Vol 15 No 11, November 2006
1009-1963/2006/15(11)/2697-09

Chinese Physics

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and IOP Publishing Ltd

Preparation and tribological properties of DLC/Ti film by pulsed laser arc deposition*

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(Received 5 January 2006; revised manuscript received 11 May 2006)

This paper reports that DLC (diamond like carbon)/Ti and DLC films were prepared by using pulsed laser arc deposition. R-ray diffraction, Auger electron spectroscopy, Raman spectroscopy, atomic force microscopy, nanoindenter, spectroscopic ellipsometer, surface profiler and micro-tribometer were employed to study the structure and tribological properties of DLC/Ti and DLC films. The results show that DLC/Ti film, with $I(D)/I(G)$ 0.28 and corresponding to 76% sp^3 content calculated by Raman spectroscopy, uniform chemical composition along depth direction, 98 at% content of carbon, hardness 8.2 GPa and Young's modulus 110.5 GPa, compressive stress 6.579 GPa, thickness 46 nm, coefficient of friction 0.08, and critical load 95mN, exhibits excellent mechanical and tribological properties.

Keywords: diamond like carbon, tribological property, pulsed laser arc deposition, Raman spectroscopy

PACC: 6855, 6115J, 6170T

1. Introduction

Diamond-like carbon (DLC) films, with high hardness, good wear resistance, high infrared penetrability, excellent chemical inertness and low electric conductivity, etc., have attracted much attention.[1−6] The usual methods to deposit DLC films are as follows: ion deposition, ion assisted sputtering, sputtering, cathodic vacuum arc, plasma deposition and pulsed laser deposition.[3] For the preparation of DLC/Ti film, Miyoshi *et al*[7] have reported that DLC/Ti film was prepared by the hybrid technique of magnetron sputtering and pulsed laser deposition, Mao *et al*[8] have presented that DLC/Ti film was prepared after annealing process, they have prepared DLC/Ti film using filtered arc deposition,[9] Wei *et al*[10] have addressed that DLC/Ti film was prepared by pulsed laser deposition (PLD), and Mao *et al*[11] have proposed that DLC/Ti was prepared by oxygen reactive etching technique. From previous presentation, optical and tribological properties and field emission feature of DLC/Ti films were investigated with different measuring instruments, in which tribological property was performed by ball-on-disc tribometer only and was not measured by nanoindentation, nanoscratch and Auger electron spectroscopy (AES) tests, etc. As seen from above presentation, DLC/Ti film prepared by pulsed laser arc deposition technique has not been reported. In this study, a pulsed laser-arc deposition (PLAD) system, with easily controllable speed of PLD[12,13] and high efficiency of cathodic vacuum arc, is used to deposit DLC/Ti film. AES, nanoindentation, nanoscratch, Raman spectroscopy, atomic force microscopy (AFM), micro-tribometer, surface profiler and spectroscopic ellipsometer as measuring tools were used to study the property of as-deposited DLC/Ti film. The results show that DLC/Ti film deposited by PLAD exhibits excellent tribological and mechanical properties.

2. Experimental

2.1. Preparation of film samples

Figure 1 shows the schematic diagram of PLAD system. Two targets, two bulks of graphite and titanium with same dimensions of 50mm×20mm×6mm, were mounted onto the target holder in the vacuum chamber. In front of the targets, there was a ring anode with inner diameter of 10mm parallel to the

*Project supported by the National Key Basic Research Program of China (Grant No 2003CB716201) and the National Natural Science Foundation of China (Grant No 50575121) and Electro–Mechanic Technology Advancing Foundation of NSK Ltd of Japan.
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target surface and was connected with target cathode through a pulse current supply circuit. Substrate, silicon (111) crystal surface, was situated on the substrate holder with a negative bias voltage range of 0–1000 volts. A resistive heater was embedded in the substrate holder to heat the substrate to a desirable temperature at the range of 300–700 K. Laser beam generated by Nd-YAG pulse laser with wavelength 1064 nm, power 245mJ and frequency 1Hz for this experiment, was transmitted into the vacuum chamber. A focusing mirror was employed to focus the laser beam at the target surface. Under the electric field condition between the ring anode and target cathode, a laser induced plasma was produced to initiate the vacuum arc which further simulated more plasma from the nearby target. To ablate the substrate uniformly, the target holder was designed to move with two dimensions, which could make multi-target deposition into truth through locating the different position precisely with precise motor and its software.

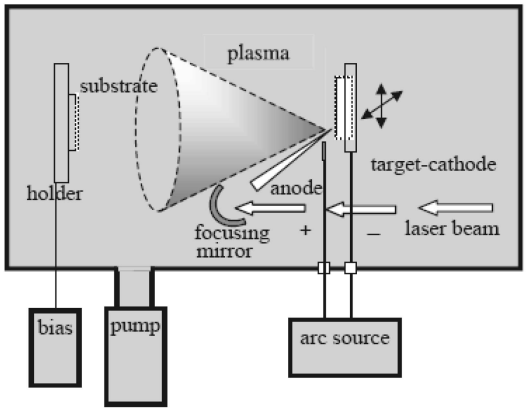


Fig.1. Schematic diagram of PLAD system.

For this DLC/Ti film deposition, the distance between the anode and target cathode and between substrate and target were 10mm and 50 mm respectively. In the deposition process, the anode working volt was 1000 V and the substrate bias volt was 150 V. Prior to deposition, the sample and substrate were treated. For substrate treatment, firstly, Si (111) substrate was dipped in the 1% (v/v) HF solution for 5min, then washed by deioned water for 3 times, at last supersonically cleaned for 10 min. After above treatment, the substrate could be mounted onto the substrate holder. For target treatment, titanium and graphite blocks were polished on the metallographic frequency conversion timing polisher, with rotating speed 200 r/min, until the un-oxidized surface was exposed, then supersonically cleaned for 10 min and mounted onto the target holder. After the target and substrate treatments, mechanical pump was started for about 3 min until the vacuum chamber presser attained about 80 Pa, then molecular pump was employed to get vacuum level of 1.4×10^{-3} Pa for about 2 h. To remove Si (111) surface oxide layer, ion bombardment was needed for 10 min with Argon gas pressure at the range of 2.0–2.6 Pa, ring anode 1500 V and substrate bias 400 V. Before and after deposition, the substrate was heated to 373 K for 10 min for improving the quality of deposited film.

For comparing the properties of DLC/Ti and DLC films, DLC was also deposited at the same condition described as above. For DLC/Ti film, prior to deposit DLC film, a thin Ti film was deposited for 15 min, then 17 min for DLC film respectively, corresponding to 600 times and 1000 times laser arc generating. Also, for DLC film, deposition time was 20 min, corresponding to 1000 times laser arc generating.

2.2. Measurements

The coefficient of friction was performed by ball-on-block tester (UMT, CETR, USA), with constant load 300mN, duration time 7 s, sliding speed 0.05 mm/s, and under ambient air and room temperature. The stress was calculated using Stoney's equation,[14]

$$\sigma = \frac{E_\mathrm{s}}{6(1-v_\mathrm{s})}\frac{t_\mathrm{s}^2}{t_\mathrm{f}}\Big(\frac{1}{R}-\frac{1}{R_0}\Big), \qquad (1)$$

where E_s (180GPa), v_s (0.26),[15] t_s, t_f are the Young's modulus, Poisson's ratio, thickness of the substrate and the thickness of the film respectively. According to Stoney's equation, t_f was measured by spectroscopic ellipsometer (GES-5, Sopra, France) with wavelength 300–900 nm and refractive index 1.7–2.6,[16] and t_s, R and R_0 were carried out by surface profiler (Talysurf 5P-120, TAYLOR — HOBSON, UK). To identify the DLC film, Raman spectroscopy was measured by a microscopic confocal Raman spectrometer (Renishaw 1000, UK), with 514 nm Ar^+ ion laser at room temperature, a 50× objective, low power density 5mW, exposure time 60 s and accumulated intensity 5 times. The surface morphology was characterized by AFM (Nanoscope®, DI, USA) with scanning speed 1 Hz, both row and column 256 pixels, and tapping mode contact style. Nanoindentation tests were carried out by a nanoindenter with a diamond Berkovich

indenter (Nanotest, MML, UK). Nanoscratch tests were performed by two tribometer (Nanotest, MML, UK; Triboindenter®, Hysitron, USA) respectively. To character the element distribution along the depth direction, AES was performed by a Auger analyzer (PHI-700, ULVAC-PHI, Japan), with vacuum level 3.9×10^{-7}Pa, scanning angle 30°, resolution 0.1 eV, sputter area 3mm×3 mm and sputter speed 13.5 nm per min calculated by silicon dioxide. x-ray diffraction (XRD) patterns were measured by a diffractometer (D/max2500, Rigaku, Japan) using Kα radiation, under tube power of 6 kW, tube current of 200 mA, tube voltage of 30 kV and scanning speed of 0.02°/s.

3. Results and discussion

3.1. XRD analysis

Figure 2 shows the XRD patterns of DLC, DLC/Ti and silicon substrate. It is observed that only silicon single-crystal peaks can be detected for DLC, DLC/Ti and silicon substrate. For DLC and DLC/Ti films, as two films are very thin, x-ray can penetrate them and attain to the silicon substrate, so the silicon peaks appear in the experimental results. According to the XRD analysis, it is believed that the two films deposited by PLAD method are non-crystal.

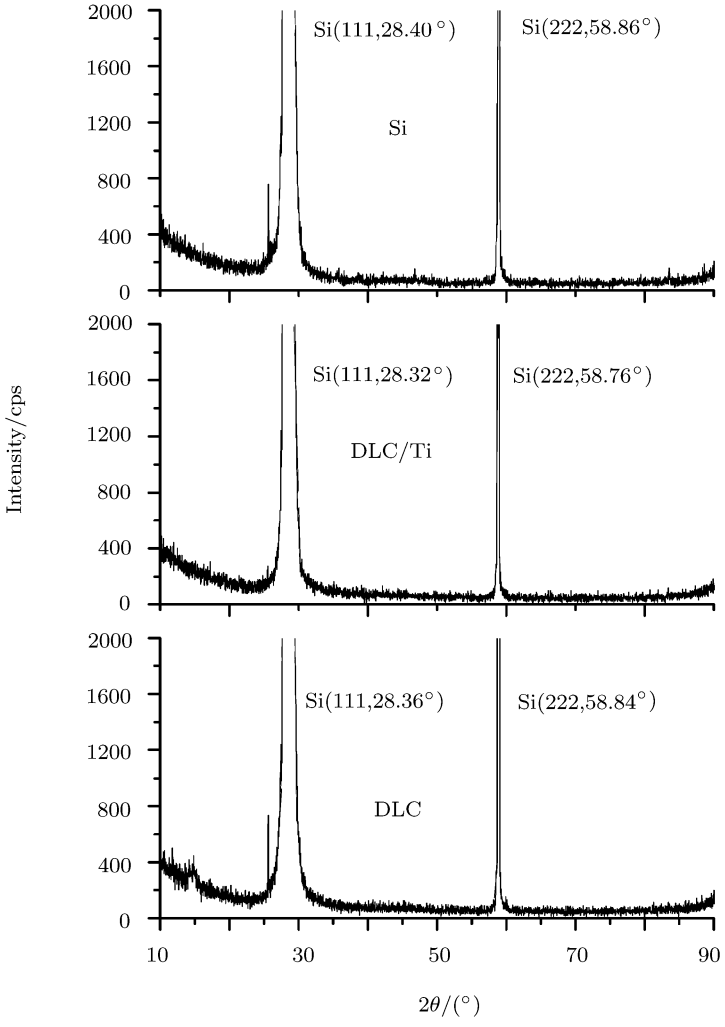


Fig.2. x-ray diffraction patterns of DLC, DLC/Ti and Si substrate.

3.2. Raman spectroscopy

Figure 3 shows the spectra of DLC and DLC/Ti films deposited on silicon substrate fitted to two Gaussian peaks using PEA KFIT-a least-squares computer program. This figure shows a broad peak centred at 1547 cm^{-1} and 1550 cm^{-1} for DLC and DLC/Ti respectively, an asymmetric shape and a shoulder peak at left side, showing a characteristic of DLC film,[17,18] which indicates that the film is amorphous. There is no noticeable difference between observed spectra. For DLC film, the actual spectra is fitted to D peak centred at 1357 cm^{-1} and G peak centred at 1556 cm^{-1} respectively, with intensity ratio, $I(D)/I(G)$ 0.36, which corresponds to 70% sp^3 content as presented by Tay *et al.*[19] Also, for DLC/Ti film, the counterpart values are D peak centred at 1349 cm^{-1}, G peak centred at 1564 cm^{-1}, $I(D)/I(G)$ 0.28 and 76% sp^3 content respectively. From above presentation, it is believed that sp^3 content of both DLC and DLC/Ti prepared by PLAD method is very high.

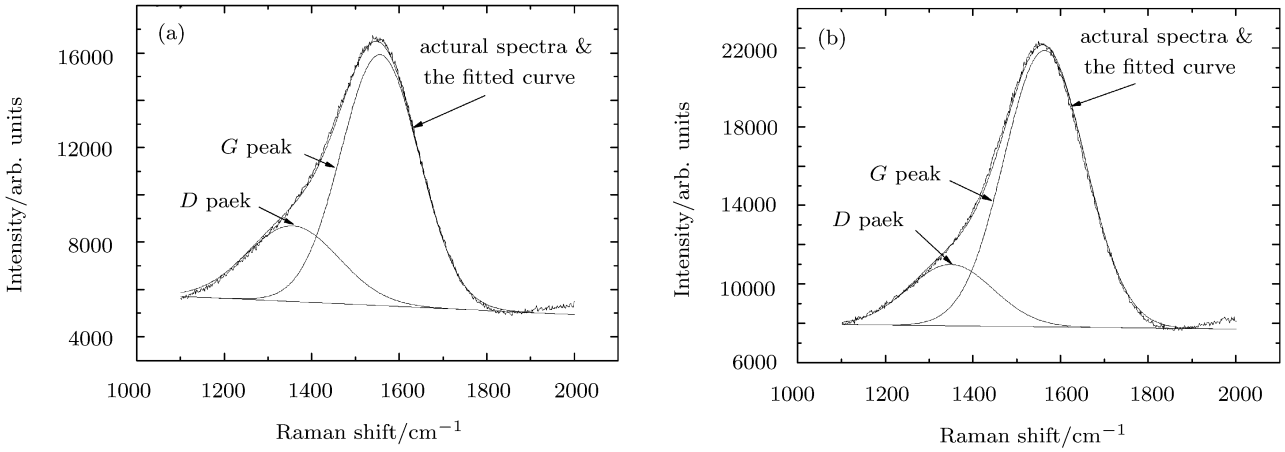


Fig.3. Raman spectra of (a) DLC film, and (b) DLC/Ti film deposited on silicon substrate.

3.3. Thickness, surface morphology and compressive stress

The thickness of DLC/Ti and DLC measured by spectroscopic ellipsometer is 39 nm and 46 nm respectively, which is the key factor of both nanoindentation and nanoscratch tests, AES sputter time and residual stress. As surface morphology includes much information of film, it is performed by AFM. Figure 4 shows the surface morphology of DLC and DLC/Ti films. Both the image size along x and y direction are 5μm×5 μm.

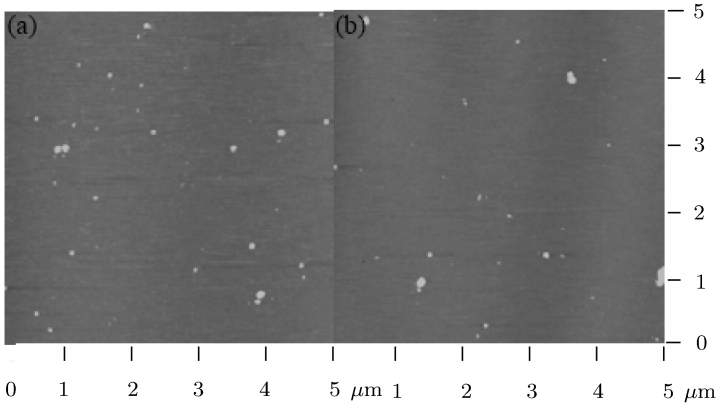


Fig.4. AFM image of (a) DLC film and (b) DLC/Ti film.

The roughness and z range of DLC are 0.265 nm and 52.463 nm, respectively. Also, they correspond to the values of DLC/Ti 0.265 nm and 27.136 nm respectively. It is seen that both the surfaces are smooth except for some defects of irradiated particles directly deposited on substrate.[20] Due to the low roughness of both surfaces of films, the hardness and Young's modulus can be measured by nanoindentation and nanoscratch tests. It is known that large compressive stress will be developed during DLC containing sp^3 bonding growth, which is believed to be due to the so-called growth induced stresses produced by the coating condensation process.[21] The compressive stresses derived from Stoney's equation, of DLC and DLC/Ti films, are 5.092GPa and 6.579GPa respectively, which is consistent with 5.74GPa proposed by Sheeja *et al.*[18]

3.4. Auger electron spectroscopy

Figure 5 shows the typical Auger spectra of DLC and DLC/Ti films.

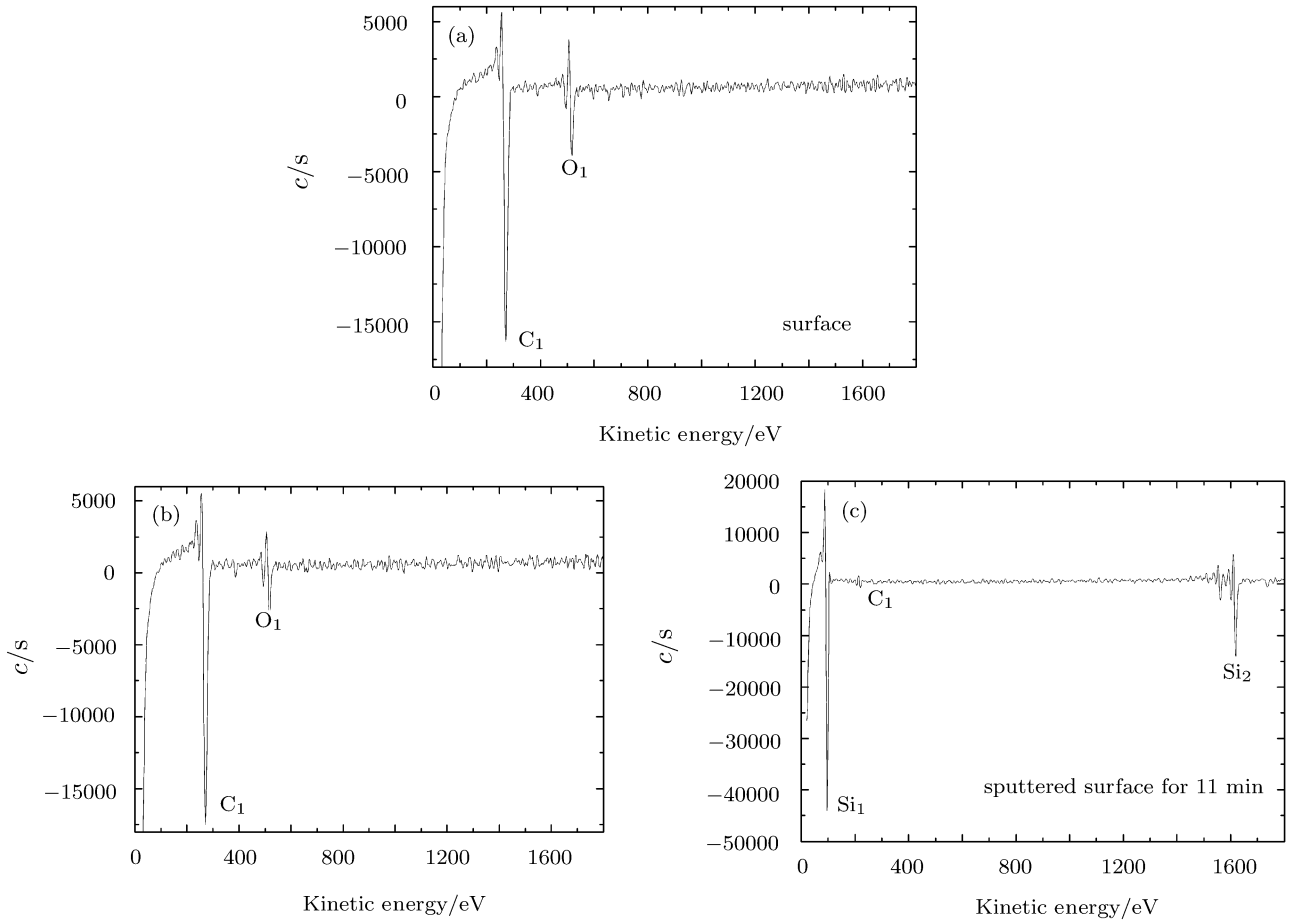


Fig.5. Auger spectra of (a) surface of DLC, (b) surface of DLC/Ti, and (c) surface of DLC/Ti for sputtering time 11 min.

It is observed that the surface Auger spectra of DLC and DLC/Ti films are similar with each other as seen in Figs.5(a) and 5(b), in which the peaks at 272 eV[22] and 510 eV [23] correspond to the KL_3L_3 transition of carbon and oxygen elements, respectively. While the spectrum of Fig.5(c) is different from above two figures, in which the peaks at 96 eV, 1621 eV and 262 eV correspond to the two kinetic energy of different electron orbits of silicon and carbidic carbon respectively at the interface containing C–Si bond as previously reported.[24] Depth profiles of DLC and DLC/Ti films are shown in Fig.6. Its sputter time was

influenced by the Ar^+ ion beam intensity, which results the longer sputter time of thinner DLC film while the shorter sputter time of DLC/Ti film. It is seen that both the content of carbon of DLC and DLC/Ti is 98 at% which is higher than that of Sedao[23] and Okada ,[22] the content of oxygen 2 at% and content of silicon 0 at%. Also, both the chemical composition of two films is uniform along the depth profiles. Both the two films is compact as the content of silicon is 0 at%. In Fig.5(a), the interface exhibits a locally high content of oxygen, which is because the thinner silicon dioxide layer was not completely removed by ion bombardment. While in Fig.5(b), it is drawn that the film forms DLC/TiO_2/Si multilayer structure as the depth profile displays two different intersected points, another reason is that the atomic concentration of oxygen after excluding that shown in Fig.6(a) is as two times as that of titanium. According to the ratio of sputter time between DLC and TiO_2, it is deduced that the thickness of titanium dioxide is 9 nm, which demonstrated that the high precision controlled by laser arc irradiation times. However, the sputter speed rate of titanium dioxide is 5.52 nm/min, which is lower than that, 5.85 nm/min derived from Fig.6(b), of DLC film.

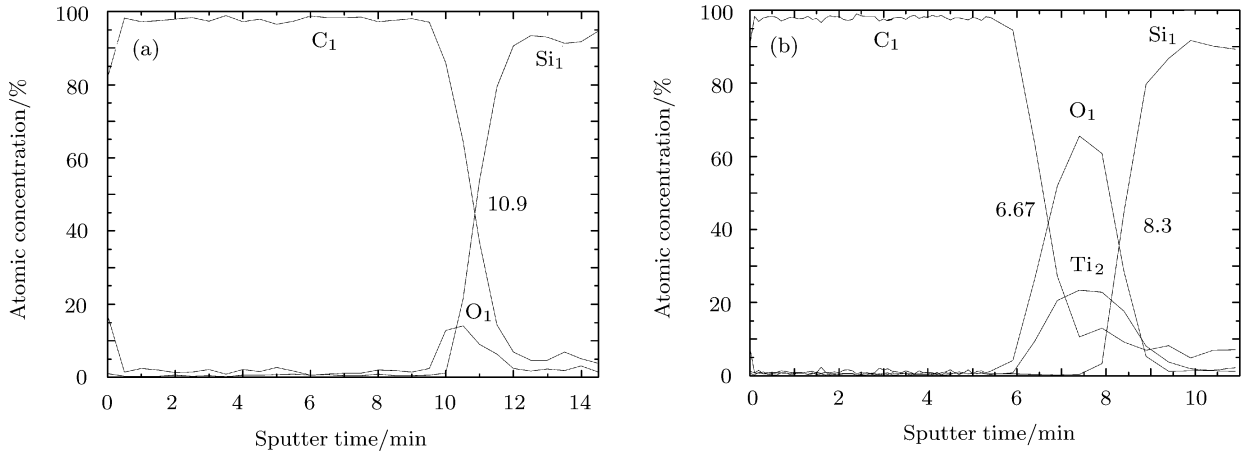


Fig.6. Depth profiles of (a) DLC, and (b) DLC/Ti.

3.5. Nanoindentation and nanoscratch characterization

To character the stability of films, five points of each film have been taken to measure the hardness and Young's modulus at the constant loading speed 0.01mN/s, and maximum load 0.2mN and 30 s temperature drift correction. The measured hardness and Young's modulus of DLC and DLC/Ti are 7.660±1.840 GPa, 111.824±12.271GPa and 8.217±0.844 GPa and 110.506±9.794GPa respectively. Hardness of DLC is lower than that of DLC/Ti, which results from the lower sp^3 bond content (see Section 3.1) of DLC compared with that of DLC/Ti.[17] In theory, Young's modulus should have the same trend with hardness, while under very small load the loading–unloading curve was influenced by the environment noise which resulted in the fluctuation of obtained data. The relatively lower hardness and Young's modulus exhibited by DLC and DLC/Ti thinner films may be influenced by silicon substrate, which is based on the fact that silicon exhibits a hardness and Young's modulus of 5.959±0.633 GPa and 89.693±6.218 GPa under the same testing parameters respectively.

3.6. Tribological property

Figure 7 shows the coefficient of friction of DLC and DLC/Ti films measured by UMT microtribometer, where DLC-1 and DLC-2 represent the different samples deposited under the same conditions, and DLC/Ti represents the DLC/Ti film. It is observed that the coefficients of friction of DLC and DLC/Ti films are approximately 0.14 and 0.08 respec-

tively, which agrees well with that of DLC deposited by filtered cathodic vacuum arc deposition (FCVA) method addressed by Sheeja,[15] and results from the thinner DLC film, 39 nm, was influenced by silicon substrate severely, while thicker DLC/Ti film, 46 nm, was influenced lightly also as argued by Sheeja.[15] According to the presentation of Sheeja, the coefficient of friction decreased as the thickness increased until it reached to 40 nm, and thereafter it kept approximately constant.

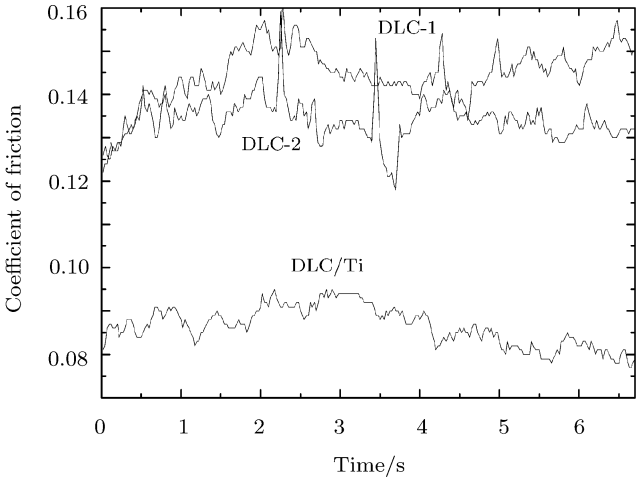


Fig.7. Coefficient of friction of DLC and DLC/Ti films varies with time.

In view of this, the coefficient of friction of DLC, DLC/Ti and Si substrate were also performed by Triboindenter®(Hysitron, USA) with maximum load 6 mN for 40 s respectively. The curves of coefficient of friction vs time of DLC/Ti are shown in Fig.8. It is observed that five curves exhibit stable coefficient of friction which is 0.12, during 5–45 s, where coefficient of friction is defined as ratio of lateral force and normal force. To remove the effect of silicon substrate on the film coefficient of friction, the maximum scratch depth is limit to 3 nm, as show in Fig.9, in which the image size is 15μm ×15 μm. In this case, the silicon substrate influence on the film can be negligible according to the micro/nano measuring rule[25] that when the measuring depth is under 1/10–1/7 of film thickness, the substrate effect can be neglected. It is noticeable that when the in-situ AFM scratch scar image is stored with digital style by the corresponding AFM software, its width keeps constant while the depth is two orders magnitude than that during scanning process, so it is necessary to record the real value of scar depth of scanning process. With the same testing parameters, five curves are taken to obtain the coefficient of friction of DLC and silicon substrate respectively, whose corresponding coefficient of friction are 0.13 and 0.16 respectively. The results show that when the scar depth is limited to 1/10 of the film thickness, the friction coefficient of DLC/Ti and DLC films is similar with each other, showing the little effect of silicon substrate. So it is believed that DLC film at thickness 40 nm is the division point with or without influence of silicon substrate.

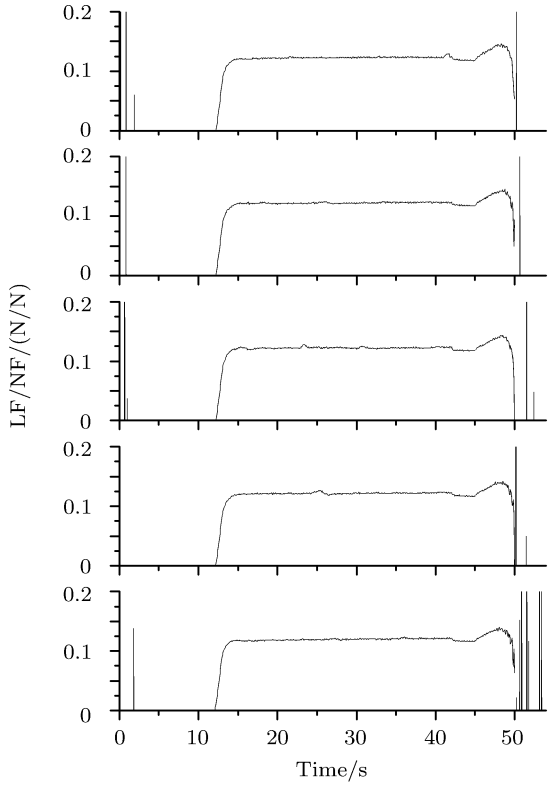


Fig.8. Coefficient of friction of DLC/Ti film.

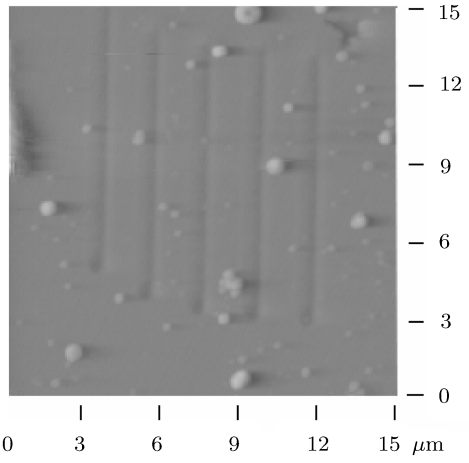


Fig.9. In-situ AFM scratch scar of DLC/Ti film.

To obtain the critical load, scratch test with maximum load of 8 mN was carried out by Triboindenter®. As the loading style is linearly loaded as the scratch distance increases, the maximum scratch depth occurs at the endpoint of scratch scar. Its in-situ AFM image scratch scar is shown in Fig.10, in which the image size is 5μm×5 μm and the maximum scratch depth is 5 nm. So it is deduced that the critical load of DLC film is approximately at 64mN according to DLC film with 39 nm thickness.

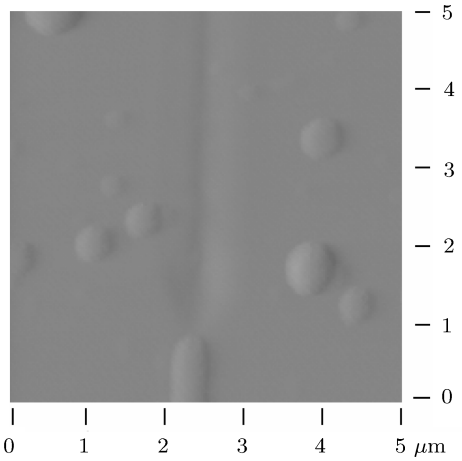


Fig.10. Scratch scar of DLC film with maximum 8 mN.

In view of this, five scratch scar curves with maximum load 100 mN were carried out by using the tribometer (NanoTest, MML, UK), as shown in Fig.11. It is observed that the five curves is similar with each other and occurs big fluctuation at scratch distance 2100 μm. As the maximum load 100 mN was completed linearly with increasing time , it is believed that the critical load is 70 mN, which agrees well with the in-situ scanning result. With the same method, critical load of DLC/Ti film is 95 mN obtained by five scratch curves, which is higher than that of DLC film. It may be caused by the high chemical reactivity of the carbon, and the metallic titanium of the adhesive interface layer, combined with the high temperatures, occurring during the frictional contact at local 'hot spots'.[26]

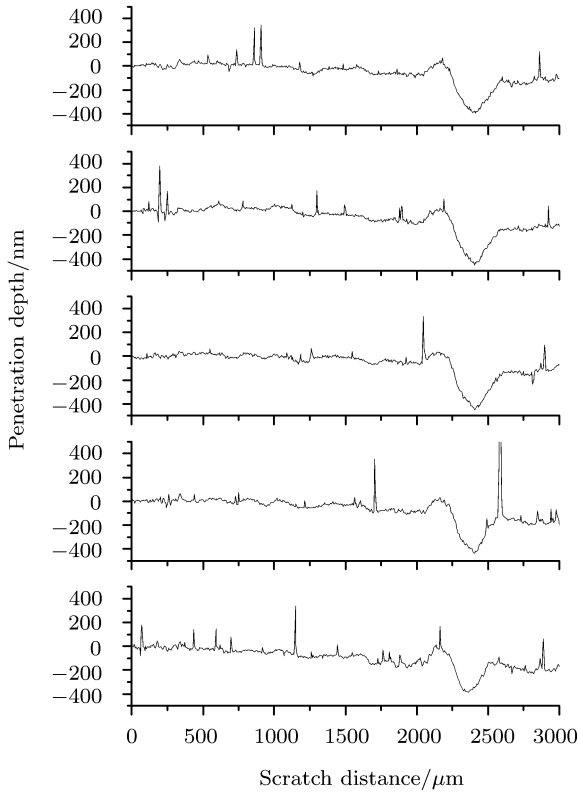


Fig.11. Scratch depth curves of DLC film with scratch distance.

4. Conclusions

A novel PLAD system developed by the State Key Laboratory of Tribology, with the advantages of PLD and vacuum arc deposition, was presented. The DLC and DLC/Ti films were prepared by using this method. The results show that both the two films exhibits compact structure, uniform chemical composition along depth direction, high atom concentration 98 at% of carbon and low oxygen content contamination in the body of film, high hardness and Young's modulus compared with that of silicon, and high sp^3 content of 70–76%. According to above presentation, both the two films prepared by PLAD method have broad prospect in the application of protective coating of cutting tools, machine tools, magnetic head of hard disc drive, and so on.

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