INFLUENCE OF DEPOSITION PARAMETERS ON MECHANICAL PROPERTIES OF SIO$_2$-LIKE PROTECTIVE COATINGS

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1. Introduction

Plasma enhanced chemical vapour deposition (PECVD) of silicon oxide thin films is of continuing interest due to numerous applications of these films, for example protective coatings on plastic materials [1, 2]. In the present work is investigated the influence of the deposition parameters on the mechanical properties of these coatings.

2. Experimental

Silicon dioxide films were prepared by PECVD from hexamethyldisiloxane (HMDSO) mixed with oxygen. The substrates used were silicon wafers, and polycarbonate (PC) plates. Plasma was generated in a parallel plate reactor capacitatively coupled to a generator at the frequency of 13.56 MHz.

Arrangement I. - The stainless steel wall surfaces of the reaction chamber formed the electrode at the ground potential. The gas feed was supplied into the reactor chamber from above by the stainless steel tube in the centre of the upper flange of the reactor. The distance between the powered bottom electrode and the upper flange was 11 cm. The end of the tube from the lower electrode was 6 cm.

Arrangement II. - The gas feed was supplied into the reactor chamber through the shower head upper electrode, which was grounded.

The microhardness measurements were made with a Hanneman (Vickers) microhardness tester in connection with Zeiss-Neophot microscope. The morphology of the surface and the thin films was studied by the optical microscope and scanning electron microscope. The thickness of the films was measured by spectroscopic elipsometry.

Deposition parameters were systematically varied to estimation their influence on the film properties.

3. Results and Discussion

The differences in property characteristics of inorganic and plastic materials resulted in tangential stresses at the interface of the PC and the hardcoating and caused cracking of the coating. To improve adhesion and for minimisation of internal stress we deposited on the PC first an intermediate layer using only organosilicon compound without mixing oxygen. The deposition conditions are summarised in the following table.

Type	P [W]	$-U_b$ [V]	Time [min]	t [nm]	Type	P [W]	$-U_b$ [V]	Time [min]	t [nm]
A	100	65	15	123	F	400	115	15	337
B	200	55	15	222	G	100	55	25	261
C	200	80	20	325	H	200	95	25	445
D	300	90	15	277	I	200	125	15	436
E	400	150	15	316	J	100	90	80	1296

Table 1. *Deposition conditions for intermediate layers (rf power P, dc bias voltage U_b, and process time) together with film thickness t. The HMDSO flow rate Q_{HMDSO} and the pressure p was 4sccm and 1.3Pa respectively. (A - B : Arr. I., H : Arr. II .-electrode distance 2.5cm, I,J: Arr.II. - electrode distance 5.5cm.).*

No	Arr.	Q_{O2} [sccm]	Power [W]	U_b [V]	p [Pa]	Time [min]	t [nm]	v_d [nm/min]
1.	I.	45	100	-5	26.4	60	1123	18.7
2.	I.	45	250	-20	26.6	150	2699	18.0
3.	I.	45	450	-25	26.2	150	2930	19.5
4.	II.	56	250	-45	32.0	90	2043	22.7
5.	II.	56	100	-20	31.7	60	1626	27.1
6.	II.	80	100	-20	42.5	60	1706	28.4
7.a	II.	-	100	-75	1.3	15		
b		56	100	-20	32.0	60	1750	23.3

Table 2. *Deposition conditions for SiO_2-like films (deposition arrangement - Arr., oxygen flow Q_{O2} rf power P, dc bias voltage U_b, and process time) together with film thickness t and deposition rate v_d. The HMDSO flow rate Q_{HMDSO} was 4sccm.*

We found out a strong dependence of mechanical properties of the polymer layers prepared without oxygen on the deposition conditions. The increase in applied power and in negative bias voltage worsened the adhesion of this layers due to thermally induced stresses during cooling down from deposition to room temperature. When the applied power was higher then 300 W and the negative self bias voltage was higher then -130 V, spontaneous fracture of films took place and all films delaminated (layers E, F, see Table 1.). The decrease in the electrode distance had a similar effect on the properties of polymer films. The layer H, which also delaminated, was deposited at the electrode distance 2.5cm. Layers A, B, C, D, I and J were smooth and transparent and showed good adhesion. These layers were used as the intermediate layers before the deposition of the protection SiO_2-like coatings. The intermediate layers also protected the PC surface against damage with oxygen plasma.

The summarised deposition conditions for SiO_2 - like thin films are in the Table 2. We prepared several different composition of the polymer layers and of the SiO_2 - like thin films

The Vickers microindentation tests were carried out to study the mechanical properties of thin SiO_2 - like films, namely hardness, brittleness and adhesion. The hardness of all films was in the range 600-1000 HV, but due to low hardness of the PC substrate and of the intermediate layer it appeared only at very low applied loads and up to relative indentation depths D/t = 1, see Fig. 1. and Fig. 2.

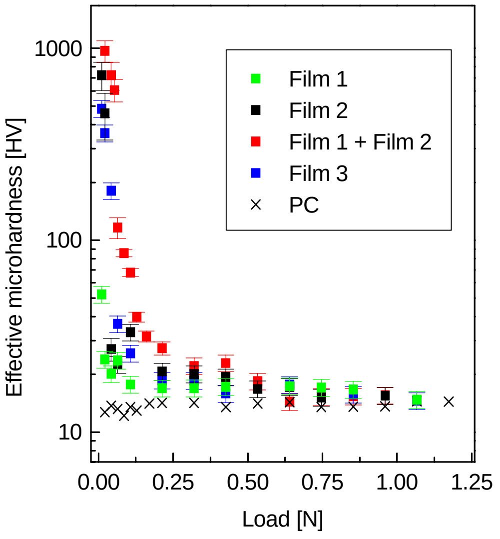

Fig. 1. Dependence of effective microhardness H_e on applied load L for films listed above in Table 2.

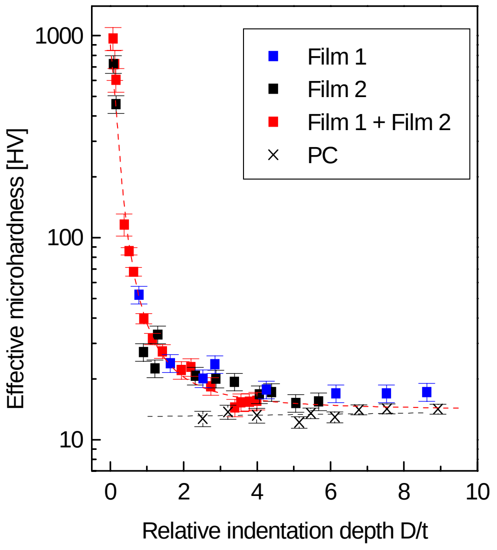

Fig. 2. Dependence of effective microhardness H_e on relative indentation depth D/t (D-indentation depth, t -film thickness) for films listed above in Table 2.

All films were very brittle and at the higher loads, the indentation surface damage was of wide range due to internal stresses in the interfacial layers. The composition of intermediate layer and the SiO_2-like film showed better adhesion than the films without intermediate layer.

4. Conclusion

Adherent protective coatings on polycarbonates were studied. To remove the interfacial stresses, polymer intermediate layer from pure HMDSO was first deposited on PC surface.

Input power, negative bias voltage and electrode distance were identified to be the decisive parameters determining the adhesion of the polymer intermediate layers.

Protective SiO_2 - like films were deposited from mixture of HMDSO monomer and oxygen on precoated polycarbonates with sufficient hardness (600 - 1000 HV) compared to the PC hardness of 14 HV. The composition of intermediate layer and the SiO_2-like film showed better adhesion than the films without intermediate layer.

Nevertheless, for practical application further increase is necessary to obtain sufficiently thick film in a reasonably short deposition time.

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