

SUMMARY

In recent time fabricated various objects are mostly coated by film deposition from a liquid or gas phase. These films have different functions and can be produced by various techniques (eg. with brush or spraying). One of the unique coating techniques is the process based on chemical deposition from a vapor phase (CVD), i.e., the remote hydrogen plasma CVD (RP CVD). This technique allows one for coating the surfaces of complex shape, even in a nanoscopic scale, which is of great importance in current miniaturization. An increasing number of the elements used in different devices is a combination of the core material and a cladding, what simultaneously improves performance, giving it a desirable new features, and extends its durability.

In the PhD thesis thin films were fabricated from 1,1,3,3-tetramethyldisiloxane (TMDSO), 1,1,3,3-tetramethyldisilane (TMDSN) and 1,1,3,3-tetramethyldisilylethane (TMDSE). The detailed studies were carried out for the films deposited from TMDSO precursor, which was used in RP CVD process for the first time. The films were examined in terms of the effect of substrate temperature (T_s), which appeared to influence markedly their kinetics of growth, structure, and surface morphology. At non-heated substrate, the film growth rate was $r_d = 7.3 \text{ nm}\cdot\text{min}^{-1}$ and decreased to a value of $r_d = 1.4 \text{ nm}\cdot\text{min}^{-1}$ at $T_s = 350 \text{ }^\circ\text{C}$. Films deposited at T_s below $200 \text{ }^\circ\text{C}$ were polymer-like (hydrogenated) materials. The increase of T_s involves a marked drop in the content of organic groups accompanied by the crosslinking, and the film structure becomes similar to that of ceramic silicon oxycarbide. This is confirmed by the results of infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and Rutherford back-scattering spectroscopy (RBS). Refractive index of the films determined by ellipsometry was found to increase with rising T_s from about 1.5 to over 1.7. These changes remain in a close relation with the film density, which increased in the range of $1 - 3 \text{ g}\cdot\text{cm}^{-3}$. AFM surface analysis showed that the films have a granular morphology. Size of grains decreased with increasing T_s , and a distinct smoothing effect of film surface was observed.

Objects coated with such film are perfectly protected against external corrosive agents and in the case of implants protect the body against the penetration of metal ions diffusing into the body. Depending on the future use the CVD film may be further functionalized, what in case of the uncoated object (eg. made of metal) would be impossible.

In this work the CVD films have been subjected to direct plasma process fed with a mixture of argon and water vapor ($\text{Ar}/\text{H}_2\text{O}$), which resulted in the surface activation by the

formation of hydroxyl groups. The activation conditions were chosen to prevent the activated films against etching and defecting. In this process a new layer of silicon oxide SiO_x was formed, and its growth was analyzed by FTIR reflectance spectroscopy and by ellipsometry. The content of resulting SiO_x structure increases at the expense of the silicon substrate. It has been found that the formation of the activated surface film takes place at relatively short activation times, less than 25 seconds.

The next step in modification of CVD films was immobilization of 3-aminopropyl triethoxysilane (APTES). APTES was used as a covalent linker forming an interface between the inorganic substrate and an organic layer. Attachment of APTES molecules to CVD activated surface was observed as the growth of additional layer of SiO_x on the surface. The silanization with APTES vapor enabled for the formation of monolayer coatings in the thickness range of 1 – 2 nm (by evaporation under reduced pressure), or thicker layers of ~ 10 nm (free evaporation under nitrogen). Silanization with APTES vapor allowed the formation of monolayer coatings with a thickness in the range of 1 – 2 nm (by evaporation under reduced pressure) or a thicker layers with a thickness of ~ 10 nm (slow evaporation under nitrogen). AFM microscopic examination showed that the deposited APTES layers are homogeneous. There are no aggregates specific to the silanization processes from solutions. For thicknesses of APTES less than 2 nm irregularities in AFM profile has sharp changes, which with increasing thickness of APTES becomes smoother.

The final modification of CVD layers, after the activation with OH groups and silanization with APTES molecules was functionalization of organic fluorescent compounds are covalently attached to amino groups of APTES using pyrene butyric acid imid ester (PyNHS). The results confirmed linking of PyNHS and proved that the chemical modification of the CVD silicon layers was achieved.

Studies on modification of CVD films were also performed for austenitic stainless steel 316L used in medicine. Similar steps were conducted as in the case of model substrates. Immobilization process was done for several silane coupling agents with different end-groups. The results of contact angle measurements revealed that the nature of the substrate (steel) does not affect the further reactions on the deposited CVD thin film. A key parameter in such cases is a good adhesion of layer to the substrate.

In addition, the results obtained for siliconoxycarbide films (from TMDSO precursor) showed that in a similar way one can modify siliconcarbide coatings prepared from tetrametylo-disilane (TMDSE) and siliconcarbonitride coatings tetramethyldisilazane (TMDSN).

A preliminary biocompatibility studies on TMDSN layers produced at substrate temperatures of 50 °C and 300 °C were also carried out. Based on the results of *E. Coli* cells culture and the interaction of the layers in contact with the blood components it can be concluded that the TMDSN films are not suitable for direct contact with blood. They may, however, be useful as the implant coatings for osseointegration, where thrombogenicity is not considered as defect. It should be noted that non modified CVD film may have a little contact with the surrounding tissues and body fluids. Such contact may have rather modifying layer.