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Improvement of adhesion of DLC coating on nitinol substrate by hybrid ion beam deposition technique

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ABSTRACT

Diamond-like carbon (DLC) films were prepared for a protective coating on nitinol substrate by hybrid ion beam deposition technique with an acetelene as a source of hydrocarbon ions. An amorphous silicon (a-Si) interlayer was deposited on the substrates to ensure better adhesion of the DLC films followed by Ar ion beam treatment. The film thickness increased with increase in ion gun anode voltage. The residual stresses in the DLC films decreased with increase in ion gun anode voltage and film thickness, while the stress values were independent of the radio frequency (RF) bias voltage. The adhesion of the DLC film was improved by surface treatment with argon ion beam for longer time and by increasing the thickness of a-Si interlayer.

1. Introduction

The performance of a biomaterial in various biomedical applications depends on its interaction with biological cells and tissues. Biomedical materials and devices are intended to benefit patients and should not impose any unnecessary adverse or toxic influence upon the patient. The existing biomaterials that are commonly used in cardiovascular applications like stainless steel and nitinol suffer from the drawback of cytotoxity, release of metal ions and corrosion [1,2]. So, a protective coating the medical device with inert, corrosion resistant and hemocompatible materials is an appropriate step to minimize any adverse effect to human body. In this context, the use of diamond-like carbon (DLC) coatings on cardiovascular devices has drawn considerable attention in recent times due to its superior tribological properties of low wear and friction, chemically inertness as well as hemocompatible properties [3–7]. DLC coatings on cardiovascular implants are reported to prevent the release of metal ions to a considerable extent [1,7]. During the implant lifetime, the medical implants for cardiovascular applications are also subjected to severe external forces inside human body. These external forces often lead to spallation and delamination of the coating due to generation of high compressive stress. To get rid of this problem some attempts were made to modify the substrate surface through surface treatment and employ an adhesive interlayer between a coating and substrate [3,8–13]. Especially Ar plasma treatment and deposition of an a-Si interlayer between substrate and film were found to improve the adhesive properties of the DLC coatings significantly [8,10–13].

In this report DLC films were synthesized by hybrid ion beam deposition technique for effective coating on a nitinol substrate, the shape memory alloy applying for stents [14] or dental parts [15]. The deposition parameters were optimized to minimize the residual compressive stress in the DLC film and an amorphous Si interlayer was used to improve the adhesion of the DLC film on the Ar plasma treated substrate. The adhesion property of the DLC coating was investigated through the scratch tests.

2. Experimental

The DLC films were prepared on silicon (100) and nitinol substrates using acetelene (or C_2H_2) as the precursor of carbon ions via hybrid ion beam deposition technique. A combination of a linear ion gun (DC 3 kV/6 kW, EN Technologies) with gases of C_2H_2 and Ar and a sputter gun for an amorphous Si deposition was used. In the ion gun, the electrons, confined in the magnetic field, collide with the gas molecules and ionize it. The positively biased anode repels the ions in the discharge area and accelerates them away from the source, creating the ion beam. At a fixed anode voltage, the ion

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beam emerges from the linear ion gun and gets deposited on the substrate maintained at a negative RF bias voltage. The plasma density and discharge currents increase with increased gas pressure and applied power. Fig. 1 showed a schematic diagram of the hybrid ion beam system. The distance between the ion source and substrate holder was about 15 cm. Base pressure in the chamber was less than 10^{-3} Pa. Prior to deposition, the substrates were initially cleaned with argon (Ar) ion beam at a chamber pressure of 0.06 Pa for the treatment time varying from 5 to 20 min. A radio frequency (RF) bias voltage was applied to the substrate holder which can be rotated at a desired speed of 3.33 rpm. An amorphous silicon (a-Si) interlayer was deposited on the substrates to ensure better adhesion of the DLC films on the nitinol substrate using DC sputtering of a silicon (Si) target (99.99% pure) at an Ar flow rate of 12 sccm and a chamber pressure of 0.26 Pa. The thickness of a-Si layer was varied by changing the deposition time and sputtering voltages. C_2H_2 was then introduced into the ion gun to obtain the hydrocarbon ions. The DLC films were deposited at a C_2H_2 rate of 8 sccm at a chamber pressure of 0.08 Pa. The ion gun anode voltage (1.5–2.5 kV), substrate bias voltage (−100 to −600 V) and deposition time was varied to study its effect on the thickness and residual stress of the DLC films. The atomic bond structure of the DLC films was analyzed using Raman spectroscopy (LabRAM HR, HORIBA Jobin–Yvon Inc.) for the determination of the D- and G-peak position.

A masked 600 μm thick silicon (100) wafer was used to measure the film thickness. The thickness of the films was measured by an alpha step profilometer. Thin silicon (Si) strips of 3 × 30 mm in size were cut from a Si (100) wafer of thickness 200 ± 5 μm and used to estimate the residual stress from the observed curvature of the film/substrate composite, measured by a laser reflection method. The residual stress of the film was estimated using the equilibrium equation for bending plates by Stoney equation [16]. The film/substrate composite was found to be convex, indicating a compressive nature in the residual stress. The DLC films on nitinol substrates were subjected to scratch tests with a scratch tester (J&L Tech, Korea). A fine diamond tip of radius 200 μm was used for scratching. The normal load is increased uniformly from 0 to 80 N for a distance of 5 mm at a scratching speed of 0.2 mm/s. The scratched path was then observed in an optical microscope mounted on the scratched tester.

3. Results and discussion

3.1. Surface treatment and deposition of amorphous Si layer

The substrates were initially cleaned with an Ar ion beam at an RF bias voltage of −100 V. Highly energetic Ar ions from the linear ion gun etch away a thin layer of substrate surface at various ion gun anode voltages. The Ar flow was kept constant at 6 sccm corresponding to a chamber pressure of 0.06 Pa. The Ar cleaning condition for silicon substrates was optimized at an anode voltage of 1.75 kV for 5 min corresponding to an etching depth of 10 nm. An amorphous silicon (a-Si) layer was deposited on the cleaned substrates to ensure better adhesion of the DLC films. The silicon films were obtained by d.c sputtering of a Si target with out any RF bias voltage. The a-Si film was found to deposit uniformly at the rate of 3.34 nm/min at a fixed d.c voltage of −590 V.

3.2. DLC film deposition

Fig. 2a showed the variation of the DLC film thickness with deposition times at a fixed anode voltage of 2.3 kV and a RF bias voltage of −100 V. The growth rate of the DLC films was measured as 15.6 nm/min. A 240 ± 9 nm thick DLC films was obtained for a deposition time of 15 min. The variations of residual stress of the DLC films with film thickness are shown in Fig. 2b. The residual compressive stress in the DLC films decreased initially from 2 to 1 GPa at lower film thickness (<100 nm) and then tended to become constant at 0.9 GPa for higher film thickness. As the thickness of a coating increase, the shear stresses near the interface shift away from the coating substrate interface. So the interface is subjected to lower stress with increase in coating thickness. Ahmed et al. also observed that increase in coating thickness influences the

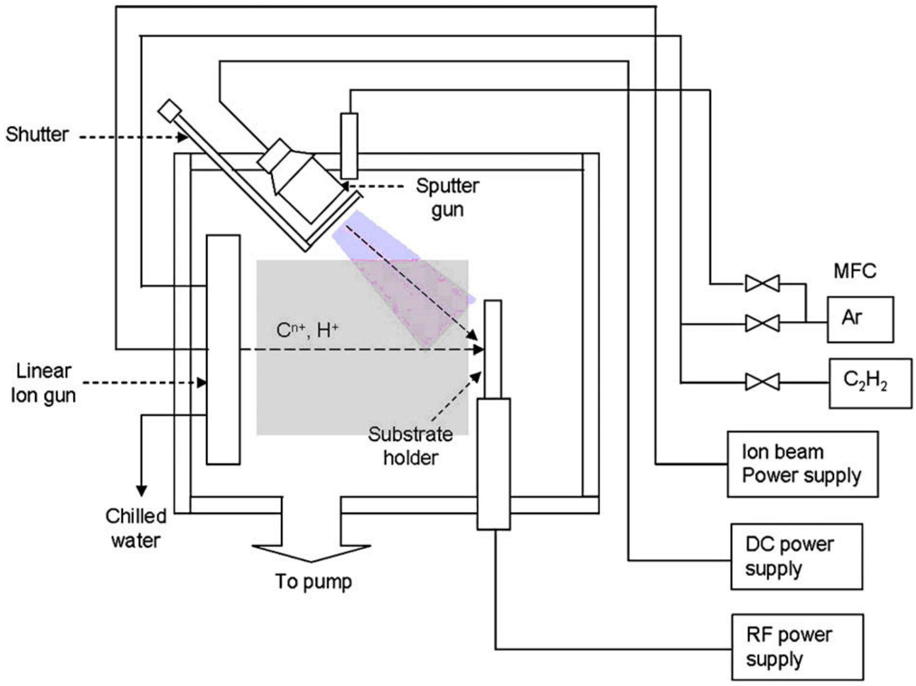

Fig. 1. Schematic diagram of hybrid ion beam deposition apparatus.

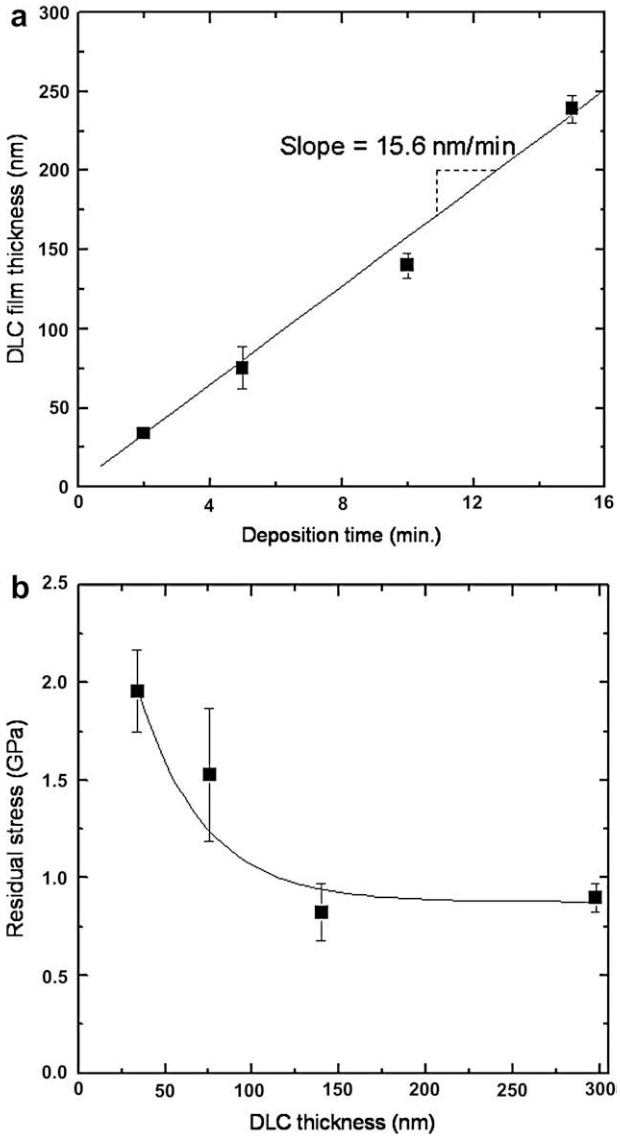

Fig. 2. (a) Thickness of DLC films at various deposition times and (b) residual stresses of DLC films with film thickness for a fixed anode voltage of 2.3 kV and RF bias voltage (V_b) of −100 V.

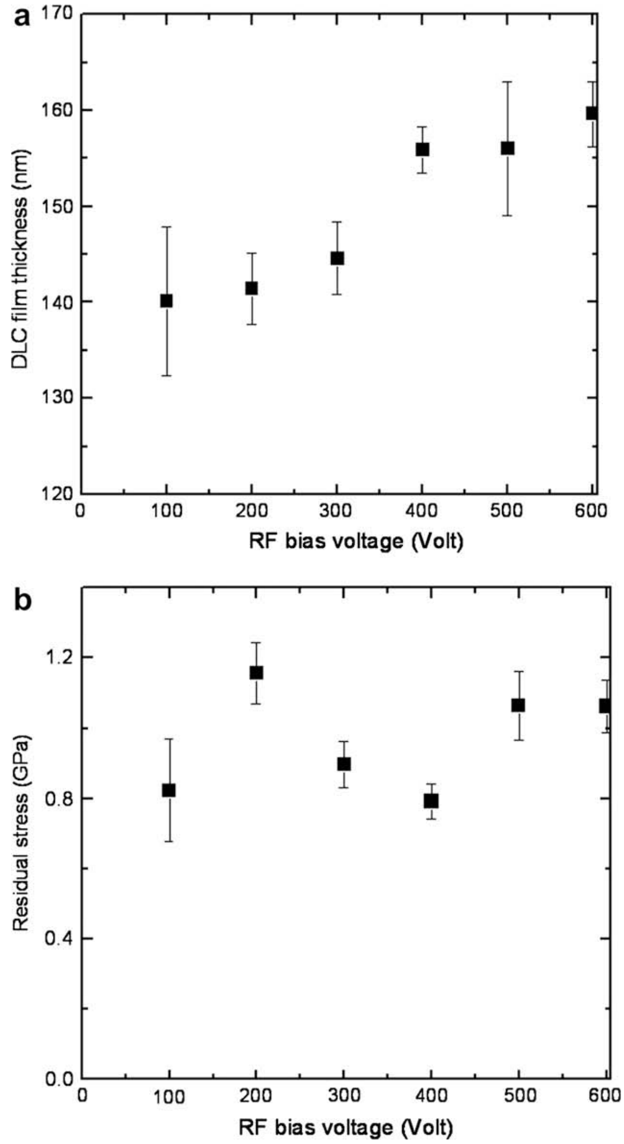

Fig. 3. (a) Thickness of DLC films at various RF bias voltage and (b) variation of residual stress of DLC films with RF bias voltage for a fixed anode voltage of 2.3 kV and 10 min deposition time.

subsurface stress distribution and minimizes the contact stress [17]. Fig. 3a showed the variation of thickness of DLC films at various RF bias voltages for a fixed anode voltage of 2.3 kV and a deposition time of 10 min. The film thickness increased slightly with increase in RF bias voltage. Fig. 3b denoted the variation of residual stress of the DLC films with RF bias voltage at a fixed anode voltage of 2.3 kV and deposition time of 10 min. The stress values revealed two small peaks at −200 and −500 V RF bias voltages. However the stress values did not vary much with change in RF bias voltage. It denoted that the RF bias voltage did not influence the energy of the incoming ions to a considerable extent.

The most significant variation in the DLC films was obtained by changing the ion gun anode voltage. It is the anode voltage which determines the energy of emerging ion beam from the ion gun and its colinearity. At lower anode voltage, a diffuse ion beam characterized by a spread and diffuse ion beam cloud outside the cathode opening is obtained. The ion energy in the diffuse mode is low. However as the anode voltage increased, a collimated and well defined beam with very small divergence is obtained. The ion energy in the collimated mode is generally considered high. Fig. 4a denoted the thickness of DLC films at various anode voltages at a fixed RF bias voltage of −100 V and deposition time of 10 min. The film thickness increased uniformly with increase in the anode voltage. The variation of residual stress of the DLC films with the ion gun anode voltages are shown in Fig. 4b. The residual compressive stress decreased with increase in the anode voltage. The stress value decreased rapidly from 3 to 1.4 GPa at the lower anode voltage (<2.0 kV) and then attain a value of 1.1 GPa at the higher anode voltages. This stress behavior is explained by the consideration of a steady state in which the stress formation by knock-on implantation of the film atoms below the film surface is balanced by stress relaxation through thermal spike excited migration of implanted atoms [18]. According to this model, the magnitude of compressive stress is strongly dependent on the ion energy and normalized flux (j/R), where j is the bombarding flux and R is the net depositing flux. For low normalized fluxes, the stress is proportional to the square root of ion energy. However for higher normalized fluxes, the stress value goes through a maximum with

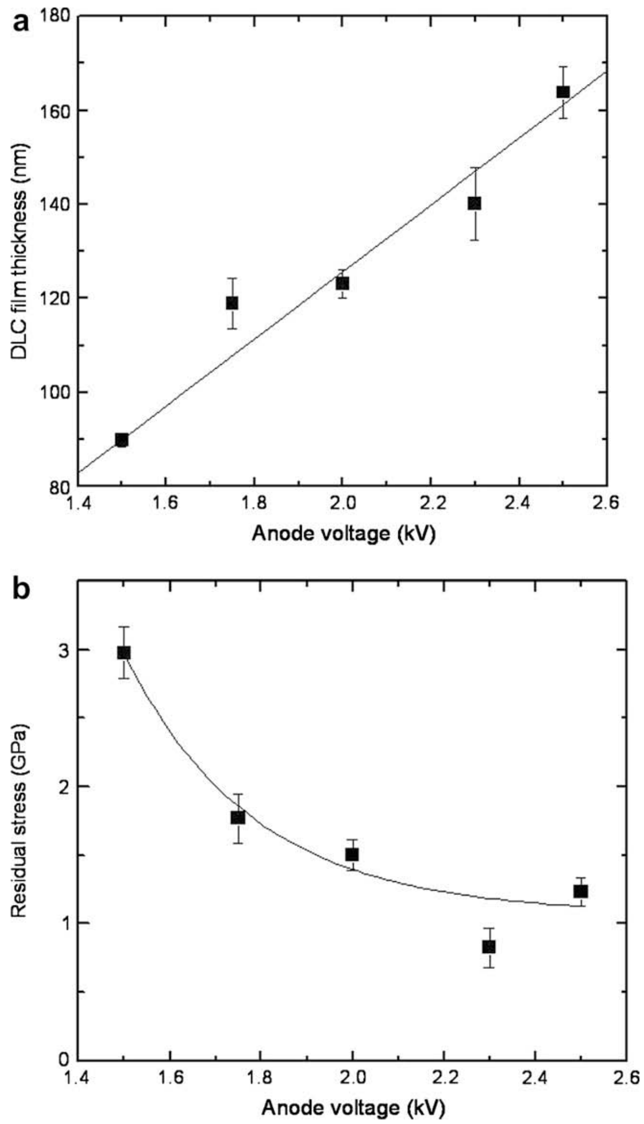

Fig. 4. (a) Variation of DLC film thickness and (b) variation of residual stress of DLC films with anode voltages for a fixed RF bias voltage (V_b) of −100 V and 10 min deposition time.

increasing ion energies with a power law decrease for large energies and fluxes. So the stress is reduced by increasing the ion energy. In our result, the compressive stress values were found to decrease with increase in the anode voltage. At higher anode voltage, the incoming ions have higher energy and are in the regime of higher normalized fluxes. So this result is consistent with that of the model proposed by Davis for high flux deposition system [18]. Increase in the bombarding energies leads to intensive local heating (thermal spike), a corresponding increase in substrate temperature and consequent reduction in the thermal stress as the structure undergoes thermal relaxation. Peng et al. [19] and Oh et al. [20] have also obtained a similar kind of stress variation in case of the DLC films deposited by capacitively coupled RF plasma enhanced chemical vapor deposition (PECVD) and ion beam deposition, respectively.

Fig. 5 shows the Raman spectra of DLC films deposited at various anode voltages. All the spectra are typical of the hydrogenated amorphous carbon (a-C:H), characterized by G-peak near 1540 cm^{-1} with broad D-peak shoulder near 1365 cm^{-1}. The

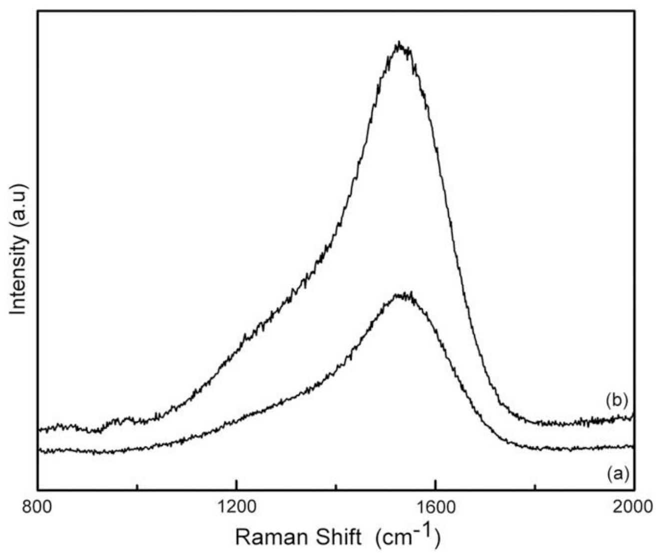

Fig. 5. (a) Raman spectra of DLC film deposited at different anode voltage (a) 1000 V and (b) 2000 V for a fixed RF bias voltage (V_b) of −200 V.

G-peak is induced by the lattice vibration in the graphite-like hexagonal ring, and the D-peak is known to be associated with the existence of graphitic clusters with a short range of crystallinity [21]. The Raman spectra were deconvoluted into D- and G-peaks, respectively using two Gaussian curves. In the Raman spectra, with increase the anode voltage the G-peak position shifted to higher wave number as well as the I_D/I_G ratio increases which mean the graphite-like sp^2 bond increases [22]. The stress in DLC is known to decrease with increasing sp^2 content [23]. So with increasing the anode voltage the sp^2 fraction increases and the stress of the DLC films decreases.

3.2.1. Optimum condition of adhesion

Based on these variations in deposition times, RF bias voltage and ion gun anode voltage, a DLC film deposition for 20 min at 2.0 kV anode voltage and −200 V RF bias voltage is considered optimum. Now to investigate the adhesion and stability of the DLC films under extreme conditions, DLC films with optimum condition were deposited on nitinol substrates at various Ar cleaning time and having a-Si interlayer of different thickness. Table 1 gives the deposition condition of four kinds of DLC films synthesized at the various Ar cleaning time, with a-Si interlayer of different thickness. The Ar cleaning of the substrate was done at 2.5 kV anode voltage and −100 V r.f. bias voltage, while the silicon sputtering for a-Si interlayer was performed at −590 V d.c voltage. The DLC coating condition was kept fixed in all the films. The resultant films were then subjected to scratch testing.

The micrographs of the scratched path of the films after scratch testing when the normal load is increased from 0 to 80 N

Table 1
Four different deposition conditions in DLC coating on nitinol substrate at various Ar cleaning time and a-Si interlayer of different thickness.

Film	Ar cleaning time (min)	Si sputtering time (min)	Thickness of a-Si interlayer (nm)
DLC-1	5	10	33.4
DLC-2	10	10	33.4
DLC-3	20	5	16.7
DLC-4	20	15	50.1

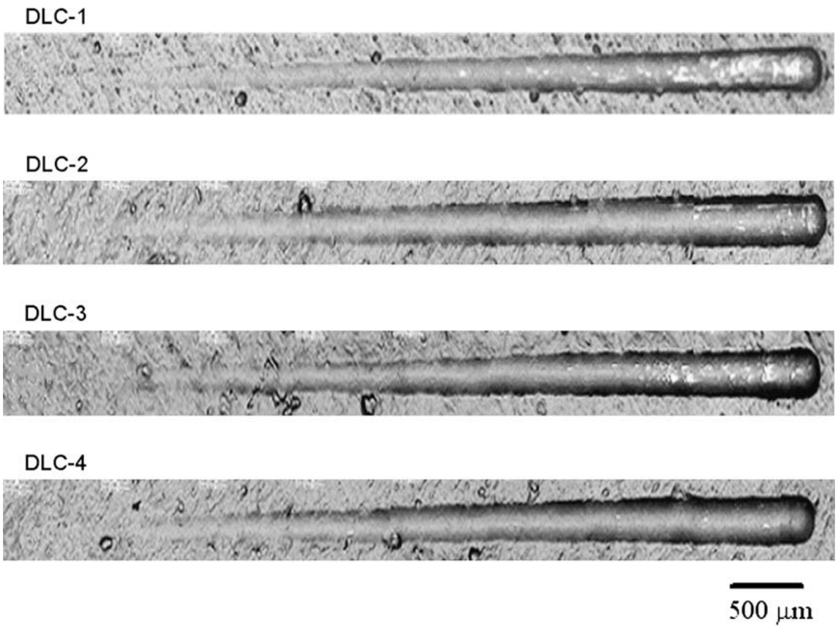

Fig. 6. Optical images of scratch tested DLC films on nitinol substrate listed on Table 1.

for a distance of 5 mm as shown in Fig. 6. The films DLC-1 and DLC-3 showed distinct spallation and delamination. The delamination and spallation were less in case of DLC-2. The DLC-4 film revealed least spallation and delamination. All these results revealed that the DLC-4 film is more stable with good adhesion to the nitinol substrate compared to the other films. It indicates that the delamination of the DLC films was minimized at higher Ar cleaning time and by using an a-Si interlayer thicker than 33 nm. It denoted that the adhesion of the DLC film improved at higher Ar cleaning time and by increasing the thickness of a-Si interlayer. Jun et al. [10] and Choi et al. [11] have also obtained a similar kind of result for RF plasma assisted chemical vapor deposited (PACVD) DLC films on spacer tool and stainless steel substrate. Addition of an a-Si interlayer of a certain thickness reduces the intrinsic stress of the DLC films and improves its adhesive properties to the substrate [12]. Initial etching of the substrate for an optimum time also minimizes the intrinsic stress without significantly affecting the film hardness [8].

4. Conclusions

DLC films were synthesized on silicon and nitinol substrate by hybrid ion beam deposition technique using acetylene as the source of hydrocarbon ions. The film thickness increased with increase in ion gun anode voltage. The residual compressive stress in the DLC films was minimized with increase in ion gun anode voltage and film thickness. However, the stress values did not vary much with change in RF bias voltage. Scratch testing revealed that the adhesion of DLC film improved by cleaning the substrate in Ar ion beam for longer time and by increasing the thickness of a-Si interlayer. By selecting the optimum condition of DLC coatings with lower residual stress and higher interfacial adhesion, DLC films have many potentials for the applications on complex structure like nitinol based stents or dental parts.

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References

[1] Gutensohn K, Beythien C, Bau J, Fenner T, Grewe P, Koester R, et al. Thromb Res 2000;99:577.
[2] Kobayashi S, Ohgoe Y, Ozeki K, Sato K, Sumiya T, Hirakuri KK, et al. Diam Relat Mater 2005;14:1094.
[3] Jones MI, McColl IR, Grant DM, Parker KG, Parker TL. Diam Relat Mater 1999;8:457.
[4] Yu LJ, Wang X, Wang XH, Liu XH. Surf Coat Technol 2000;128-129:484.
[5] Nurdin N, Francois P, Morret M, Unal K, Krumeich J, Aronson BO, et al. Euro Cells Mater 2003;5:17.
[6] Jones MI, McColl IR, Grant DM, Parker KG, Parker TL. J Biomedical Mater Res 2000;52:413.
[7] Cheng Y, Zheng YF. Surf Coat Technol 2006;200:4543.
[8] Morshed MM, McNamara BP, Cameron DC, Hashmi MSJ. Surf Coat Technol 2003;163-164:541.
[9] Podgornik B, Vizintin J, Ronkainen H, Holmberg K. Thin Solid Films 2000; 377-378:254.
[10] Jun Y, Choi JY, Lee KR, Jeong BK, Kwon SK, Hwang CH. Thin Solid Films 2000;377-378:233.
[11] Choi HW, Lee KR, Wang R, Oh KH. Diam Relat Mater 2006;15:38.
[12] Bonetti LF, Capote G, Santos LV, Corat EJ, Airoldi VJT. Thin Solid Films 2006;515:375.
[13] Kim HJ, Moon MW, Kim DI, Lee KR, Oh KH. Scripta Mater 2007;57:1016.
[14] Cwikiel W, Stridbeck H, Tranberg KG, Holstein CSV, Hambraeus G, Gil RL, et al. Radiology 1993;187:661.
[15] Thompson SA. Intl Endodontic J 2000;33:297.
[16] Stoney GG. Proc Roy Soc London A 1909;82:172.
[17] Ahmed R, Hadfield M. Wear 1999;230:39.
[18] Davis CA. Thin Solid Films 1993;226:30.
[19] Peng XL, Clyne TW. Thin Solid Films 1998;312:207.
[20] Oh JU, Lee KR, Yun KY. Thin Solid Films 1995;270:173.
[21] Choi HW, Choi JH, Lee KR, Ahn JP, Oh KH. Thin Solid Films 2007;516:248.
[22] Kahn M, Cekada M, Berghauser R, Waldhauser W, Bauer C, Mitterer C, et al. Diam Relat Mater 2008;17:1647.
[23] Robertson J. Mater Sci Eng R 2002;37:129.