CHARACTERISATION OF SURFACE AND BULK PROPERTIES OF POLYMER-LIKE THIN FILMS PREPARED USING PECVD ON VARIOUS SUBSTRATES

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Abstract

The aim of the present work was to deposit thin polymer-like films fulfilling several criteria in order to enable their industrial application as protective coatings on various materials, for example plastic substrates. Therefore the films have to be stable, wear resistant with good adherence to the substrate materials and they have to be resistant against mechanical damage. The thin films presented in this work were prepared from mixture of hexamethyldisilazane and nitrogen using plasma enhanced chemical vapor deposition technique.

The silicon, glass and polycarbonate substrates were plasma treated in low pressure glow discharge using hydrogen or nitrogen discharge in order to increase the adhesion of the coatings to the substrates. An extended study of surface free energy on polycarbonate was carried out in order to find the optimum substrate surface treatment process before deposition of thin film. Once the process of pre-treatment was optimized, large number thin films was prepared with various mechanical and surface properties.

Keywords: PECVD, polycarbonate, glass, mechanical properties, TDS, XPS, HMDSZ

1. INTRODUCTION

Recently, there is a great industrial interest in the development of multi functional thin wear and scratch resistant coating deposition techniques [1-3]. One of the prospective industrial application areas is the use of theses techniques for development of protective coatings for plastics for example polycarbonates [4]. Polycarbonate (PC) substrates compared to glasses offer several advantages (fracture resistance, low weight, low cost, easy manufacturing etc.), however, their use is limited to relatively non-abrasive and chemical free environments, because of its low hardness, low scratch resistance and low resistance to aggressive chemical environments.

Plasma-chemical methods using radio-frequency discharges in mixture of organosilicon or organosilazane are often used to deposit protective coatings on plastic substrates [4-6]. Hard-coatings such as amorphous diamond-like carbon (a-C:H or DLC) deposited directly onto plastics may have performance problems when the system is subjected to stresses produced by mechanical or thermal effects. Polymer-like films prepared from organosilicon or organosilazane precursors may exhibit high hardness, high wear resistance and low friction coefficient similar to DLC coatings as well as good adhesion to polymer materials, low internal stress and high fracture toughness close to the properties of polymer materials. Silicon and nitrogen incorporated amorphous hydrogenated carbon materials have a great potential for solving some of the major drawbacks of pure DLC films, because they present reduced residual internal stress, high hardness, high deposition rates and good adhesion to PC. In the present work hexamethyldisilazane (HMDSZ) precursor was used to modify the properties of amorphous diamond-like carbon coatings.

2. EXPERIMENTAL PART

The films were prepared by means of plasma enhanced chemical vapor technology (PECVD) using low pressure r.f. glow discharge. The deposition reactor used consisted of glass cylinder 310 mm in diameter, 210 mm height, closed by two stainless steel flanges. The diameter of the graphite electrodes was 150 mm and distance between them was 55 mm. The bottom electrode was capacitively coupled to the r.f. generator

working on frequency 13.56 MHz [6]. The vacuum system consisted of rotary pump and diffusion pump. The working pressure depended on the gas mixture used and was kept around 17 Pa. Minimum pressure achieved by diffusion pump was 0.1 Pa. The flow rate of the hydrogen was kept at 0.7 sccm, the flow rate of the HMDSZ ranged from 0 to 0.4 sccm. The applied power was 50 W. The negative self-bias voltage changed from -100 to -250 V. The samples were prepared onto crystalline silicon, glass and polycarbonate substrates placed on the bottom electrode of the reactor. The atomic composition of the prepared films was studied using X-ray photoelectron spectroscopy technique.

A Fischercope H100 instrumented indentation tester was used to study the indentation response of the prepared films. Several different testing conditions were used in order to find the optimum procedure allowing the suppression of the substrate influence. The loading period of 20 s was followed by a hold time of 5s, an unloading period of 5 s and finished after holding the minimum load for 5 s. The tests were made for several different indentation loads in order to study the composite mechanical properties of the film/substrate system from near surface up to film-substrate interface. The applied load varied from 1 to 100 mN. Each test was repeated at least 9 times in order to minimize the experimental errors.

The internal stress was calculated from measurements of a bending curvature of single crystal silicon (111) strips coated with the studied films using the Stoney formula. The samples were subjected to heating with heating rate of 2 K/min. The temperature dependence of the bending curvature was determined using X-ray diffraction technique for both heating and cooling process. The films on silicon substrates were annealed in the laboratory furnace Classic Clare 4.0. The furnace chamber was evacuated by turbomolecular pump down to minimum pressure of about 10^{-5} Pa. The studied samples were subjected to heating with constant heating rates in the rage from 2 to 10 K/min [7]. The mass spectrometer Pfeiffer Vacuum Prisma 80 was set in order to follow the evolution in time of 8 specific masses. These specific masses are associated to the ions originated from desorbed gas mixture.

3. RESULTS AND DISCUSSION

A large set of films was prepared in order to find the optimum amount of HMDSZ in the gaseous deposition mixture enabling to prepare hard film with enhanced adhesion and minimized compressive stress. In order to extend the study on protective coatings deposited on polycarbonates, the surface treatment of polycarbonate was studied and optimized first to enhance the adhesion between the substrate and the deposited films. The hydrogen plasma treatment with 1 sccm of hydrogen and at applied power of 50 W lasting 1 minute was found to be the more effective. The total surface free energy was increased from 34 mJ/m^2 to 61 mJ/m^2. This value did not decrease even after 3 hour of storage. The time between the treatment and the film deposition was around 30 minute. The deposition conditions are listed in **Table 1**. For these depositions polycarbonate, glass and silicon substrates were used. In order to determine the composition of the deposited thin films, XPS analyses were carried out on samples prepared on silicon. On the basis of the XPS measurements it was found that carbon in these films is predominantly bonded to nitrogen, evidenced particularly by the broadened silicon peak towards higher energies. Both single and double bonds with nitrogen atoms occurred. On the other hand, carbon bonds to silicon can be considered as minor. From the asymmetry of the oxygen peak towards higher energies it is possible to assume the existence of numerous bonds with silicon, which is also evidenced by the silicon peak asymmetry. It can be concluded that the layer contains a large amount of silicon suboxides. In **Table 1** there are presented the results on film composition obtained from XPS measurements. These coatings were prepared at the same flow rates of hydrogen and methane while increasing the HMDSZ flow rate. The dependence of deposition rate v_{dep} on the HMDSZ flow rate Q_{HMDSZ} was approximately linear and it is possible to describe with the following formula: v_{dep}= (13 + 98.Q_{HMDSZ})nm/min. The film thickness was in the range from 500 to 1400 nm depending on the deposition time.

The mechanical behavior was studied using instrumented indentation method. This method enables the determination of the so-called universal hardness HU, which is the measure of the indentation resistance against plastic and elastic deformation. Comparing the universal hardness values, HU, of the uncoated and

coated PC substrates, it was found that by depositing the protective films, the hardness near the surface of the sample increased more than by one order of magnitude. Thin film hardness ranged from 15 to 22 GPa and the elastic modulus between 80 and 140 GPa. The dependence of the film hardness on the HMDSZ flow rate is given in **Fig. 1** and the dependence of the film elastic modulus on the HMDSZ flow rate is given in **Fig. 2.** Both the hardness and elastic modulus have decreasing tendency with increasing amount of HMDSZ precursor in the deposition mixture. However, both values are more than one order of magnitude higher, than that of the polycarbonate substrate (H = 0.2 GPa, E = 3 GPa).

Table 1 Summary of the varied deposition parameters (flow rate of HMDSZ Q_{HMDSZ} and negative self bias voltage U_b) and the resulted film atomic composition obtained by XPS analysis. The deposition power P was 50 W, the flow rate of methane was kept at 2.7 sccm, the flow rate of hydrogen was kept at 0.7 sccm

Sample	Q_{HMDSZ} [sccm]	U_b [sccm]	C [at%]	Si [at%]	O [at%]	N [at%]
N1	0.00	-260	81.7	0.4	10.6	7.3
N2	0.15	-216	79.5	2.4	13.4	4.7
N3	0.19	-201	68.8	6.8	16.8	7.6
N4	0.19	-160	69.1	7.1	16.6	7.2
N5	0.37	-249	59.6	9.6	22.1	8.8
N6	0.37	-213	64.0	8.4	19.7	7.9
N7	0.40	-195	57.2	11.0	21.5	10.2
N8	0.15	-206	71.5	5.2	16.9	6.3

The films prepared in this series generally presented relatively high internal stress. It had compressive character and ranged from -0.6 to -1.2 GPa. The thermal desorption experiments showed, that the annealing decreases the internal stress, the internal stress after annealing at 500 °C decreased to values near to 0 GPa.

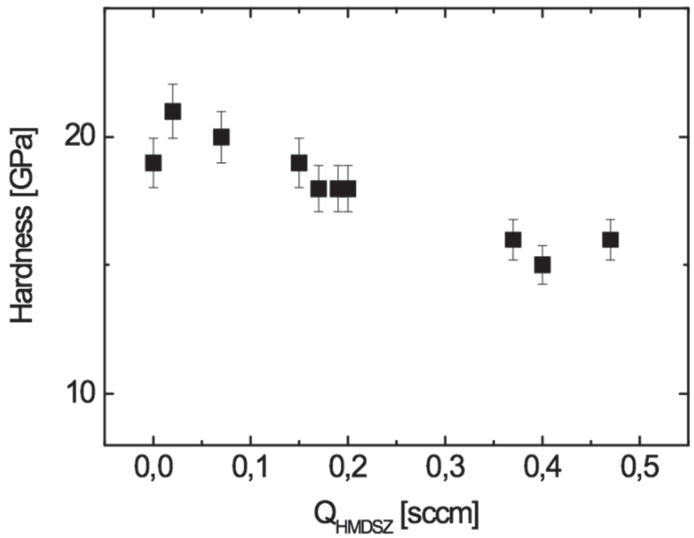

Fig. 1 The dependence of the film hardness on the flow rate of hexamethyldisilazane HMDSZ

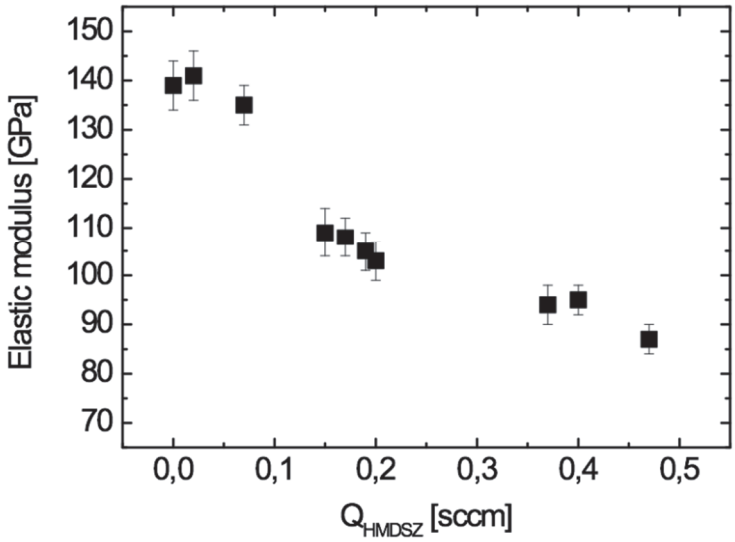

Fig. 2 The dependence of the film elastic modulus on the flow rate of hexamethyldisilazane HMDSZ

The thermal stability and the internal stress of films deposited on single crystal silicon substrate were studied using thermal desorption spectroscopy and X-ray diffraction technique, respectively. The relatively low compressive stress of the as-deposited films decreased during heating. The decrease in compressive stress with temperature was accompanied by desorption of H_2O, OH, CO and CO_2. **Fig. 3** shows the temperature dependence of hydrogen and hydrocarbon fragment desorption. The desorption peak around 550 °C corresponds to the start of the decrease in compressive stress. Further heating caused an increase in tensile stress and decrease in hardness and elastic modulus. These films were not delaminated or cracked after heating, however, during indentation testing showed less resistance against indentation induced cracking, than as-deposited films or films heated up to temperatures below 500 °C.

Fig. 3 present the desorption curves of several m/Z ratios for sample N8.

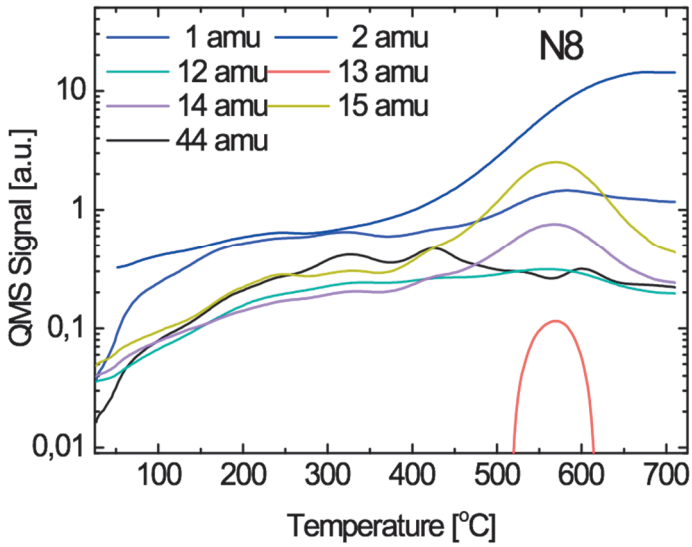

Fig. 3 Results of thermal desorption spectroscopy obtained on sample N8. The graph illustrates the temperature dependence of the desorption of carbon based species from the sample

The surface topography was studied on films deposited on silicon substrates. The films deposited with low amount of HMDSZ were very smooth and their roughness was almost the same as the roughness of the substrate. When the amount of the HMDSZ content increased in the deposition mixture, then some small organosilazane particles started to incorporate into the amorphous matrix and the surface roughness of the films increased. The values of surface roughness for sample in **Fig. 4** were Ra = 3.7±0.5 nm (Ra is average roughness) and Rq= 10.3±0.7 nm (Rq is root mean square roughness].

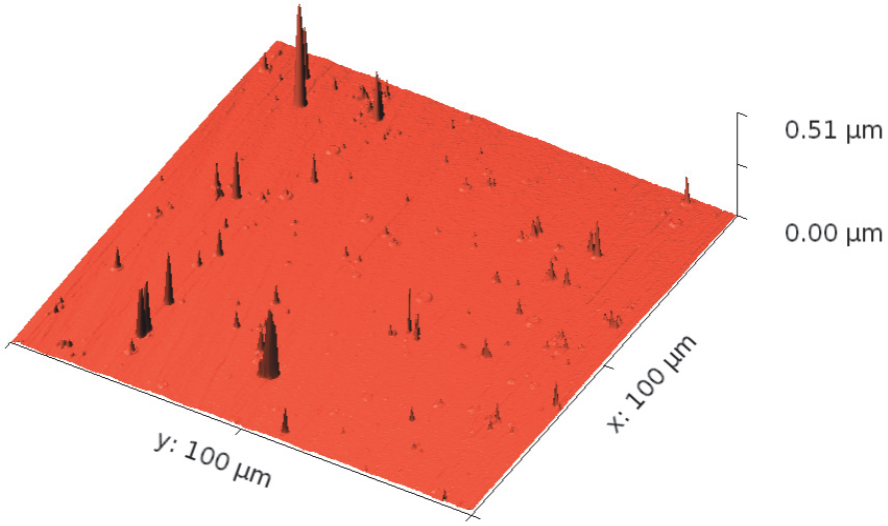

Fig. 4 AFM image of the sample prepared with HMDSz flow rate of 0.4 sccm

4. CONCLUSION

Plasma polymer films were prepared from mixture of methane, hydrogen and hexamethyldisilazane using low pressure r.f. discharges. Optimum deposition condition for deposition of smooth, hard, wear resistant thin films suitable for protection of the polycarbonate substrates were found. These films prepared under optimum conditions exhibited excellent fracture resistance and low intrinsic stress. The prepared films have all the properties needed for excellent protective coatings including high hardness, low friction coefficient, excellent chemical and thermal stability and transparency in the visible spectrum.

ACKNOWLEDGEMENTS

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