spectrum decreases from 63.3 to 56.7 nm, and the intensity of the SPR band increased due to the annealing treatment process. It is supposed that both intrinsic cluster-size effects ($R < 10$ nm) and extrinsic cluster-size effects ($R > 10$ nm) have effect on the change of SPR band [1]. Concerning the change in SPR band there are two effects included in this case study. On the one hand the slight increase in nanoparticle size
induces the red shift and broadening of the SPR band. On the other hand the blue shift, decrease of FWHW and the increased intensity of SPR band result from the increase of the shape factor ($S$) of nanoparticles [2]. The shift of the band position and the change of FWHM after annealing can be understood as the results of the competition between the two effects. In this case study, the latter is more prominent than the former. Therefore, the intensity of SPR band increases, FWHM narrows and the SPR band blue shifts.

8.3.3 Barrier Properties of HDFD Plasma Polymer Films and Thin Ag/HDFD-Plasma Polymer Nanocomposite Films

8.3.3.1 Barrier properties of HDFD plasma polymer films in borate buffer solution

The barrier properties of HDFD plasma polymer films were investigated by electrochemical impedance spectroscopy in the borate buffer solution for up to three hours as shown in figure 8-7. The typical Bode plots of HDFD plasma polymers as a function of the immersion time in borate buffer solution are given in figure 8-7 a). Figure 8-7 b) illustrates the evolution of the coating capacitance of HDFD plasma polymer films versus the immersion time in borate buffer solution. The coating capacitance of the HDFD plasma polymer film increased with time at the initial stage of the immersion and reached a constant plateau after approx. 50 minutes. As shown in figure 8-7 c) the water uptake of the HDFD plasma polymer film was at about 0.15% in the first 5 minutes of exposure to borate buffer solution, rising to a value of 0.7% after 50 minutes of exposure. The logarithmic $C_p$ values versus the square root of the immersion time for HDFD plasma polymer film immersed in borate buffer solution are shown in figure 8-7 d). The diffusion coefficient was determined to be $D = 1.4 \times 10^{-14}$ cm$^2$·s$^{-1}$ by the slop of the linear fitting according to equation 8-4. This value is very small in comparison to those obtained for organic primers such as epoxy films and polyester which show values between $10^{-9}$ and $10^{-11}$ cm$^2$·s$^{-1}$ [24] and reflects the strong barrier effects of the HDFD plasma polymer films.
Figure 8-7: a) Bode plots of the reference silver-covered Si-wafer substrates and 76.5 nm HDFD plasma polymer film deposited on silver-covered Si-wafer substrates in borate buffer solution; b) evolution of the coating capacitance within the first three hours of immersion in borate buffer solution for HDFD plasma polymer films; c) evolution of the water uptake of the HDFD plasma polymer film within the first three hours of immersion in borate buffer solution; d) film capacitance vs. the square root of the immersion time for the HDFD plasma polymer films during the immersion.

8.3.3.2 Barrier properties of thin Ag/HDFD-plasma polymer nanocomposite films during the ageing process in PBS solution

The electrochemical impedance spectra of the thin Ag/HDFD-plasma polymer nanocomposite film were measured during immersion in phosphate buffered saline (PBS) solution. As presented in figure 8-8 a), the film impedances of the Ag/HDFD-plasma polymer nanocomposite films are two orders of magnitude higher than that of the ITO
substrate. With increasing thickness of the HDFD plasma polymer film, the film impedances of the Ag/HDFD-plasma polymer nanocomposite films increased as shown in figure 8-8 a)-c).

**Figure 8-8:** Bode plots of the reference ITO-covered glass substrates and the ITO-covered glass-supported thin Ag/HDFD-plasma polymer nanocomposite films with HDFD plasma polymers of different thicknesses immersed in the PBS solution within 10 days: a) 4 nm HDFD/10 nm Ag/4 nm HDFD; b) 19 nm HDFD/10 nm Ag/19 nm HDFD; c) 35 nm HDFD/10 nm Ag/35 nm HDFD.

With increasing time of immersion in PBS electrolyte, the film impedance decreases very slowly as the PBS electrolyte penetrates the coating through the pores in the coating. Furthermore, the thicker the HDFD plasma polymer film, the slower the film impedance decreases. As shown in figure 8-8 c), with 35 nm HDFD plasma polymer film as sub layer and top layer of the thin Ag/HDFD-plasma polymer nanocomposite film, the film impedance changed only very slightly after the ageing process in PBS solution for 235
hours. However, the impedance spectra of the coating system are still pure capacitive and this leads to the conclusion that the thin Ag/HDFD-plasma nanocomposite films are quite stable during the ageing process in the PBS solution. This is mainly due to the high barrier properties and the high chemical inertness of the HDFD plasma polymer matrix.

8.3.4 Optical Properties of Thin Ag/HDFD-Plasma Polymer Nanocomposite Films during the Ageing Process

8.3.4.1 Ex-situ UV-Vis spectroscopy measurements

To investigate the change in optical properties of the thin Ag/HDFD-plasma polymer nanocomposite films during the ageing process, UV-Vis spectra of the Ag/HDFD-plasma polymer nanocomposite films were measured as a function of the immersion time in PBS solution. Both the as-measured spectra and the second-derivative spectra are shown in figure 8-9 a) and b). Second-derivatives of UV-Vis absorption spectra were used to study the change of optical properties during the ageing process. It was shown that after the ageing process the chemical compositions of the HDFD plasma polymer films were not substantially changed (see figure 8-3 b) and table 8-1). After the immersion in PBS solution for 42 hours, the SPR band red shifted from 452.5 to 457.0 nm and SPR band intensity increased (second-derivative of the absorption decreased). This is very likely induced by the matrix effect, because during the immersion the relative dielectric constant of the HDFD plasma polymer increases from 1.82 to 2.56 due to the 0.7% water uptake. In this case study of silver, the maximum of the absorption is given by

\[
C_{abs,max}(\Omega) = \frac{9V}{c} \frac{\varepsilon_m^{3/2}}{(1 + \chi_1^{ib} + 2\varepsilon_m)} \frac{\Omega^2}{\gamma} 
\]

(8-6),

where \(V\) is the volume of the particle, \(\varepsilon_m\) represents the dielectric function of the embedding matrix, \(c\) is the speed of light, \(\chi_1^{ib}\) is the real part of the dielectric permittivity caused by interband electronic transitions (\(\chi_1^{ib} = 3-5\)), \(\gamma\) is the rate of electron collisions, and the resonance frequency is defined by

\[
\Omega = \frac{\omega_p}{\sqrt{1 + \chi_1^{ib} + 2\varepsilon_m}} 
\]

(8-7),

where \(\omega_p\) is the plasma frequency of the conduction electrons in the particle [1, 25]. Therefore, the increase of \(\varepsilon_m\) leads to an increase of SPR band intensity and a red shift of SPR band according to equation 8-6 and 8-7. Moreover, the adsorbed water at the interface
between the Ag nanoparticles and the HDFD plasma polymer matrix could also be another effect resulting in the red shift of the SPR band [26, 27]. With the further increasing immersion time from 42 to 173 hours, the SPR band position did not shift much, but the SPR band intensity decreased (second-derivative of the absorption increased). The decrease in absorption suggests the release of silver from the thin Ag/HDFD-plasma polymer nanocomposite films. As the immersion time increased from 173 to 238 hours, the SPR band position shifted further to 460.0 nm and the peak intensity also displayed a further decrease. The change in the second derivative of absorption (inversely proportional to absorption) as a function of the immersion time in the PBS solution is shown in figure 8-9 c). The minimum of the second-derivative absorption $A_{\text{min}}$ increased with the immersion time after the initial stage of immersion (42 hours later), i.e. the absorption decreased relative to the immersion time because of the release of silver.

![UV-Vis spectra of Ag/HDFD-plasma polymer nanocomposite films as a function of the immersion time in PBS solution: a) as-measured UV-Vis spectra; b) second-derivative of the UV-Vis spectra in a); c) change in the minimum of second-derivative absorption ($A_{\text{min}}$) with respect to that at the beginning of the immersion.](image)

**Figure 8-9:** UV-Vis spectra of Ag/HDFD-plasma polymer nanocomposite films as a function of the immersion time in PBS solution: a) as-measured UV-Vis spectra; b) second-derivative of the UV-Vis spectra in a); c) change in the minimum of second-derivative absorption ($A_{\text{min}}$) with respect to that at the beginning of the immersion.
8.3.4.2 Effect of the thickness of HDFD plasma polymer films

To investigate the effect of the thickness of HDFD plasma polymer films on the optical properties of the thin Ag/HDFD-plasma polymer nanocomposite films during the ageing process in PBS solution, HDFD plasma polymer films with thicknesses of 4, 19 and 35 nm were used as the sub layers and top layers, respectively. The as-deposited thin Ag/HDFD-plasma polymer nanocomposite films with three different HDFD plasma polymer film thicknesses were annealed at 120 °C in vacuum for one, two and four hours. The as-measured and second-derivative UV-Vis spectra of the thin Ag/HDFD-plasma polymer nanocomposite films are shown in figure 8-10.

![Graphs showing UV-Vis spectra](image)

**Figure 8-10:** a) As-measured UV-Vis spectra of annealed thin Ag/HDFD-plasma polymer nanocomposite films with different HDFD film thicknesses; b) second-derivative of UV-Vis spectra in a); c) as-measured UV-Vis spectra of the annealed thin Ag/HDFD-plasma polymer nanocomposite films with different HDFD film thicknesses after the ageing process in PBS solution for 10 days; d) second-derivative of UV-Vis spectra in c).
It is apparent that the SPR peak red shifted from 447.5 to 456.0 nm with increasing thickness of the HDFD plasma polymer film from 4 to 19 nm. SPR peak read shifted further to 459.0 nm, as the thickness of the HDFD plasma polymer film increased to 35 nm. On the other hand, the SPR peak intensity increased (second-derivative of the absorption decreased) with the increasing thickness of the HDFD plasma polymer film from 4 to 35 nm (see figure 8-10 a) and b)). This is very likely due to the increase in the local refractive index around the particles according to equation 8-6 and 8-7. After the immersion in PBS solution for 10 days, the SPR band read shifted to 453.5, 459.0 and 465 nm for the thin Ag/HDFD-plasma polymer nanocomposite films with HDFD plasma polymer films of 4, 19 and 35 nm thicknesses. It is induced by the water uptake during the immersion, which increased the local refractive index of the matrix around the silver nanoparticles. The SPR band intensity of the Ag/HDFD-plasma polymer nanocomposite film decreased (second-derivative of the absorption increased), respectively, most likely due to the release of silver from the Ag/HDFD-plasma polymer nanocomposite films. It is shown that the difference in the SPR band intensity between the Ag/HDFD-plasma polymer nanocomposite films with different HDFD film thicknesses after the ageing process in PBS solution (see figure 8-10 d)) is not so obvious as that before the ageing process (see figure 8-10 b)). This might be explained by the fact that the effect of the immersion in PBS solution on the refractive index of the matrix is stronger than the effect of the increasing thickness of the matrix layer surrounding the silver nanoparticles [27, 28].

8.3.4.3 In-situ UV-Vis spectroscopy measurements

To investigate the optical properties of the thin Ag/HDFD-plasma polymer nanocomposite films with HDFD plasma polymer films of different thicknesses during the ageing process in PBS solution, the samples were measured using an in-situ cell shown in figure 8-2. Second-derivatives of UV-Vis absorption spectra during the ageing process for the thin Ag/HDFD-plasma polymer nanocomposite films with HDFD plasma polymer films of different thicknesses are shown in figure 8-11 a)-c). As discussed in section 8.3.4.1 at the initial stage of the immersion the intensity of the SPR band increased up to a maximum (second-derivative of the absorption decreased to a minimum) due to the matrix effect. Later the intensity of the SPR band decreased (second-derivative of the absorption increased) because of the release of silver from the thin Ag/HDFD-plasma polymer nanocomposite films. However, for the thin Ag/HDFD-plasma polymer nanocomposite films with HDFD plasma polymer films of different thicknesses, the time for the SPR band
intensity to reach the maximum (second-derivative of the absorption reached the minimum) was different. For the Ag/HDFD-plasma polymer nanocomposite film with 4 nm HDFD plasma polymer film, after 6.3 hours the SPR band intensity started to decrease. The thin Ag/HDFD-plasma polymer nanocomposite films with 19 and 35 nm HDFD plasma polymer films displayed decreases of the SPR band intensity after 8 and 17 hours, respectively. The variations of the minimum of the second-derivative of the absorption with the ageing time for the thin Ag/HDFD-plasma polymer nanocomposite films are shown in figure 8-11 d). It can be observed that the starting point of the decrease of SPR band intensity (the increase of the second-derivative of absorption) can be adjusted by varying the thicknesses of HDFD plasma polymer films. The thicker the HDFD plasma polymer film, the more time is needed for the PBS solution to penetrate the coating, to reach the interface between the silver nanoparticles and the HDFD plasma polymer matrix, thereafter to reach the saturation of the water uptake of the film. Figure 8-11 d) showed that after the SPR band intensity started to decrease (second-derivative of the absorption started to increase), the release rate of silver for the Ag/HDFD-plasma polymer nanocomposite films with different HDFD film thicknesses is almost the same, because the slope of each curve is nearly the same.

However, while the SPR band red shifted due to the increasing refractive index resuled from the immersion in PBS solution shown by the ex-situ measurements in section 8.3.4.1, the SPR band in figure 8-11 d) blue shifted during the ageing process in the PBS solution. This was probably induced by the presence of the phosphate and chloride ions in the PBS solution. The trace amount of precipitates such as AgCl could be built on the sample surface and the depletion of chloride and phosphate ions changed the dielectric index of the PBS solution and the reference of the in-situ UV-Vis measurements. In the future, the in-situ UV-Vis measurements with a continuous circulation of the PBS solution will be designed for the further investigation of the optical properties of the Ag/HDFD-plasma polymer nanocomposite films during the ageing process.

Moreover, the change in the microstructure of silver nanoparticles in the thin Ag/HDFD-plasma polymer nanocomposite films during the immersion in PBS solution could contribute to the shift in band position and the change of SPR peak intensity as well, which is discussed in the following section.
Figure 8-11: Second-derivative of in-situ UV-Vis absorption spectra of annealed Ag/HDFD-plasma polymer nanocomposite films with different HDFD plasma polymer film thicknesses during ageing process in PBS solution: a) 4 nm HDFD/6 nm Ag/4 nm HDFD; b) 19 nm HDFD/6 nm Ag/19 nm HDFD; c) 35 nm HDFD/6 nm Ag/35 nm HDFD; d) change in the minimum of second-derivative of the UV-Vis absorption \(A_{\text{min}}\) spectra with time of ageing process.

8.3.5 Morphological Changes of Thin Ag/HDFD-Plasma Polymer Nanocomposite Films during the Immersion in Water

To investigate the microstructural change of silver nanoparticles in thin Ag/HDFD-plasma polymer nanocomposite films during the immersion in water-base electrolytes, thin Ag/HDFD-plasma polymer nanocomposite films were immersed into ultra pure water. For an ageing process under ambient conditions, the thin Ag/HDFD-plasma polymer nanocomposite films did not show any change in the microstructure of silver nanoparticles. However, after the immersion in ultra pure water for twelve days as shown in figure 8-12 a) and b), some of the silver nanoparticles presented in figure 8-5 a) and b) grew into some
larger faceted structures. The size of the larger particles is approximately four times larger than the size of the largest nanoparticle before the immersion. Figure 8-12 c) and d) demonstrate more clearly the fine microstructure of the larger silver nanoparticles. For the immersed non-annealed films, the size of silver nanoparticle shown in figure 8-12 c) is approximately 135 nm × 182.5 nm. For the immersed annealed films, the size of silver nanoparticle shown in figure 8-12 d) is approximately 125 nm × 125 nm. The large faceted nanoparticles in figure 8-12 b) are more spherical in comparison to those in figure 8-12 a), which agrees with the effect of annealing on the microstructure of nanoparticles discussed previously. The EDX elemental analysis determined the faceted structures to be pure silver metal. The electron diffraction investigations demonstrated some of the larger faceted particles (see figure 8-12 e) and f)) to be single crystals.
When taking a closer look at figure 8-12 c) and d), it can be observed that the small silver nanoparticles were scavenged by the larger ones. This phenomenon is probably induced by a mechanism similar to Ostwald ripening. The depletion of the smaller nanoparticles next to the larger nanoparticles after the immersion (marked in circles and shown in figure 8-12 g) clearly shows that the microstructural changes are indeed similar to Ostwald ripening. However, the formation of the larger particles cannot be fully explained by the diffusion of the silver atoms, otherwise the free zones around the larger particles should be much larger.
than those observed in figure 8-12 g) considering the size of the formed larger silver nanoparticles. For reasons of comparison a FE-SEM image of the Ag/HDFD-plasma polymer nanocomposite film on ITO substrate immersed in water for 12 days is shown in figure 8-12 h). It can be observed that some larger silver nanoparticles formed as well after the immersion with comparable size to the larger silver particles shown in figure 8-12 g). A possible reason could be the accelerated atomic diffusion by the absorbed water at the interface between silver nanoparticles and the HDFD plasma polymer matrix during the immersion. Moreover, when particles are in contact to each other (in circles in figure 8-5 a)), the diffusion of silver atoms along the particle surface or the grain boundaries inside the polycrystalline silver particles takes place in order to minimize the particle surface energy. Therefore, coalescence also contributes to the size increase of the nanoparticles. Once the nanoparticles are in contact with each other, the process can also be accelerated through an electrochemical Ostwald ripening mechanism, by the size dependence of the work function and standard electrode potential as reported by Redmond et al. [29].

Electrochemical Ostwald ripening is, in principle, due to the localized electrochemical reactions of metal dissolution/deposition on the surface of silver nanoparticles. Redmond et al. concluded that the existence of the silver ions in the solution and the conductive substrate are the preconditions for the electrochemical Ostwald ripening [29]. The reduction of bulk silver is described by the half-cell reaction $\text{Ag}^+ (\text{aq}) + e^- \leftrightarrow \text{Ag}^0(\text{surface})$ with $E_{\text{bulk}}^0 = +0.80 \text{ V versus SHE}$. According to Plieth [30], the standard electrode potential $E_p^0$ of a small metal particle shifts negatively according to the following equation, where $\gamma$ is the surface tension, $\nu_M$ represents the molar volume, $z$ is the lowest valence state, $F$ is Farady’s constant and $r$ is the particle radius,

$$E_p^0 = \left(E_{\text{bulk}}^0 - \frac{2\gamma
u_M}{zFr}\right)$$

(8-8).

The negative shift in the standard electrode potential of small particles means that smaller metal nanoparticles are more easily oxidized than bulk material. When larger and smaller particles are electrochemically connected to each other, they will then function as cathode and anode in a galvanic cell when an electrolyte and reducible species are present. The existence of the trace amount of silver ions has been shown before resulting from the slow oxidation of silver in ambient conditions by Cai et al. and Schmidt et al. [31, 32]. However, the conductivity can only result from the coalescence of the silver nanoparticles in the Ag/HDFD-plasma polymer nanocomposite films. Moreover, the microstructural
reformation of silver nanoparticles depends on the potential, pH value of the solution, concentration of the silver ions and the ionic conductivity of the solution [29, 33]. At a certain point, the silver nanoparticle becomes so large that the very thin HDFD plasma polymer film can not cover it anymore because of the limited elasticity of the HDFD plasma polymer films. The large silver nanoparticles are exposed to the solution, in which some silver ions have been released. From that moment on, the electrochemical Ostwald ripening will proceed even much faster, because large silver particles principally assume the role of the conductive substrate. The electrochemical Ostwald ripening process proceeds between the scavenged smaller nanoparticles, and the diffusion across the particle surface or the grain boundaries make the silver nanoparticle become even larger. It has been shown that the standard exchange rate of $\text{Ag}^+(\text{aq}) + e^- \leftrightarrow \text{Ag}^0(\text{surface})$ at polycrystalline electrode is 3 to 4 orders of magnitude faster than at bulk-terminated Ag(100) surfaces. The polycrystalline silver surface contains active sites with an extremely high rate constant for the above-mentioned reaction, but these sites are absent from the surfaces of single crystalline silver. Thus the system is kinetically and thermodynamically biased toward the formation of larger single crystals [29, 34]. Therefore, large single crystalline particles can be formed as shown in figure 8-12 e).

### 8.3.6 Morphological Changes of the Ag/HDFD-Plasma Polymer Nanocomposite Films during the Immersion in PBS Solution

To investigate the microstructural change of silver nanoparticles during the ageing process of the thin Ag/HDFD-plasma polymer nanocomposite films in PBS solution, the Ag/HDFD-plasma polymer films were deposited on TEM gold grids. The TEM images of the as-deposited and annealed samples, as well as the annealed sample immersed in PBS solution for 12 days are presented in figure 8-13. In figure 8-13 a) isolated silver nanoparticles can be observed and the size of the silver nanoparticles is similar to that shown in figure 8-5 a). After annealing at 120 °C for one hour most of the silver nanoparticles agglomerated into several larger silver nanoparticles and the interparticle distance increased in comparison to before annealing, although some smaller ones still existed. The scavenging of the smaller nanoparticles can be observed in figure 8-13 b), where some scavenged nanoparticles were just adsorbed on the larger nanoparticles but did not diffuse into the larger nanoparticle yet. In addition, some particles are connected to each other due to the diffusion along the particle surface resulting from the Ostwald ripening.
During the annealing process (shown in circles in figure 8-13 b)). Figure 8-13 c) shows the TEM image of the thin Ag/HDFD-plasma polymer nanocomposite film after the ageing in PBS solution. The size of silver nanoparticles decreased a lot due to the release of silver during the ageing process. The scavenging of the smaller nanoparticles by the larger ones as shown in figure 8-12 c) and d) was not observed in figure 8-13 c). The reason could be that the silver ions released into the PBS solution were consumed by forming AgCl precipitate in the solution, so that the above-mentioned electrochemical Ostwald ripening could not happen.

**Figure 8-13:** Bright field TEM images of the thin Ag/HDFD-plasma polymer nanocomposite films: a) Ag/HDFD-plasma polymer nanocomposite films as-deposited on TEM gold grids; b) Ag/HDFD-plasma polymer nanocomposite samples in a) annealed at 120 °C for one hour; c) Ag/HDFD-plasma polymer nanocomposite films in b) immersed in PBS solution for 12 days.
8.4 Conclusions

In summary, the mean diameter of silver nanoparticles in thin Ag/HDFD-plasma polymer nanocomposite films synthesized by electron beam evaporation is determined to be about 12.0 nm. HR-TEM results demonstrated that annealing treatment leads to the increase of the size and shape factor of the silver nanoparticles, broadening of the size distribution and the increase of the interparticle distance. This results from the Ostwald ripening process and the diffusion of metal atoms along the particle surface. UV-Vis spectra showed that the optical properties of the Ag/HDFD-plasma polymer nanocomposite films change due to the microstructural change of silver nanoparticles resulting, in turn, from the annealing treatment. The SPR band blue shifted from 465.0 to 452.0 nm and the FWHM of the SPR band decreased from 63.3 to 56.7 nm. Furthermore the intensity of the SPR band increased due to the annealing treatment.

EIS measurements lead to the conclusion that the Ag/HDFD-plasma nanocomposite films are quite stable during the ageing process in the PBS solution, which is mainly due to the high barrier properties and the chemical inertness of the HDFD plasma polymer matrix. At the initial stage of the ageing process the SPR band read shifted from 452.5 to 457.0 nm mainly due to the matrix effect resulting from the water uptake of the Ag/HDFD-plasma polymer nanocomposite films. Due to the further increase of the immersion time the SPR band position slowly shifted from 457.0 to 460.0 nm and the peak intensity decreased as a result of the release of silver from the Ag/HDFD-plasma polymer nanocomposite films and the microstructural change of silver nanoparticles. In addition, the starting point of the release of silver from the Ag/HDFD-plasma polymer nanocomposite films can be adjusted by varying the thickness of the HDFD plasma polymer films, although the release rate could not be adjusted by the same approach.

The HR-TEM results showed the microstructure of silver nanoparticles reforms during the immersion in water through a complex mechanism based on the combination of the atomic metal diffusion, coalescence-inducing increase of the particle size and the electrochemical Ostwald ripening driven by the size dependence of the work function and standard electrode potential. The scavenging of the smaller nanoparticles by the larger ones was not observed during the ageing of the thin Ag/HDFD-plasma polymer nanocomposite films in PBS solution. The reason could be that the silver ions released into the PBS solution were consumed by forming AgCl precipitate in the solution, so that the above-mentioned
electrochemical Ostwald ripening could not happen.

References


Chapter 9: Overall Conclusions & Outlook

The present work is based on the functionalities of the thin plasma polymer and metal/plasma polymer nanocomposite films. Different functional film systems were developed, such as pure fluorocarbon or organosilicon plasma polymer films, thin fluorocarbon and organosilicon bilayer plasma polymer films and fluorocarbon plasma polymer-supported silver nanoparticles, as well as silver/fluorocarbon plasma polymer nanocomposite films. Various surface-sensitive analytical methods, such as FT-IR, UV-Vis spectroscopy, XPS, ToF-SIMS, AFM, SEM and electrochemical impedance spectroscopy, HR-TEM etc., were intensively applied to characterize the thin functional films.

In chapter 4 thin HDFD and HMDSO plasma polymers films were synthesized and their chemical compositions were determined to be C_{10}F_{11.4}H_x and SiO_{0.8}C_{0.8}H_x by means of XPS, respectively. FT-IR results showed that CF, CF_2, CF_3 and CH_x functional groups mainly exist in the HDFD plasma polymer films and Si(CH_3)_x and Si-O-Si functional groups are main components of the HMDSO plasma polymer films. The densities of the HDFD and HMDSO plasma polymer films were determined to be 2.46 and 1.46 g·cm^{-3}, respectively. AFM results demonstrated very smooth surfaces of the thin HDFD and HMDSO plasma polymer films with RMS < 1 nm. The surface energy of HDFD plasma polymer films was calculated to be 10.69 mJ/m^2 by the contact angle measurements. In addition, refractive indices of the thin HDFD and HMDSO plasma polymer films were determined to be in the range between 1.3 and 1.5 in the wavelength ranging from 300 to 800 nm.

The etching effect of Ar-plasma on the chemical structure, morphology and the wettability of the thin HDFD plasma polymer films was investigated in chapter 5. An etching rate of about 7 nm/min for the Ar-plasma was determined by the QCM measurements. During the Ar-plasma etching process cross-linking takes place at the expense of the CF_2 and CF_3 functional groups. The roughness of the Teflon-like HDFD plasma polymer films increases as a function of the etching time and the initially very smooth surface morphology changes into an island-like structure. The values of the advancing and receding contact angles decrease with the time of Ar-plasma etching due to the loss of -CF_2- and -CF_3 functional groups, whereas the hysteresis increases with the generated roughness during the etching process.

In chapter 6 spontaneous formations of the worm-like structures were achieved by the
deposition of thin organosilicon and fluorocarbon bilayer plasma polymer films. The formation of the island-like HMDSO plasma polymer structure during the initial stage of the film formation can be explained by the inhomogeneous distribution of HMDSO layer on the low energy surface of the HDFD plasma polymer films. In the second stage of the film growth, the formation of a laterally continuous HMDSO plasma polymer film is based on the buckling theory to release the compressive stress in plasma polymer films.

Well-defined silver nanoparticles with narrow size distribution were generated by means of electron beam evaporation of silver on ultra-thin fluorocarbon plasma polymer films in chapter 7. The size of nanoparticles increased from 4.2 to 15.8 nm and the size distribution broadened from 3.6 to 13.4 nm with increasing amount of deposited silver from m to 4m (m represents the change in mass corresponding to 5 nm continuous silver film per unit area). The comparison of the growth of PVD silver nanoparticles on ultra-thin HDFD plasma polymer films and on fluorinated SAMs indicated a better stability of the cross-linked HDFD plasma polymer films against the penetration of silver during the silver deposition process. FE-SEM results demonstrated that the annealing treatment leads to the morphological change of silver nanoparticles such as the increase of size and the interparticle distance of the silver nanoparticles, as well as the change of the particle shape. This results from the Ostwald ripening process and the diffusion of metal atoms along the particle surface. UV-Vis spectroscopy was applied to investigate the change in the optical properties of silver films due to the microstructural change of silver nanoparticles resulting from the annealing treatment. Moreover, spectroscopic ellipsometry was used to investigate the impact of the silver morphology on the optical properties of silver nanoparticle-covered thin HDFD plasma polymer films. For the silver nanoparticle-covered HDFD plasma polymer films, an SPR band appears in the extinction coefficient curve and the real part of the refractive index n shows an anomalous dispersion at the SPR peak maximum. The SPR band red shifts and broadens with increasing amount of the deposited silver. This correlates to an increase in the size of silver nanoparticles and the broadening of the size distribution.

In chapter 8, HR-TEM was applied to better clarify the microstructure of the silver nanoparticles in the thin Ag/HDFD plasma polymer nanocomposite films. HR-TEM results proved that the annealing treatment leads to the increase of silver nanoparticle size and shape factor, broadening of the size distribution and the increase of the interparticle distance shown previously in chapter 7. UV-Vis spectra showed that the SPR band blue
shifted from 465.0 to 452.0 nm and the FWHM of the SPR band decreases from 63.3 to 56.7 nm. Furthermore the intensity of the SPR band increases due to the annealing treatment.

More importantly, chapter 8 focused on the ageing process of the thin Ag/HDFD plasma polymer nanocomposite films exposed in water-based electrolytes. EIS measurements lead to the conclusion that the thin Ag/HDFD-plasma polymer nanocomposite films are quite stable during the ageing process in the PBS solution, which is mainly due to the high barrier properties and the chemical inertness of the HDFD plasma polymer matrix. From the UV-Vis spectroscopy results it was found that at the initial stage of the ageing process the SPR band read shifts from 452.5 to 457.0 nm and the SPR peak intensity increases mainly due to the matrix effect resulting from the water uptake of the Ag/HDFD-plasma polymer nanocomposite films. With the further increasing immersion time the SPR band position slowly shifts from 457.0 to 460.0 nm and the peak intensity decreases due to the release of silver from the Ag/HDFD-plasma polymer nanocomposite films and the microstructural change of silver nanoparticles. In addition, the starting point of the release of silver from the Ag/HDFD-plasma polymer nanocomposite films can be adjusted by varying the thickness of the HDFD plasma polymer films, although the release rate could not be adjusted by the same approach.

HR-TEM results showed that the microstructure of silver nanoparticles reforms during the immersion in water through a complex mechanism based on the combination of the atomic metal diffusion, coalescence-inducing increase of the particle size and the electrochemical Ostwald ripening driven by the size dependence of the work function and standard electrode potential. The scavenging of the smaller nanoparticles by the larger ones did not take place during the ageing of the thin Ag/HDFD-plasma polymer nanocomposite films in PBS solution. The most possible reason might be that the silver ions released into the PBS solution were consumed by forming AgCl precipitate in the solution, so that the above-mentioned electrochemical Ostwald ripening could not happen.

The release of silver and the antibacterial properties of the thin Ag/HDFD-plasma polymer nanocomposite films should be studied for their applications in household or medical field as antibacterial materials. Especially the quantitative determination of the silver release rate during the ageing process in humidity or in water-based solution would provide more reliable database for the long-term use of the Ag/HDFD-plasma polymer nanocomposite
films as antibacterial coatings. The anodic stripping voltammetry would be a promising method to determine the very low concentration of silver ions released from the thin Ag/HDFD-plasma polymer nanocomposite films. In addition, the mechanical properties, such as the tribology properties, surface friction and the forming behavior of the thin Ag/HDFD-plasma polymer nanocomposite films are of great interest for the long-term technological applications of such silver/fluorocarbon plasma polymer nanocomposite films.
## Chapter 10: Appendices

### 10.1 Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Full Form</th>
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<tbody>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>BE</td>
<td>Binding energy</td>
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<tr>
<td>CVD</td>
<td>Chemical vapor deposition</td>
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<tr>
<td>DDA</td>
<td>Discrete dipole approximation</td>
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<tr>
<td>DMAP</td>
<td>4-(dimethylamino) pyridine</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy-dispersive X-ray analysis</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron spectroscopy for chemical analysis</td>
</tr>
<tr>
<td>FAS-17</td>
<td>Heptadecafluorodecyl-trimethoxysilane</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>Field emission scanning electron microscopy</td>
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<tr>
<td>FT-IR</td>
<td>Fourier transform infrared</td>
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<tr>
<td>FT-IRRAS</td>
<td>Fourier transform infrared reflection absorbance spectroscopy</td>
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<tr>
<td>FWHM</td>
<td>The full width at half maximum</td>
</tr>
<tr>
<td>HDFD</td>
<td>Heptadecafluoro-1-decene</td>
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<tr>
<td>HMDSO</td>
<td>Hexamethyldisiloxane</td>
</tr>
<tr>
<td>HR-TEM</td>
<td>High resolution transmission electron microscopy</td>
</tr>
<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
</tr>
<tr>
<td>LBL</td>
<td>Layer-by-layer</td>
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<tr>
<td>PAA</td>
<td>Poly(acrylic acid)</td>
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<tr>
<td>PAMAM</td>
<td>Poly(amidoamine)</td>
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<tr>
<td>PBS</td>
<td>Phosphate buffered saline</td>
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<tr>
<td>PDMS</td>
<td>Poly(dimethylsiloxane)</td>
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<tr>
<td>PMMA</td>
<td>Poly(methyl methacrylate)</td>
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<tr>
<td>PSS</td>
<td>Poly(styrenesulfonate)</td>
</tr>
<tr>
<td>PTFE</td>
<td>Polytetrafluoroethylene</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical vapor deposition</td>
</tr>
<tr>
<td>QCM</td>
<td>Quartz crystal microbalance</td>
</tr>
<tr>
<td>RMS</td>
<td>Root mean square</td>
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<tr>
<td>SAED</td>
<td>Selected area electron diffraction</td>
</tr>
<tr>
<td>SAMs</td>
<td>Self-assembled monolayers</td>
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</table>
SEM  Scanning electron microscopy
SHE  Standard hydrogen electrode
SPM  Scanning probe microscopy
SPR  Surface plasmon resonance
STM  Scanning tunneling microscopy
TEM  Transmission electron microscopy
ToF-SIMS  Time of flight secondary ion mass spectroscopy
UHV  Ultra high vacuum
XPS  X-ray photoelectron spectroscopy

10.2 Latin Symbols

$A$  Area
$A(\lambda)$  Absorbance
$A_{min}$  The minimum of second-derivative absorption
$A_p$ and $A_s$  The FT-IR absorbance spectra in parallel and vertical polarization
$c$  The concentration of materials
$c$  The speed of light
$C$  The condensation coefficient
$C$  The coating capacitance
$C_{abs}(\omega)$  The absorption cross section
$C_{abs,\text{max}}(\Omega)$  The maximum of the absorption cross section
$C_f$  Constant in the Sauerbrey equation
$C_p$  The coating capacitance during the measurement
$C_{p0}$  The coating capacitance for the dry film
$C_s$  The coating capacitance at the saturation stage of the immersion
$d$  The film thickness
$d$  The critical wavelength of the wave-like structure
$D$  Diffusion coefficient
$E_A$  Energy of the Auger electron
$E_b$  Binding energy
$E_f$  The Young’s modulus of the film
$E_i$  The internal field $E_i$
$E_k$  Kinetic energy
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\begin{align*}
E_s & \quad \text{The Young’s modulus of the substrate} \\
E_0 & \quad \text{The external field} \\
E_{\text{bulk}}^0 & \quad \text{The standard electrode potential of the bulk metal} \\
E_p^0 & \quad \text{The standard electrode potential of a small metal particle} \\
E_1, E_2 & \quad \text{Binding energies of the atom in the singly ionized state} \\
E_3^* & \quad \text{Binding energy of the atom in the doubly ionised state} \\
f & \quad \text{Frequency} \\
f_0 & \quad \text{The resonance frequency of the quartz crystal} \\
F & \quad \text{Farady’s constant} \\
h & \quad \text{The Planck constant} \\
h & \quad \text{The thickness of the upper film} \\
I & \quad \text{The number of photoelectrons per second in a specific spectra peak} \\
I & \quad \text{The transmitted intensity} \\
I_0 & \quad \text{The original photoelectron intensity} \\
I_0 & \quad \text{The intensity of the incident light} \\
I(x) & \quad \text{The remaining intensity of photoelectron after travelling through material} \\
k & \quad \text{Extinction coefficient} \\
K & \quad \text{Kelvin} \\
L_q & \quad \text{The thickness of the bare quartz disk} \\
m/z & \quad \text{Mass-to-charge ratio} \\
n & \quad \text{The electron density inside the nanoparticle} \\
n & \quad \text{The number of atoms of the element per cm}^3 \text{ of the sample} \\
n & \quad \text{Refractive index} \\
N & \quad \text{The frequency constant of quartz crystal} \\
r & \quad \text{The radius of the particle} \\
R & \quad \text{The radius of the particle} \\
R^p, R^s & \quad \text{The total reflection coefficients} \\
S & \quad \text{Shape factor of the particle} \\
S & \quad \text{Atomic sensitivity factor} \\
t & \quad \text{Time} \\
T & \quad \text{The detection efficiency for electrons emitted from the sample} \\
U & \quad \text{The particle perimeter}
\end{align*}
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\( V \) \hspace{1cm} \text{The volume of the particle}

\( x \) \hspace{1cm} \text{Thickness of the material}

\( y \) \hspace{1cm} \text{The efficiency in the photoelectric process for formation of photoelectrons of the normal photoelectron energy}

\( z \) \hspace{1cm} \text{The lowest valence state}

\( |Z| \) \hspace{1cm} \text{The magnitude of the impedance}

10.3 Greek Symbols

\( \alpha(\omega) \) \hspace{1cm} \text{The dipolar polarizability of the spherical particle}

\( \gamma \) \hspace{1cm} \text{The surface tension}

\( \gamma \) \hspace{1cm} \text{The rate of electron collisions}

\( \gamma_1, \gamma_2 \) \hspace{1cm} \text{The surface energies of the respective liquid and the solid surface}

\( \gamma'_d, \gamma'_p \) \hspace{1cm} \text{The dispersion part and the polar part of the surface energy}

\( \delta_1, \delta_2 \) \hspace{1cm} \text{The phase differences between the p-wave and the s-wave before and after the reflection}

\( \varepsilon \) \hspace{1cm} \text{The molar absorptivity of the absorbing species}

\( \varepsilon \) \hspace{1cm} \text{The dielectric constant of the coating}

\( \varepsilon_m \) \hspace{1cm} \text{The dielectric constant of the embedding medium}

\( \varepsilon_w \) \hspace{1cm} \text{The dielectric constant of water}

\( \varepsilon_0 \) \hspace{1cm} \text{The dielectric constant of free space}

\( \varepsilon(\omega) \) \hspace{1cm} \text{The dielectric constant of the embedded metal particles}

\( \varepsilon_1(\omega) \) \hspace{1cm} \text{The real part of the dielectric constant of the embedded metal particles}

\( \varepsilon_2(\omega) \) \hspace{1cm} \text{The imaginary part of the dielectric constant of the embedded metal particles}

\( \theta \) \hspace{1cm} \text{The contact angle}

\( \theta \) \hspace{1cm} \text{The angle of emission with respect to the surface normal}

\( \theta \) \hspace{1cm} \text{An angular efficiency factor for the instrumental arrangement based on the angle between the photon path and detected electron}

\( \lambda \) \hspace{1cm} \text{The mean free path of the photoelectrons in the sample}

\( \lambda = (E_k, Z) \) \hspace{1cm} \text{The inelastic mean free path}

\( \nu \) \hspace{1cm} \text{Frequency}

\( \nu_f \) \hspace{1cm} \text{Poisson’s ratio of the film}
\( \nu_M \) The molar volume
\( \nu_s \) Poisson’s ratio of the substrate
\( \rho_q \) The density of the quartz crystal
\( \sigma \) The photoelectric cross-section for the atomic orbital of interest in cm²
\( \varphi \) The water uptake
\( \phi_{spec} \) Work function of the spectrometer
\( \chi^{ib}(\omega) \) The complex interband susceptibility
\( \chi^{ib}_1(\omega) \) The real part of the interband susceptibility
\( \chi^{ib}_2(\omega) \) The imaginary part of the interband susceptibility
\( \omega \) Frequency
\( \omega_i \) Interband transition edge
\( \omega_p \) Plasma frequency of the conduction electrons in the particle
\( \omega_{res} \) The resonance frequency
\( \omega_1, \omega_2 \) The frequencies defining the FWHM of the resonant curve
\( \Gamma \) FWHM of the resonant curve
\( \Delta \) (\( \Delta = \delta_1 - \delta_2 \), where \( \delta_1 \) and \( \delta_2 \) represent the phase difference between the p-wave and the s-wave before and after the reflection)
\( \Delta f \) The mean frequency shift
\( \Delta_m \) The change in mass per unit area
\( \Psi \) (\( \tan \Psi = |R^p|/|R^s| \), where \( R^p \) and \( R^s \) are the total reflection coefficients, i.e. the ratio of the amplitude of the outgoing resultant wave to the amplitude of the incoming wave for p-waves and s-waves)
\( \Im \) The imaginary part of the polarizability of the particle
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Publications Related to This Work


4. “Ageing of thin Ag/fluorocarbon plasma polymer nanocomposite films exposed to water-based electrolytes” Xuemei Wang, Christoph Somsen and Guido Grundmeier, Accepted for publication, Acta Materialia.
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