J MATER SCI 41 (2006) 1705–1709

Nano-mechanical properties and nano-tribological behaviors of nitrogen-doped diamond-like carbon (DLC) coatings

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Published online: 24 February 2006

Diamond-like carbon (DLC) coatings doped with different nitrogen contents were prepared by an ECWR-CVD deposition technique, and their chemical compositions, nano-mechanical properties and nano-tribological behaviors were characterized using Auger Electron Spectrometer and Hysitron Triboindenter, respectively. The results have shown that, higher nitrogen contents in the N-doped DLC coatings can be obtained by increasing the N2 flow rate in the reactive gas mixture. The nitrogen addition in the DLC coatings decreases evidently the nano-mechanical properties, including nano-hardness and reduced modulus. In addition, the depths for the scratched tracks produced during the scratch testing depend heavily on the nitrogen content in the N-doped DLC coatings, and, at the same applied loads, the higher the doped nitrogen content, the deeper the resulting scratched tracks. For the DLC coatings doped with different nitrogen contents, however, the frictional coefficients (LF/INF) deduced from nano-scratch testing at same loads are similar, and, therefore, seem to be independent of the added nitrogen content.

Diamond-like carbon (DLC) coatings are a novel type of carbon materials, which have witnessed rapid developments over the past few years. DLC coatings possess remarkably high hardness corresponding to that of diamond, extremely low friction coefficient, satisfactory thermal conductivity and chemical inertness. The unique combination of these properties make DLC coatings suitable for applications in wear resistant coatings, metal cutting and forming tools, and magnetic hard disc device [1–3]. Research shows that doping of certain chemical elements, including nitrogen (NDLC or CNx coatings), silicon (SiDLC), fluorine (FDLC), and metal atoms, into DLC coatings can improve effectively their structures and properties, such as internal thermal stress and thermal stability, and thus greatly broaden their application fields. Many investigations have been dedicated to the introduction of nitrogen element in the carbonaceous structure to improve the properties of conventional DLC coatings [4–7]. For example, the N-containing DLC coatings have been proposed to be used as protective coatings for MEMS. However, up to now, investigations into the nano-mechanical properties and nano-tribological behaviors for the nitrogen-doped DLC coatings are very limited. In this work, the diamond-like carbon (DLC) coatings with different nitrogen contents produced by using an ECWR-CVD deposition technique were prepared and characterized with respect to their compositions, nano-mechanical properties and nano-tribological behaviors.

Nitrogen-doped DLC coatings were prepared onto silicon substrates by using a DLC150N type ECWR-CVD deposition equipment (Shimadzu Corp., Kyoto, Japan). During the deposition of the coatings, a gas mixture of methane (CH_4) and nitrogen (N_2) was used as the reactive atmosphere, and the chemical compositions for the N-doped DLC coatings were controlled by the variation of N_2 flow rate in the reactive atmosphere. Table I summarizes the deposition conditions for the coatings. The measurements of the chemical compositions

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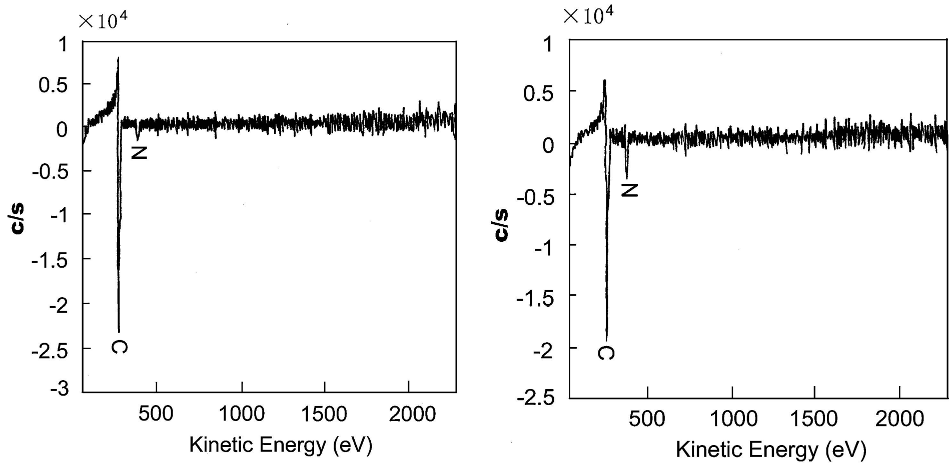
0022-2461 © *2006 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-006-2874-6

TABLE I Parameters for the preparation of N-doped DLC coatings

CH_4 flow rate (sccm)	N2 flow rate (sccm)	Radio-frequency power (W)	Microwave power (W)	Coil current (A)	Atmosphere pressure (Pa)	Bias voltage (-V)
100	10–50	80	100	16.5	1.5	170



a) 10% N_2 b) 50%N_2

Figure 1 The AES analytical results for the DLC coatings in the case of different N_2 flow rates.

for the nitrogen-doped coatings were performed on a Perkin-Elmer PHI-680 Auger electron spectroscope. The nano-mechanical properties and nano-tribological behaviors for the N-doped coatings were determined using a Triboindenter system (Hysitron Corporation, USA).

Fig. 1a and b present the AES spectra for the resultant N-doped DLC coatings in the case of 10 and 50% N_2 flow rates, respectively. Obviously, there exists much more nitrogen in the N-doped DLC coating prepared at a N_2 flow rate of 50%.

Fig. 2 shows the variation of the nitrogen contents in the DLC coatings with the N_2 flow rate in the reactive atmosphere. When the N_2 flow rate is at 10%, the nitrogen content in the coating is about 4.1 at%. The nitrogen content monotonically increases with the N_2 flow rate, and can reach to about 9.2 at% in the case of 50% N_2 flow rate, indicating the nitrogen content in the DLC coatings can be controlled through the N_2 flow rate in the reactive gas mixture.

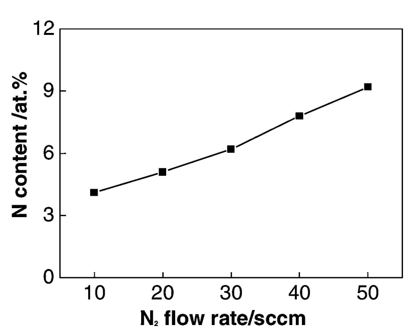
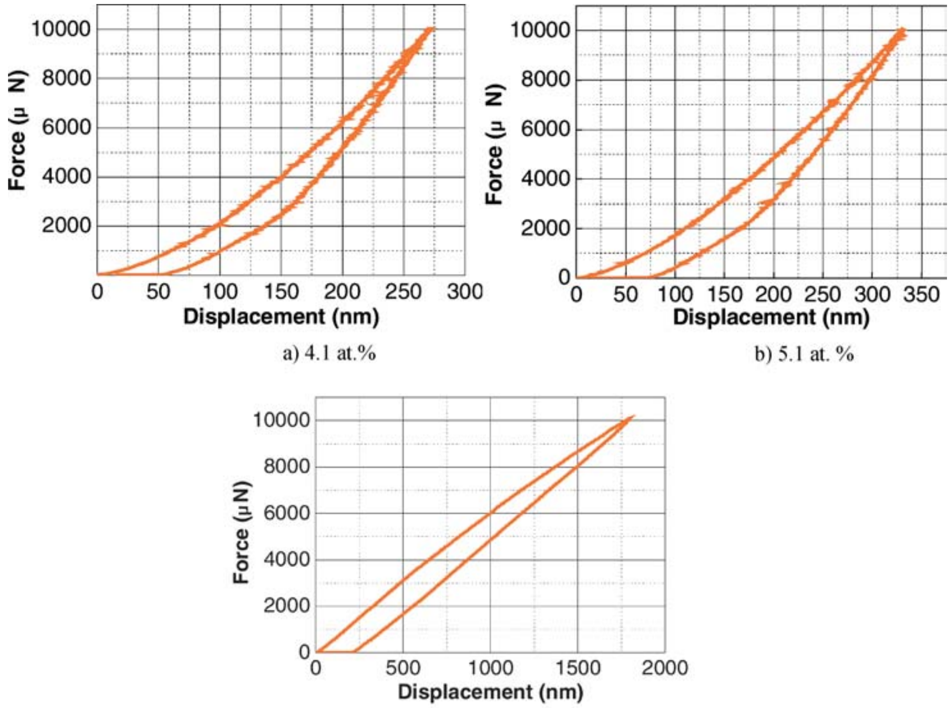


Figure 2 Correlation between the N content in the N-doped DLC coatings and the N_2 flow rate in the reactive gas mixture.

Nanoindentation testing on the nitrogen-doped DLC coatings having different nitrogen contents was carried out using a Hysitron nanoindentation system equipped with a Berkovich diamond tip. Fig. 3a, b and c) show the results of the nanoindentation experiments for the DLC coatings containing 4.1, 5.1 at% and 7.8 at% nitrogen, respectively.

The nano-mechanical properties for the nitrogen-doped DLC coatings, including nano-hardness and reduced modulus, can be determined based on the nano-hardness curves shown in Fig. 3, and are listed in Table II. The nano-hardness and the reduced modulus for the nitrogen-doped DLC coatings are greatly dependent on the nitrogen content. The more the doped nitrogen, the lower the nano-hardness and the reduced modulus for the N-doped DLC coatings. In addition, it should be noted that, when the N content rises from 4.1 to 7.8 at%, the nano-hardness and reduced modulus decrease surprisingly up to 10.3 and 38.9 times, respectively. This result suggests that, for the purpose of sustaining the excellent nano-mechanical properties, there should not exist too high nitrogen content in the nitrogen-doped DLC coatings.

Nano-scratch testing on the nitrogen-doped DLC coatings was carried out using a Hysitron nanoindentation system equipped with a conical diamond tip. The applied normal load (N_F) is 1000, 5000 and 10000 μN, respectively. Fig. 4 shows the scratched morphologies for the DLC coatings with different N contents under these three applied loads. It should be pointed out that, in the course of the nano-scratch testing, according to the left to right sequence, the applied normal load increases gradually from 1000 to 5000 μN, and then to 10000 μN. However, on the AFM images for the scratched DLC coatings having



c) 7.8 at. %

Figure 3 Nano-hardness curves for the DLC coatings with different N contents.

different nitrogen contents, there occurs no the scratched tracks corresponding to the applied load of 1000 μN. This indicates that, in the case of small applied load (e.g., 1000 μN), even though the nano-hardness for the DLC coating containing 7.8 at% nitrogen drops greatly, it still exhibits superior anti-scratch property.

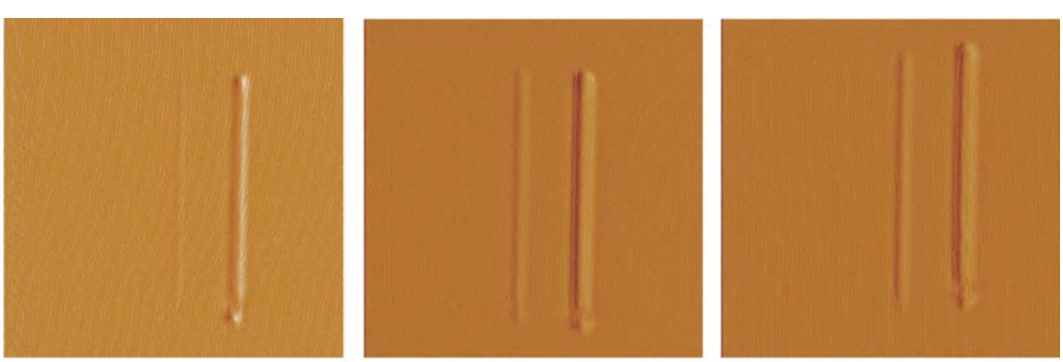
Table III gives the scratched depths for the N-doped DLC coatings at different normal loads. When the applied load is less than or equal to 1000 μN, the scratched depths for the DLC coatings with different nitrogen contents are approximately zero. At the loads of more than 5000 μN, the scratched tracks become deeper with increasing the applied loads. In addition, the scratched depth varies depending on the doped nitrogen amount in the DLC coatings. At the same applied load, higher nitrogen contents correspond to deeper scratched tracks. Obviously, this is

TABLE II Nano-hardness (H) and reduced modulus (Er) measurements for the DLC coatings having different nitrogen contents

Nitrogen content (at%)	H (GPa)	Er(GPa)
4.1	9.07	65.43
5.1	6.64	43.78
7.8	0.874	1.68

TABLE III Scratched depths for the the N-doped DLC coatings at different loads

	Scratched depth (nm)		
Nitrogen content (at%)	1000 μN	5000 μN	10000 μN
4.1	0	3	12
5.1	0	5	15
7.8	0	6.5	17



a) 4.1 at.% b) 5.1 at.% c) 7.8 at.%

Figure 4 Scratched morphologies for the N-doped DLC coatings having different N contents.

owing to the drop in the nano-hardness for the DLC coatings with higher N contents.

Figs. 5 and 6 present temporal behaviors of frictional coefficient (L_F/N_F, i.e., the ratio of lateral force (L_F) to normal force (N_F)) for the N-doped DLC coatings at the normal loads of 1000 and 10000 μN, respectively.

It can be observed that, in the course of scratch testing, the nitrogen-doped DLC coatings having different nitro-

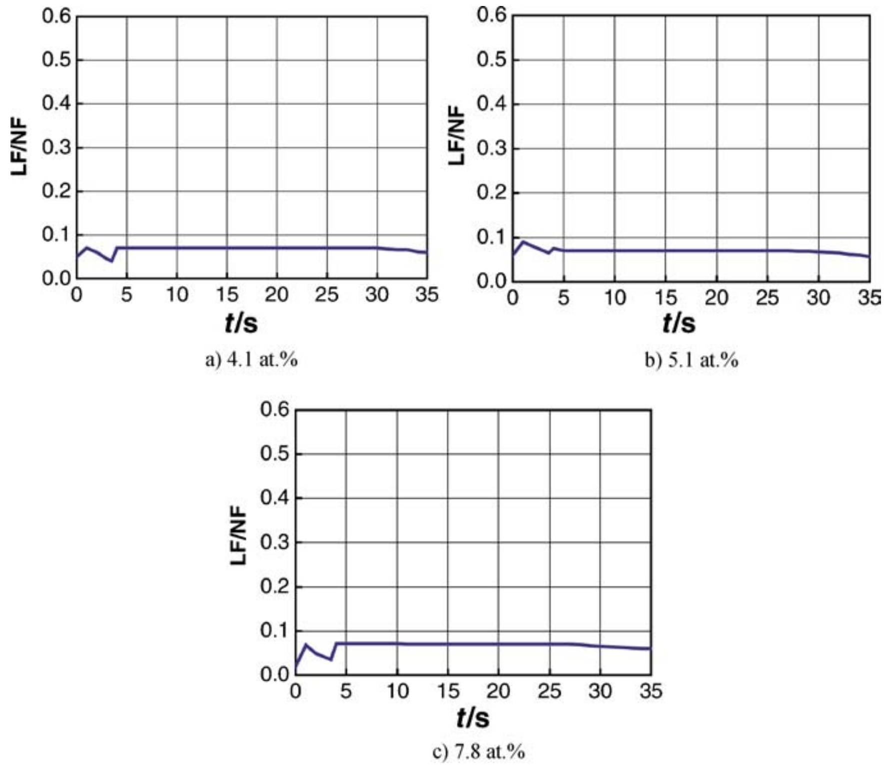


Figure 5 Temporal behaviors of frictional coefficient (L_F/N_F) for the the N-doped DLC coatings at a load of 1000 μN.

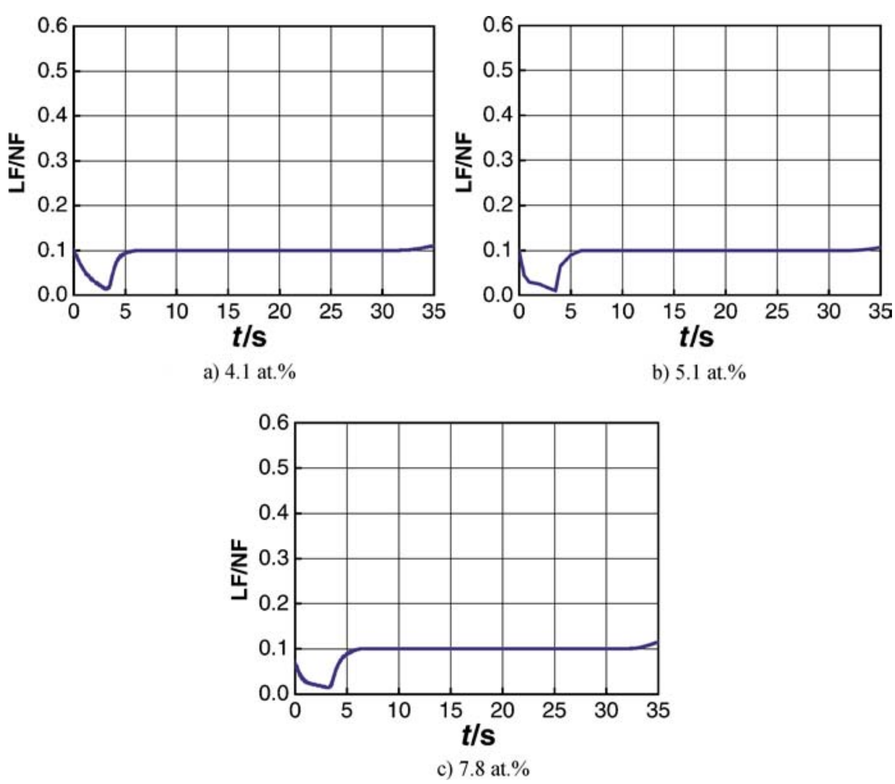


Figure 6 Temporal behaviors of frictional coefficient (L_F/N_F) for the the N-doped DLC coatings at a load of 10000 μN.

gen contents show considerably stable friction states, and their frictional coefficients (L_F/N_F) keep basically invariable during most of the scratching duration. The frictional coefficients (L_F/N_F) vary with the applied normal load, and, the L_F/N_F values become larger when the normal loads increase. However, at the same applied loads, the nitrogen-doped DLC coatings having different nitrogen contents exhibit similar L_F/N_F values. This indicates that the frictional coefficients (L_F/N_F) seem to be independent of the doped nitrogen amounts in the DCL coatings under the present testing conditions.

In summary, higher nitrogen contents in the N-doped DLC coatings can be obtained by increasing the N_2 flow rate in the reactive gas mixture. The nitrogen addition in the DLC coatings evidently decreases the nano-mechanical properties, including nano-hardness and reduced modulus. In addition, the depths for the scratched tracks produced during the scratch testing depend heavily on the nitrogen content in the N-doped DLC coatings, and, at the same applied loads, the higher the doped nitrogen content, the deeper the resulting scratched tracks. For the DLC coatings doped with different nitrogen contents, however, the frictional coefficients (L_F/N_F) deduced from nano-scratch testing at the same loads are similar, and, therefore, seem to be independent of the added nitrogen content.

Acknowledgments

The authors are grateful to the Research Project (Grant No. 2002204) of Education Office, Hebei Province, China and the Doctorate Funds of Yanshan University, China.

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Received 25 March
and accepted 7 June 2005