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ELECTRON-IRRADIATION-INDUCED ORDERING IN TETRAHEDRAL-AMORPHOUS CARBON FILMS

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We investigated in detail the structural ordering developed in films of tetrahedral amorphous carbon (ta-C) under 100 kV to 200 kV electron beams of transmission electron microscopes (TEM). From systematic measurements of electron diffraction and electron energy loss spectra (EELS), in selected areas the ordered structures were concluded to be multi-walled carbon nanotubes or warped graphitic platelets containing a high density of defects. The electron-irradiation-induced ordering can neither be accounted for by a sample heating nor be explained only by displacement damage caused by 200 kV electron irradiation. The essential process, that is enhanced, appears the atomic diffusion induced by electronic excitations due to the electron irradiation.

Keywords: tetrahedral amorphous carbon; nanotubes; graphite; electronic excitations; transmission electron microscopy; electron energy loss spectroscopy

INTRODUCTION

Carbon is a unique material that has a large variety of allotropic structures, the electronic properties of which depend strongly on the bonding nature of the solids. The conversion of one structure to the others occurs usually under severe conditions such as at extremely high temperatures and high pressures. In some cases, it has been suggested that electronic excitation effects are involved in the conversion: e.g., Ugarte [1] alluded that some electronic process may mediate the conversion of graphite to carbon onions that occurs during irradiation of electrons used for transmission electron microscopic observations. In the present paper, we report results of our experimental exploration of this problem in tetrahedral amorphous carbon (ta-C), showing that an electronic excitation effect appears really present.

EXPERIMENTS AND DISCUSSION

The ta-C films, we used, were prepared by the Filtered Cathodic Vacuum Arc (FCVA) method [2]: C^+ions accelerated at 100 V, the voltage at which the highest fraction of sp^3 bonding is achieved, were deposited onto Si (111) substrates up to a thickness of 70 nm. The thin ta-C films were removed from the Si substrates by etching with fluoronitric acid and were examined by a transmission electron microscope (JEM-2010F) installed with a thermal field emission gun. Selected area diffraction (SAD) patterns were recorded by imaging plates for quantitative analysis, and electron energy loss spectra (EELS) were acquired by using a parallel EELS system (Gatan, DigiPEELS 766).

Room temperature irradiation of the TEM electron beam at the acceleration voltage of 200 kV with a current density of $5 \times 10^4 A/m^2$ (2.7 nA in the area of $5.3 \times 10^4 nm^2$) for 35 minutes induced a structural change in the ta-C film as shown by a typical high-resolution image in Figure 1. The image, that had no features before irradiation, turned to exhibit contrasts of curled fringes or partially concentric patterns of a dimension of several nanometers.

Electron irradiation for 10 min induced a new halo ring inside the rings in the SAD patterns observed in as-grown samples (Figs. 2(a) and 2(b)). In the dark field image from the new ring appeared bright spot contrasts of a nanometer size indicating the occurrence of structural ordering in the irradiated area. The smallest interplanar spacing evaluated from the diffraction ring size was 0.36 nm, which is quite different from that (0.22 nm) of diamond and is considerably larger than the interlayer spacing (0.33 nm) of crystalline graphite; however it is close to the inter-wall spacing

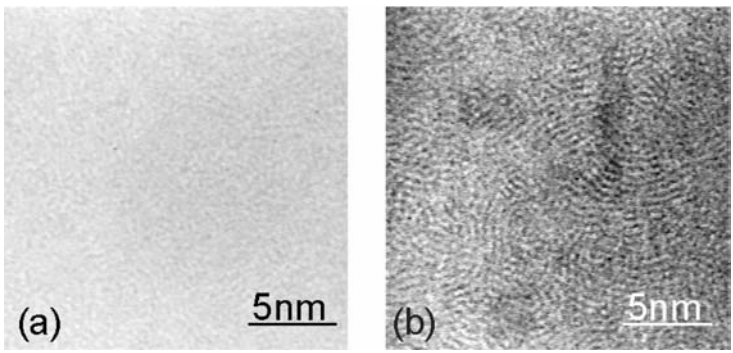

FIGURE 1 High-resolution images of a sample area before (a) and after (b) electron irradiation.

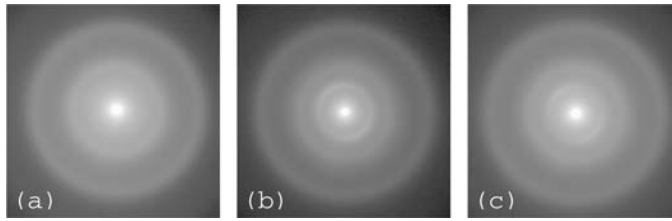

FIGURE 2 SAD patterns before (a) and after (b) electron irradiation. (c) A SAD pattern from an irradiated area of a sample tilted by 25°.

(0.36 nm) of multi-walled carbon nanotubes of the similar dimension (≈5 nm in diameter) [3].

Figure 3 shows the EELS spectra in the carbon K-edge core loss range in which 200 kV electron irradiation is seen to induce a growth of the π* peak that represents the presence of carbon-carbon bonds of sp^2 character.

When the sample was tilted by 25°, the new ring in the SAD pattern became anisotropic, indicating that the ordered structures are not spherical like carbon onions. This fact together with the smallest SAD ring size and the increase of π* core loss strongly suggests that the ordered structures induced by electron irradiation are those close to multi-walled carbon nanotubes or warped graphitic platelets containing a high density of defects [4].

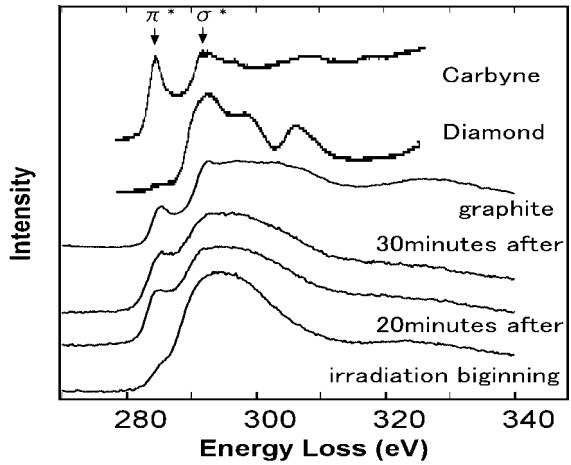

FIGURE 3 Growth of π* peak in EELS Spectra.

The electron irradiation at 100 kV brought about less significant effects, but, if the irradiation was prolonged, it yet induced ordering of ta-C with less efficiency. Figure 4 shows the effect of the acceleration voltage on the growth of ordered structures quantified by the relative intensity of the SAD ring with respect to the background. In all plots, the current density was fixed at the same value of 5×10^4 A/m^2 for the same sample.

Since the displacement threshold voltage for ta-C is considered to be located between 100 kV and 200 kV, Figure 4 indicates that the structural ordering is enhanced by atomic displacements. For the structural ordering to develop, however, the diffusion of atoms over some distance must take place. Although atomic diffusion is usually activated thermally, experiments at elevated temperatures showed that the structural ordering does not occur at temperatures below 300°C. The possible temperature rise due to the electron irradiation estimated from the energy deposit by the electron energy loss is at most 0.1 K for the current density of 1×10^4 A/m^2, too small for the electron-irradiation-induced ordering to be interpreted in terms of a sample heating effect. It should be noted that irradiation with less penetrable electrons accelerated at lower voltages would cause a rather larger sample heating and also stronger electronic excitations. These lead us to an idea that some electronic excitations caused by the electron irradiation are responsible for the enhanced diffusion of carbon atoms. The enhancement of ordering at 100 kV by the pre-irradiation at 200 kV ((b) in Fig. 4) and the persistent progress of ordering under 200 kV irradiation ((a) in Fig. 4) imply that the irradiation damage is not a requisite for the structural ordering but assists the electronic-excitation-enhanced diffusion by introducing free volumes that serve as sites for atomic diffusion.

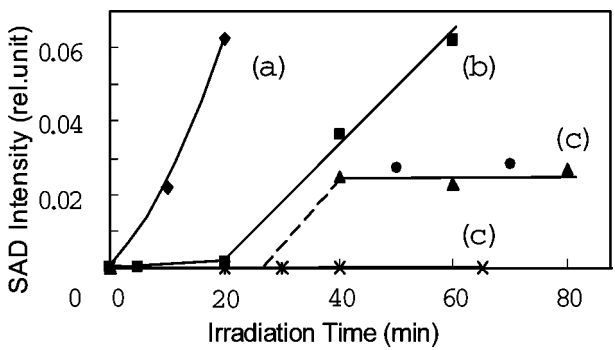

FIGURE 4 The growth of ordered structures with irradiation time. (a) irradiated all through at 200 kV (b) pre-irradiated at 200 kV for 5 min and irradiated at 100 kV (c) irradiated all through at 100 kV.

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