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 $\text{C}_{10}\text{F}_{11.4}\text{H}_x$ and $\text{SiO}_{0.8}\text{C}_{0.8}\text{H}_x$ 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.