Field Emission Characteristics of Nitrogen-Doped and Micro-Patterned Diamond-Like Carbon Films Prepared by Pulsed Laser Deposition

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Abstract

Effect of nitrogen doping on field emission characteristics of patterned Diamond-like Carbon (DLC) films was studied. The patterned DLC films were fabricated by the method reported previously[1]. Nitrogen doping in DLC film was carried out by introducing N_2 gas into the vacuum chamber during deposition. Higher emission current density of 0.3~0.4 mA/cm^2 was observed for the films with 6 at % N than the undoped films but the emission current density decreased with further increase of N contents. Some changes in CN bonding characteristics with increasing N contents were observed. The CN bonding characteristics which seem to affect the electron emission properties of these films were studied by Raman spectroscopy, x-ray photoemission spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR). The electrical resistivity and the optical band gap measurements showed consistence with the above analyses.

Introduction

DLC films are mechanically hard, chemically inert and of great interest as cold cathodes for field emission display. Because of low threshold field and high current density, electron field emission behaviors of DLC films have been widely investigated by many researchers.[2][3] In the previous paper[1], improved field emission characteristics of pulse laser deposited DLC films by the micro-patterning were reported.

In the present work, nitrogen-doped DLC films were obtained by introducing N_2 gas into the deposition chamber and effects of nitrogen doping on field emission characteristics of patterned DLC films were studied.

To analyze the effects of nitrogen on bonding characteristics of CN bonds, Raman spectra, XPS and FT-IR analyses were employed. Also effects of nitrogen on the electrical properties and the optical band gap were studied. These effects are discussed in connection with portion of C-N bond and C=N bond.

Experiment

DLC films were deposited by a pulsed Nd-YAG ablation technique using oscillating 5 N graphite target. The oscillating of the target was employed to facilitate a spatially stable plume formation by avoiding the laser shooting the same spot twice during one run. The focused power density, 3×10^{12} W/cm^2 for wavelength of 532 nm was used. The vacuum chamber was maintained at a low 10^{-7} torr range during deposition process. Patterning method was the same as that of the previous report[1].

Field emission measurements were carried out at a pressure of 2-3 $\times$ 10^{-7} torr by a diode type arrangement. The nitrogen content in the DLC films was determined by elastic recoil spectrometry using incident ion of ^{35}Cl.

For the electrical resistivity measurement, DLC films were deposited on thermally oxidized Si with 0.6 µm thick oxide layer to avoid the influence of the conductive substrates.

Result and Discussion

As shown in Fig. 1, high emission current density of 0.3-0.4 mA/cm^2 has been obtained at the applied field of 8.5 MV/m. The emission current density of nitrogen-doped film with 6 at % nitrogen is higher than that of the undoped film. However, further increase of nitrogen content decreased emission current density. The increase in the emission current density up to nitrogen content of 6 at % and the reduction in the emission current density at higher nitrogen content are shown.

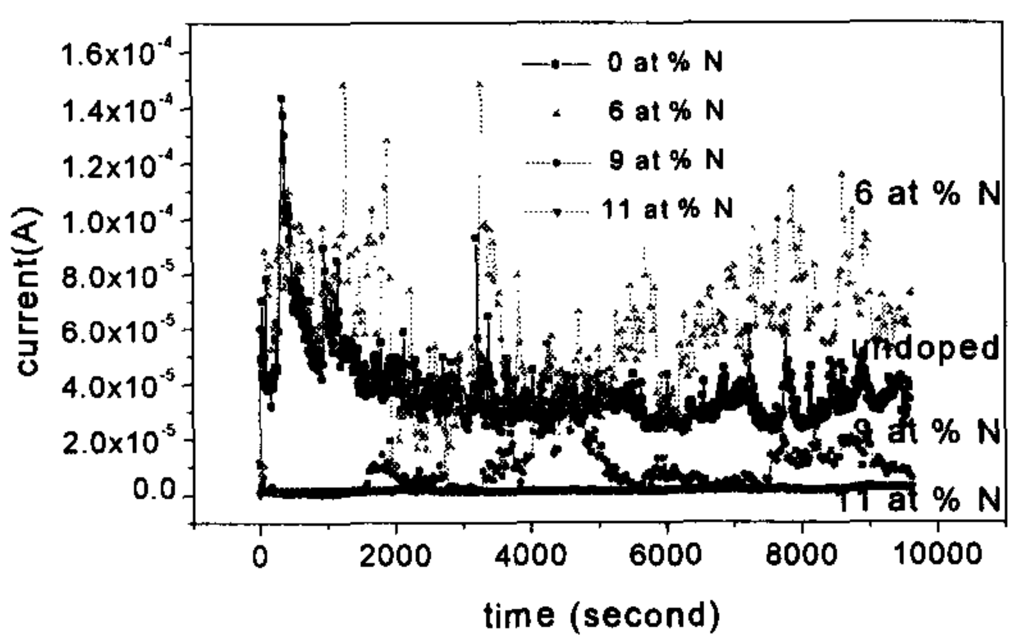

Fig. 1. The emission current vs bias annealing time for a series of the nitrogen content.

These suggest that there is some change of CN bonding characteristics with increasing N content and the bonding characteristics may change the electron emission properties. Also the dominant CN bonding type such as C=N double bonds with the sp^2 hybridization and C-N single bonds with the sp^3 hybridization may be varied by the extent of incorporated nitrogen contents.

The I(D)/I(G) ratio and G-band width of the Raman spectra of the nitrogen-doped DLC films as a function of the nitrogen content are shown in Fig. 2. The I(D)/I(G) ratio increases and G-band width decreases with the increasing nitrogen content but the both showed a plateau-like region at 4 to 6 at %. The strong decrease of the G-band width and the increase of the I(D)/I(G) are observed at 6 to 9 at % nitrogen. These phenomena are consistent with the results reported by R. O. Dillon[4] suggesting the formation of sp^2 clusters.

Fig. 3 shows C1s spectra of the DLC films measured by XPS. A shift of peak position of the carbon core electron excitation energy towards higher binding energy in the specimen doped with 6 at % nitrogen content was observed. This suggests that more diamond-like bond was formed[5]. Therefore, this result indicates that nitrogen is forming C-N bonds with the tetrahedral bonded carbon atoms[6] up to 6 at % of nitrogen. Further increase of nitrogen content results in shifts of the C1s peaks towards lower binding energy, e.g. more graphite-like bonding[5].

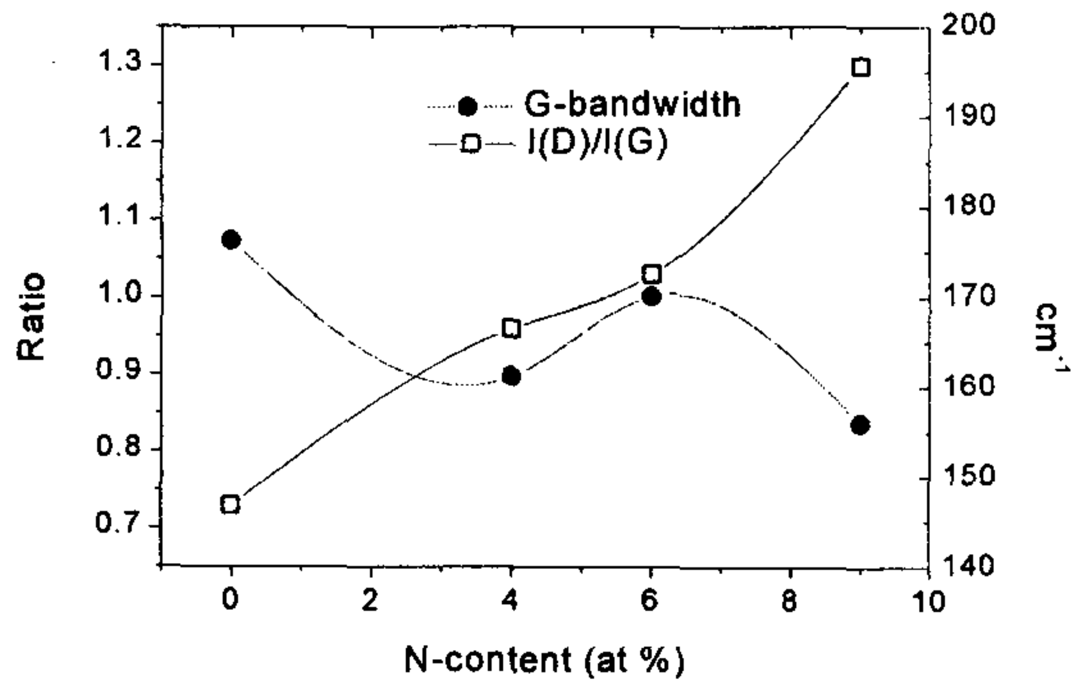

Fig. 2. The I(D)/I(G) ratio and G-bandwidth as a function of the nitrogen content

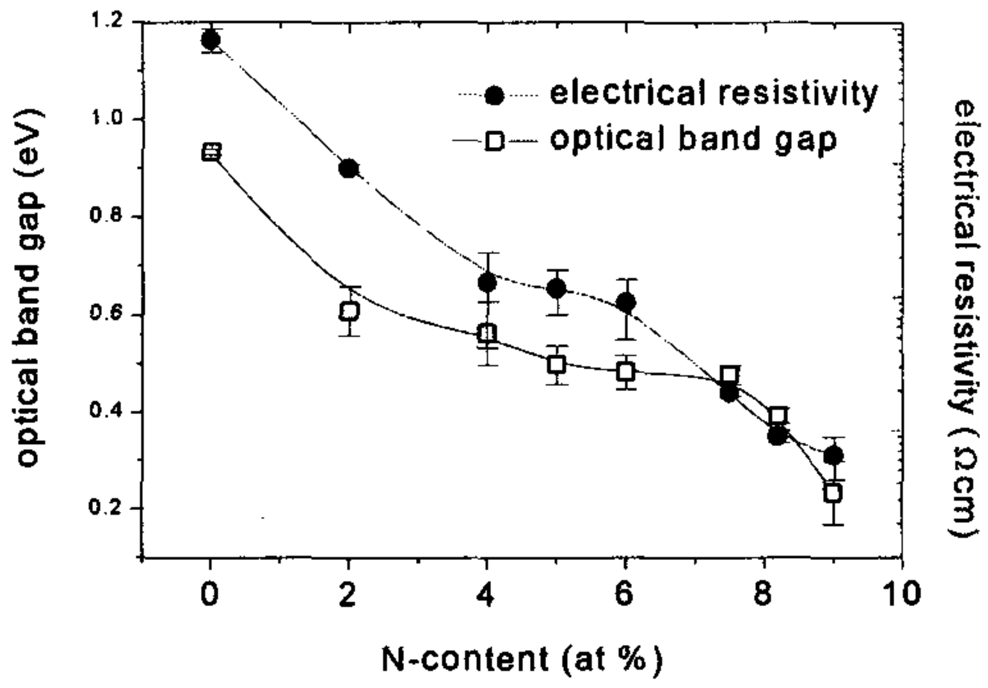

Fig. 5. Electrical resistivity and optical band gap as a function of the nitrogen content.

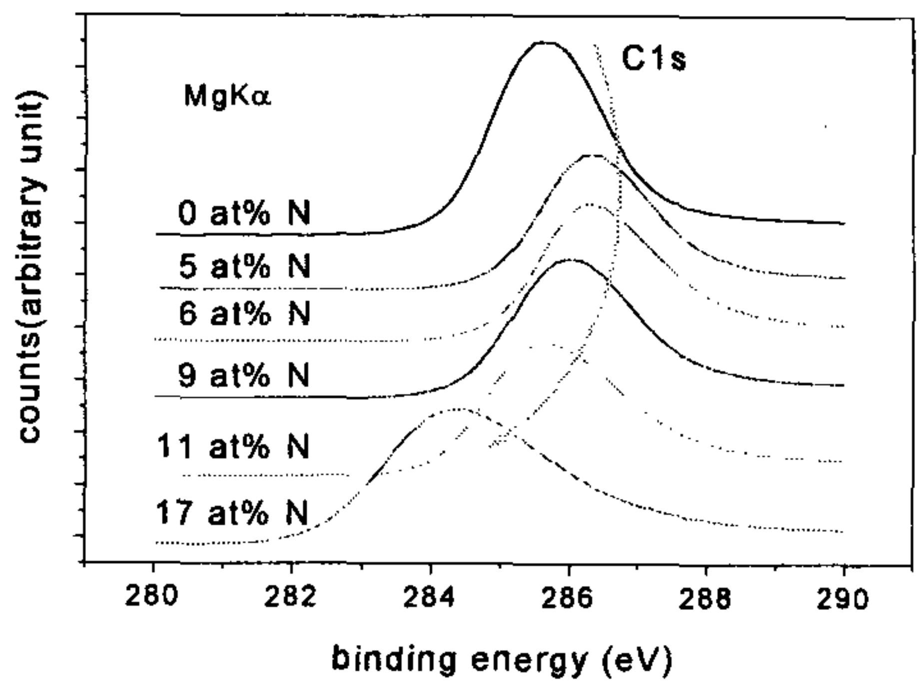

Fig. 3. XPS C1s core-level electron spectra for DLC films

In Fig. 4, the deconvoluted IR spectra of the DLC films with 7.5 and 9 at % mitrogen are shown together with the whole spectra. This result shows the existence of strong C-N bonds absorption peak together with weaker C=N peak at the 6 at % N film. However, as N content increase up to 9 at %, stronger C=N bond absorption peak has been developed. It indicates that the content of C=N bond in the film with nitrogen content of 9 at % is higher than the film with 7.5 at % N. The FT-IR results are in consistent with the above mentioned Raman and XPS results.

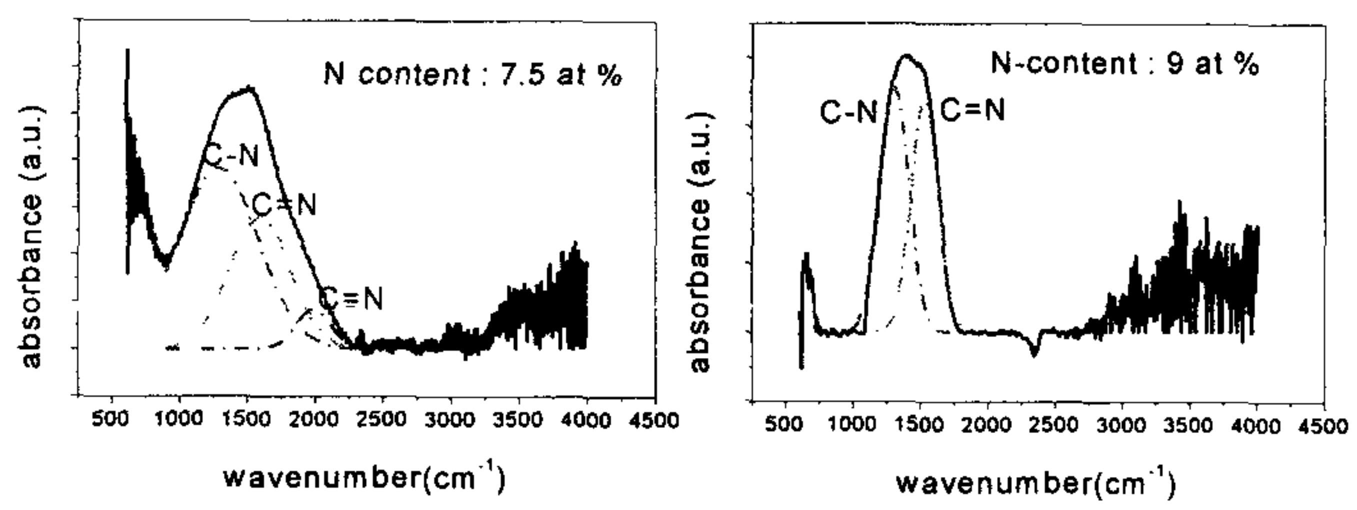

Fig. 4. Deconvoluted IR spectra for DLC films.

Changes of electrical resistivity and optical band gap with varying nitrogen content are appeared in Fig. 5. Overall feature of the curves shows that electrical resistivity and optical band gap decrease with increasing nitrogen content. But a plateau-like region at 4 to 6 at % range and more rapid decreases with further increase of nitrogen content are observed.

It has been reported that the variation of sp^2 fraction for C and N sites as a function of N content was reported by Silva, et al[7]. They argued that the C sp^2 fraction increased at a high nitrogen content and it corresponded to graphitization. Also, in the present work, the rapid decrease of electrical resistivity and optical band gap may be associated with the formation of sp^2 bond regions in the specimens over nitrogen content of 6 at %. For more detail analyses regarding distribution of sp^2 and sp^3 bonds in the films, DLC films are being investigated by transmittance electron microscopy and electron energy loss spectroscopy.

Conclusion

The incorporation of nitrogen into the DLC films fabricated by pulsed laser deposition increased the emission current density of the films when the nitrogen content was lower than 6 at %. Further increase of nitrogen content lowered emission current density of the films abruptly. The FT-IR measurements showed that the C=N bond portion of the films increased with increase of N contents over 6 at %. This is consistent with the results of the Raman and XPS measurement. The sp^2 bond regions seem to be formed over the 6 at % N. The electrical resistivity and the optical band gap measurements supported the above mentioned analyses.

Consequently, it is deduced that the enhancement effect on the field emission properties by the incorporation of the nitrogen is restricted by the formation of sp^2 bond regions.

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