

Thin and Ultrathin Plasma Polymer Films and Their Characterization

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Abstract One often mentioned advantage of plasma polymerization is the possibility to coat any type of substrate. In addition, it is often supposed that films of plasma polymers grow independently of the substrate material. As will be discussed in this contribution, this assumption is not valid for ultrathin films (up to 20 nm). In this case properties of growing film may be influenced by substrate material and may change with increasing thickness of the film. This will be demonstrated in this study by an example of plasma polymerized polytetrafluorethylene. Results of measuring chemical composition, water contact angle and barrier properties towards oxygen are presented in dependence on film thickness.

Introduction

Surface modification of various materials is in the center of scientific interest for many decades [1]. This is due to the possibility of modifying the physical, chemical, or recently also bio-responsive properties of surfaces without changing the bulk properties of the whole object. One way to modify solid surfaces is to coat them with a thin plasma polymer layer deposited by means of low temperature plasma.

Plasma polymers, which are created as a result of the passage of an organic gas or vapors through plasma, are used in many applications — such as protective, barrier and decorative coatings. Since the sixties of the 20th century thin layers of plasma polymers enjoy growing interest also in biomedical applications (e.g. coating contact lenses, joint and vascular prostheses, catheters, biosensors production ...) [1], where they are used to control adsorption of biomolecules or cells [2]. The main advantages of plasma polymer films are their relatively easy preparation without the use of toxic substances and the possibility to control precisely their resulting properties by adjusting parameters of preparation (e. g. power, pressure, used working gas). Other frequently mentioned advantages are the very good homogeneity and low surface roughness of the deposited layers and the fact that films grow independently of the substrate material. However, as shown by recent studies [3–5], these characteristics are not generally valid for ultrathin films of plasma polymers, i.e. films with a thickness below 20 nm.

For instance, the smoothness and homogeneity of plasma polymer layers has limited validity. For example, Micheltore et al. [4] reported island growth of plasma polymerized n-heptylamine: it was found that films are smooth only when their thickness exceeds 8 nm. Another and often studied example is the formation of nanotextured plasma polymerized fluorocarbon films [e.g., 6–8]. The creation of nanostructured layers of plasma polymers were observed during the deposition on smooth substrates at certain deposition conditions (pulsed power delivered to the discharge or deposition in the afterglow regime). Drabik et al. [8] in their study reported a transition between smooth and nanotextured films of RF magnetron sputtered polytetrafluorethylene (PTFE) with increasing pressure and increasing distance between sputtered target and the substrate. The next reason for formation of nanostructured layers is the deposition on the substrate which is already nanostructured. This effect was demonstrated on hydrocarbon layers with a columnar structure [9]. Their deposition took place under a large angle on the substrate coated by Ti nano-columns.

Also the assumption of chemical uniformity of the films of plasma polymers is not necessarily fulfilled. For instance, Vasilev et al. [3] have shown that the chemical composition of deposited layers of plasma polymerized n-heptylamine and allylamine and their rate of growth may depend on the substrate material. It was shown in this study that the chemical composition of plasma polymers changes continuously with their thickness, until it reaches a stable value. Another study was performed by Micheltore et al. [4], who studied the growth of plasma polymerized n-heptylamine and allylamine on Si substrates. These authors demonstrated the gradient of the chemical composition

from the substrate to the surface of the thin film. An interesting method for measuring the chemical composition of the interface layer between the plasma polymer film and the substrate was shown by Chen et al. [5]. Plasma polymers from allylamine and 1-bromopropane were deposited on NaCl single crystal substrate and after the deposition they were delaminated from the substrate with double-sided carbon adhesive tape. In such way it was possible to measure the chemical composition of the bottom side of the plasma polymer film. The differences in the chemical composition between the interface layer and the surface of the plasma polymer thin film were reported.

The main aim of this study is to present the first results related to the investigation of properties of plasma polymerized polytetrafluorethylene (pPTFE) thin and ultrathin films in dependence on their thickness. The main attention is devoted to the determination of their chemical composition, wettability and barrier properties.

Experimental details

Deposition of plasma polymerized polytetrafluorethylene films

The experimental set-up schematically depicted in Figure 1 was used for the deposition of pPTFE films. It consists of a vacuum chamber of volume approximately 0.05 m³, which is equipped with a water cooled planar RF magnetron and pumped by rotary and diffusion pumps. As a target material a standard PTFE sheet (Goodfellow) of diameter 81 mm was used. The sputtering was done in an argon atmosphere of pressure 5 Pa. Applied RF power was 100 W. The distance between a RF magnetron and a substrate was 12 cm. Under these conditions the deposited pPTFE are smooth [10]. The substrate material used were polypropylene (PP) foils and Si wafers coated with amorphous hydrocarbon (a-C:H) film. The a-C:H coatings were prepared by plasma polymerization on the RF powered electrode in argon/n-hexane gas mixture. More details about deposition of a-C:H coatings can be found in [11].

Characterization of deposited samples

The chemical composition of prepared coatings was measured by X-ray photoelectron spectroscopy (XPS) using Al K α X-ray source (1486.6 eV, Specs) equipped with a hemispherical energy analyzer (Phoibos 100, Specs). The XPS spectra were acquired at a constant take-off angle of 90° with pass energy of 40 eV (wide spectra) and 10 eV (high-resolution spectra). Peak fitting of the high-resolution spectra was performed by using CasaXPS software. The XPS spectra were referenced to C–C/H peak at 285.0 eV.

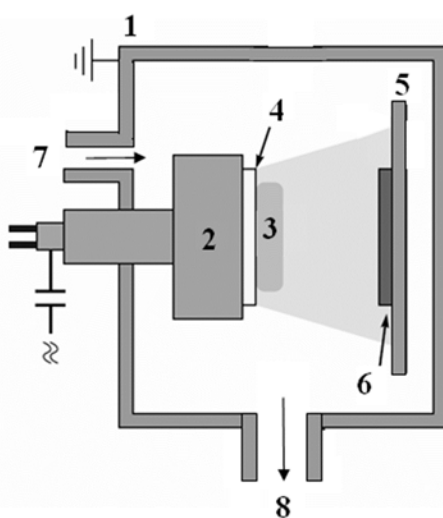


Figure 1. Schematics of the experimental set-up. 1 — vacuum chamber, 2 — water cooled magnetron, 3 — plasma, 4 — PTFE target, 5 — substrate holder, 6 — sample, 7 — working gas supply, 8 — pumping.

The thickness of deposited films was measured by spectroscopic ellipsometry (Woollam, M-2000DI). The static water contact angles of the films were determined by a sessile droplet method using home-build goniometer and computer software (SolariusWettability [12]). The barrier properties were measured by ExtraSolution MultiPerm single cell apparatus. Measurement was done at 0 % of humidity, temperature of 25 °C and a gas flow of N₂ 75 ml/min.

Results and discussion

Chemical composition

The first parameter studied was the surface chemical composition of RF magnetron sputtered fluorocarbon thin and ultrathin films in dependence on their thickness. The results for coatings deposited on PP foil are given in Figure 2, where high resolution XPS spectra of the C1s peak are presented, and in Table 1 where the XPS analysis results are summarized. For comparison, the spectrum of the PP foil substrate is also presented (thickness 0 nm).

As can be seen, the amount of various CF_x moieties increases with increasing thickness of pPTFE films. However, distinct changes in the chemical composition of the films with their thickness were observed. The most important change is in the relative abundance of –CF₃ functional groups: for example, whereas for the thickness of 2 nm was the ratio of –CF to –CF₃ bonds 3.25, for films with the thickness 20 nm this ratio was 1.21. In other words, XPS analysis proved that the chemical composition of the films deposited on PP foil is dependent on their thickness.

On the other hand, XPS analysis of pPTFE films deposited on the a-C:H surface revealed that the ratio of the relative abundance of different –CF_x functional groups is much less sensitive to the thickness of deposited pPTFE film (see Table 2). For instance, the ratio of –CF to –CF₃ changed from 1.4 for 2 nm thick pPTFE film to 1.2 measured in case of pPTFE thickness of 20 nm. However, it is important to note that in spite of differences in thickness dependence of surface chemical composition of pPTFE films deposited on to PP foil and a-C:H surface, the chemical composition of sufficiently thick films (≈ 20 nm) is very similar on both substrate materials. This suggests that the substrate material plays a role solely for very thin pPTFE films.

Water contact angle

The thickness of the plasma polymer film also affects the water contact angle (WCA) of the resulting surface, which is the key parameter in many applications [1]. From this point of view it is important to determine the minimal thickness of the fluorocarbon coating that assures stable value of WCA.

Table 1. Chemical composition of pPTFE films on PP foil.

Thickness of pPTFE film [nm]	CF ₃ [%]	CF ₂ [%]	CF [%]	C–O, C–CF [%]	C–C, C–H [%]
0	0	0	0	16	83
2	4	12	13	25	46
5	10	20	18	24	28
10	16	28	21	21	14
20	19	32	23	22	4

Table 2. Chemical composition of pPTFE films on a-C:H surface.

Thickness of pPTFE film [nm]	CF ₃ [%]	CF ₂ [%]	CF [%]	C–O, C–CF [%]	C–C, C–H [%]
2	5	9	7	10	69
3	7	14	10	15	54
4	10	18	15	18	38
12	17	24	22	22	15
20	20	30	24	24	3

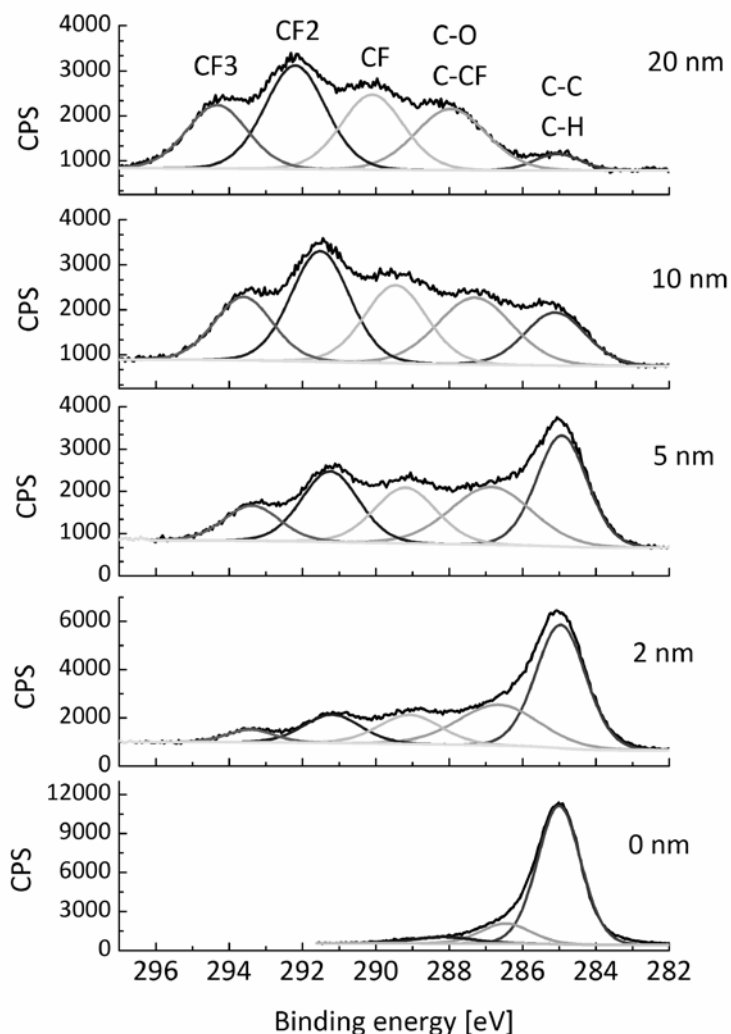


Figure 2. XPS C1s scan of pPTFE films on PP foil. The thickness of pPTFE films is indicated at the right side of the graphs.

Values of static water contact angle measured in dependence on the thickness of pPTFE coatings deposited on PP foil are presented in Figure 3. It was found that even the thickness of the film as low as 2 nm is enough for changing the WCA of the foil itself (around 80°) to the WCA typical for smooth fluorocarbon plasma polymer films (around 115° – 120°). When the thickness of the pPTFE film is further increased, the wettability of the resulting surface remains approximately the same. This result clearly shows that already ultrathin pPTFE coating is sufficient for changing the wettability of PP foils.

Barrier properties

The last parameter studied of thin pPTFE films was their barrier properties towards oxygen, i.e., topic important, for instance, in the field of food packaging. As can be seen in Figure 4, where are presented relative oxygen permeabilities, already the pPTFE film of the thickness 7 nm is enough to reduce the oxygen permeability of the PP foil to one third. Further increase of thickness of pPTFE coating has no significant effect on the barrier properties.

Conclusion

In this work we presented a short review of the state-of-the-art in the field of thin and ultrathin plasma polymer films. By means of XPS analysis of early stages of pPTFE films growth it was found that the chemical composition of such films depends both on the thickness of the film and on the substrate material. Confirmation of this result for other substrate materials is the subject of on-going studies.

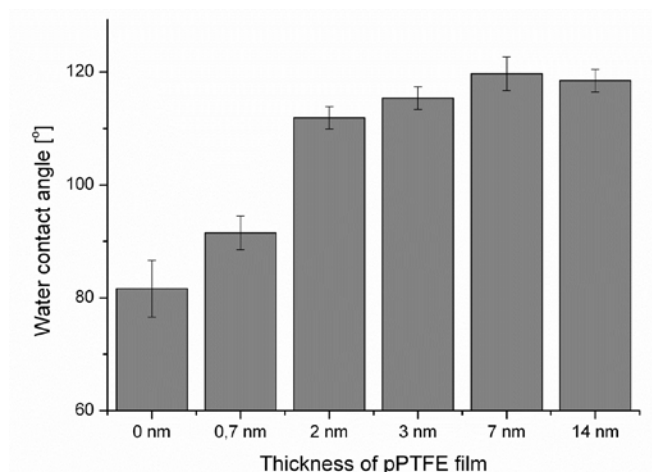


Figure 3. Water contact angle on PP foil coated with pPTFE films with different thickness.

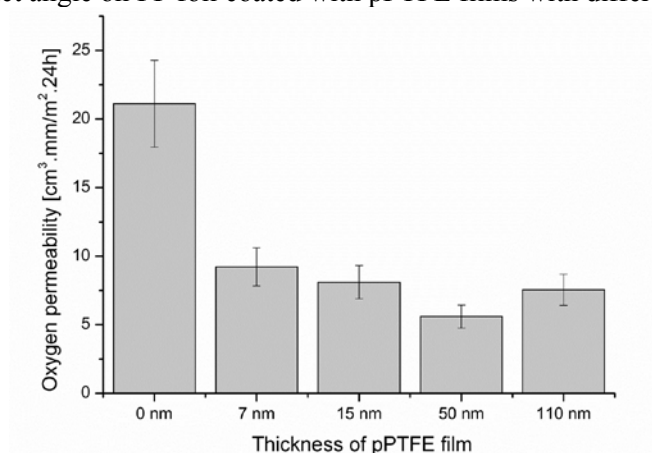


Figure 4. Barrier properties of PP foil coated with pPTFE films with different thickness.

In addition, two examples of properties of ultrathin pPTFE films were presented, concretely their wettability and barrier properties when they were deposited on to PP foil. In both cases it was shown that already very thin coatings with the thicknesses lower than 10 nm significantly decrease both the wettability and the barrier properties of PP foil. Moreover, it was demonstrated that further increase of thickness of pPTFE film does not lead to additional improvement of these two properties. This is an important result from the point of view of possible applications, since it shows that it is not necessary to deposit thicker coatings, which leads to both time and cost savings.

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