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Influence of plasma discharge on the structure of polytetrafluoroethylene film and step coverage on polymer substrate

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Abstract

Polytetrafluoroethylene (PTFE) films have been deposited onto polycarbonate (PC) substrates from the products of PTFE evaporation, activated by a cloud of accelerated electrons. A 40.68 MHz glow discharge was used during the deposition process. The polymer films have been characterised by XPS, FTIR and AFM. The use of the low power plasma during film growth led to the formation of PTFE films with modified structure. Films are amorphous and contain more cross-links, but in general, the structure of their macromolecules is still linear. An increase of RF-power leads to the formation of films with large amount of double bonds and enhanced internal stresses.

Deposition of PTFE on PC without plasma treatment led to the formation of PTFE clusters up to 50 nm in diameter. The RMS roughness of the films, deposited without plasma, was about 4 nm, while the films deposited with plasma treatment had a roughness of 1.5 nm. The use of plasma has an additional effect if a PTFE coating is deposited on the PC substrate with submicrometer-sized steps. Without plasma the steps retain a rectangular shape. Deposited with the RF-discharge the PTFE layers resemble plasma-polymerised films. Under certain conditions the deposited films can fill trenches in the substrate like a wetting liquid, while under other conditions they avoid trenches and grow in between them.

Keywords: Polytetrafluoroethylene; PTFE; Vacuum deposition; Plasma; Discharge; Film

1. Introduction

Low-*k* dielectric thin films and technology of their deposition is highly necessary for the semiconductor industry for the next generation of microchips [1]. PTFE is the best suitable material due to its excellent dielectric properties and stability. PTFE films can serve as dielectric, barrier and protective coatings in organic light emitting devices (OLED) and organic field effect transistors (OFET) [2,3]. The most promising use of PTFE is its application in the novel advanced research branch – plastic electronics on flexible polymer substrate. However, deposition of PTFE thin film is a difficult problem due to it is insolubility with any solvent. One way to deposit perfluoropolymer film is by plasma polymerisation of various perfluoromonomers [4,5]. Films deposited by means of plasma polymerisation are highly cross-linked and have no linear macrochains at all.

Gritsenko proposed film deposition from the products of PTFE thermal evaporation, activated by a cloud of accelerated electrons [6,7]. Under this action, the composition of the destruction products was changed. The concentration of the CF_3 and C_3F_5 fragments correlates well with film deposition rate. So the suggestion was made, i.e., these fragments are responsible for the film growth [5]. Although the origin of the transformations is still not clear, this mechanism of PTFE deposit growth was later confirmed by Wijesundara and co-authors [8]. Further modification of PTFE film properties can be done by non-self-sustained radiofrequency (RF) discharge [7].

The aim of the research is the modification of PTFE film growth on plastic substrate with RF discharge.

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2. Experimental

Research-scale vacuum deposition installation of VUP-5M was used. Films were deposited by evaporating bulk PTFE in vacuum and activating vapor using an electron cloud. Additional activation of both vapors and substrate surface was done using RF discharge. The discharge frequency of 40.68 MHz was chosen as it is suitable for PTFE vacuum deposition conditions. The higher the frequency, the higher electron concentration will be, and thus the lower their energy will be [5]. Such conditions are favorable for polymerisation. This method was described in detail elsewhere [7,9]. This method allows tuning of the PTFE film structure. Bare DVD polycarbonate (PC) disc (made by OTB Engineering) was used as a model of plastic micro-patterned (period is 800 nm) surface. Gold films were deposited using a tantalum boat. Homemade quartz microbalance thickness monitor (10 MHz) was used for determining film thickness.

Fourier transform infrared (FTIR) spectroscopy was carried out with a reflection mode using a Perkin-Elmer 2000 spectrometer. XPS spectra were recorded by SAGE 100 system with no chromatic radiation of Mg Kα anode. The surface relief of the films was studied using an atomic force microscope (AFM) operated in air at room temperature in a tapping mode (NanoScope IIIa Dimension 3000™). Mechanical properties of the PTFE films were tested using nanoindentation. A diamond tip with a 25 nm apex radius and 96° cone angle was applied. Hardness values were measured using both indent shape measurements and load–penetration curves (LPC) extracted from AFM force–distance curves.

3. Results

Plasma treatment does not significantly influence film growth rate, if substrate was placed between RF electrodes. Fig. 1 shows XPS spectra for PTFE films, deposited with and without optimal RF discharge, both between RF electrodes and on the electrode. XPS spectra reveal differences in the film structure.

Film grown between RF electrodes have a C_{1s} main peak at 293,2 eV, which is attributed to CF_2–CF_2 groups. Other peaks, related to end groups or cross-links, are present but at minor percentages. Oxygen is at less than 1%. The chemical composition of the surface of the films is like that of bulk PTFE. However, an increase of discharge power to 70 W led to the formation of classic plasma-polymerised deposit with a consequent shape of XPS spectrum. When a substrate was placed onto the RF electrode, film growth rate decreased proportionately to RF power. The sputtering of growing film was already not small at 20 W. At 70 W no film growth was detected at all. Therefore, at the same period, the thickness of the film deposited with RF plasma was thinner compared to the film deposited without plasma. Fig. 2 presents FTIR spectra of these films.

For all three spectra bands located near the next wavelengths: 526, 555, 640, 729, 1151, and 1213 cm^{-1} were attributed to 15_7 PTFE conformation [10,11]. The band near 980 cm^{-1} was assigned to $–CF_3$ groups, 1352 cm^{-1} to –C=C– groups. Increase of RF discharge power leads to 980 cm^{-1} and 1352 cm^{-1} bands relative intensity growth and therefore, increase of concentration of $–CF_3$ and –C=C– groups. The relative intensities of the 555, 625, 777 and 1150 cm^{-1} bands decreased. On the other hand, relative intensities of the 530, 703, 737, 738 and 1260 cm^{-1} bands increased. The content of the crystal phase decreased, while the content of the amorphous phase increased. The quantity of $–CF_2–$ groups was decreased. Electron diffraction patterns showed that the film deposited without plasma contains some quantity of the crystal phase, while films deposited with plasma are completely amorphous. More data about differences in the structure of these films were obtained by XPS. Fig. 1c presents the C_{1s} spectrum of the film grown on the RF electrode. Spectrum shows a main peak at 288.52 eV, which is attributed to unsaturated C=CF groups with fluorine deficit. The peaks at 285.8 eV, 284 eV and 282 eV are attributed to C=CF, C–C in fluorinated environment and hydrocarbons. The spectrum resembles well the spectrum of plasma-polymerised or sputtered perfluorocarbon film [4,12] and reveals a cross-linked and branched structure. The next conclusions have to be made for additional activation by RF discharge: 1 – films deposited with RF plasma on electrode have the structure like that of plasma-polymerised films; 2 – films deposited with low RF power between electrodes have a mainly linear structure close to that of bulk PTFE with minimal concentration of double bonds and branches.

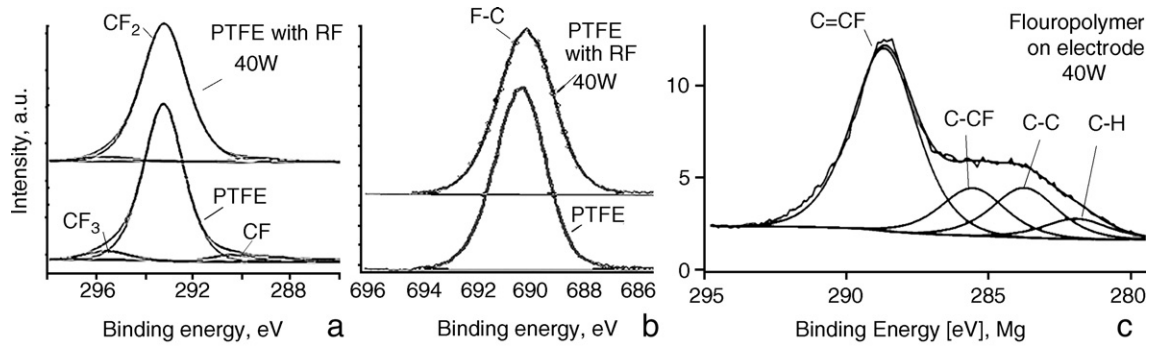

Fig. 1. C_{1s} and F_{1s} XPS peaks of PTFE films: a and b – PTFE films deposited between electrodes without and with 40 W discharge, c – perfluoropolymer film grown on RF electrode.