PREPARATION AND CHARACTERISATION OF CARBON FILMS PREPARED FROM HMDSZ/METHANE/NITROGEN OR HYDROGEN MIXTURE USING PECVD

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1. Introduction

Recently, there is a great industrial interest in the development of thin film deposition techniques improving the wear and scratch resistance of plastics such as polycarbonate. Polycarbonate (PC) substrates in contrary to glasses offer the additional advantages of lower cost, less chance of damage due to breakage, longer durability, manufacturing of lightweight products suitable for many applications in the growing market of large area displays, as well as a number of new product applications, such as compact disks, paper, cell phones and plastic electronics. PC is thermally stable in temperature range from –100 °C to +120 °C. However, its use is limited to relatively non-abrasive and chemical free environments, because of its low hardness, low scratch resistance and high susceptibility to aggressive chemical environments.

There are a rather limited number of methods for improving the scratch – resistance of plastics such as polycarbonate. Plasma-chemical methods are generally using radio-frequency discharges in mixture of hard-coating precursors for deposition of a very thin film directly on a PC substrate. However, hard-coatings such as amorphous diamond-like carbon (a-C:H or DLC) deposited directly onto plastics such as polycarbonate have performance problems when the system is subjected to stresses produced by mechanical or thermal effects. These problems are due to the difference in property characteristics of inorganic and plastic materials. There is a continuing interest in improving methods for forming hard-coatings having still greater abrasion resistance while also exhibiting improvements in various other physical properties1-5. It is therefore an object of the present work to study the indentation response of DLC films on PC substrates. Several different testing conditions were used in order to find the optimum procedure allowing the suppression of the influence of the time dependent indentation response of PC substrate. The loading period of 20 s was followed by a hold time of 5 s, an unloading period of 5 s and finished after holding the minimum load for 5 s. The tests were repeated at least 9 times in order to minimize the experimental errors.

The optical measurements were done with Horiba Jobin Yvon ellipsometer in the spectral range from 190 to 2100 nm at the incidence angles from 55° to 75°.

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⁻¹. 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⁻¹. 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 CH4/H2 deposition mixture enabling to prepare hard film with enhanced adhesion and minimised compressive stress. The dependence of the deposition rate on HMDSZ flow rate is shown in Fig. 1.

The film prepared in optimum conditions (0.4 sccm HMDSZ, 0.7 sccm H2, 2.7 sccm CH4, 17 Pa, 50 W, Ubias = −215 V) exhibited very interesting properties on PC substrate. The bulk concentrations of carbon, hydrogen, silicon and oxygen atoms, composing the prepared films were obtained by combination RBS and ERDA. The film with optimum mechanical properties consisted 65 at% of carbon, 18 at% of hydrogen, 8 at% of silicon, 5 at% of silicon and 4 at% of oxygen.

The mechanical behaviour was studied by DSI method enabling the determination of the so-called universal hardness $H_U$, which is the measure of the indentation resistance against plastic and elastic deformation. The comparison of the universal dependence on the indentation depth for uncoated and coated PC in Fig. 2 shows, that $H_U$ at the surface was increased of one order of magnitude by the help of the protective film.

There are some specific problems with interpretation of nanoindentation dates related to system of viscoelastoplastic substrate and hard film. Except elastic and plastic response these types of film/substrate systems exhibit a considerable time dependent plastic deformation, and may show also time dependent reversible (anelastic) behaviour. The prints done with low loads can heal out.
This effect was observed also in the case of our hard and elastic film on polycarbonate substrate, with prevalent viscoplastic properties. It is illustrated in Fig. 3, where the loading and unloading hysteresis obtained on the studied LD2 sample shows almost complete elastic deformation for loads up to 17 mN and indentation depths up to 900 nm. This depth almost corresponds with the thickness of the prepared film. Hence the system of HMDSZ modified DLC film on PC substrate exhibited the so-called “plate-bending model”6,7, i.e. the hard film on plastic substrate acted as a hard, elastic membrane with extremely high fracture toughness. Due to anelastic behaviour of sample LD2 the indentation prints made with loads lower than 30 mN disappeared after a short time, i.e. they were healed out.

The DSI method is a very powerful technique. It enables also the determination of the film fracture toughness and the interfacial fracture toughness4-8. If the studied sample undergoes some fracture events, part of the irreversibly dissipated energy is related to the creation and propagation of cracks and may be used for calculation of the fracture toughness. Moreover, the differential hardness \( H_{\text{dif}} \) (\( H_{\text{dif}} = k \partial L / \partial (h^2) \)), here \( L \) is the load, \( k \) is a constant value dependent on the indenter geometry and \( h \) is the indentation depth) dependence on the indentation depth may be used to visualise the crack creation or the penetration through film/substrate interface. The differential hardness \( H_{\text{dif}} \) represents the ratio of the instantaneous load increase to the corresponding change in the square of the indentation depth (i.e. change in contact area of the indenter and the tested material). Therefore, the abrupt changes appear on the depth dependence of \( H_{\text{dif}} \) as abrupt jumps. In Fig. 5 the depth dependence of \( H_{\text{dif}} \) for studied film/substrate system is shown. According to this graph the indentation induced failures at the interface began to create mostly at maximum load of 17 mN and at indentation depth of approximately 900 nm. Achieving this depth, which corresponded with the film thickness, the strong influence of the PC substrate on measured values started.

The maximum load may be kept constant during a certain time period and from the time dependence of the indentation depth it is possible to evaluate the indentation creep resistance of the tested material. In Fig. 6 the results of indentation creep are shown for three different indentation loads. The increase in creep strain for higher loads was caused by the increasing influence of the PC substrate. In Fig. 6 the SEM image of the indentation print made with load of 500 mN is shown. The SEM image demonstrates the high resistance of the sample against indentation induced cracking and delamination.

The thermal stability of films deposited on single crystal silicon substrate was studied using thermal desorption spectroscopy and X-ray diffraction technique.

![Fig. 5. Results obtained on study of indentation creep (time dependent plastic deformation at constant load) at several different loads.](image)

![Fig. 6. SEM image illustrating the high indentation resistance of the film against indentation induced cracking and delamination.](image)

![Fig. 7. Comparison of the thermal desorption spectroscopy results with the intrinsic stress dependence on the temperature for sample prepared from HMDSZ/methane/nitrogen mixture](image)
The compressive stress of the as-deposited films was relatively low, it was around \(-0.3\) GPa. The compressive stress decreased during heating and reached the zero value for temperatures around 300 °C. The decrease in compressive stress with temperature was accompanied with desorption of water, OH, CO and CO$_2$. The maximum in water desorption at around 300 °C corresponds to the start of the decrease in compressive stress. Further heating caused increase in tensile stress (see Fig. 7). The tensile stress of $\sigma = 0.1$ GPa remained in films even after cooling down to room temperature. The films were not deteriorated after heating, however during indentation testing showed less resistance against indentation induced cracking, than as-deposited films or films heated up to 300 °C.

4. Conclusion

We have deposited a large set of diamond like carbon films with incorporation of silicon, oxygen and nitrogen. The optimum deposition condition for deposition of smooth, hard, wear resistant thin films suitable for protection of the polycarbonate substrates were found. The film 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.

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REFERENCES