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Diamond & Related Materials 15 (2006) 38 – 43

DIAMOND AND RELATED MATERIALS

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Fracture behavior of diamond-like carbon films on stainless steel under a micro-tensile test condition

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Received 18 March 2005; received in revised form 15 June 2005; accepted 1 July 2005
Available online 15 August 2005

Abstract

We investigated the stability of the DLC film coated on 304 stainless steel substrate by r.f. PACVD method. Fracture and spallation behaviors of the coating were observed during micro-tensile test of the film/substrate composite. As the tensile deformation proceeded, the cracks of the film appeared in the perpendicular direction to the tensile axis. Further deformation resulting in the local necking with shear band of 55° inclined to the tensile axis, induced the spallation of the film, which was initiated at the cracks of the film, and was aligned along the slip directions. We found that both the cracking and the spallation behaviors are strongly dependent on the pretreatment condition, such as Ar plasma pretreatment or Si buffer layer deposition. The spallation of the film was significantly suppressed in an optimized condition of the substrate cleaning by Ar glow discharge. These results show that the spallation behavior during the tensile test can be used to estimate the interfacial strength of the coating with relatively poor adhesion.

Keywords: Diamond-like carbon; Stainless steel; Crack and spallation; Adhesion; Micro-tensile test

1. Introduction

Diamond-like carbon (DLC) film, also referred to as hydrogenated amorphous carbon (a-C:H) film, has been considered as a strong candidate for a protective coating of various biomedical implants and devices. For example, DLC coatings on femoral head of artificial hip joint, heart valve, or vascular stents are being intensively investigated [1–4]. The biomedical implants should prevent infections and uncontrolled cell growth, maintain their integrity inside the body, and avoid formation of debris. Owing to chemical inertness, biocompatibility and excellent mechanical properties, the DLC coating on the implants is expected to reduce the corrosion and the wear, and extends the lifetime of implants to the benefit of the patients. For the biomedical applications, stability of the DLC coating is of crucial importance. Delamination of the coating or adhesive wear during service should degrade the overall performance of the implants, which ultimately limits the lifetime of the coated implants [5]. The instability is closely related to the high level of residual compressive stress and/or the poor adhesion of DLC coating. The film spontaneously buckles when the energy release rate of the delamination exceeds the interfacial toughness. It is widely known that the instability of DLC coating is more significant in aqueous environment or in saline solution. Furthermore, the DLC coating on vascular stent to prevent elution of Ni and Cr should survive the plastic deformation (maximum 2%) of the stainless steel substrate.

In the present work, we investigated the failure behaviors of the DLC film deposited on 304 stainless steel after having imposed tensile strain on the coated specimen. Since Agrawal and Raj proposed the tensile test to evaluate adhesion strength of thin film on ductile substrate [6], this

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doi:10.1016/j.diamond.2005.07.002

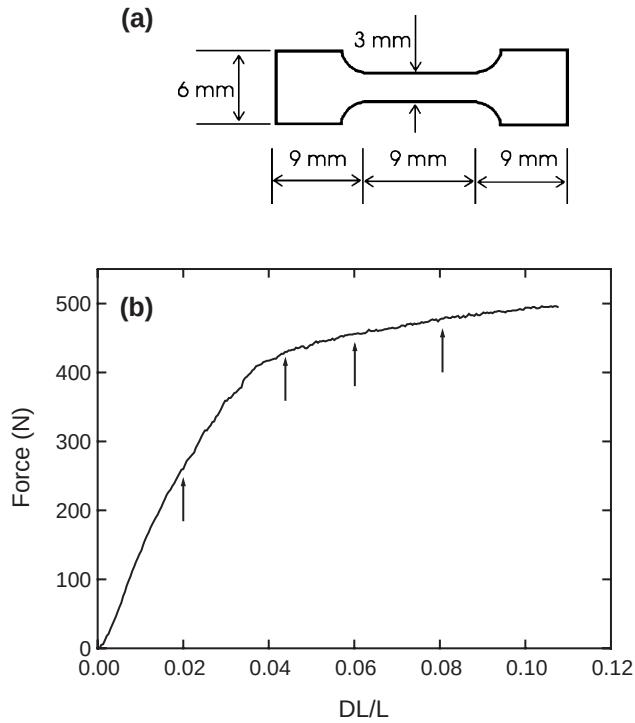

Fig. 1. (a) Schematics of tensile specimen used in the present work (thickness 0.1 mm). (b) A typical force–strain curve of the tensile test.

method has been developed in both theoretical and experimental aspects [7–12]. This method is useful for hard coating on soft substrate where scratch test or indentation method failed due to severe deformation of the substrate. Chen et al. applied this method to evaluate adhesion of TiN film using a modified theoretical model considering the effect of residual stress [10]. Ohmura and Matsuoka compared this method with nanoindentation when evaluating the adhesion of TiN coatings on stainless steel [11]. They suggested that the tensile test is superior in detecting the difference in adhesion of the film/substrate interface. This method was also employed to investigate the cracking behavior of SiO_2 film on Al alloy of various surface roughnesses [12].

If the tensile strength and elastic modulus of the film are exact, this method will provide a simple and reliable method to estimate the adhesion of film/substrate interface. However, application of this method is limited when the mechanical properties of the film can be hardly determined as in DLC films. Furthermore, in poor adhesive films, the cracking normal to the strain axis is combined with cross-linked cracking or spallation of the coating that would considerably affect the stress environment. One should carefully consider these factors when evaluating the interfacial strength using the crack spacing.

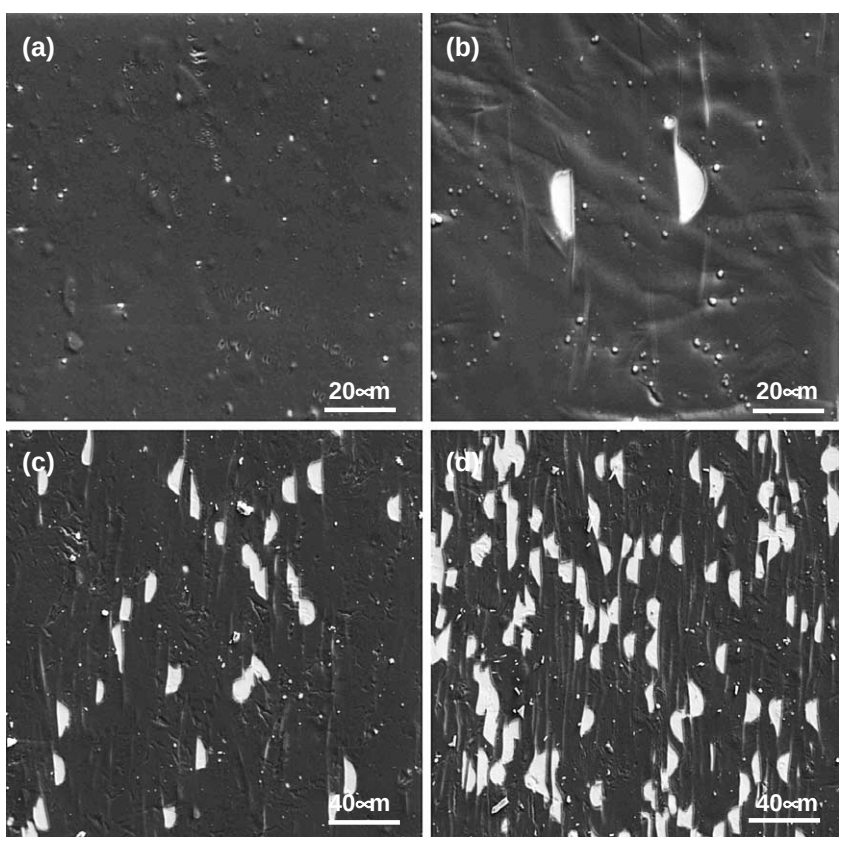

Fig. 2. SEM microstructure of the specimen surface after imposing tensile strain of (a) 2%, (b) 4%, (c) 6% and (d) 8%.

In the present work, we investigated the failure behaviors of the DLC film during tensile test of the coated stainless steel substrate in the range of the strain up to 10%. This experiment is to simulate the situation experienced by the DLC coating during expansion of the vascular stent. We observed that the spallation of DLC coating occurs along the slip direction of the tensile specimen and is highly sensitive to the pretreatment condition. We showed that the spallation behavior can be used to optimize the pretreatment process to improve the stability of the DLC coating. Ar sputter cleaning of the substrate followed by the deposition of amorphous Si interlayer was the pretreatment process considered in the present work.

2. Experimental

The DLC films were deposited by a radio frequency plasma-assisted chemical vapor deposition (r.f. PACVD) method using benzene as the precursor gas. Details of the experimental setup were reported elsewhere [13]. Tensile specimens of 304 stainless steel with thickness 0.1 mm were used for the substrates. Dimensions of the tensile specimen were shown in Fig. 1(a). The specimens were electrochemically polished to obtain a surface of roughness less than 0.1 μm in rms value. DLC film was deposited at the bias voltage of −400 V and the deposition pressure 1.33 Pa. The residual stress and the mechanical properties of the DLC films were strongly dependent on the kinetic energy of the deposited carbon atoms, which in turn depends on the substrate bias voltage, the deposition pressure and the precursor gas molecules [14]. DLC films with a residual compressive stress of 0.9 ± 0.2 GPa and a hardness of 10.0 ± 1.0 GPa were used in this work. Thickness of the film was kept constant, 1.0 ± 0.1 μm for all specimens.

Prior to the film deposition, the substrates were sputter cleaned by Ar plasma followed by a thin amorphous Si interlayer deposition. This pretreatment process is essential to obtain a stable DLC coating on the stainless steel substrate. In the present work, we investigated the fracture behavior of the DLC coating for various process parameters during Ar plasma cleaning and Si interlayer deposition. During Ar plasma cleaning, pressure was kept at 0.4 Pa while the negative bias voltage was varied from 200 to 900 V by adjusting the r.f. power. Cleaning time was also varied from 15 to 60 min. After Ar cleaning, Si interlayer was deposited from r.f. glow discharge of diluted silane (SiH_4/H_2 = 10:90) at a fixed deposition pressure 2.66 Pa and the negative bias voltage ranging from 200 to 600 V. The thickness of the Si interlayer was varied from 19 to 84 nm. When investigating the effect of Ar sputter cleaning condition, Si interlayer was deposited at a fixed condition: negative bias voltage 200 V, pressure 2.66 Pa and the thickness 19 nm. On the other hand, when the thickness of Si interlayer and the applied bias voltage were varied, Ar sputter cleaning condition was fixed: negative bias voltage 600 V, pressure 0.4 Pa and the cleaning time 15 min.

A miniature materials tester (MINIMAT, Rheometic Scientific Co.) was employed for the tensile test of the coated specimen. The coated tensile specimen was pulled with a strain rate of 0.2 mm/min. Maximum strain was fixed at 10%, which is much larger than the yield point of the specimen. Typical force–strain curve of the specimen was shown in Fig. 1(b). The force–strain curve is essentially the same as that of 304 stainless steel substrate because the thickness of the film was much smaller than that of the substrate. Surface of the tensile specimen was monitored during tensile test by high speed CCD camera with high magnification zoom lens. After the tensile test, the specimen surface was observed by an optical microscope and a scanning electron microscope (SEM). A scanning Auger spectroscopy was employed to characterize the surface of the damaged area.

3. Results and discussion

Fig. 2 shows typical evolution of the crack and the spallation of the DLC coating with increasing the strain. The horizontal direction is the tensile axis. The tests paused at various strain levels of 2.0%, 4.0%, 6.0% and 8.0%, as

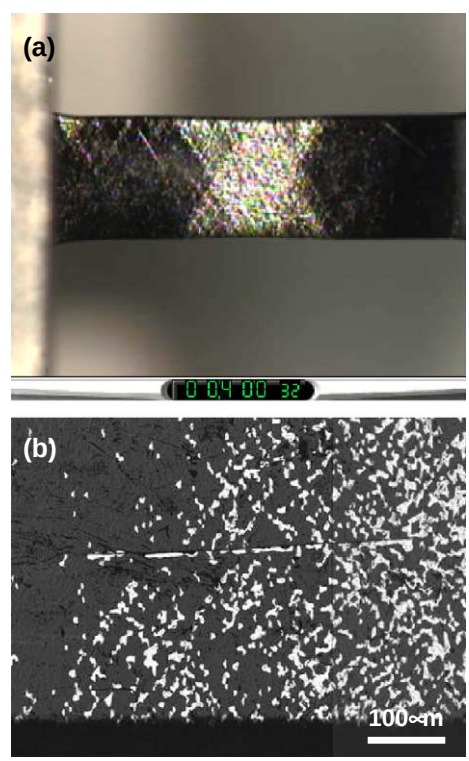

Fig. 3. (a) A snapshot of the specimen surface observed by high magnification video during tensile test. (b) An optical microstructure of the specimen surface near the boundary of the shear band. Note that the spallations are aligned along the shear direction which inclined about 55° to the tensile axis (horizontal direction).

indicated by arrows in Fig. 1(b). When the strain was 2.0% where no significant yielding occurs in the substrate, no defects in the film were observed (Fig. 2(a)). However, surface speckles were observed in the specimen, presumably due to local deformation in the polycrystalline substrate. When the strain increased to 4.0%, crack propagation occurred in perpendicular direction to the tensile axis regardless of the orientation of the underlying grains in the substrate. Fig. 2(b) shows array of the cracks in this specimen. It is also noted that spallation of the film occurred with the crack propagation, although the number density of the spallation is very low. Further increasing the strain to 6% and 8% increased both the crack density and the number of the spallation site as shown in Fig. 2(c) and (d), respectively.

In the previous works, the maximum crack spacing in the saturated crack density was measured to estimate the adhesion of the film [6]. In the case of the DLC coating on stainless steel substrate where the adhesion is relatively low, not only multiplication of the crack but also spallation of the film occurred simultaneously (see Fig. 2(c) and (d)). Since the spallation affects the stress state in cracking, characterization of the interfacial shear strength by measuring the maximum crack spacing is impossible for the DLC coatings. In the present work, we could not observe a systematic change of the crack spacing with the pretreatment condition. In the case of TiN films, transverse cracks were observed before the spallation occurred [10,11]. Transverse cracks were inclined approximately 45° to the tensile axis, which might be associated with the shearing action of the film due to the compressive stress generated by the necking of substrate [10,11]. In contrast, spallation of the coating dominates in DLC films presumably due to high level of residual compressive stress and poor adhesion on the stainless steel substrate.

Spallation of the DLC coating is closely related to the shear deformation of the substrate. Fig. 3(a) is a typical snapshot of the video image when local necking occurs in the tensile specimen. Along the shear band inclined by 55° to the tensile axis, bright lines were evolved during tensile test. In situ observation revealed that multiplication of the bright lines occurred as the tensile test proceeded, which enlarged the bright region on the specimen surface. Surface microstructure of high magnification (Fig. 3(b)) shows that the bright lines are composed of the spallations aligned along the slip direction. It can be thus said that the spallation is caused by the localized shear of the substrate. Because the total strain was fixed at 10%, we assumed that the spallation within the shear band represents the delamination of the film caused by the same amount of the shear strain. The spallation area in the slip band was compared to characterize

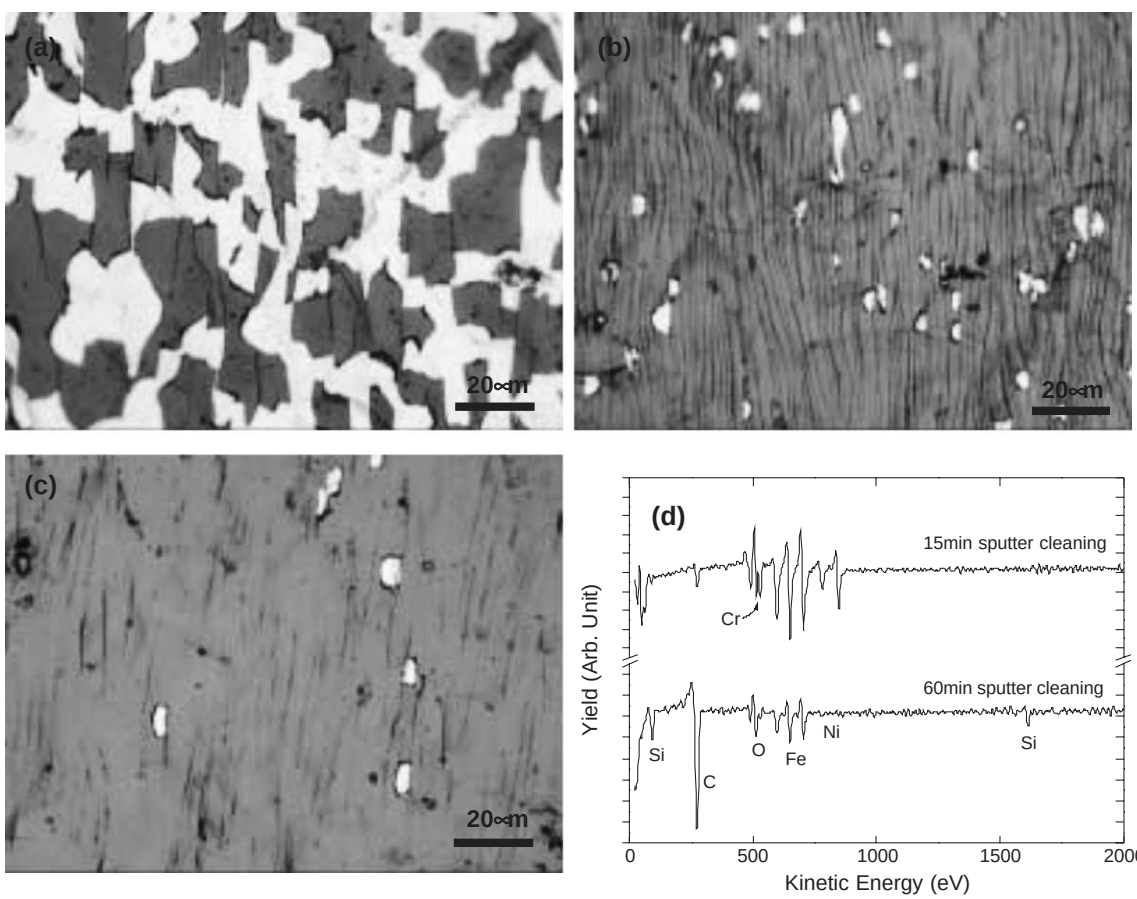

Fig. 4. Microstructures of the spallated region of the specimen after imposing tensile strain of 10% for various Ar sputter cleaning times: (a) 15 min; (b) 30 min; (c) 60 min. (d) Auger spectra of the spallated surface of the specimens (a) and (c).

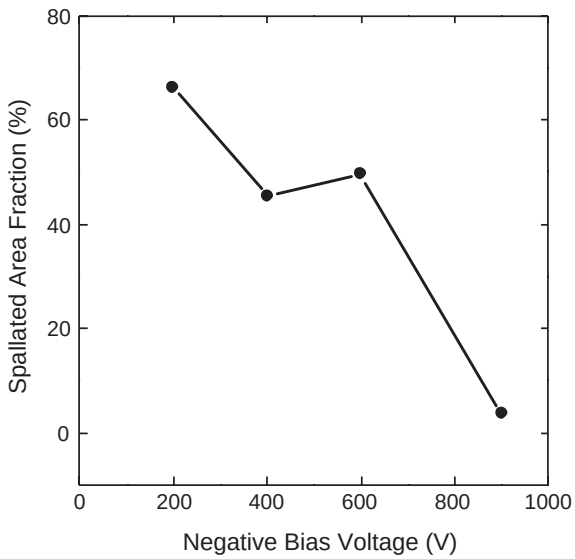

Fig. 5. Fraction of the spallated area for various negative bias voltages during Ar sputter cleaning. Sputter cleaning time was fixed at 15 min.

the adhesion of the DLC coatings between the specimens of various pretreatment conditions.

Fig. 4(a)–(c) show the spallation behaviors of the specimen for various Ar sputter cleaning time. The surface microstructure was observed by an optical microscope after the tensile test. For these specimens, the Si interlayer of thickness 19 nm was deposited at the negative bias voltage of 200 V. When Ar cleaning time was 15 min, severe spallation occurred through the whole area of the slip band. However, spallation area significantly decreased as the cleaning time increased. Statistical analysis showed that the fraction of the spallated area reduced from 41.7% to 4.0% as the cleaning time increased from 15 to 30 min. Further increasing the cleaning time to 60 min reduced the spallated area to 0.3%. The result shows that the increasing the Ar cleaning time is very effective to enhance the adhesion of the DLC coatings. One should note that the crack spacing in Fig. 4(a) is much larger than in other specimens of better adhesion. This result reveals that the crack spacing was not saturated due to the spallation when the adhesion of the coating is not sufficient.

Fig. 4(d) summarizes the Auger spectra of the spallated area of the specimen of Fig. 4(a) and (c). Prior to the analysis, thin surface layer of about 2 nm was sputter etched by Ar ion beam in the analysis chamber to remove the surface contaminant. On the spallated surface of the specimen (a), Fe, Cr and Ni are the dominant elements, showing that the stainless steel surface is exposed. In contrast, significant amount of Si and C were observed on the spallated surface of the specimen (c). Large peak of C implies that the fracture within the DLC film even occurred during spallation. The Auger analysis shows that the adhesion between the Si interlayer and the DLC film is so high that the overall adhesion is determined by the interface between the Si interlayer and the substrate.

Fig. 5 shows the spallation behavior for various substrate bias voltages during Ar sputter cleaning. The sputter cleaning time and the thickness of Si interlayer were fixed at 15 min and 19 nm, respectively. As the negative bias voltage increased from 200 to 600 V, the fraction of the spallation area slightly decreased from 66.2% to 49.7%. However, the spallation was significantly suppressed at the negative bias voltage of 900 V. In r.f. PACVD, higher negative bias voltage results in higher kinetic energy of Ar ion and higher plasma density. It is thus expected that the efficiency of the surface cleaning or surface modification is enhanced when using higher negative bias voltage. The present result shows that the effect of the bias voltage is significant when the negative bias voltage was larger than at least 600 V.

It was observed that the adhesion of the DLC coating is also dependent on the deposition condition of Si interlayer.

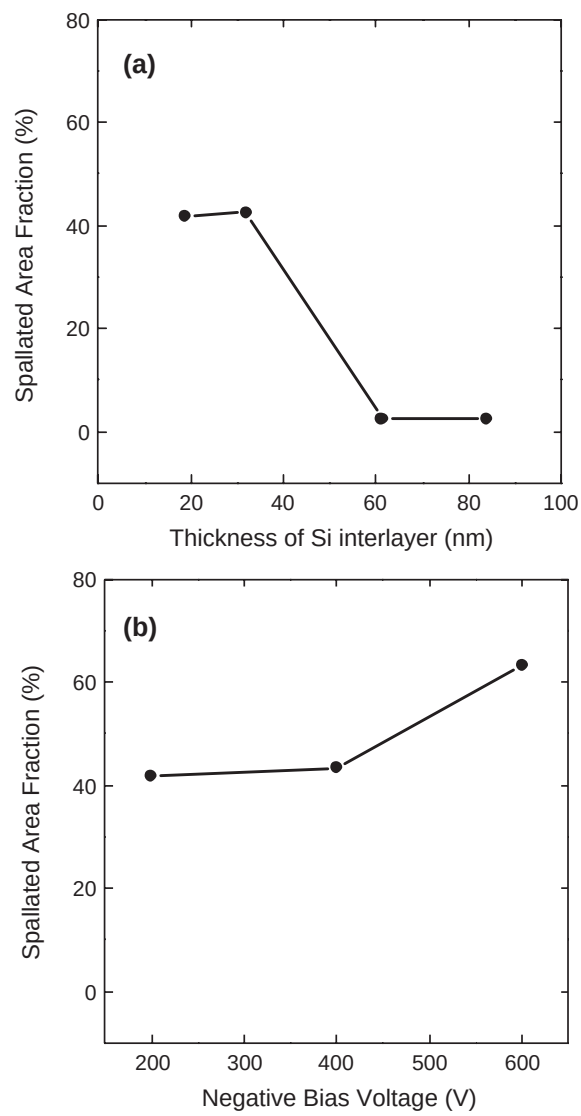

Fig. 6. (a) Fraction of the spallated area for various thicknesses of the Si interlayer deposited at the negative bias voltage −200 V. (b) Fraction of the spallated area for various negative bias voltages during the Si interlayer deposition.

Fig. 6(a) represents the spallation behavior with increasing thickness of the Si interlayer. The Si layer was deposited at the negative bias voltage of 200 V after Ar sputter cleaning at the negative bias voltage of 600 V for 15 min. Adhesion of the film was improved with increasing Si interlayer thickness. The fraction of the spallated area was about 42% when the Si layer thickness was thinner than 32 nm. However, the spallation was considerably suppressed when the Si interlayer was thicker than 32 nm. The present results are consistent with those of the scratch test for the DLC films deposited on tool steel substrate under similar deposition condition [15]. Increasing negative bias voltage during the Si interlayer deposition slightly degrades the adhesion as shown in Fig. 6(b). As the negative bias voltage increased from 200 to 600 V, spallated area fraction increased from 41% to 61%.

4. Conclusions

Fracture behaviors of DLC coating under tensile strain condition were investigated to simulate the stability of DLC coating on vascular stent. Because the adhesion of DLC coating on stainless steel substrate is relatively poor, spallation of the film was concomitant with the parallel cracking perpendicular to the tensile axis. It was thus impossible to apply Agrawal and Raj's method to estimate the interfacial strength between the DLC film and the stainless steel substrate. However, we found that the spallation of the film which occurred due to the shear strain along the shear band was strongly dependent on the pretreatment condition of the substrate. Optimized pretreatment condition for improved adhesion could be determined by selecting the condition for the minimized spallation in the shear band.

Acknowledgement

Authors gratefully acknowledge the financial support from the Ministry of Science and Technology of Korea through the Program for International Cooperation in Science and Technology.

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