



Influence of bias voltage on microstructure and properties of Al-containing diamond-like carbon films deposited by a hybrid ion beam system

Wei Dai ^{a,b}, Peiling Ke ^a, Aiyang Wang ^{a,*}

^a Division of Surface Engineering, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, China

^b State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

ARTICLE INFO

Available online 4 April 2012

Keywords:

Diamond-like carbon
Bias voltage
Microstructure
Tribology

ABSTRACT

Al-containing diamond-like carbon films were deposited using a hybrid ion beam system composed of an anode-layer ion source and a magnetron sputtering with various bias voltages. XPS, TEM and Raman spectroscopy were applied to characterize the film composition, microstructure, and carbon atom bond. Nano-indentation and ball-on-disk tribo-tester were also used to study the mechanical properties and tribological behavior, respectively. The results showed that the bias voltage played a significant role on the microstructure of the films, and nano-stripe structures were observed in the DLC films, which resulted in the relatively high hardness of the films. The friction tests revealed that the films possessed a superior friction performance with a friction coefficient of about 0.02. Specially, the film with the nano-stripe clusters exhibited a good wear resistance, though those nano-clusters seemed to increase the friction coefficient.

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1. Introduction

Diamond-like carbon (DLC) films have been expected to have potential applications in many industrial fields, such as data storage in magnetic and optical disks, micro-electromechanical devices (MEMs), and biomedical coatings due to their high hardness, wear resistance, low friction coefficient, chemical inertness and so on [1–3]. However, high internal stress derived from the formation of sp³ bonds during film deposition leads to poor adhesion to the substrate, and thus limits the extended utilization of DLC films [4–6]. The incorporation of metal atoms has been considered as one of the most effective methods to stress relaxation [7,8]. Furthermore, the doped atoms can bond with carbon or form composite nano-structure embedded in the DLC matrix. This will endow the DLC films with some additional properties, including field emission, magnetic property, and adjustable permittivity, which further expand the application range of the films. Recently, nano-structures or nano-particles imbedding in metal-doping DLC (Me-DLC) films have been reported by many researchers [9–11]. Wang and co-workers [9] have successfully acquired Co nanorods in Co-DLC films using plasma-assisted magnetron sputtering. In another work, nanoscale multilayer was found in Cr-DLC films deposited by the combined steered cathodic arc/unbalanced magnetron sputtering technique in conditions of high ion irradiation [10]. And the DLC films with nano-columnar and granular pattern structures were synthesized by Corbella et al. [11] via a pulsed DC reactive magnetron sputtering method. It could be said that the nanostructure or nanocomposite in

DLC films has attracted the attention of a large number of research groups in the scientific community.

Al has been expected to be one of the best candidates for metal atom doping in stress relaxation, and the incorporation of Al can significantly improve the toughness of the DLC films [12,13]. Furthermore, Al may be easily separated out from the DLC matrix to form nanostructure precipitation due to low solubility and wettability between Al and C, which would modify the mechanical and tribological properties of the DLC films. On the other hand, the applied bias voltage in the deposition process strongly influences the microstructure and composition [14,15]. Accordingly, in this paper, Al-containing DLC (Al-DLC) films were fabricated using a hybrid ion beam system, which consists of an anode-layer ion source and a DC magnetron sputtering of Al target. During film deposition, a negative bias voltage was applied to the substrates. The influences of the bias voltage on microstructure, mechanical properties and tribological characters of the films were studied systematically.

2. Experimental details

Al-DLC films were deposited on Si wafers by the anode-layer ion source combining with the DC magnetron sputtering [16]. The anode-layer ion source has been widely used in the industrial field, and it can be scaled to any desired length and thus can produce ion beams for treating large-area samples [17,18]. Before film deposition, the chamber was first evacuated down to 2.7×10^{-3} Pa and the silicon substrates were sputter-cleaned for 10 min using Ar⁺ ion. During deposition, the C₂H₂ gas of 10 sccm was introduced into the ion source to obtain the hydrocarbon ions, and the Ar gas of 70 sccm was supplied to the magnetron sputtering to sputter the Al target. The work pressure was kept at about 0.5 Pa. A typical current of the

* Corresponding author. Tel.: +86 574 87913381; fax: +86 574 87910728.
E-mail address: aywang@nimte.ac.cn (A. Wang).

anode-layer ion source and magnetron sputtering was 0.2 A and 3 A, respectively. A pulsed negative bias voltage ranging from 0 (floating state) to -300 V (350 kHz, 1.1 μ s) was applied onto the substrate, keeping other parameters fixed among all the coatings.

A surface profilometer was used to measure the thicknesses of the deposited films through a step formed by a shadow mask. In general, all film thicknesses were more than 850 nm. The composition and chemical bond state of the films were characterized using an X-ray photoelectron spectroscopy (XPS, Japan, Axis UltraDLD) with Al (mono) K α irradiation at a pass energy of 160 eV. Before commencing the measurement, Ar⁺ ion beam with an energy of 3 keV was used to etch the sample surface for 5 min to remove contaminants. High-resolution transmission electron microscopy (TEM, US, Tecnai F20) operated at 200 keV with a point-to-point resolution of 0.24 nm was used to observe the microstructure of the films. The TEM specimens with a thickness of about 60 nm were prepared by peeling off the films from the NaCl crystalline substrates, which were dissolved in deionized water. Raman spectroscopy with a 514.5 nm Ar⁺ laser was employed to evaluate the carbon atomic bonds of films.

The hardness and elastic modulus of the films were measured by the nano-indentation technique (MTS-G200) in a continuous stiffness measurement (CSM) mode using a Berkovich diamond tip. The maximum indentation depth was 500 nm, and the characteristic hardness of the films was chosen in the depth around 1/10th of the film thickness to minimize the substrate contribution. Six replicate indentations were made for each sample. A ball-on-disk tribometer was employed to test the tribological behavior of the films in atmosphere with a relative humidity of about 60%. A steel ball (SUJ-2, HRC60) with a diameter of 6 mm was used as the counter body. The applied load was 3 N and sliding velocity was 0.2 ms⁻¹. The sliding distance was 300 m. After the friction test, the wear traces were observed by a 3D scanning surface profiler (AEP, US) and the wear scars on the counter balls were studied using an optics microscope (Leica DM2500 M, German).

3. Results and discussion

Fig. 1(a) displays the typical XPS survey scan for the Al-DLC films deposited at the bias voltage of 0 V, -100 V and -300 V. It can be seen that the films are mainly composed of C, Al, and O. With the bias voltage increased from 0 to -300 V, the Al concentration shows a slight increase from 13.33 to 14.87 at.%, while the C concentration decreases from 79.35 to 76.21 at.% (see Table 1). This may correlate with the carbon re-sputtering caused by the high-energy ion bombardment. It was reported that the weakly bonded and light carbon atoms would be more easily re-sputtered away by incident ions during the film growth stage [19]. Fig. 1(b) and (c) presents the C 1s and Al 2p spectra of the films, respectively. The C 1s peak can be fitted by three components, which center around 284 eV, 285 eV and 286 eV corresponding to sp²-C, sp³-C and C–O, respectively. However, neither aluminum carbide peak (around 281.5 eV [20]) nor aluminum oxycarbide (around 282.5 eV [21]) is detected in the C 1s spectra of the films. Fig. 1(c) reveals that the Al 2p XPS spectra have a binding energy at about 74.5 eV, corresponding to Al–O peak, which indicates that the doped Al in the carbon matrix exists mainly in the form of oxide rather than carbide. The formation of the oxidized aluminum may result from the decomposition of O₂ or H₂O during the plasma deposition process due to the insufficient vacuum.

Fig. 2 shows the TEM micrographs of the Al-DLC films deposited with different bias voltages. The image of the film deposited at 0 V is composed of grains, observably different from that of pure DLC which presents a smooth surface and consists of granular contrast [22]. The magnified view (Fig. 2(e)) reveals that there are some grain-like bright regions, which may be oxidized Al clusters. As the bias voltage was changed to -100 V, the grain microstructure evolves into a nano-stripe structure and the oxidized Al clusters get sharper. When bias voltage is further increased, those stripes become weak. This implies that the bias voltage plays a dominant role in the microstructure evolution of the

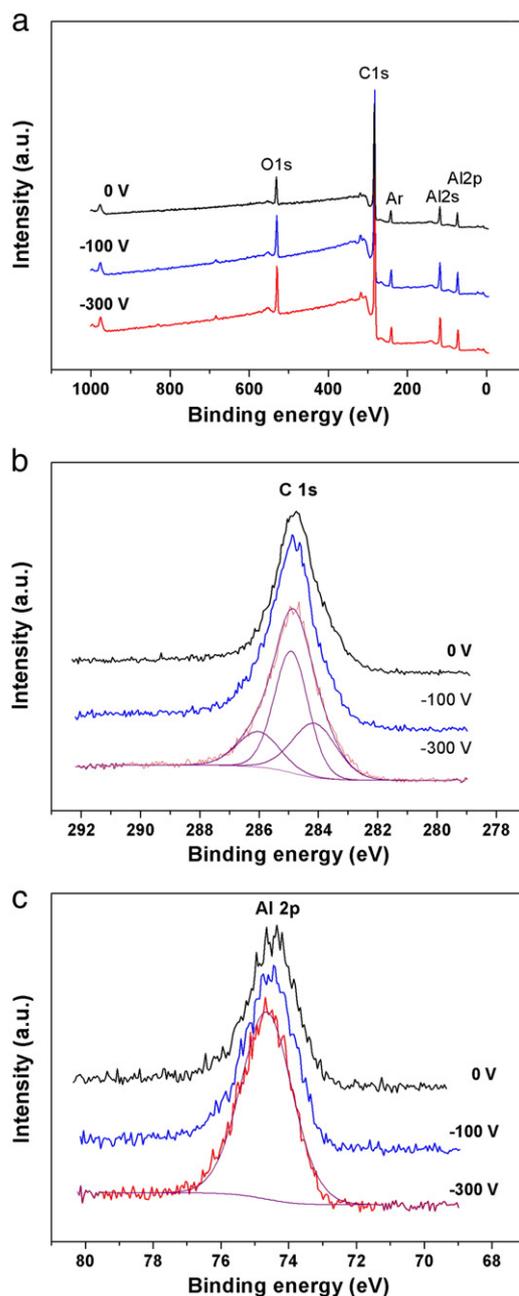


Fig. 1. Typical XPS results for the films deposited with various bias voltages: (a) survey scan spectrum, (b) high-resolution C 1s, and (c) high-resolution Al 2p.

films. Without the bias voltage (floating state), the ion energy is so low that the ions are difficult to move. Accordingly, the film growth is characterized as grain feature. When the bias voltage was changed to -100 V, the ions possess sufficient energy to move, which causes oxidized Al to be separated from the DLC matrix and thus results in the growth of the nano-stripe structure. With the bias voltage further increasing (> -100 V), the high energy ions will bombard the film

Table 1

The concentration of Al, C and O in the Al-DLC films deposited with various bias voltages obtained by XPS.

Bias (V)	Al (at.%)	C (at.%)	O (at.%)
0	13.33	79.39	7.28
-100	13.38	79.35	7.28
-300	14.87	76.21	8.91

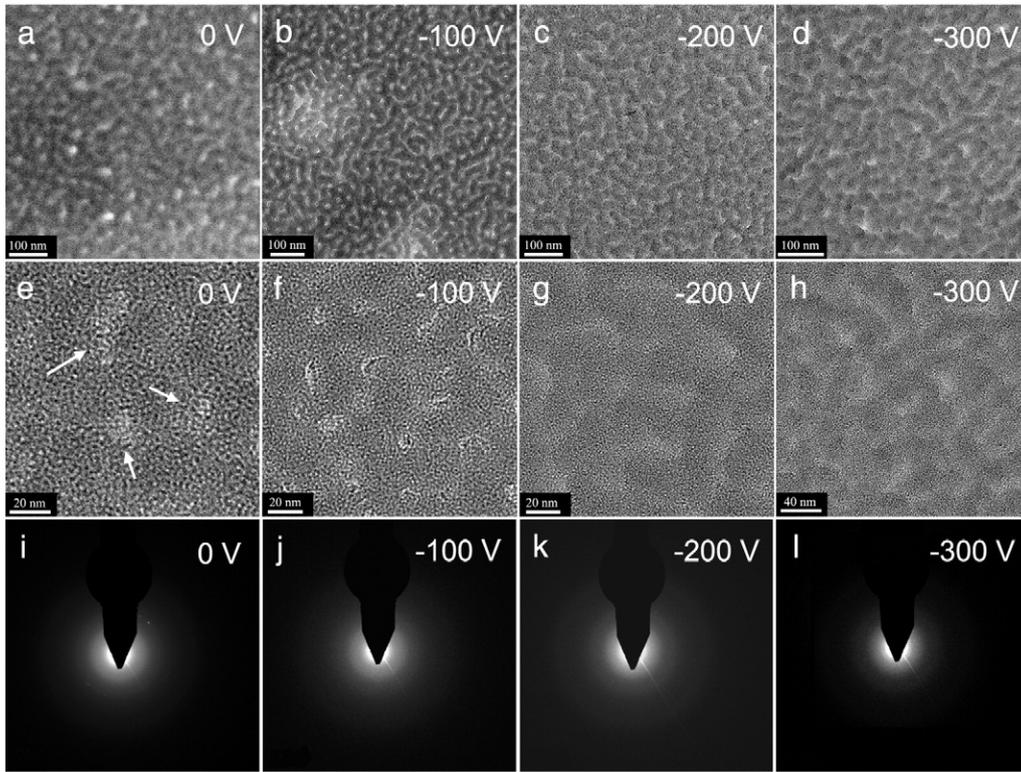


Fig. 2. (a)–(h) TEM micrographs and (i)–(l) electron diffraction patterns of the films as a function of bias voltage.

strongly and accelerate the atom diffusion, which can break the nano-stripe structures. Fig. 2(i)–(l) presents the electron diffraction pattern of the films. It should be noted that all the films present a diffuse halo, representing a typical amorphous structure, implying that the nano-stripe structures separated from the DLC matrix are also amorphous.

Raman spectroscopy is usually employed to characterize the atomic bonds of carbon films. Fig. 3 shows the representative Raman spectrums of the Al-DLC films with different bias voltages. There is a broad asymmetric Raman scattering band in the range from 1000 to 1700 cm^{-1} , consistent with the typical characteristic of amorphous carbon films [1]. Normally, the Raman spectra can be fitted by two Gaussian peaks, D peak around 1350 cm^{-1} and G peak around 1550 cm^{-1} . The D peak is attributed to the breathing modes of sp^2 atoms only in aromatic rings (graphitic cluster), while the G peak is attributed to the bond stretching of all pairs of sp^2 atoms in both aromatic rings and chains. Therefore, the intensity ratio of D peak to G peak (I_D/I_G) will increase as the graphitic component increased [23]. The

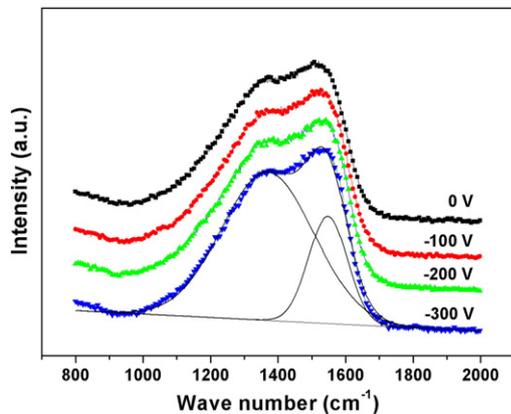


Fig. 3. Raman spectrum of the films deposited with different voltages and typical Gaussian fitting.

I_D/I_G value of the films varies over a small range from 1.55 to 1.41 with increasing bias voltage from 0 to -300 V. It can be concluded that the carbon bond structure of the films is not affected greatly by the bias voltage.

Fig. 4 demonstrates the hardness and elastic modulus of the films as a function of the bias voltage. It is characteristic to note that the hardness and elastic modulus show an increase as the bias voltage was changed from 0 to -100 V, and present a maximum value at bias voltage of -100 V followed by a monotonic decrease with further increase of the bias voltage. The formation of the oxidized Al nano-clusters (nano-stripe structures) in the films is suggested to have a significant influence on the film mechanical properties. According to the TEM results, the sharp oxidized Al nano-stripe structures are observed in the film deposited with the bias voltage of -100 V. These nano-stripe structures embedding in the DLC matrix could construct the nano-composite structures of DLC and oxidized Al nano-cluster, and therefore resulted in the high hardness of the film. In either

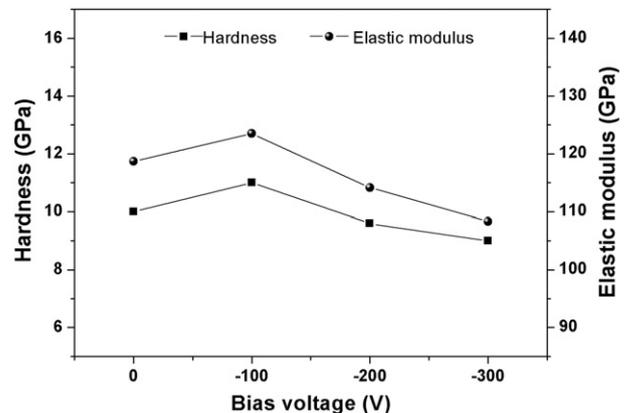


Fig. 4. Hardness and elastic modulus of the films as a function of bias voltage.

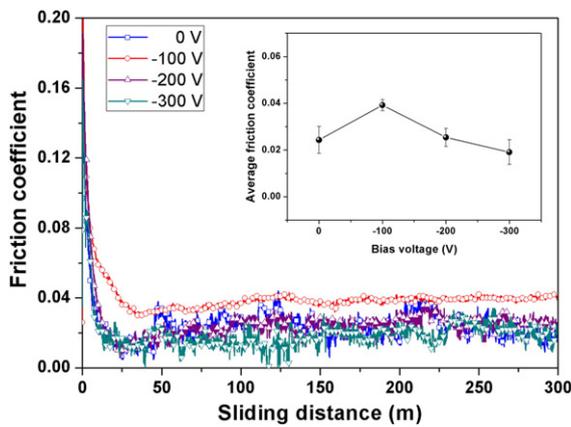


Fig. 5. Friction coefficient of the films against sliding distance and the average friction coefficient of the films as a function of bias voltage.

increasing or decreasing bias voltage, these nanostructures tended to disappear, and caused the film hardness to decrease.

Fig. 5 presents the friction coefficient of the films against the sliding distance. The average friction coefficient (calculated after 50 m of sliding distance) as a function of the bias voltage is also given in the inset of Fig. 5. It can be seen that all films exhibit an excellent lubrication performance with a friction coefficient of about 0.02, although the film deposited at -100 V possesses a slightly higher friction coefficient of about 0.04. Thick transfer-layers were found in the contact balls (as shown in Fig. 6). Previous works indicated that the transfer-layers formed in the friction of DLC films were rich in graphitic component, which could significantly decrease the friction and have been expected to account for the superior friction performance [24,25]. The increase of

the friction coefficient of the film deposited at -100 V might be correlated with the oxidized Al nano-stripe structures since the aluminum oxide always shows a high friction coefficient. Accordingly, the film deposited at the bias voltage of -100 V shows the highest friction coefficient among the present experiments.

The wear tracks within the films after friction testing are shown in Fig. 7. The film deposited with the bias voltage of -100 V exhibits a narrow and shallow wear track, while the films deposited with other bias voltages show a wider and deeper wear track. Fig. 8 presents the wear rate of the films as a function of bias voltage. With the bias voltage increasing, the wear rate of the films is decreasing firstly and then increasing. It can be seen that the film deposited at the bias voltage of -100 V reveals a minimum value, although it possesses a relatively high friction coefficient due to the existence of the oxidized Al nano-stripe clusters. It is suggested that the film hardness has a significant relationship with the wear behavior of the films, which also shows the maximum value at -100 V.

4. Conclusions

Al-DLC films were deposited by a hybrid ion beam system using different negative bias voltages. The microstructure evolution of the films was strongly affected by the bias voltage that would increase the mobility of the deposited ions. The oxidized Al nano-stripe structure was observed in the film deposited at the bias voltage of -100 V, which resulted in the relatively high hardness. In general, the Al-DLC films exhibited an excellent lubrication performance with a friction coefficient of about 0.02, but the film deposited with the bias voltage of -100 V exhibited a slightly higher friction coefficient due to the oxidized Al nano-stripe structure. The wear rate of the films seems to correlate with the mechanical properties, and the

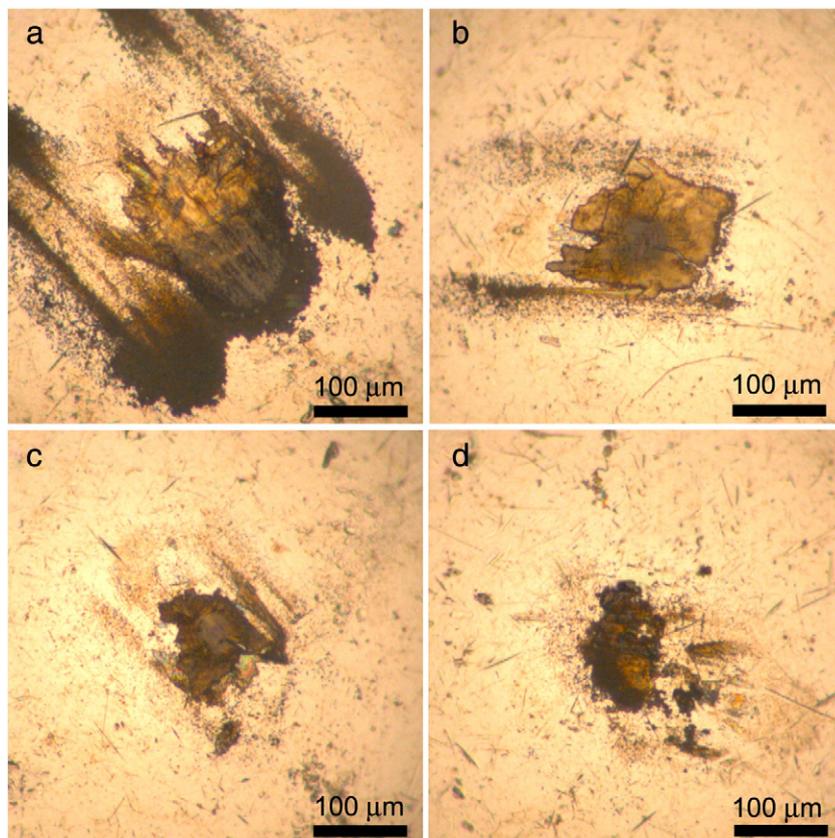


Fig. 6. The wear scar on the contact balls after friction test: (a) 0, (b) -100 V, (c) -200 V, and (d) -300 V.

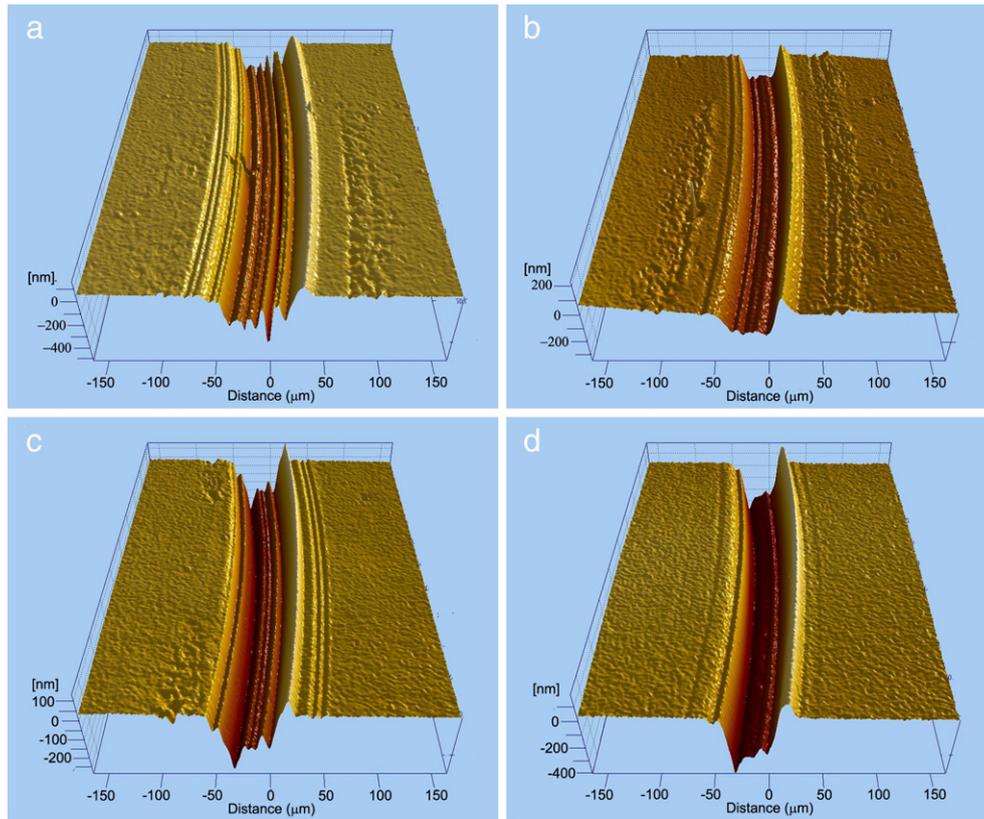


Fig. 7. The wear tracks on the films after friction test: (a) 0, (b) –100 V, (c) –200 V, and (d) –300 V.

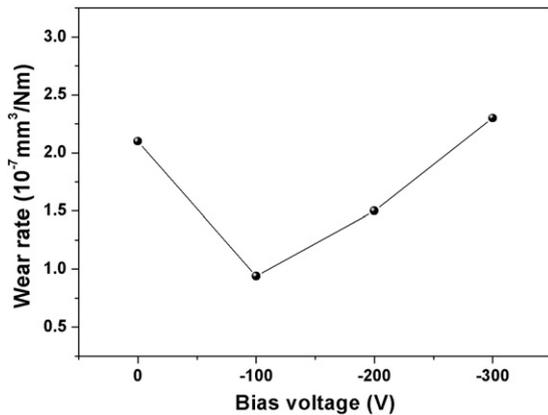


Fig. 8. The average wear rate of the films as a function of bias voltage.

lowest wear rate was shown by the film deposited at –100 V, which possessed the highest hardness among the present deposited films.

Acknowledgments

This work was financially supported by the project of the Natural Science Foundation of China (grant no: 51072205), the Natural Science Foundation (grant no: 2010A610161) and International Cooperation Foundation (grant no: 2010D10015) of Ningbo government. Furthermore, the authors would like to acknowledge the help provided by Dr. Guosong Wu (associate professor).

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