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STRUCTURE MODIFICATION OF HYDROGENATED CARBON NITRIDE FILMS BY HIGH-ENERGY He^{2+} IRRADIATION

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It is well known that amorphous carbon and related films consist of nano-sized carbon clusters. With the incorporation of hydrogen into these films, the hydrogen termination limits the cluster size and decreases the bond strength among clusters. In this study, dehydrogenation from amorphous hydrogenated carbon nitride films was accomplished using 3.75 MeV-He^{2+} irradiation. The hydrogen atoms forming methyl and ethylene groups were mainly removed from the film during the irradiation procedure. With the progress of dehydrogenation from methyl and ethylene groups, the degree of order of the atomic configuration became large, resulting in an increase of the cluster size. The mechanical properties of amorphous films were improved due to cluster growth.

Keywords: carbon nitride; ion irradiation; ERDA; hardness; infrared absorption; Raman scattering spectroscopy

INTRODUCTION

It is well known that amorphous carbon and related films consist of nano-sized carbon clusters. With the incorporation of hydrogen into these films, the hydrogen termination limits the cluster size and decreases the bond strength among clusters. In this study, dehydrogenation from amorphous hydrogenated carbon nitride films decreased from 0.50 to 0.30 by He^{2+} ion irradiation as a dose of 4.86×10^{15} ion/cm^2.

The IR spectra are obtained from the a-CN_x:H films before and after He^{2+} irradiation, as shown in Figure 2. The absorption at the wave number

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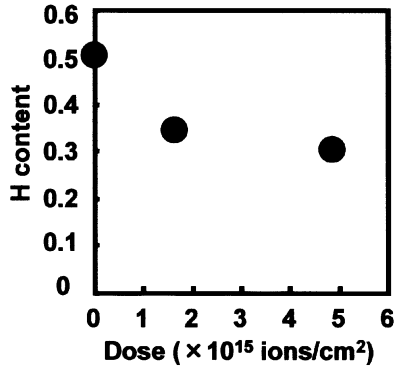

FIGURE 1 Hydrogen content in the a-CN_x:H films as a function of He^{2+} dose.

in the range of 1500 cm^{-1}–1600 cm^{-1} can be assigned to the stretching vibration mode of C=N and C=C, respectively. Other absorptions at the wave numbers around 3300 cm^{-1}, and 2800–3000 cm^{-1} are assigned to the stretching vibration modes of the N-H bond, and CH_2 and CH_3 bonds, respectively. Furthermore, the absorption band at the wave number around 1400–1500 cm^{-1} is attributable to the bending vibration mode of the CH_2 and CH_3 bonds. The intensity of stretching and bending vibrations for CH_2 and CH_3 bonds markedly decreased with increasing He^{2+} dose. It finally almost disappeared. It is likely that the cluster size grows in the films by hydrogen elimination due to the termination followed by the progress of polymerization of dangling bonds. If the cluster size grows in the

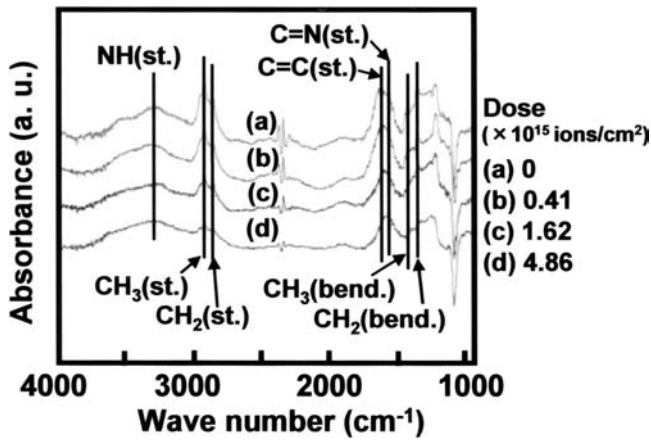

FIGURE 2 IR spectra of the a-CN_x:H films as a function of He^{2+} dose.

amorphous films, structural changes can be confirmed by Raman spectroscopy and the measurement of mechanical properties.

Figure 3 shows the Raman spectra obtained from α-CN_x:H films before and after He^{2+} irradiation. Prior to He^{2+} irradiation, the fluorescence background was confined by the Raman spectrum, implying the presence of a hydrogen-containing polymer structure. The intensity of the fluorescence background decreased to one-fifteenth at the He^{2+} dose of 4.86×10^{15} ions/cm^2. After He^{2+} irradiation, two new broad bands appear: the G(graphiti) band at around 1550 cm^{-1} and the D(disorder) band at around 1360 cm^{-1}, implying the presence of the structure of diamond-like carbon (DLC). There are no sharp graphite peaks that are clearly visible at 1576 cm^{-1} and 1327 cm^{-1} [2]. These results show that high-energy He^{2+} irradiation promotes dehydrogenation of α-CN_x:H films without graphitization. These also suggested that the cluster size was increased by more than 2–3 nm by polymerization due to hydrogen elimination [3].

Figure 4 shows the hardness value obtained from the α-CN_x:H films. Before He^{2+} irradiation, the hardness value of the sample was 1.0 GPa. It increased to 5.2 GPa at a He^{2+} dose of 4.86×10^{15} ions/cm^2. Although this hardness value is lower than that of DLC, which is in the range of 10–25 GPa [4–6], it is clear that the hardness value of the α-CN_x:H films increased with the lack of hydrogen. This result along with the Raman results suggests the increase in the cluster size in the α-CN_x:H film with He^{2+} irradiation. These results are well explained using the cluster model previously proposed by us [1].

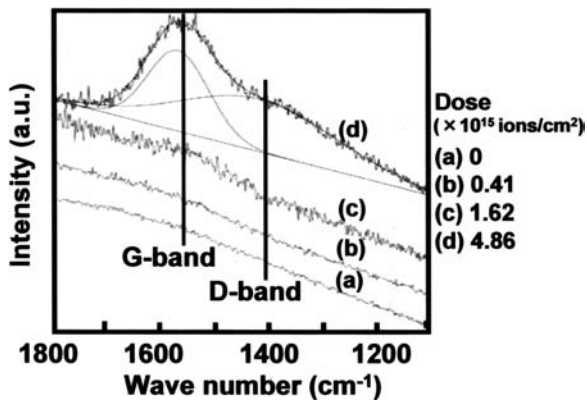

FIGURE 3 Raman spectra of the α-CN_x:H films as a function of He^{2+} dose.

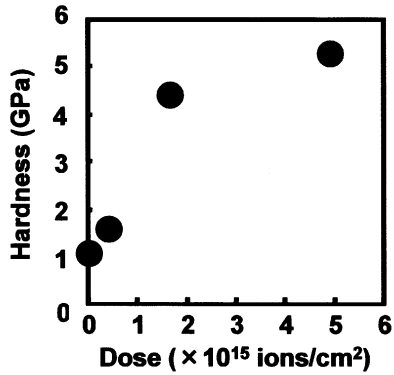

FIGURE 4 Hardness of the a-CN_x:H films as a function of He^{2+} dose.

SUMMARY

In this study, hydrogen terminating the nano-cluster in the a-CN_x:H films was eliminated using He^{2+} ion beam irradiation. In addition, structural analyses were performed by spectroscopy and mechanical measurements. The hydrogen atoms forming methyl and ethylene groups were mainly removed from the film during the irradiation procedure. With the progress of dehydrogenation from methyl and ethylene groups, the degree of order of the atomic configuration became large, resulting in an increase of the cluster size. The mechanical properties of amorphous films were improved due to cluster growth. These results are well explained using the cluster model previously proposed by us.

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