Effect of precursor flow rate on physical and mechanical properties of a-C:H:SiO$_x$ films deposited by PACVD method

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Abstract. In this paper the deposition of a-C:H:SiO$_x$ films by plasma activated chemical vapour deposition in a mixture of argon and polyphenylmethylsiloxane (PPMS) vapor with the impulse bipolar bias voltage applied to the substrate is presented. The paper discusses the dependence of the physico-mechanical properties of the deposited films on the flow rate of the PPMS precursor. The structure of the deposited films was determined by Fourier transform infrared spectroscopy and Raman spectroscopy. Mechanical properties characterization of a-C:H:SiO$_x$ films (hardness and elastic modulus) was made using the nanoindentation method. Hardness and elastic modulus were used to evaluate the endurance capability ($H/E$) and resistance to plastic deformation ($H/E^2$). The elastic recovery was calculated based on loading and unloading curves. It is shown that with an increase in the PPMS flow rate in the range of 35-287 µl/min, the films deposition rate increases from 17 to 221 nm/min. At this films mechanical properties, such as hardness, elastic modulus and elastic recovery did not deteriorate. The maximum values of the endurance capability and resistance to plastic deformation are obtained at a flow rate of 175 µl/min and equal to 0.12 and 203 MPa, respectively.

1. Introduction

Amorphous silicon-carbon (a-C:H:SiO$_x$) films have recently attracted considerable attention due to their wide range of technological uses. Typically, such films consist of two interpenetrating networks such as diamond-like a-C:H and SiO$_x$, which makes them a new class of diamond-like materials [1, 2]. The a-C:H:SiO$_x$ films have attractive mechanical, tribological, optical, and electrical properties, comparable with the diamond-like films characteristics [3-6]. One of the main advantages of these films is low internal stresses (less than 1 GPa), which allow forming films with a few micrometers tens thickness with good adhesion [7]. The most common method for the formation of a-C:H:SiO$_x$ films is plasma activated chemical vapour deposition (PACVD) with RF bias voltage. However the deposition on large area substrates makes the industrial application of RF PACVD processes difficult. From this point of view it is more advantageous to use impulse bipolar plasma technologies [8], because they allow working at higher power and without matching networks.

Santra et al [9] investigated the hexamethyldisiloxane (HMDSO) flow rate effect on the mechanical and optical properties of a-C:H:SiO$_x$ films deposited by RF PACVD technique. It is shown that there is an optimal precursor flow rate, at which the hardness reaches the maximum value (13 GPa). The maximum growth rate of the obtained films was 26 nm/min. Barve et al [10] also
studied the mechanical and optical characteristics of a-C:H:SiO$_x$ films formed by the RF PACVD method under different RF self bias (-25 to -225 V). Diamond like nature of films was enhanced with the RF bias. The maximum films hardness was 12 GPa, and the growth rate did not exceed 30 nm/min. Batory et al [7] have shown that depending on the amplitude of the applied substrate bias voltage (-200 to -800 V), the hardness varies from 5 to 17 GPa, endurance capability (H/E) increases from 0.08 to 0.15, resistance to plastic deformation ($H/E^2$) increases from 70 to 320 MPa. In this case, the deposition rate did not exceed 59 nm/min. Jedrzejczak et al [11] showed that the tribological properties of a-C:H:SiO$_x$ films formed by RF PACVD also depend on the oxygen and silicon content. Films with better tribological characteristics were obtained at a bias voltage of -600 and -800 V.

It can be concluded that the a-C:H:SiO$_x$ films properties depend on the many factors: deposition method, precursor composition (Si and O content), deposition parameters, such as substrate bias voltage, carrier gas (Ar) pressure, precursor flow rate. The purpose of this work was to investigate the dependence of the a-C:H:SiO$_x$ films physico-mechanical properties, prepared by the PACVD method with the use of polyphenylmethylsiloxane (PPMS) as a precursor, on the PPMS flow rate.

2. Materials and Methods
A plasma assisted chemical vapor deposition system, used to synthesize a-C:H:SiO$_x$ films, has been described in detail in [12]. It consists of a stainless steel vacuum chamber with oil-free pumping system and plasma generator working in a mixture of argon and polyphenylmethylsiloxane vapors. The plasma generator with a thermionic or so-called hot cathode is equipped with an electromagnetic coil used for additional plasma confinement, increase in plasma density and, consequently, increase the flow of ions bombarding the surface of the growing film. The tungsten filament used as the cathode of the discharge system was also used to heat and vaporize the liquid precursor.

Monocrystalline silicon (100) wafers with thickness of 0.5 mm and size of 20×20 mm$^2$ were used as substrates. The substrates were installed at a distance of 100 mm from the plasma generator. Before the films deposition, the substrates were cleaned with argon ions for 5 minutes. In this case, the working Ar pressure was 0.28 Pa and a bipolar bias voltage with a frequency of 100 kHz and the amplitude of the negative pulse of -1000 V was applied to the substrate. The amplitude of the positive pulse was 15–20% of the negative pulse amplitude and its duration was 4 µs. During film deposition, the working Ar pressure and the amplitude of the negative pulse of the bipolar bias voltage were reduced to 0.1 Pa and -500 V, respectively. PPMS was fed to the plasma generator with flow rates from 35 to 287 µl/min.

The obtained films were investigated by the Raman spectroscopy on the Centaur U HR complex to estimate the content of sp$^3$- and sp$^2$-hybridized carbon atoms in the film. The Raman spectrum was obtained using a 532-nm Ar$^+$ laser focused into a beam with a diameter of 50 µm and a power of 10 mW. The spectra were recorded in the range of 800–2000 cm$^{-1}$ with a resolution of 1.5 cm$^{-1}$. The hardness and elastic modulus of films were determined by the Oliver-Pharr method [13] with the help of NanoTest 600 nanoindenter (MicroMaterials, UK) at a load from 2 to 20 mN. The value of elastic recovery $W_e$ was calculated from the load/unloading curves. The Nicolet 5700 Fourier transform infrared spectrometer (Thermo Scientific) was used for the determination of functional group in the obtained films. The spectra were recorded in the range of 500–4000 cm$^{-1}$ with a resolution of 4 cm$^{-1}$ in the transmission mode. The atomic force microscope Solver P47 (NT-MDT, Russia) was used to study the surface morphology of the obtained a-C:H:SiO$_x$ films in semi-contact mode. The films thickness was determined using the Linnik microinterferometer MII-4 (LOMO, Russia).

3. Results and Discussion
In the experiments, the growth rate dependence on the PPMS flow rate was revealed, shown in figure 1. It can be seen that with the increase in the precursor flow rate from 35 to 287 µl/min, the films growth rate increases from 17 to 221 nm/min. The hardness and elasticity modulus of the obtained films were 14±0.8 and 123.5±6 GPa, respectively, and were weakly dependent on the precursor flow rate in a wide range of its values (figure 2). However, maximum hardness and elasticity...
modulus values of can be observed at a flow rate of 95 µl/min. Thus, increasing the PPMS flow rate increases the growth rate of a-C:H:SiO_x films by an order of magnitude without significant changes in their hardness.

Figure 1. The dependence of the growth rate of a-C:H:SiO_x films on the PPMS flow rate.

Figure 2. The dependence of hardness and elastic modulus of a-C:H:SiO_x films on the PPMS flow rate.

Elastic-plastic properties of deposited films can be characterized with the help of hardness and elasticity modulus values. The hardness to elasticity modulus (H/E) ratio, so called endurance capability or elastic strain to failure, usually used to estimate the resistance to plastic deformation (H/E^2). In order to obtain a material with high resistance to plastic deformation, H must be large, and E is small, i.e., the ratio H/E is large. The H/E^2 determines film resistance to wear, a high H/E^2 values mean a high film resistance to plastic deformation and, apparently, a high wear resistance [11]. The dependence of the endurance capability and resistance to plastic deformation of a-C:H:SiO_x films on the PPMS flow rate shown in figure 3.

Figure 3. The dependence of the endurance capability H/E and resistance to plastic deformation H/E^2 of a-C:H:SiO_x films on the PPMS flow rate.

It is seen that there is an optimal PPMS flow rate (175 µl/min), at which the endurance capability H/E and the resistance to plastic deformation H/E^2 of a-C:H:SiO_x films have maximum values of 0.119 and 203 MPa, respectively. For comparison, H/E and H/E^2 values of a-C:H:SiO_x films, obtained
in [7], varied between 0.12 and 0.15 and between 66 and 237 MPa, respectively, depending on HMDSO flow rate and self-bias voltage.

Another important solid films parameter is the elastic recovery $W_e$, expressed as a percentage. This parameter is calculated from the load/unload curves using the following formula:

$$W_e = \frac{h_m - h_f}{h_m} \cdot 100\%,$$

$h_m$ – the maximum indenter penetration depth under load, $h_f$ – the residual penetration depth of the indenter after load removal.

Elastic recovery $W_e$ shows how film recovered after its deformation. The elastic recovery variations of a-C:H:SiO$_x$ films deposited at different PPMS flow rates are presented in figure 4. Data are obtained for several loads on the indenter. It can be seen that at a relatively low load of 2 mN $W_e$ is more than 90–93%, i.e. the film is very well recovered after deformation. With increasing load up to 20 mN, $W_e$ is reduced to 73–78%. However, the obtained $W_e$ values are superior to those obtained in [7] for a-C:H:SiO$_x$ films, which do not exceed 67% for a load of 0.5 mN.

**Figure 4.** The variations of the elastic recovery $W_e$ of a-C:H:SiO$_x$ films deposited at different PPMS flow rates.

Figure 5 shows the loading /unloading curves of the obtained a-C:H:SiO$_x$ films. It can be noted that the curves for all films deposited at different PPMS flow rates overlap. This suggests that at increasing the PPMS flow rate, the films growth rate significantly increases, but their mechanical and elastic-plastic properties practically do not change.

To understand the changes in the films structure with increasing PPMS flow rate, the Raman and IR-Fourier spectroscopy results were analyzed. The location and intensity of D and G peaks in the Raman spectra are correlated with the ratio of sp$^3$/sp$^2$ hybridized carbon in diamond-like films, which determines their mechanical and electrical properties [14]. In amorphous carbon structure $\pi$-bond in sp$^2$-site controls the films electronic properties, while in sp$^3$-site, the $\sigma$-bond controls the films mechanical properties [15]. Consequently, the D and G peaks location reflects the physical properties of the films. In fact, the D and G peaks location can be shifted towards higher or lower energies due to the different films structure, Raman spectrometer light source, the Gaussian decompositions of the Raman spectra, etc. It is known that the G peak shift towards low energies and the the $I_D/I_G$ ratio decrease show an increase in the sp$^3$-hybridized carbon atoms in the film [16]. Figure 6 shows the Raman spectra of the obtained films.
Figure 5. Loading/unloading curves of a-C:H:SiO$_x$ films obtained at different PPMS flow rates.

Figure 6. Raman spectra of a-C:H:SiO$_x$ films obtained at different PPMS flow rates.

Figure 7. FT-IR transmission spectra of a-C:H:SiO$_x$ films deposited at different PPMS flow rates.

It is seen that with increase of PPMS flow rate, the $I_D/I_G$ ratio decreases, and G peak moves towards low energies, indicating increase of content of sp$^3$-hybridized carbon atoms in the film. In addition, the $I_D/I_G$ ratio, as well as hardness and elasticity modulus may decrease due to an increase in the Si content in the diamond-like carbon film [17]. Increased Si content leads to polymer-like structure formation.

According to the results of IR-Fourier spectroscopy (figure 7), in all obtained a-C:H:SiO$_x$ films there is a valence oscillation Si-O at wavenumbers 600±10 cm$^{-1}$ and 1070±10 cm$^{-1}$, which indicates a noticeable amount of oxygen primarily bonded to silicon. In addition, the valent oscillation of SiC fragments, located at wavenumbers 720±10 cm$^{-1}$ and typical for silicon incorporated carbon films, was
found. The silicon is also chemically bonded to hydrogen and forms Si–H group at 2100 cm\(^{-1}\) [18], which appears at high PPMS flow rates. There is a band of stretching vibration C=C with a center at 1445±10 cm\(^{-1}\). With an increase in the PPMS flow rate, the intensity of Si-C, Si-H and C=C bands increases, indicating an increase in the amount of corresponding bonds in the film.

4. Conclusion
In this paper the a-C:H:SiO\(_x\) films with a high value of the elastic recovery were obtained by method of plasma-assisted chemical vapor deposition at different precursor flow rates. With an increase in the PPMS flow rate in the range 35-287 \(\mu\)l/min, the deposition rate of a-C:H:SiO\(_x\) films is increased from 17 to 221 nm/min without significant deterioration of the mechanical properties of the films. In particular, the hardness of films is 14±0.8 GPa, the elastic modulus is 123.5±6 GPa, and the elastic recovery at a load of 2 mN is 90-93%. We believe that with an increase in the PPMS flow rate two processes occur during the film growth. On the one hand, the content of sp\(^3\) bonded carbon in film is increased, which leads to an increase in the film hardness. On the other hand, the silicon content in the film increases, which reduces its hardness. As a result of these processes, with an increase in the PPMS flow rate, the mechanical properties of the film vary insignificantly. The endurance capability \(H/E\) and the and resistance to plastic deformation \(H^3/E^2\) increase with PPMS flow rate increasing and reach a maximum of 0.12 and 203 MPa, respectively, at a flow rate of 175 \(\mu\)l/min.

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