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Optical Properties of DLC:SiO_x and Ag Multilayer Films: Surface Plasmon Resonance Effect

Arvydas ČIEGIS *, Vitoldas KOPUSTINSKAS, Šarūnas MEŠKINIS, Andrius VASILIAUSKAS

Institute of Materials Science of Kaunas University of Technology, Baršausko 59, LT-51423 Kaunas, Lithuania

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Diamond like carbon films containing silicon (DLC:SiO_x) and „conventional“ hydrogenated diamond like carbon (DLC) films were deposited by direct ion beam using anode layer ion source. Ag films were grown by unbalanced direct current magnetron sputtering. Structure of DLC:SiO_x films was investigated by Raman scattering spectroscopy. In the case of DLC:SiO_x film deposited on Ag layer surface enhanced Raman scattering effect was observed. Optical properties of the different diamond like carbon and silver multilayers were studied. Annealing effects were investigated. Influence of the thickness of the diamond like carbon and Ag layers was investigated. Position of the plasmonic absorbance peak maximum of DLC:SiO_x and multilayers in all cases was redshifted in comparison with “conventional” diamond like nanocomposite films containing silver nanoclusters. It was explained by increase of the Ag nanoparticle size and/or increased probability of the oxidation of the embedded Ag due to the higher amount of oxygen in DLC:SiO_x film in comparison with “conventional” diamond like carbon film.

Keywords: diamond like carbon, diamond like carbon nanocomposite containing silicon oxide, silver, multilayer film, Raman spectroscopy, surface plasmon resonance effect.

1. INTRODUCTION

Surface plasmon resonance effect received considerable attention of the researchers due to the very broad range of the possible applications including different elements of the optical nanocircuits [1 – 4], selective photo sensors of the increased sensitivity [5], biomedicine [6] and photovoltaics [4].

Nanoparticles of the noble metals (silver and gold) are the most often used plasmonic materials. In this case silver nanoparticles as a plasmonic material have their own advantages over gold nanoparticles. Particularly higher intensity of the surface plasmon resonance can be mentioned [7]. It should be mentioned that oxidation resistance of the silver nanoparticles can be increased by using ultra-thin protective coating [8 – 10]. Alternative approach is to use plasmonic multilayer films, which can be grown by widely used physical vapor deposition methods compatible with semiconductor device fabrication technology such as magnetron sputtering [4]. Such plasmonic multilayers can be easier integrated into the different microelectronic and optoelectronic devices in comparison with nanoparticles synthesized by wet chemical methods. Usually insulator/metal/insulator and metal/insulator/metal multilayers are used [4]. In this case surface plasmon resonance is excited at the metal layer and insulator layer interface [4].

One of the prospective insulator materials in this case is diamond like carbon (DLC). It is amorphous allotrope of carbon consisting of the sp^3 bonded and sp^2 bonded carbon atoms [11, 12]. Hydrogenated diamond like carbon films in addition contain up to several tens atomic percent of hydrogen [11, 12]. DLC films are hard, wear and corrosion resistant, chemically inert and biocompatible [11, 12]. Optical and electrical properties of DLC films can be changed in a broad range [11, 12]. Position of the nanoparticle surface plasmon resonance peak can be controlled by setting appropriate nanoparticle shape, size and inter particle distance [4]. In the case of the plasmonic multilayer position of the plasmonic peak depends on the refractive index of the insulator layer [4]. It should be mentioned that refractive index of DLC films (at 632 nm wavelength) can be changed in 1.6 – 2.5 range while maintaining high optical transparency [11 – 14]. Optical transparency of the diamond like carbon films can be increased while reducing internal stress by growing diamond like carbon films containing silicon oxide (DLC:SiO_x) [13]. There are a lot of the studies on plasmonic properties of the diamond like carbon films containing silver nanoparticles (see e.g., [15 – 19]). However diamond like carbon and silver multilayer films are less investigated [20]. Particularly there are no studies on DLC:SiO_x and Ag multilayers or nanocomposite films. Therefore in the present research structure and optical properties of the diamond like carbon (or DLC:SiO_x) and Ag multilayers were investigated.

2. EXPERIMENTAL TECHNIQUES

In the present study hydrogenated diamond like carbon films were deposited by direct current ion beam deposition using anode layer ion source. DLC:SiO_x films were synthesized by using hexamethyldisiloxane ($(CH_3)_3SiOSi(CH_3)_3$ vapor and hydrogen gas mixture. „Conventional“ DLC films were grown for comparison purposes by using acetylene gas. Ag films were deposited by unbalanced magnetron sputtering of the silver target.

* Corresponding author. Tel.: +370-37-313432; fax: +370-37-314423.
E-mail address: *arvydas.ciegis@ktu.lt* (A. Ciegis)

Samples for the investigation of the optical properties were deposited on fused silica substrates, while samples for measurement of the Raman scattering spectra were grown on monocrystalline silicon substrates. For more information on fabricated and studied samples please see Table 1.

Table 1. Thickness of DLC and Ag multilayers investigated in the present study

No	Multilayer	d_{DLC}, nm	d_{Ag}, nm
1	DLC:SiO_x/Ag/DLC:SiO_x	53	10
2	DLC:SiO_x/Ag/DLC:SiO_x	52	5
3	DLC:SiO_x/Ag/DLC:SiO_x	52	5
4	Ag/DLC:SiO_x	52	5
5	Ag/DLC:SiO_x	27	5
6	Ag/DLC	28	5
7	DLC/Ag/DLC	26	5

Thickness of Ag (d_{Ag}) layers was controlled by using quartz resonator. Thickness of DLC (d_{DLC}) films was controlled by using deposition rate known from the previous studies [14] and setting appropriate deposition time. More information on deposition conditions, chemical composition and optical properties of DLC:SiOx films can be found in [14].

Raman scattering measurements were performed using a Raman microscope inVia (Renishaw) with 532 nm excitation. Integration time was 100 s, power was 0.3 mW, and grating groove density was 2400 grooves/mm.

Optical properties of the films were investigated using an optical spectrometer Avantes that is composed of a deuterium halogen light source (AvaLight DHc) and spectrometer (Avaspec-2048). The absorbance and reflectance of the films was analyzed in the wavelength region from 180 nm to 1100 nm.

3. EXPERIMENTAL RESULTS

Structure of DLC:SiO_x films deposited on Ag layer as well as DLC:SiO_x films deposited directly onto the monocrystalline silicon substrate was studied by Raman scattering spectroscopy (Fig. 1). It can be seen that shape of the spectra in both cases is the same. Raman scattering spectra are typical for diamond like carbon [11, 12] with peculiarities common for DLC:SiO_x films [13]. Particularly in all cases maximum of the main Raman scattering spectra peak is at the 1470 cm^{-1}. Such a shifting from the position typical for G peak of the conventional DLC film (~ 1530 cm^{-1}) can be explained by presence of the transpolyacetylene chains [13]. In the case of the Raman scattering spectra of DLC:SiO_x film deposited on Ag layer surface enhanced Raman scattering (SERS) effect can be seen: intensity of the Raman spectra of DLC:SiO_x film deposited on Ag layer is significantly higher than the intensity of the Raman spectra of DLC:SiO_x film deposited directly on Si substrate. Optical absorbance and reflectance spectra of the plasmonic multilayers were studied. It can be seen in Fig. 2 that in the case of multilayer DLC:SiO_x/Ag/DLC:SiO_x containing 10 nm thickness Ag interlayer, strong absorbance peak in 800 – 1100 nm range can be seen. However it can be seen in Fig. 2 a that reflectance of the multilayer in the same region is ~ 100 %. Thus it seems that this multilayer acts as perfect mirror in 800 – 1100 nm range. It is impossible correctly evaluate film absorbance due to such high reflectance.

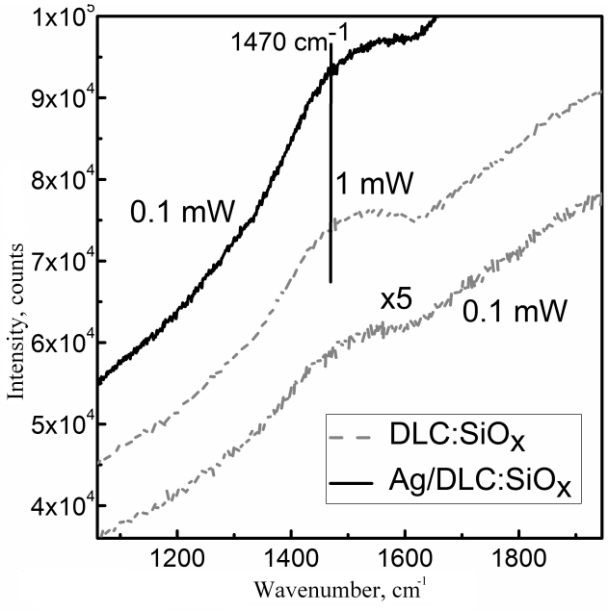

Fig. 1. Raman scattering spectra of DLC:SiO_x film and DLC:SiO_x/Ag multilayer

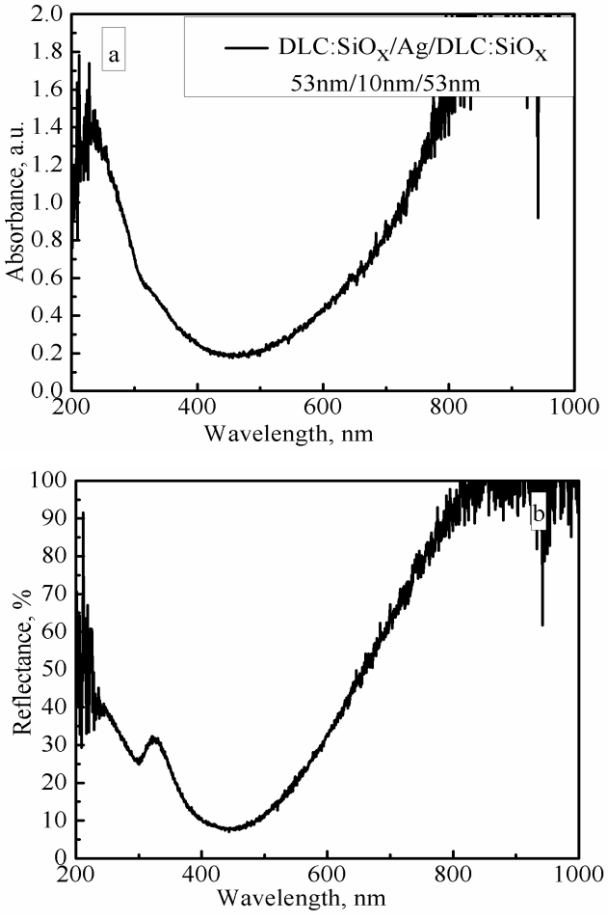

Fig. 2. Absorbance (a) and reflectance (b) spectra of multilayer DLC:SiO_x-Ag- DLC:SiO_x. Thickness of DLC:SiO_x layer is 53 nm, thickness of Ag film is 10 nm

In the following experiments thickness of Ag layer was decreased from 10 nm to 5 nm. It can be seen in Fig. 3 that in this case plasmonic absorbance peak redshifted.

However, reflectance of the multilayers significantly decreased and did not exceed 30 – 35 %. Thus in this case absorbance spectra measurement data was reliable. It can be supposed that in this case 10 nm Ag layer was continuous while 5 nm Ag layer was non-continuous and consisted of the nanoclusters. Such an assumption is in good accordance with [21]. According to [21] transmittance and extinction spectra of 5 nm thickness Ag film were similar to the respective spectra of silver nanoparticles with surface plasmon resonance peak, while transmittance and extinction spectra of 10 nm thickness Ag film were typical to the continuous silver films. In addition, in [22] there were shown that 5 nm thickness Ag films consist of the isolated nanometric islands. It can be seen in Fig. 3 that plasmonic peak redshifted in the case of Ag/DLC:SiO_x bilayers in comparison with the DLC:SiO_x/Ag/DLC:SiO_x multilayer. In the case of the bilayer films both absorbance and reflectance was lower in 180 – 500 nm range. It should be mentioned that decrease of the DLC:SiO_x layer thickness in Ag/DLC:SiO_x bilayer from 52 to 27 nm had no significant influence on absorbance and reflectance spectra of the bilayer films.

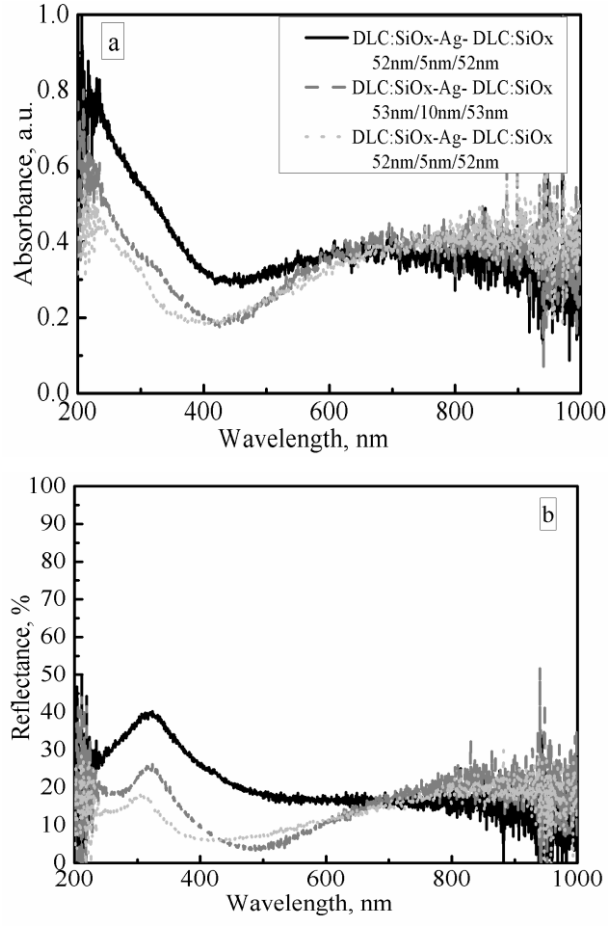

Fig. 3. Absorbance (a) and reflectance (b) spectra of multilayer DLC:SiO_x-Ag- DLC:SiO_x (thickness of DLC:SiO_x layer is 53 nm, thickness of Ag film is 5 nm) as well as Ag-DLC:SiO_x bilayers

Multilayers deposited by using DLC:SiO_x and "conventional" hydrogenated DLC films are compared in Fig. 4, Fig. 5. It can be seen that in the case of DLC/Ag/DLC multilayer film no clearly pronounced plasmonic absorbance peak can be seen. Probably it can be explained by higher absorbance of DLC film in comparison with DLC:SiO_x [14]. Alternative explanation would be differences of the Ag film growth modes on DLC and DLC:SiO_x surfaces. It can be mentioned that according to [23] minimal thickness of the continuous Ag film deposited on Ge layer is substantially than minimal thickness of the continuous Ag layer deposited on silicon dioxide. Surprisingly for DLC/Ag/DLC multilayer film some kind of the reflectance peak with maximum at ~ 850 nm can be seen.

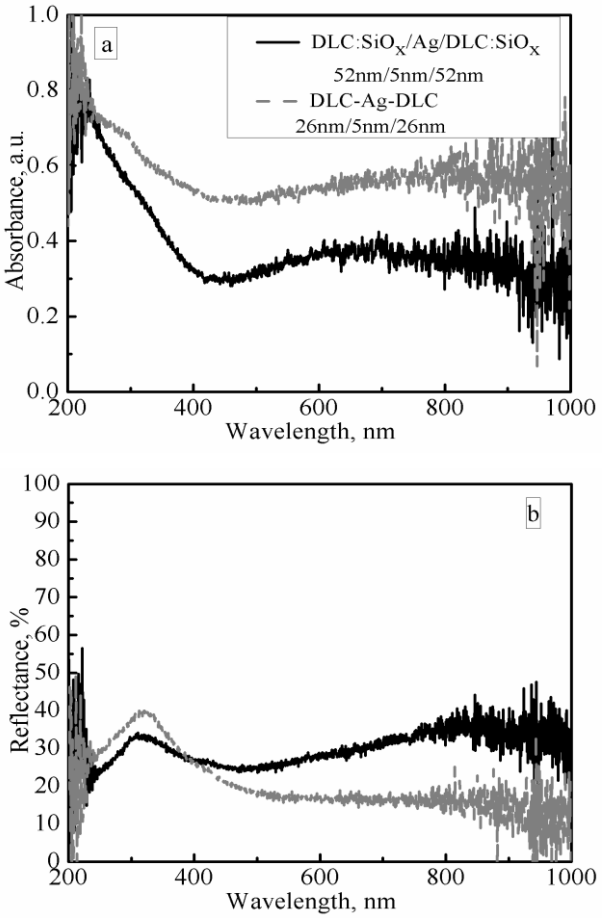

Fig. 4. Absorbance (a) and reflectance (b) spectra of multilayer DLC:SiO_x/Ag/DLC:SiO_x and DLC/Ag/DLC films

In the case of the bilayer Ag/DLC:SiO_x and Ag/DLC films plasmonic peak of the absorbance spectra of bilayer Ag/DLC film is redshifted and less pronounced in comparison with the case of Ag/DLC:SiO_x bilayer.

Annealing in air at 200 °C temperature of Ag/DLC bilayer resulted in appearance of the pronounced plasmonic peak with maximum in 550 – 600 nm range. It can be mentioned that vacuum evaporation of thin continuous Ag films followed by annealing results in the formation of nanoparticles in the form of islands [24, 25]. In addition, laser annealing of the ZnO/Ag/ZnO multilayer results in the formation of the Ag nanoparticles layer embedded between ZnO films [26]. Thus in our case it can be supposed that formation of the Ag nanoclusters took place as a result of the annealing, too. It should be mentioned that in this study in all cases position of the plasmonic peak maximum was at wavelengths > 600 nm.

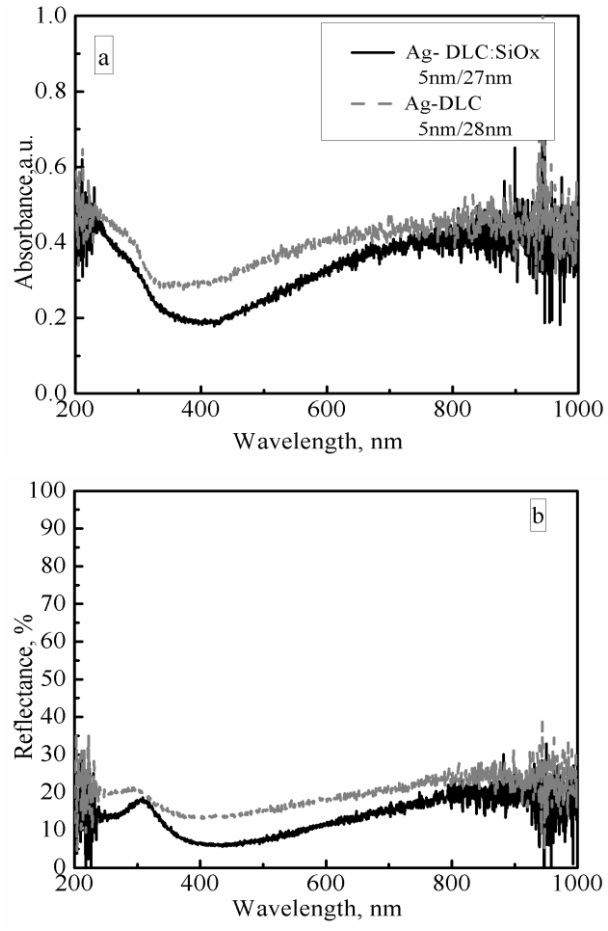

Fig. 5. Absorbance (a) and reflectance (b) spectra of bilayer Ag/DLC:SiO_x and Ag/DLC films

On the other hand, in the case of the DLC:Ag nanocomposites deposited by reactive magnetron sputtering position of the plasmonic peak was blueshifted. It was located at wavelengths < 500 nm [18, 19]. In addition in present study in all cases position of the plasmonic absorbance peak was located at the range of the higher wavenumbers in the case of the plasmonic multilayers fabricated by using DLC:SiO_x is in comparison with multilayers containing DLC. Thus in the present study plasmonic peak position is redshifted despite refractive index of DLC:SiO_x is lower than the refractive index of DLC [14]. There are two possible explanations of such behavior. Position of the surface plasmon resonance peak can redshift with increase of the Ag nanoparticle size [4]. Thus it can be supposed that size of the silver nanoclusters in the present study is higher than in [18, 19]. On the other hand, oxidation of the silver nanoparticles results in redshift of the plasmonic peak, too [19, 27]. In such a case use of DLC:SiO_x instead of the "conventional" DLC results in the increased probability of the oxidation of the embedded Ag due to the higher amount of the oxygen in the film. While in the case of the Fig. 6 oxidation of the silver nanoparticles can occur due to the annealing similarly to the [27].

4. CONCLUSIONS

Raman scattering spectra of DLC:SiO_x films deposited on Ag layer was typical for DLC:SiO_x films deposited directly onto the monocrystalline silicon substrate. In the case of the films deposited on both silver film and monocrystalline Si substrate maximum of the main Raman scattering spectra peak was at the 1470 cm^{-1}. Such a shifting from the position typical for G peak of the conventional DLC film (~ 1530 cm^{-1}) was be explained by presence of the transpolyacetylene chains.

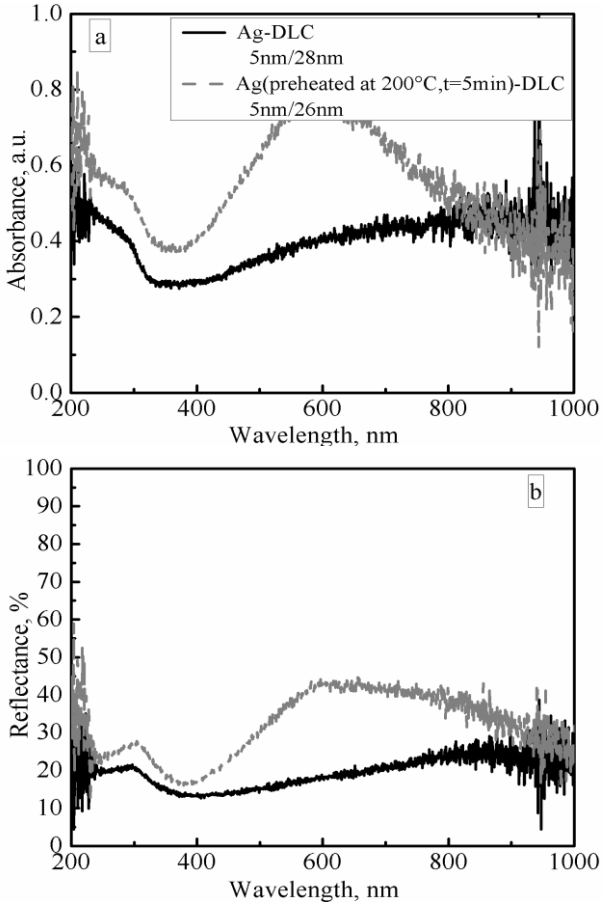

Fig. 6. Annealing effects on absorbance (a) and reflectance (b) spectra of bilayer Ag/DLC films

In the case of the Raman scattering spectra of DLC:SiO_x film deposited on Ag layer surface enhanced Raman scattering (SERS) effect was observed.

Study of the optical absorbance and reflectance spectra of the plasmonic multilayers DLC:SiO_x/Ag/DLC:SiO_x containing 10 nm thickness Ag interlayer revealed strong (~ 100 %) reflectance. Decreased of Ag film thickness to 5 nm resulted in substantially decreased reflectance. It can be supposed that 10 nm Ag layer was continuous while 5 nm Ag layer consisted from the nanoclusters. Air annealing at 200 °C temperature of Ag/DLC bilayer resulted in appearance of the pronounced plasmonic peak with maximum in 550 – 600 nm range. It can be explained by formation of the Ag nanoclusters as a result of the annealing.

In this study in all cases position of the plasmonic peak maximum was at wavelengths > 600 nm while in the case of the DLC:Ag nanocomposites deposited by reactive magnetron sputtering position of the plasmonic peak was located at wavelengths < 500 nm. Plasmonic peak position was redshifted despite refractive index of DLC:SiO_x is lower than refractive index of DLC. It can be explained by

increase of the Ag nanoparticle size and/or increased probability of the oxidation of the embedded Ag due to the higher amount of the oxygen in DLC:SiO_x film in comparison with "conventional" diamond like carbon C film.

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