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Effect of Silver Clusters Deposition on Wettability and Optical Properties of Diamond-like Carbon Films

E. Mohagheghpour*[a], M. M. Larijani[b], M. Rajabi[c], R. Gholamipour[c]

[a] *Radiation Applications Research School, Nuclear Sciences and Technology Research Institute, Tehran, Iran*
[b] *Physics and Accelerators Research school, Nuclear Sciences and Technology Research Institute, Tehran, Iran*
[c] *Department of Advanced Materials and Renewable Energy, Iranian Research Organization for Science and Technology (IROST), Tehran, Iran*

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ABSTRACT

In this study, the effect of silver clusters deposition was investigated on optical, wettability and surface properties of diamond-like carbon (DLC) films. Silver clusters and DLC films were deposited on Ni-Cu (70.4-29.6;W/W) alloy substrates by ion beam sputtering deposition (IBSD) technique. Optical and structural properties were measured using UV-visible spectroscopy and Raman spectroscopy, respectively. The wettability and surface free energy of films were determined by the contact angle (CA) measurements. Raman spectra of DLC thin film with 121±6nm thickness without accumulated Ag showed that the size of the graphite crystallites with sp^2 bands (L_a) was 3.36Å by the I_D/I_G ratio equal to 0.062 with large optical band gap equal 3eV extracted from Tauc relation. The results of the deposition Ag in the various ion beam energy between 0.6 to 2keV showed the Ag clusters were accumulated uniformity on the surface of DLC films at 0.9keV. The volume percentage of silver clusters was varied from 5.0±2.01 to 16.3±1.4. The variation was caused by controlling the screen voltage and the deposition time. The CA of the deposited films increases from 79°±2 to 95°±2 as well as the reflection values in the visible and near-infrared region due to the increase in the Ag concentration in the surface of DLC films; while the surface free energy decrease from 86±1 to 66±2mJ/m^2 and the optical transmittance is almost constant. Our results demonstrate that the deposition of silver particles on DLC films is potentially useful for biomedical applications having good hydrophobic characteristics without causing a destructive effect on the optical properties of DLC films.

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1. INTRODUCTION

Diamond-like carbon (DLC) film is an interesting protective coating for modifying the surface properties of biomedical implants [1-3] due to their excellent mechanical properties such as wear and corrosion resistance, low friction coefficient, excellent chemical inertness and biocompatibility [4, 5]. Also, due to the optical properties, DLC films have widespread application in optical lens, anti-reflection coatings for optical devices, photodiodes and electroluminescence devices [5, 6].

In medical implants, the chemical properties of a protective coating at the interface strongly affect the biological behavior of coating [7]. Thus, controlling the surface chemistry of an implant and investigation about effective factors on it, for producing a specific surface with a well-defined biological reaction, is very important. On the other hand, there are reports that hydrophobic surfaces are better than hydrophilic ones for coating medical tools such as medical guide-wire and protein absorption, platelet attachment and activation for cardiovascular applications [8].

Doped DLC films have recently attracted a lot of attention [9] because of the addition of the other elements into DLC can change the surface free energy. Among the large number of NPs investigated, Ag is a powerful antibacterial agent that increases surface hydrophobic properties, improves hemocompatibility [10-12] and enhances the electron field emission property with

*Corresponding Author Institutional Email: *emohagheghh@aeoi.org.ir* (E. Mohagheghpour)

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lowering the work function [13]. Ag incorporation in the DLC films reduces surface free energy [14, 15], decreases the residual stress, improve the wear performance [14-16], and promote faster biointegration of DLC films [17]. Although the surface modification of diamond like carbon film by silver (Ag:DLC) can solve some of the major drawbacks of pure DLC films, this process has a destructive effect on the transparency, optical and structural properties of these films [18] due to the decreasing of the fraction of sp^3 bonds in the carbon structure [14, 16]. Koutsokeras et al. [19] reported that by limiting the interactions between metal (Ag, Cu) and carbon during deposition can retain the transparency level of the hydrogenated diamond like carbon films.

So, it is valuable to find a process that improves the surface properties without changing the DLC film properties. In this research that follows our previous work [20]. We want to introduce a new method for modifying the surface properties of DLC thin films by depositing silver particles without optical properties disturbance.

Although, several researches have been investigated the deposition of silver particles, in the recent years, the synthesis of silver particles is usually done by wet chemical reduction starting from a molecular precursor containing Ag in an oxidized state [21, 22]. This method has several drawbacks such as the presence of impurities, high cost of synthesis process and weak adhesion of the obtained nano particles to the substrate [22, 23]. In addition, Liu et al. [24] have reported the use of silver nano particles to decorate the surface of graphene oxide. In order to enhanced catalytic applications Ag nanoparticles, Jeon et al. [25] and Lim et al. [26] dispersed Ag nanoparticles on graphene oxide nanosheets and reduced graphene oxide, respectively. So, there is lack of systematic studies about of Ag deposition on DLC film and investigation about of the relation between Ag concentration and surface properties of DLC film.

In the present study, we deposited silver clusters via ion beam sputtering deposition (IBSD) method directly on the surface of DLC films which were deposited on the Ni-Cu alloy and microscope slides for studying the optical properties of thin films. IBSD method has been used for silver particles deposition with excellent adhesion to DLC thin film which is a result of controlling energetic particles precisely by adjusting the particle flux, energy and incidence angle, independently [27].

We investigated the effect of Ag concentration on the surface of DLC films on the optical and wetting properties of DLC films deposited on Ni-Cu (70.4-29.6; W/W) alloy by IBSD method. The optical property, the wetting behavior and the surface free energy dependence on the Ag concentration and the existing relations are systematically determined.

2. EXPERIMENTAL

DLC thin films were deposited on the Ni–Cu alloy substrate by ion beam sputtering deposition technique. Nickel with a purity higher than 99% and copper with purity higher than 99.9% produced at Mes Sarcheshmeh (Rafsanjan, Iran) were used to make Ni-Cu (70.4-29.6; W/W) alloy by a vacuum arc remelting (VAR) furnace and were homogenized with four times remelting. After rolling, the samples were cut into pieces with an approximate size of 10 × 20 mm and 0.5 mm thickness, and then were mechanically wet ground, polished and smoothed with Al_2O_3 to get a finished mirror surface.
These substrates were cleaned ultrasonically with acetone, ethanol, and deionized water prior to film deposition.

The carbon source for deposition DLC films was a high purity graphite plate (>99%; 12 cm × 15 cm) produced by SGL carbon group. During the deposition process of DLC film, the pressure was kept constant at 2×10^{-5} Torr by introducing a high purity argon gas. Eight sets of DLC films were prepared under identical conditions. The accelerator voltage, the ion current, the substrate temperature and the deposition time were 2200V, 25 mA, 100 ºC, and 30 min, respectively. After that, for determining the appropriate parameters for depositing silver particles, the ion beam energy and deposition time were changed in the ranges of 0.6 to 2 keV and 10 to 90s, respectively. During the deposition of silver particles, the pressure and the ion current were kept constant at 2×10^{-5} and 10 mA, respectively.

The thickness of DLC films as a surface for deposition of Ag was determined by reflection measurement (AvaSpec-2048). The AFM was operated in a tapping mode (DME dual scope DS 95, Danish Micro Engineering, Herlev, Denmark) with a scan rate of approximately 3 Hz and 0.1 nN force in the typical scan area of $1\times1\mu m^2$. The surface roughness of Ni–Cu alloy substrates was measured by the portable surface roughness tester (TR 200, Time Instruments, Beijing, China). The Raman spectra were measured using the 785 nm excitation wavelength of Nd: YLF laser with a power of 30 mW. The optical properties of DLC films were obtained by simultaneous deposition of the films on the glass substrate (microscope slides). The optical properties were investigated from the reflectance and transmittance data using a UV/visible spectrophotometer (Cary 500, Varian, Palo Alto, and California). The optical microscope (Olympus BX_60), a field emission gun SEM (MIRA3\\TESCAN) and scanning electron microscopy (VEGA\\TESCAN-LMU, RONTEC) was employed to evaluate the amount and manner of Ag accumulation on the surface of DLC thin films. The amount of Ag on the DLC films was determined by energy dispersive spectrometer (EDS;

VEGA\\TESCAN-LMU, RONTEC). The wetting test was carried out at room temperature by using a contact angle-measuring device (CAM). The contact angle (CA) was determined from digital images taken by a $DFK_{23}U_{618}$ $USB_{3.0}$ color industrial camera with the help of an a_2X lens. An open-source image processing software, ImageJ1.46v, was used to measure contact angles.

3. RESULTS AND DISCUSSION

Figure 1 shows the Raman spectra of DLC film deposited on the Ni-Cu (70.4-29.6; W/W) alloy and the glass substrate. The average surface roughness of the Ni–Cu alloy substrates was 272± 20 nm before the coating. The accelerator voltage, the ion current and the substrate temperature were 2200V, 25 mA, and 100 ºC, respectively. The deposition time was 30 min that generated a DLC thin film with 121±6 nm thickness.

The Raman spectra of the carbon film are mainly composed of two broad peaks that are associated with D and G peaks. The D peak contributed to the disordered graphitic carbon and G peak contributed to the graphite carbon in aromatic (rings) and olefinic (chains) molecules [2, 28].

The spectra were deconvoluted by Gaussian functions to determine the I_D/I_G ratio, as well as D and G peak positions. The data extracted from the Raman deconvolution of DLC film on Ni-Cu alloy and glass substrate are reported in Table S1. It is observed that the integrated intensity ratio I_D/I_G increases from 0.062 to 0.072 while the G peak band shifts from 1577.9 to 1541.7 cm^{-1} due to DLC film deposition on the Ni-Cu alloy and glass substrate, respectively.

According to amorphization trajectory proposed by Ferrari and Robertson [29], structural evolutions from graphite to diamond consist of three stages. When the I_D/I_G ratio is very small and the decrease in the I_D/I_G ratio associated with the G peak band shifts to the greater values, the structure changes from amorphous carbon to DLC. Therefore, in this research, the structure of the deposited film is diamond-like amorphous carbon with large optical band gap (3 eV) extracted from Tauc relation [2, 30] (Figure 2).

On the other hand, according to this trajectory [29], in very low I_D/I_G ratio, there exists a simple relation between the I_D/I_G ratio and optical band gap given in Equation (1):

$$\frac{I_D}{I_G} = \frac{C''}{E_g^2} \quad (1)$$

According to the Raman deconvoluted spectra, since the integrated intensity ratio I_D/I_G is very low- with a small increase from 0.062 to 0.072 which is due to deposition of DLC film on the Ni-Cu alloy and glass substrate, respectively. We can use this equation for predicting the evolution of optical properties of deposited DLC thin film on the Ni-Cu alloy by the optical properties study of the deposited DLC thin film on the glass substrate.

The surface free energy is an important parameter in controlling the adsorption, wetting and surface adhesion of DLC film that depends on the amount and nature of surface bonds. This parameter can be determined by the CA of a surface [31]

Here, we investigated the effect of silver accumulation on the wettability properties of DLC thin film. With the deposition of Ag at 2keV ion beam energy, a continuous thin layer was formed. The microscopic images of accumulated clusters at 1.2 keV ion beam energy (Figure S1) show high percentage coverage of the surface of DLC film by silver clusters with a diameter of about 50-100 microns. In addition, according to FESEM images of deposited Ag at 0.6 keV ion beam energy (Figure S2), the accumulation of SNPs was done only in the surface defect regions that have higher energy levels in comparison with the other parts of the deposited layer. Therefore, the investigation was done at 0.9

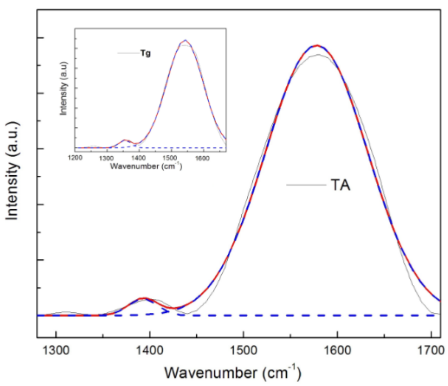


Figure 1. Raman spectra of DLC films deposited on Ni-Cu alloy (TA) and glass substrate (Tg),(ion beam energy, Gussian fit peak, deconvoluted peaks)

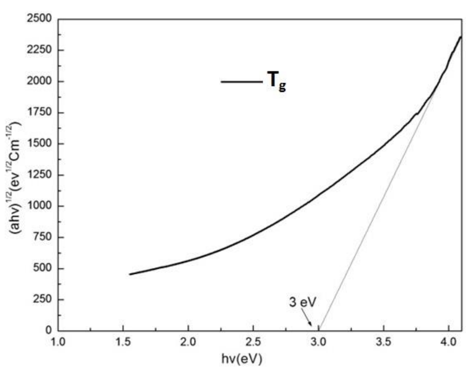
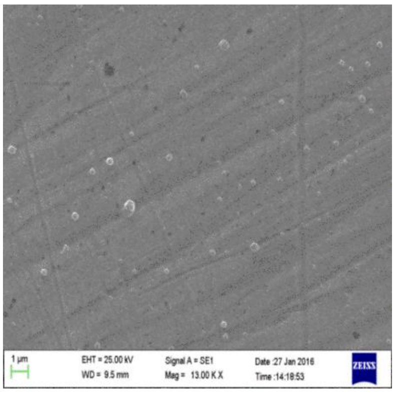


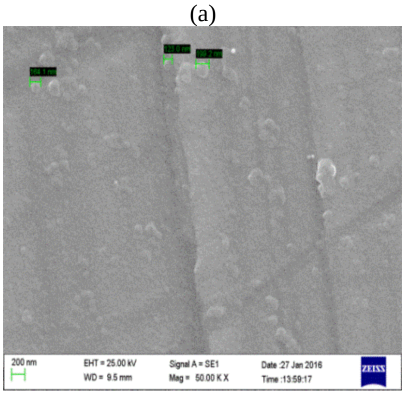
Figure 2. Tauc plot to determine the optical band gap of DLC thin film without accumulation of silver nanoparticles (SNPs)

keV ion beam energy in different deposition times ranging from 10 to 30 s (Figure 3).

Figure 4 shows the profile of the distilled liquid water drop and its contact angle on the DLC thin films as a function of Ag weight percentage in the surface. The corresponding values of the contact angle are presented in Table 1. The CA measurements indicated that the hydrophobicity of the DLC films increased with the silver clusters deposition on its surface.



(a)



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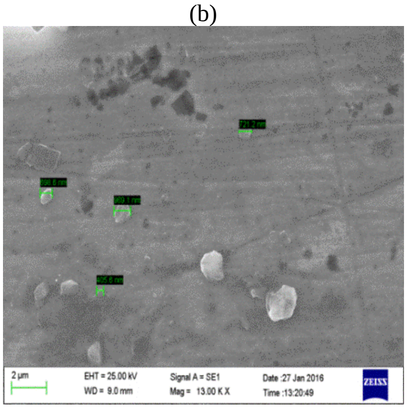

(c)

Figure 3. Scanning Electron Microscopy (SEM) image of accumulated SNPs at 0.9 keV ion beam energy (a) after 10s deposition time (T_A-Ag_{10}) with magnification13KX and 40 KX, (b) after 20s deposition time (T_A-Ag_{20})with magnification13KX and 50 KX, (c) after 30s deposition time (T_A-Ag_{30}) with magnification13KX and 40 KX

Since a hydrophobic surface usually has a contact angle higher than 70°, while a hydrophilic surface has a contact angle lower than 70°[32] and CA of the uncoated substrate (Ni-Cu alloy), shown in our previous work, is around 62° [20], this surface has the hydrophilic nature before coating. By DLC coating of the substrates, the hydrophobic property is induced to the surface due to the hydrophobic nature of the amorphous carbon films [33]. By depositing Ag clusters on the surface of DLC films, the value of the CA will vary between 79°±2–95°±2 by increasing the volume percentage of Ag from 5.0±2.01 to 16.3±1.4%.

The surface free energy can be calculated using Young–Dupre Equation (2) [34]:

$$E = \gamma(1 + \cos\theta) \quad (2)$$

where γ is the surface tension of water at 20°C (γ = 72.8 mJ/m^2), and θ is the contact angle (∘).

The volume percentage of the DLC films covered by Ag clusters was calculated by image analysis software (Table 1). In addition, the weight percentage of Ag calculated by EDC analysis is reported in Table 1. As expected, the volume percentage and the weight percentage of Ag increase in the surface by increasing the deposition time of SNPs.

The result of calculating surface free energy by Equation 2 shows that the surface free energy decreases with the increase in the volume percentage and the weight percentage of Ag due to the increase in the deposition time on the surface of DLC film (Table 1).

When silver nanoparticles or silver ions accelerate towards the substrate, they first accumulate in high-energy areas of the surface. FESEM images of silver nanoparticles on the surface of DLC thin films (Figure S2) confirm this phenomenon. Therefore, with the accumulation of particles in high-energy areas, the reaction centers (dangling bonds) decrease on the surface, and as a result, the surface free energy decreases.

Since any factor that reduces the surface free energy of the interface increases the wetting angle and hydrophobic property [35, 36], hence, the increase in CA caused by silver particles deposition on the surface of DLC thin films is explained. This trend continues with an increase in concentration of Ag to a point that CA reaches

TABLE 1. The contact angle (CA), surface free energy, weight and volume percentage of accumulated Ag extracted from EDS analysis

Sample code	Contact angel (°)	surface free energy (mJ/m^2)	Weight percentage (%)	Volume percentage (%)
T_A	74°±1	92±1	0.00	0.0
T_A-Ag_{10}	79°±2	86±2	0.29	5.0±2.01
T_A-Ag_{20}	87°±1	75±1	0.37	7.4±0.35
T_A-Ag_{30}	95°±2	66±2	0.57	16.3±1.4

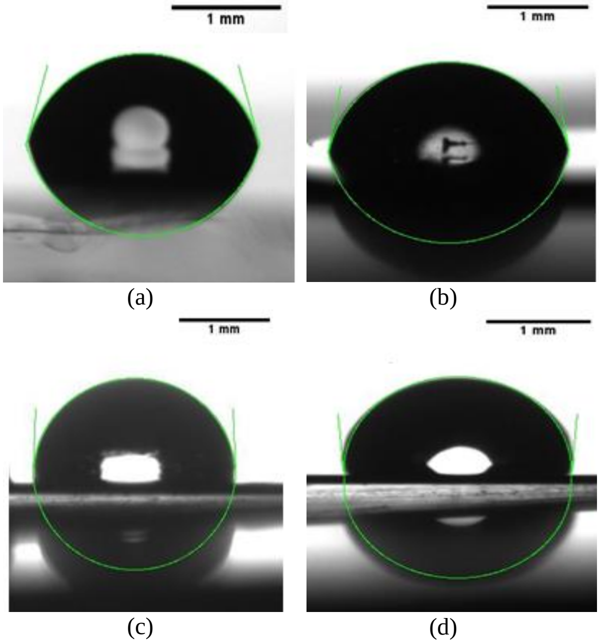

Figure 4. Profiles of the liquid distilled water droplet on DLC films deposited by different SNPs content (a) T_A (b) T_A-Ag_{10} (c) T_A-Ag_{20} and (d) T_A-Ag_{30}

95°±2 as a result of the increase in the Ag up to 16.3% volume percentage on the surface of DLC thin films.

Cavaliere et al. [12] deposited highly bactericidal Ag nanoparticle films on the glass by cluster beam deposition method.

Since there are several reports about improving hemocompatibility of the surface with antibacterial properties [32, 37], it can be concluded that with the accumulation of Ag on the surface of DLC film, hemocompatibility of the surface increases as a result of the increased hydrophobicity. The results from the other studies confirm our findings [24, 29, 38-40].

Figure 5 shows the transmittance and reflection spectra of DLC films deposited on a glass substrate at the same condition of Ni–Cu substrates. The values of optical density (OD) of DLC are presented in Figure S3. It was observed that the optical transmittance stays almost constant, but the reflection values increase in the visible and near-infrared region due to Ag deposition on the surface of DLC films. It means that, there are no significant physical changes in DLC films, but with an increase in light reflection from the surface, the amount of light absorption and hence the optical density in the DLC films decreases (Figure S3). We found that in addition to the increase in hydrophobicity of the DLC thin films caused by deposition of Ag, the optical density of DLC increases without any reduction in the transparency of DLC films; while according to the other studies [32] the transparency and optical band gap of DLC film decreased due to Ag incorporation in the film. The reduction in the total

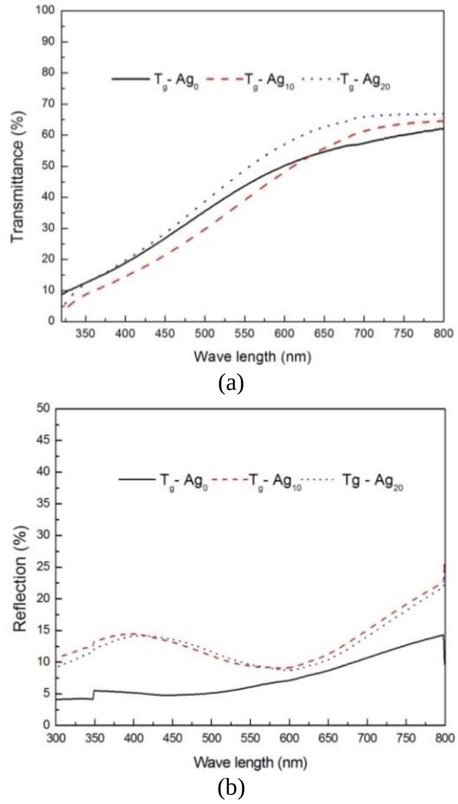

Figure 5. (a) Optical transmission and (b) the reflection of DLC films deposited on glass substrates

surface energy of Ag-incorporated DLC films are attributed to the decrease in both polar and dispersive component [32]; but due to the increase in sp^2/sp^3 ratio of the DLC films and the changes in electronic structure by the incorporation of substitutional defect states in the films, the transparency and optical band gap of Ag:DLC film is lower than pure DLC film [15, 16, 18].

Thus, as noted in the other research [8, 10], the hydrophobic surface is better than the hydrophilic surface for coating on medical device. Similarly, according to the results of this research the hydrophobicity of DLC films improved by accumulation Ag on the surface without destructive effects on the optical properties; it can be said that this coating method is an excellent candidate for a wide variety of engineering applications in optical devices and biomedical implantation.

4. CONCLUSION

Deposition of silver clusters on the DLC films was done uniformity at 0.9 keV ion beam energy by ion beam sputtering method.

The hydrophobicity of the DLC thin film on the Ni-Cu (70.4-29.6; W/W) alloy substrate has improved because of the deposition of silver clusters on the surface of thin film. The contact angle shifted from 79°±2 to 95°±2 due to the increase in the Ag volume percentage in the surface of DLC films from 5.0±2.01 to 16.3±1.4.

The reflection values increased in the visible and near-infrared region due to deposition of Ag on the surface of DLC thin films while the optical transmittance stayed almost constant. Therefore, an increase in the hydrophobicity and the optical density of the DLC thin films without any decrease in the transparency of DLC films is due to the deposition of Ag clusters.

In fact, with the accumulation of Ag in the high-energy areas on the surface of the DLC films, the reaction centers (dangling bonds) on the surface reduced and CA increased because of the decrease in the surface free energy. This kind of nanostructured DLC film is an excellent candidate for a wide variety of engineering applications in optical devices and biomedical applications.

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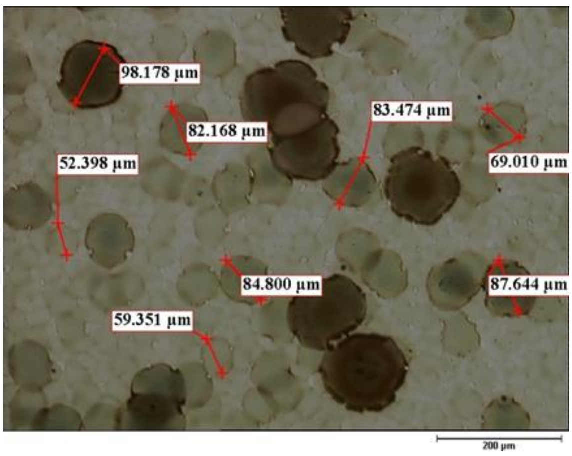
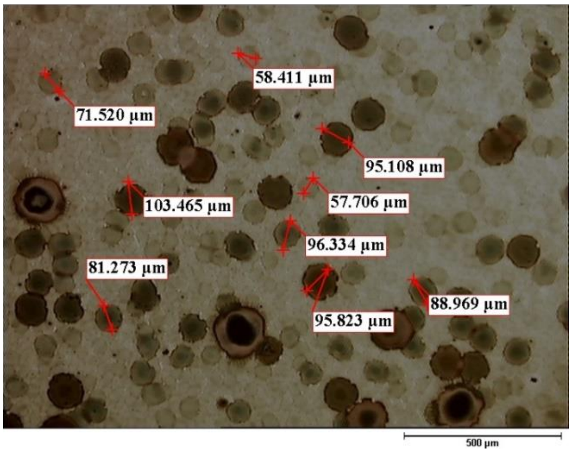
7. APPENDIX

TABLE S1. The data extracted from Gaussian deconvolution of Ramman spectra

Sample code	G- peak (cm-1)	I_D/I_G ratio	La(Å)
Tg	1541.7	0.072	3.62
TA	1577.9	0.062	3.36



(a)



(b)

Figure S1. Microscopic images of accumulated silver cluster at 1.2 keV ion beam energy

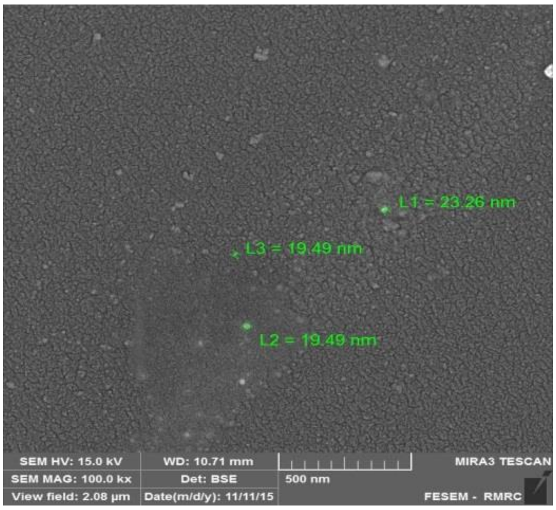
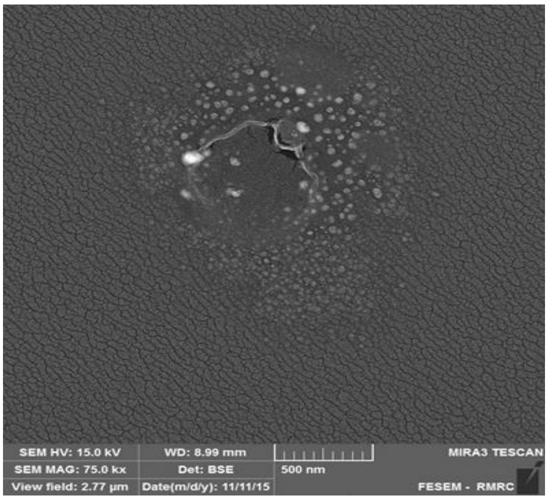


Figure S2. Field Emission Scanning Electron Microscopy (FESEM) image of accumulated silver nano particles at 0.6 keV ion beam energy



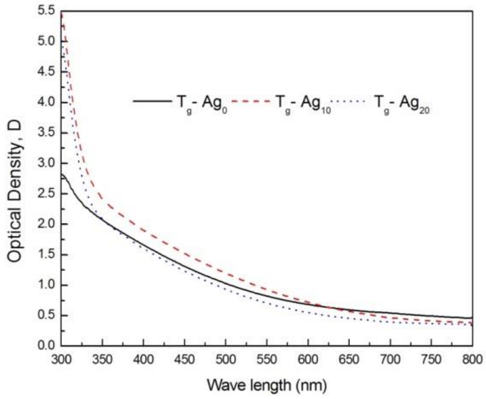


Figure S3. Optical density of DLC films with accumulated SNPs on the surface

Persian Abstract

چکیده

در تحقیق حاضر، تاثیر انباشت خوشه‌های نقره بر خواص نوری، ترشوندگی و خواص سطحی فیلم کربن شبه‌الماسی (DLC) بررسی شده است. نقره و فیلم DLC بر زیرلایه آلیاژ نیکل-مس (70/4-29/6؛ W/W) با استفاده از روش کندوپاش پرتو یونی (IBSD) انباشت شد. خواص نوری و ساختاری به ترتیب با استفاده از طیف سنجی فرابنفش-مرئی و رامان انجام شد. ترشوندگی و خواص سطحی لایه‌ها با استفاده از زاویه ترشوندگی (CA) اندازه‌گیری شد. طیف رامان فیلم DLC با ضخامت 6±121 nm بدون انباشت نقره نشان می‌دهد که اندازه کریستالهای گرافیت با پیوندهای sp^2، 3/36 Å با نسبت I_D/I_G برابر با 0/062 و انرژی‌باند گپ 3eV می‌باشد که با استفاده از معادله تاک بدست آمده است. نتیجه انباشت نقره در انرژی یون متفاوت بین 0/6keV تا 2 keV نشاندهنده انباشت خوشه‌های نقره به صورت یکنواخت برروی فیلم DLC در 0/9 keV می‌باشد. درصد حجمی خوشه‌های نقره از 5/0±2/01 تا 16±1/40٪ تغییر می‌کند. تغییرات با کنترل ولتاژ شتابدهنده و زمان انباشت ایجاد می‌شود. CA در فیلمهای انباشت شده از 2± °79 به 2± °95 افزایش می‌یابد و مقادیر انعکاس در محدوده مرئی و فروسرخ نزدیک در نتیجه افزایش غلظت نقره در سطح فیلم DLC افزایش می‌یابد در حالی که انرژی آزاد سطح از $1±86mJ/m^2$ به $1±66mJ/m^2$ کاهش می‌یابد و میزان عبور نور تقریبا ثابت می‌ماند. نتایج نشان می‌دهد که انباشت ذرات نقره بر فیلم‌های DLC با توجه به ویژگی آبگریزی خوب بدون تاثیر مخرب بر خواص نوری فیلم DLC پتانسیل استفاده برای کاربردهای بیوپزشکی را دارا می‌باشد.