NANO-MECHANICAL PROPERTY AND NANO-TRIBOLOGICAL BEHAVIORS OF NITROGEN-DOPED DIAMOND-LIKE (DLC) COATINGS

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ABSTRACT
Diamond-like carbon (DLC) films doped with different nitrogen contents were prepared by an ECWR-CVD deposition technique, and their composition, structure, nano-mechanical property and nano-tribological behaviors were characterized using PHI680 type Auger Electron Spectrometer (AES), Renishaw Raman system 1000 type Laser Raman Spectroscopic technique and Hysitron Nano-indentor, respectively. It has been found that, with the increasing of nitrogen content in the films, the resultant N-doped DLC films show a monotonous drop in the sp³ ratio and a significant increase in the sp² ratio, and, accordingly, their nano-mechanical property, including nano-hardness and reduced modulus, decreases evidently. In addition, the depths for the scratched tracks produced during the nano-scratch testing depend heavily on the nitrogen content in the N-doped DLC films, and, in the case of the same applied loads, the higher the doped nitrogen content, the deeper the resulting scratched tracks. However, at the same applied loads, the DLC films doped with different nitrogen contents exhibit similar nominal coefficients of friction (L_F /N_F), indicating that the amount of doped nitrogen has little effect on the nano-frictional behavior for the N-doped DLC films.

1. INTRODUCTION
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]. Researches show 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 as protective coating 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 by using an ECWR-CVD deposition technique were prepared and characterized with respect to their compositions, structures, nano-mechanical properties and nano-tribological behaviors.

2. EXPERIMENTAL
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 (CH₄) and nitrogen (N₂) was used as the reactive atmosphere, and the chemical compositions for the N-doped DLC coatings were controlled by the variation of N₂ flow rate in the reactive atmosphere.

3. RESULTS AND DISCUSSION
Compositional analysis for the nitrogen-doped coatings performed on a Perkin-Elmer PHI-680 Auger electron spectroscopy has confirmed that the nitrogen content monotonously increases with the \( N_2 \) flow rate, indicating the nitrogen content in the DLC coatings can be controlled through the \( N_2 \) flow rate in the reactive gas mixture.

Raman spectra for the N-doped DLC coatings having different nitrogen contents show that the G peak position monotonously increases with the rising of the nitrogen content in the doped DLC coatings. Therefore, it can be deduced that, as the nitrogen content in the DLC coatings becomes higher, the content of the sp\(^3\) carbon atoms reduces while the content of the sp\(^2\) carbon atoms increases.

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. Referring to the aforesaid structural analytical results of the doped DLC coatings, it can be supposed that the variation of the nano-mechanical properties with the N can be supposed that the variation of the nano-mechanical properties with the N content should be related to the sp\(^3\) to sp\(^2\) ratios. In addition, the results of the scratched depths for the N-doped DLC coatings at different normal loads show that, at the same applied load, higher nitrogen contents correspond to deeper scratched tracks. Obviously, this is owing to the drop in the nano-hardness for the DLC coatings with higher N contents.

Nano-tribological testing on the N-doped DLC coatings shows that, frictional coefficient (\( L_F/N_F \), i.e., the ratio of lateral force (\( L_F \)) to normal force (\( N_F \))) varies 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 (e.g., see Fig. 1). This indicates that the frictional coefficients (\( L_F/N_F \)) seem to be independent of the doped nitrogen amounts in the DLC 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 promotes the increase in the sp\(^2\) ratio and 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 coefficients of friction (\( LF/NF \)) deduced from nano-scratch testing at the same loads are similar, and, therefore, seem to be independent of the added nitrogen content.