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Effect of deposition conditions on optical properties of a-C:H:SiO_x films prepared by plasma-assisted chemical vapor deposition method

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ABSTRACT

The a-C:H:SiO_x films were deposited on glass substrates by plasma-assisted chemical vapor deposition from mixtures of argon and polyphenylmethylsiloxane vapor. Optical properties of a-C:H:SiO_x films were investigated by varying deposition parameters, such as Ar pressure and amplitude of negative pulse of bipolar substrate bias. Optical properties were determined using the transmission spectra *T(λ)*, measured in the spectral range 300–800 nm. It was shown that the integrated transmittance of a-C:H:SiO_x films in the visible wavelength range 380–780 nm is 69–89%, depending on the deposition conditions. On the basis of the transmission spectra Tauc optical band gap, wavelength of absorption edge and Urbach energy were calculated. The resulting films exhibit a wide range of properties including hydrogen content from 35% to 39%, optical band gap from 2.3 to 2.6 eV, wavelength of absorption edge from 477 to 537 nm and Urbach energy from 547 to 718 meV. The change in optical properties of a-C:H:SiO_x films is associated with a decrease in the size and concentration of graphite-like clusters in the films as a result of the enhancement of ion bombardment of a growing film with increasing of argon pressure and amplitude of negative pulse of bipolar substrate bias. The study of the optical properties of a-C:H:SiO_x films showed that they can be used as protective and antireflection films on optical instruments, in particular, on solar cells.

1. Introduction

Nowadays researchers are giving much more attention to develop new kind of thin films like a-C:H:SiO_x due to their unique mechanical, tribological and optical properties [1–4]. This film represents a new class of diamond-like materials and consists of two interpenetrating networks, one being a diamond-like carbon (a-C:H) network and the other a glass-like a-SiO_x network [5,6]. The a-C:H:SiO_x films in their performance characteristics are similar to those well-known undoped hydrogenated diamond-like carbon films (a-C:H, DLC). DLC films are useful as optical, antireflective and wear resistive films for IR optics due to their transparency in IR range [7]. One of the main advantages of a-C:H:SiO_x films in comparison with the DLC is low internal stresses (less than 1 GPa), which allow forming thick films of a few to a few tens of micrometers with excellent adhesion [8,9]. In general, the DLC film suffers from low thermal stability. The sp^3 bond converted to sp^2 at relatively lower temperature (300 °C) [10]. But, this type of bond conversion could

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be prevented by incorporation of Si which formed Si−C bond, as Si does not form sp^2 bonding, i.e. Si-doped DLC film stability increases [11]. In addition, a-C:H:SiO_x films can have a high transmittance not only in the IR wavelength region but also in the visible one. Therefore, they can be used as protective and antireflective coatings on optical instruments [12]. The a-C:H:SiO_x films can be deposited by different techniques like radio frequency and direct current plasma assisted chemical vapor deposition (RF and DC PACVD), thermally activated chemical vapor deposition, ion beam assisted deposition and have refractive index of 1.5–2.5 and band gap in the range 1.1–3.58 eV [1,12–17].

Santra et al. [18] investigated the influence of flow rate of hexamethyldisiloxane (HMDSO) based liquid precursor on mechanical and optical properties of a-C:H:SiO_x films, deposited by RF plasma enhanced chemical vapor deposition (PECVD) technique. It was shown that there is an optimal flow rate of HMDSO, at which the film hardness is increased to 13 GPa. Increasing the flow rate of HMDSO causes a shift in the absorption edge of the films toward low wavelengths, i.e. high photon energies. This improves the transmittance of a-C:H:SiO_x films at a wavelength of 550 nm to 70–75%. Randeniya et al. [1] investigated the influence of Si content for SiO_x–DLC films prepared using DC-PECVD method on optical properties of these films, in particular optical band gap. For films with Si concentrations up to 13 at.% band gap increases slowly from 1.1 to 1.5 eV. For higher Si concentrations (17–25 at.%), optical gap reaches approximately 2.9–3.4 eV. Barve et al. [13] studied the influence of RF bias on structure and properties of films formed using a capacitively coupled RF generated plasma of argon, methane and HMDSO gases. Characterization of deposited films by Raman spectroscopy indicated that sp^3-bonded carbon content in the films is increased with the RF self-bias values on the substrates and this improves the optical and mechanical properties of the deposited films. The resulting films have a refractive index in the range from 1.6 to 2.2, which varies depending on the deposition conditions. Meskinis et al. [19] investigated the effect of ion beam energy on properties of a-C:H:SiO_x films, prepared from HMDSO vapor by ion beam assisted deposition. It was shown that an increase in the ion energy from 350 to 800 eV leads to a decrease in the resistivity and band gap from $2\,10^{10}$ to $9.7\,10^7$ Ω cm and from 2.44 to 1.45 eV, respectively. Decreased optical bandgap and resistivity authors associate with the decreased sp^3/sp^2 ratio of the film as well as decreased atomic concentration of oxygen and increased concentration of carbon. Jana et al. [16] stydied the annealing effect on structural and optical properties of the a-C:H:SiO_x films, deposited by HF PACVD using a liquid precursor (2,3,4-triphenyl nonamethyl pentasiloxane). It was shown that the refractive index of the films increases gradually from 1.79 to 2.84 with annealing temperature due to out-diffusion of hydrogen from the films, breaking of Si−H and C−H bonds and formation of Si−C bonds. At high temperatures graphitization of the film also contributes to the refractive index increasing. The optical band gap defined by the Tauc method up to 400 °C initially increases from 3.05 to 3.20 eV and then decreases due to graphitization.

In this paper, the effect of argon pressure (p_{Ar}) and amplitude of negative pulse of bipolar substrate bias (U_{bias}) on the optical properties of a-C:H:SiO_x films were investigated. Films were synthesized by plasma-assisted chemical vapor deposition from mixtures of argon and polyphenylmethylsiloxane (PPMS) vapor. This technique has advantages over the conventional radio-frequency (RF) plasma methods because it is more adapted to industrial-scale applications. Understanding of how the differences in deposition parameters influence the resulting optical properties is requirement for the applications of these films into the industry.

2. Experimental

The a-C:H:SiO_x films were deposited on a 1.2 mm thick optical quality soda lime glass substrates (75 × 26 mm). A vacuum unit with turbomolecular pumping was used for the deposition of films. It was equipped with a plasma generator with a hot cathode operating in polyphenylmethylsiloxane vapor. PACVD deposition system has been described in detail in Ref. [4]. The substrates were attached to a conductive sample holder located 300 mm from the plasma generator. Before deposition of the films, the substrates were cleaned with argon ions for 6 min. In this case, the working pressure of argon was 0.28 Pa. A bipolar bias voltage was applied to the substrate with a pulse repetition rate of 100 kHz, negative pulse amplitude of 650 V, positive pulse amplitude of 15–20% of the negative pulse value and positive pulse duration of 4 μs.

Two series of experiments on the deposition of a-C:H:SiO_x films were carried out. The first one was performed by varying the argon pressure in the working chamber from 0.025 to 0.28 Pa at a constant flow rate of the liquid precursor (PPMS). The discharge current I_d was 6 A, and the discharge voltage U_d varied from 80 to 200 V, depending on the Ar pressure. The amplitude of the negative pulse of the bipolar bias voltage U_{bias} applied to the substrate was 100 V, since an absence of bias voltage results in the formation of a polymer-like structure of the film [4].

The second series of experiments was done with a change in the amplitude of the negative pulse of the bipolar bias voltage U_{bias} from 100 to 650 V. In this case, the Ar pressure was 0.025 Pa, the discharge current I_d was 6 A, and the discharge voltage U_d was 200 V. The temperature of the substrates during the deposition, as measured by the thermocouple, did not exceed 150 °C. The thickness of all films was 1 ± 0.2 μm.

The bonding structure of the deposited films was characterized using Raman spectroscopy. The Raman spectra were recorded using Centaur U HR spectrometer (Nano Scan Technology, Russia) with 532 nm wavelength. Raman spectra were recorded with a laser power of 10 mW and within a spectral range of 800–1800 cm^{-1} with a spectral resolution better than 1.5 cm^{-1}. For this purpose, films deposited on a monocrystalline silicon substrate were used.

UV–VIS spectrometer AvaSpec-2048 has been used for the measurement of optical transmittance of the a-C:H:SiO_x films in the wavelength range 300–800 nm. Integrated area under each spectrum was used to determine the integrated transmittance of films $T_{380\text{-}780}$ in the visible range, i.e., 380–780 nm. Subsequent calculations and estimates were based on absorption spectra converted from transparency spectra using the Beer-Lambert law. The band gap value was estimated using the Tauc's method, and the width of band tails of localized states in the band gap (Urbach energy) was determined using the Urbach's empirical rule. Thickness of the deposited films was measured by MII-4 interference microscope (LOMO Corp., Russia).