Plasma deposition of nanocomposite protective coatings on polymer substrates

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There is a continuing interest in improving methods for deposition of hard coatings having still greater abrasion resistance while also exhibiting improvements in various other physical properties. It is therefore an object of the present work to provide a method for forming protective coatings on the surfaces of plastics such as polycarbonates, having a high level of abrasion resistance, with improved resistance against cracking under exposure to thermal and mechanical stresses. Plasma-chemical methods are generally using a mixture of hard-coating precursors (e.g. organosililicon or organosilazane mixtures with oxygen in the case of transparent coatings) in a high-frequency or corona discharges and depositing the product directly on a plastic substrate as a very thin film. Using this method, thin films with a wide range of mechanical properties can be produced from hard inorganic SiO_2-like to soft polymerlike $SiO_xC_yH_z$ films properties just varying the plasma conditions. Moreover, under specific conditions films with special structures, such nanocomposite SiOCH or nanocomposite SiO_2-containing diamond-like carbon films may be prepared [1-3].

The main objective of the present work was to prepare protective films from hexamethyldisiloxane ($C_6H_{18}Si_20$- HMDSO) oxygen mixtures. These types of films are of particular interest in various applications because they exhibit a number of desirable properties: good adherence to polymer substrates, relatively high deposition rate, good transparency to visible radiation, good thermomechanical stability etc. The studied films were prepared by plasma enhanced chemical vapour deposition (PECVD) from HMDSO and oxygen with oxygen-to-HMDSO flow rate ratio ($q=Q_{O2}/(Q_{HMDSO}+Q_{O2})$) ranging from 0 to 0.95. The substrates were silicon wafers, glass and polycarbonate plates. Capacitive r.f. discharges (13.56 MHz) were generated in a parallel plate reactor. The HMDSO flow rate QHMDSO varied from 3 to 10 sccm, the oxygen flow rate was varied from 0 to 20 sccm. The working pressure was in the range from 1 to 40 Pa depending on q. The applied power P was varied from 50 to 150 W and the negative bias voltage was in the range from –10 to –300 V.

The optical properties of the films were studied using ellipsometer. The composition of the films was studied by FTIR, RBS and ERDA techniques. The instrumented indentation technique was used to study the mechanical properties of the films. The morphology of the film surface and the indentation prints was studied by means of Zeiss-Neophot optical microscope, a Nicon SMZ - 2T optical stereo-microscope, a Philips SEM 505 scanning electron microscope and by AFM. The surface energy of the deposited films was calculated from contact angle measurement using See System. Time of flight mass spectrometer equipped with nitrogen laser (337 nm) was used to characterize nanocomposite layers composition via laser desorption ionization (LDI) and/or laser ablation. The stoichiometry of positively or negatively charged species was confirmed via isotopic pattern simulation. The mass spectra of tested material obtained show mainly carbon spectral patterns similar to other carbon-containing materials such as diamond, carbon nanotubes, diamond like carbon, etc. but also several other positively or negatively charged $O_mSi_nC_oH_p$ species were observed.

Inorganic hard-coatings such as silicon dioxide (SiO_2) 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. We overcame these difficulties developing a very elastic film with nanocomposite character. In Figure 1 there is an example of loading-unloading dependence obtained nanoindentation test. We can see, that the tested film exhibited almost fully elastic behavior, at relatively high indentation depth there was almost no plastic deformation.

The deposition conditions suitable for nanocomposite film preparation were achieved due to relatively high HMDSO to oxygen flow rate ratio, which led to the creation of dusty plasma because of the relatively low applied power. The fragmentation of HMDSO molecules during this deposition process was low. The dissociative ionization of the HMDSO molecule and the electron attachment, followed by consecutive ion-neutral reactions led to the creation of high mass anions. These anions were trapped in the plasma and homogeneous reactions finally caused a growth of solid amorphous particles which were incorporated into the growing amorphous $SiO_xC_yH_z$ film. The composite character of the produced film improved its mechanical stability, however the particles embedded in the amorphous $SiO_xC_yH_z$ matrix increased little bit the film roughness as it can be seen on the Figure 2, were an example of AFM

image of the sample surface is shown. The surface energy studies showed that the films have hydrophobic and under optimum plasma conditions even ultrahydrophobic properties.

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References

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Figures

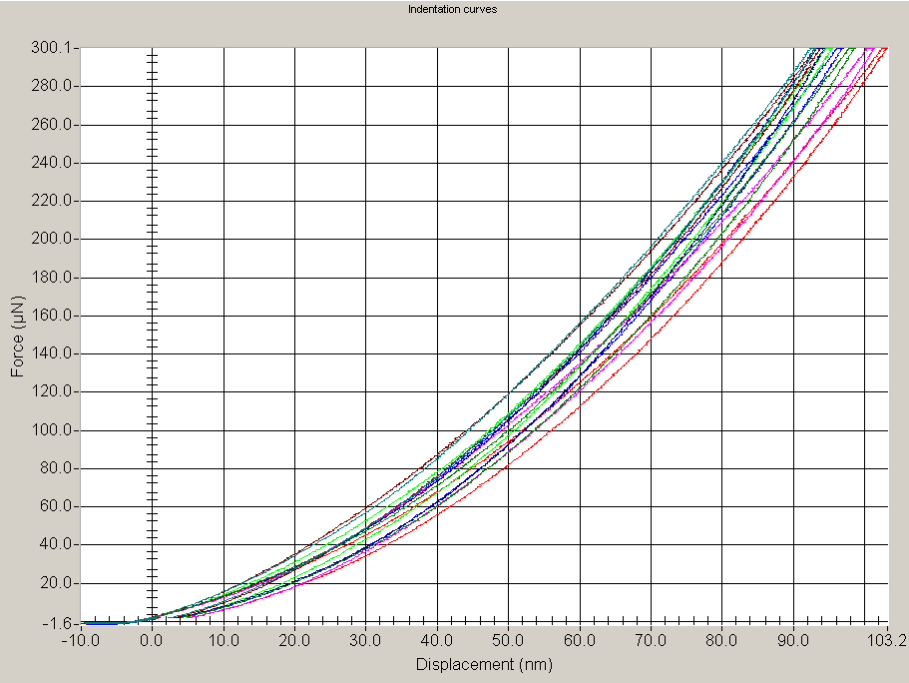

Figure 1 Examples of force-displacement curves obtained using nanoindentation with maximum force of 0.3 mN. Nanomechanical instrument Hysitron TI 950 TriboIndenter™ was used for testing the mechanical properties of the sample VI49.

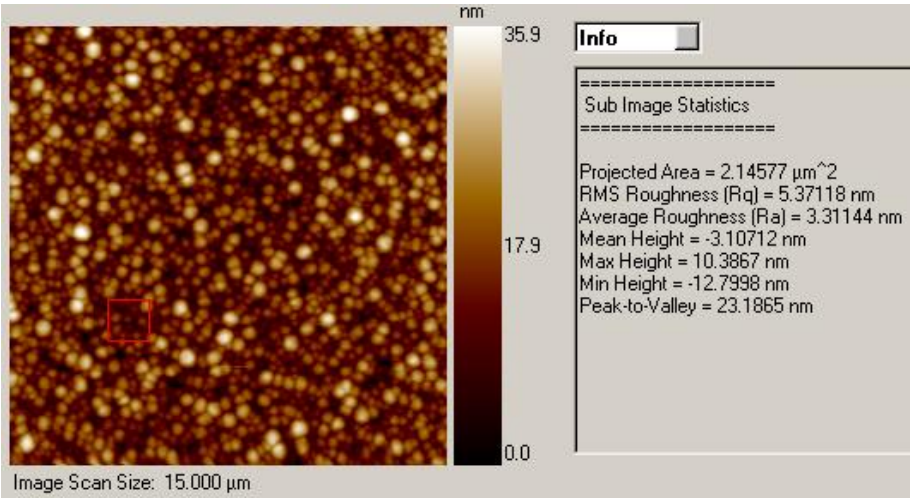

Figure 2 Example of SPM image of the film surface (sample VI49) with sub region roughness analysis indicated by the red square.