The preparation of ultra hard nitrogenated DLC film by N_2^+ implantation

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Hydrogen free diamond like carbon (DLC) films were prepared on steel substrates by using a single ion beam in a configuration that allowed sputtering of a graphite target and at the same time allowed to impact the substrate at a grazing angle. The DLC films so prepared have improved properties with increased disorder and with modest hardness that is slightly higher than previously reported values. We have studied the effects of N_2^+ ions implantation on such films. It is found that the implantations of nitrogen ions into DLC films lead to chemical modifications that allowed N atoms to be incorporated into the carbon network to produce a nitrogenated DLC. Nano-indentation experiments indicated that the nitrogenated films have consistently higher hardnesses ranging from 30 to 45GPa, which represents a considerable increase in surface hardness, compared with non-nitrogenated precursor films. The investigations by XPS and Raman spectroscopy suggests that the N_2^+ implanted DLCs had undergone both chemical and structural modifications through the incorporation of N atoms and the increased ratio of sp^3/sp^2 type bonding. The observed high hardness was therefore attributable to these structural and chemical modifications. This result has implication for the preparation of super hard wear resistant films required for tribological functions in devices.

Key words: Ion beam deposition, thin film, DLC, surface modification, ion implantation, carbon nitride

1. INTRODUCTION

Nitrogenated diamonlike carbon (a-C:N), or amorphous carbon nitride is a versatile tribo-material with potential applications where wear or corrosion cannot be ignored[1–3]. During the past decade, a variety of processes have been explored to synthesise a-C:N. These include among others, ion beam[4], plasma enhanced chemical vapour deposition [5], magnetic sputtering [6], electroplating from organic solution [7]. However, a-C:N is very sensitive to the process and its properties vary widely from one process to another. Nevertheless, application-oriented evaluation of a-C:N, including a better understanding of the nitrogenation process of the precursor DLC and of the difference between different processes need to be elucidated.

The utilization of ion implantation, in the manufacturing of a-C:N has not yet been fully explored, in the areas of varying nitrogeneous ionic species and the different DLC substrate in its various forms. This paper focuses on N_2^+ ion implantation onto DLC film manufactured by using ion beam sputtering deposition (IBSD). Comparison is made with a-C:N from reactive IBSD (ie. RIBSD) process.

2. EXPERIMENTAL

Synthesis of a-C:N by ion implantation was conducted on a 50 KV ion implanter. DLC, deposited previously on steel substrate by using ion beam sputtering deposition (IBSD), was used as the precursor sample. In the ion implantation process, the nitrogen ion spectrum was filtered with the aid of an electromagnet, to allow mass selection of N_2^+ specie from the ion beam spectrum. The implanted dose was varied from $5–2 \times 10^3$ mC, scanned over an area of $40 \times 40cm^2$.

Nanoindentation was conducted to assess the micromechanical properties of the films using a Berkovich indenter and a maximum load of 5mN. Raman spectroscopy was performed using a Renishaw Ramascope with a 10mW helium-neon laser excitation source of wavelength 633 nm. X-ray Photoelectron Spectroscopy (XPS) was performed on a Phi-Spectrometer with non-monochromatic Mg Kα radiation (1253.6eV).

3. RESULTS AND DISCUSSION

Fig 1 shows indentation depth profile, where the doted line shows the result collected on a RIBSD sample for comparison. All the profiles show a common trend that the hardness value rapidly reaching a maximum value and then decreases with increasing penetrating depth. The maximum hardness observed on the profile is indicative of the true hardness of the film. As shown on Fig. 1, N_2^+ ion implanted samples showed maximum hardness values, which varied between 27 – 45 GPa. These were significantly higher than maximum hardness values observed for the RIBSD samples, which are typically in the range of 20-30 GPa [7].

Fig 2 showed a typical Raman spectrum of N_2^+ ion implanted sample. It shows a broad peak ranging from 1100 to 1700 cm^{-1}, which is a typical feature for amorphous carbon.

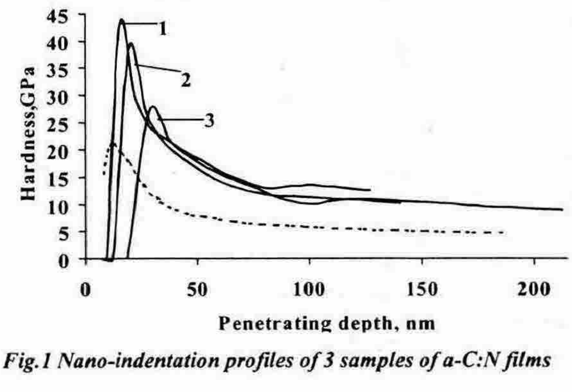

Fig.1 Nano-indentation profiles of 3 samples of a-C:N films

The broad peak is considered as an overlap of multi-components, which is usually deconvoluted into two peaks centering at around 1340 and 1580 cm^{-1} and corresponding to D- and G-line, respectively. The intensity ratio of D line to G line, (i.e, I_d/I_g) has been correlated with the proportion of sp^3 type bonding in the carbon network and it is believed that the sp^3 increases with a decrease in I_d/I_g [8]. The Raman spectrum from an a-C:N by RIBSD is also shown (doted line) for comparison. The preparation of a-C:N by ion implantation does not change the amorphous structure, but did change the Raman parameters by affecting the asymmetry and the I_d/I_g ratio. The a-C:N via N_2^+ ion implantation has a higher asymmetry and a smaller I_d/I_g value than the a-C:N from the RIBSD process. This evidence would indicate that the N_2^+ ion implanted a-C:N has a higher proportion of sp^3, and would be consistent with the higher hardness observed in the implanted samples.

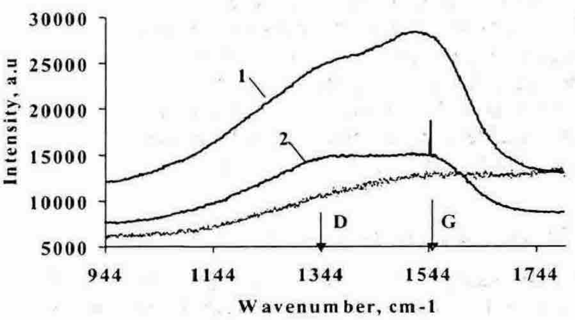

Fig. 2 Raman spectra for DLC, a-C:N by ion implantation (1) and a-C:N from RISBD, showing the characteristic D and G lines

Fig 3 shows the C1s core level XPS spectra of a-C:N films. It is generally found that, C1s peak for amorphous carbon (DLC) centers at about 284.6 eV, and that for a-C:N from RIBSD at 285 eV with an asymmetry toward higher binding energy. Here, for a-C:N ion implanted the C1s peak is centered around 285eV but the shift is found to be accompanied with an increased asymmetry toward higher binding energy, which may be an indication of higher proportion of sp^3 bonded C.

The XPS data for N1s core level of a-C:N films are shown in Fig 4. By comparing with RIBSD sample, N1s peak for ion implanted shows the tendency of down-shift and decrease in asymmetry.

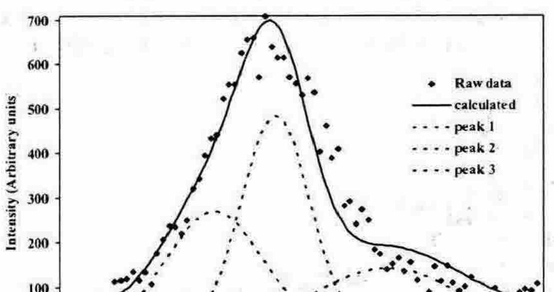

Fig.3 XPS C1s for a-C:N by ion implantation, with in increased asymmetry towards higher binding energy.

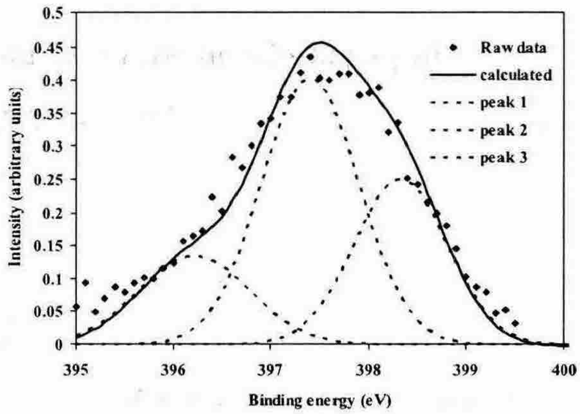

Fig. 4. N1s XPS spectrum for a-C:N, showing two major peaks corresponding to N^1 and N^2

The peak for RIBSD has been shown to be deconvoluted into 3 peaks, centering at 397.4, 399, and 401.4 eV (correspondingly denoted as N^1, N^2 and N^3), respectively. While in this ion implanted sample we can resolve the raw data into two major peaks around N^1 and N^2 without the N^3 peak at 401.4 eV . The peaks N^1 and N^2 could be assigned to the bonding structures of nitrogen to sp^2- and sp^3- carbon, respectively[9]. Combined evidences from our present results suggest that the nitrogen atoms in a-C:N from the ion implanted film are mostly in chemical bonding with carbon atoms, and there is less free N_2 incorporated when compared with similar a-C:N in film from the RIBSD process .

4. CONCLUSION

Implantation of N_2^+ into a-C films offers a higher hardness than that the directly synthesized by RIBSD, probably through an increase in sp^3/sp^2 ratio and in the proportion of nitrogen atoms chemically bonded to the carbon atoms. However, both methods can be used for the surface modification of the steel substrate.

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