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Structural change in graphite under electron irradiation at low temperatures

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Abstract

Changes in crystallographic and electronic structure of electron-irradiated graphite were examined at low temperatures by means of transmission electron microscopy (TEM) and electron energy-loss spectroscopy (EELS). The long range order *within* the basal planes at the low temperatures was lost more quickly than at room temperature, which hardly affected the continuous changes in electronic and short range structures. This was mainly caused by the faster fragmentation of the crystal into pieces with the local structure maintained. The basal plane buckling and lattice dilation in the *c*-direction, similar to the previous results obtained at room temperature, suggest the local formation of non-hexagonal atomic rings, on the analogy of fullerenes, by the displacement damage incorporated with electronic excitations. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Carbon-based materials have been utilized as representatives of low-*Z* materials in the nuclear environment [1]. Their usefulness, from the practical point of view, probably consists in the flexibility in their properties, such as light but hard enough for use as structural materials, high-corrosion resistance, high or moderate heat and electrical conductivities even under high-energy particle irradiation. These practically utilized carbon materials are often mixtures of disordered graphite and other impurities partly because homogeneous and isotropic properties are required.

On the other hand, continuous efforts to understand the physical and chemical properties of carbon materials in well-defined structures (i.e. crystalline states) have been made from the fundamental point of view. In this respect graphite shows a variety of interesting characters because of its uniaxial anisotropy where the covalent bonding within the graphitic sheet (basal or *c*-plane) and the van der Waals interaction between them. If limiting the subjects to radiation effects in graphite, there still remain a number of issues to be understood, for instance, anomalous swelling in the *c*-direction, drastic reduction of heat and electrical conductivities, increase in resistance for cleavage, etc [2]. These effects cannot be fully understood by applying the conventional concept of crystal defect physics, i.e. the formation and annihilation of point defects and their agglomeration, which has been successful for most metals and alloys.

Present authors' group has claimed that these above mentioned radiation effects above are partly ascribed to a transition of the local chemical bonding from the sp^2 to sp^3 hybridization to construct 3-dimensional bridging between the *c*-planes [2]. An attempt to take such effects of covalent bonding and its highly anisotropic character into account has recently started, primarily using transmission electron microscopy (TEM) and electron energy-loss spectroscopy (EELS) under electron irradiation [3–7]. The main results obtained at room temperature are summarized as follows: (i) The [0 0 0 1] electron diffraction pattern turned to complete halo rings at the electron dose of about 1 dpa (displacements per atom) [5]. (ii) High-resolution electron microscopy

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(HREM) and electron diffraction parallel to the *c*-planes showed that the lattice spacing between the *c*-plane was homogeneously increased by up to 11% with the irradiation [4]. (iii) The crystal was fragmented into pieces, a few nanometers in size and the basal planes were buckled, while the layered structure was still well maintained [4]. (iv) The analyses of the extended energy-loss fine structure (EXELFS) on the EELS spectrum showed that the covalent bonds between carbon atoms changed their nature into several kinds incorporated with slightly different bond lengths [7]. (v) The energy-loss near edge structure (ELNES) characteristic of crystalline graphite disappeared and then exhibited new broad structures peaked around 293 and 297 eV after the prolonged irradiation [7], which well agreed with the ELNES (or NEXAFS: near edge X-ray absorption fine structure) of higher fullerenes [8,9]. All these results above suggest that the overall change in electronic structure accompanies the formation of non-hexagonal atomic rings involved by electron irradiation [3].

In the present study we conduct similar experiments at low temperatures, where it is expected that the evolution of displacement damage varies in some manner, which could be helpful for a further understanding of the phenomena.

2. Experimental

Samples used in the present study were highly oriented pyrolytic graphite (HOPG) and highly graphitized carbon fibers (HGCF). The sample preparation procedures and experimental conditions, which have been described in the series of our papers in detail [3–7], are not extensively repeated here.

Electron irradiation and TEM–EELS experiments were simultaneously performed in an electron microscope operated at an accelerating voltage of 200 kV, which is well above the threshold for the displacement of carbon atoms in the graphite lattice (130 kV). The irradiation temperatures were around 90 and 120 K. The irradiation doses are shown hereafter in the unit of displacements per atom (dpa), estimated from the cross-section for elastic electron scattering, 1.0×10^{-23} dpa/electron at the accelerating voltage of 200 kV. The electron flux was about 2×10^{19} electrons cm^{-2} s^{-1} which corresponds to about 2×10^{-4} dpa s^{-1}.

We used two types of microscope for different experiments: a Hitachi H-800 electron microscope equipped with a serial EELS spectrometer in Nagoya University and a JEOL JEM2000F electron microscope equipped with a field emission gun and a parallel EELS spectrometer (Gatan Model 666) in Japan Atomic Energy Research Institute (JAERI). The former was used for acquiring the EXELFS data, where the structural change due to the irradiation damage was monitored by electron diffraction, and the latter for in situ HREM and ELNES observations which need better spatial and energy resolution. Because of the different performance of specimen cooling holders available for the two microscopes, the former experiments were done at ~120 K and the latter at ~95 K.

3. Results

3.1. Analyses of EXELFS and ELNES spectra

The analyses of core loss spectra in EELS were done along the same procedures as those of X-ray absorption fine structure (XAFS) [10,11]: EXELFS is a phenomenon similar to extended X-ray absorption fine structure (EXAFS) originated from short range atomic configurations, and ELNES to NEXAFS or XANES (X-ray absorption near edge structure), sensitive to chemical environments of the excited atoms of interest.

The radial distribution functions (RDF) derived from the EXELFS spectra for as-prepared and 0.2 dpa irradiated HOPG samples are shown in Fig. 1, in which the corresponding diffraction pattern for each stage is inset. The direction of the incident electron beam was along the *c*-axis. The original sharp Bragg reflections turned to complete halos at a dose of ~0.2 dpa, much lower than

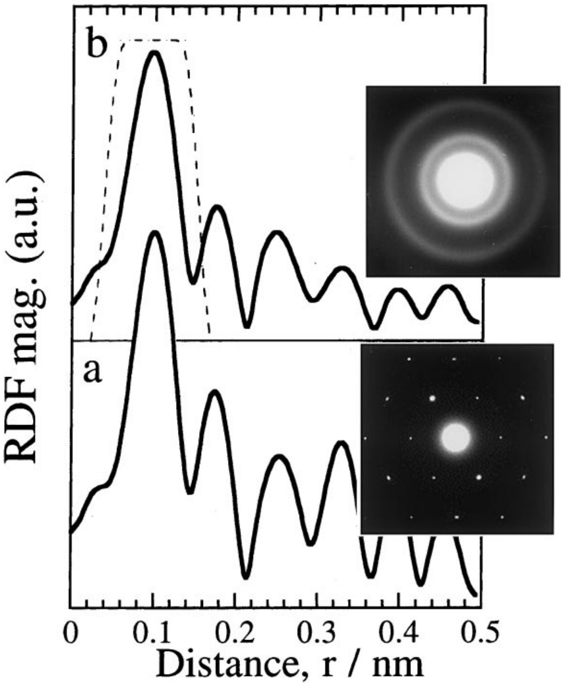

Fig. 1. Radial distribution functions at 120 K for as-prepared (a) and 0.2 dpa-irradiated samples, respectively. Electron diffraction patterns from the corresponding stages are inset.

the dose at room temperature (~1 dpa) [5], presumably due to the slower recovery rate at low temperatures. It is seen that the peak positions of the co-ordination shells did not exhibit a significant change against the irradiation up to the dose of 0.2 dpa.

We next followed the standard EXELFS analysis procedure to extract the change in the co-ordination number and the mean square displacement of the first neighbor co-ordination shell [12]. This can be done first by extracting the first peak in the RDF with a smooth window (shown in Fig. 1 by the dashed line), and then applying the inverse Fourier transformation to obtain the interference function, $\chi(k)$, of the first neighbor co-ordination shell only. The amplitude, $A(k)$, of $\chi(k)$ for the only one co-ordination shell of interest is expressed as

$$A_s(k) = \frac{N_s}{r_s^2}\frac{f(k)}{k}\exp(-2r_s/\lambda)\exp(-2\sigma_s^2k^2),$$

where N is the co-ordination number, r the radius of the co-ordination shell, $f(k)$ the form factor, λ the mean free path for inelastic scattering, and σ^2 the mean square displacement in the radial direction. A plot of $\ln(A_u/A_s)$ vs. k^2, where subscripts u and s are referred respectively to the sample of interest with unknown structure and the standard with well-known structure, must follow a straight line. Hence one can estimate the relative change of N and σ^2 from its slope and intercept with the ordinate respectively.

The plots were done for the as-prepared state as the standard and 0.2 dpa irradiation as the unknown. The relative changes in N and σ^2 was estimated from the plot to be −22% and $+0.3 \times 10^{-5}$ nm^{-2}, respectively. The decrease in the co-ordination number can be interpreted simply by the introduction of unsaturated bonds due to the displacement damage. The change in σ^2 is not significant within the experimental accuracy. The above results indicate that the chemical bonding between neighboring carbon atoms was not appreciably changed at a dose of 0.2 dpa even though the loss of the long range order was significant at the low temperature.

The ELNES spectra for the corresponding doses above are shown in Fig. 2. The fine structure in the sp^2-σ^* state gradually disappeared, representing again the deterioration of the long range translational symmetry within the basal plane. The fine structure characteristic of higher fullerenes, which was observed for room temperature irradiation [7], did not appear at this stage. It should be noted that the sp^2-π^* core loss peak was still well retained even after prolonged irradiation, as was also seen at room temperature [5].

3.2. Lattice image observation of the basal planes

A sequential change in the lattice fringes of the *c*-planes under electron irradiation was recorded on a video tape at 94 K. Excerpted snapshots from the video recording are shown in Fig. 3(a) and (b), which were processed to filter out the disturbing low-frequency noises. The overall features are very similar to those at room temperature [4,6], in that the original straight lattice fringes were gradually buckled and lost the long range coherency, though the definite layered structure was still locally maintained within a scale of a few nanometers.

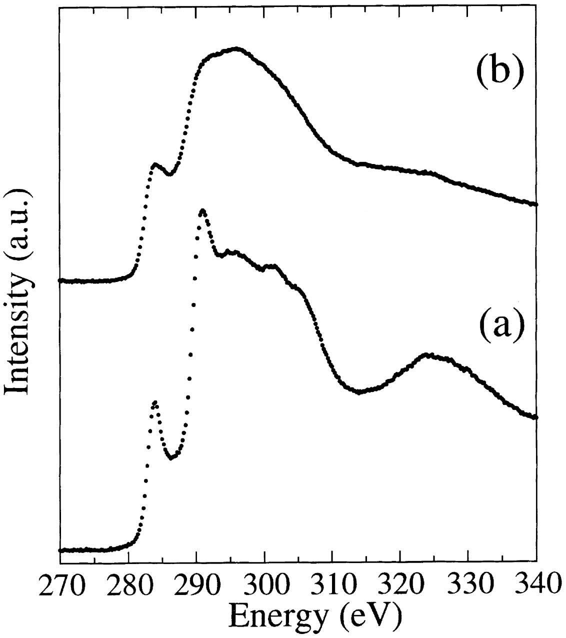

Fig. 2. ELNES spectra at 120 K for as-prepared (a) and 0.2 dpa-irradiated samples, respectively.

The average interplanar spacing of the basal planes was calculated from the distance between the spots in 2D-Fourier transform (power spectra) of the lattice images, where the initial (unirradiated) spacing was assumed to be the ideal value (0.335 nm) of graphite. In Fig. 4 are shown those changes vs. the irradiation dose at 94 K and room temperature [4]. Both curves show a similar tendency though the increase in the interplanar spacing seems less conspicuous at 94 K than that at room temperature.

In contrast with the quicker structural deterioration within the basal plane at low temperatures, as mentioned in Section 3.1, the change in the lattice spacing showed much less significant difference between the low and room temperatures.

4. Discussion

Since we ceased the EELS experiments when the complete halo rings were observed in electron diffrac-

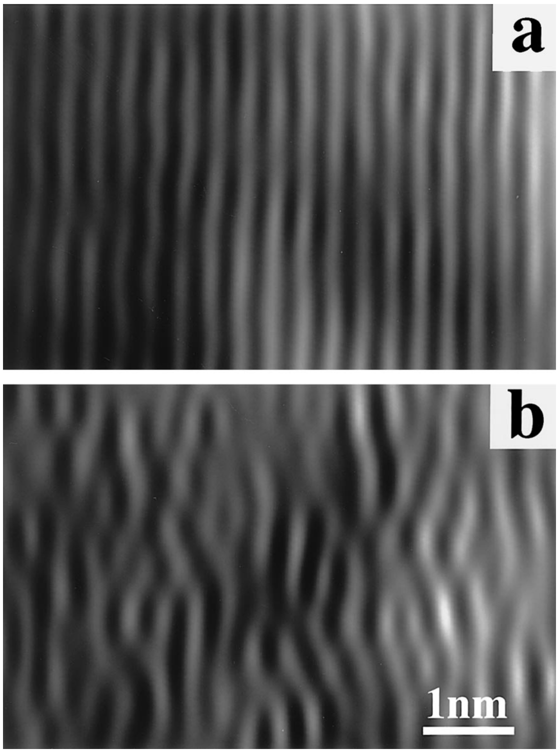

Fig. 3. Lattice images of HGCF at 94 K. (a) initial (b) after 1.2 dpa irradiation. The images were processed to reduce the underlying noises and enhance the contrasts.

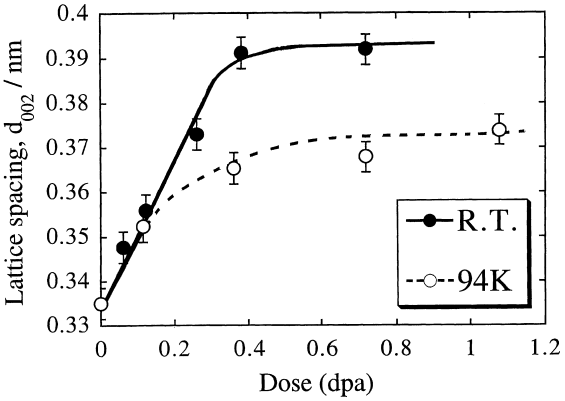

Fig. 4. Plots for interplanar spacing of basal planes vs. irradiation dose at room temperature (solid line) and 94 K (dashed line).

tion, the EXELFS and ELNES spectra at low temperatures for the dose more than 0.2 dpa are not available now. Nevertheless the present results indicate that the loss of the *in-plane* long range order is not essential for the changes in the chemical bonding states which have been observed at room temperature [7]. The *interplanar* change with the irradiation actually behaved similarly for both room and low temperatures irrespective of the halo formation, as shown in Section 3.2.

This homogeneous interplanar dilation in the *c*-direction should be interpreted in terms of the in-plane electronic structure because the cohesive force between the basal planes originates from the van der Waals interaction between the π-orbitals with no direct chemical bonding. Hence the homogeneous dilation must be ascribed to the overall change in electronic structure within the basal plane with the sp^2 hybridization basically maintained. This naturally reminds us of the formation of non-hexagonal atomic rings on the analogy of fullerenes [13,14].

Now it is realized that the in-plane disordering proceeds in two different scales: the fragmentation into small pieces of crystallites with random orientations in micron-scale, and the buckling of the *c*-planes within the fragmented crystallites with the formation of odd-member atomic rings involved in atomic scale. The former gives rise to the formation of halo rings in electron diffraction without altering the short range structure, while the latter to the variation of the bond lengths and the characteristic split of the ELNES spectrum. At lower temperatures the former proceeds faster because of the generally slower recovery rate of the displacement damage, while the latter exhibits less temperature dependence because the process must involves electronic excitations. The apparent decrease in the co-ordination number, described in Section 3.1, is considered to derive mainly from the highly incoherent peripheral regions between the fragmented crystallites rather than the unsaturated bonds within them.

5. Summary and conclusions

TEM–EELS experiments were performed at low temperatures to investigate the changes in the spatial and electronic structure of graphite under high-energy electron irradiation. Although the [0 0 0 1] diffraction pattern was transformed to complete halos much more quickly than at room temperature, the other radiation effects in atomic scale observed at room temperature experiments, such as the development of other types of chemical bonding and homogeneous lattice dilation in the *c*-direction, were not enhanced by the loss of the long range order within the basal planes. These suggest that the displacement damage plays two types of roles, the fragmentation of the crystals with random orientations and the reconstruction of non-hexagonal atomic rings in combination with electronic excitations, in the whole damaging process.

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References

[1] For review, see T.D. Burchell, MRS Bull. 22 (1997) 29 and references therein.
[2] T. Tanabe, Phys. Scripta T64 (1996) 7.
[3] S. Muto, M. Takeuchi, T. Tanabe, J. Surf. Anal. 3 (1997) 420.
[4] S. Muto, T. Tanabe, Philos. Mag. A 76 (1997) 679.
[5] M. Takeuchi, S. Muto, T. Tanabe, S. Arai, T. Kuroyanagi, Philos. Mag. A 76 (1997) 691.
[6] S. Muto, T. Tanabe, M. Takeuchi, S. Horiuchi, H. Kurata, K. Hojou, S. Arai, T. Kuroyanagi, Proc. of 5th NIRIM Int'l. Symp. on Advanced Materials, ISAM'98, March 1998, Tsukuba, p. 129.
[7] S. Muto, M. Takeuchi, T. Tanabe, H. Kurata, K. Hojou, Jpn. J. Appl. Phys., to be published.
[8] R. Kuzuo, M. Terauchi, M. Tanaka, Y. Saito, Y. Achiba, Phys. Rev. B 51 (1995) 11018.
[9] R. Mitsumoto, H. Oji, I. Mori, Y. Yamamoto, K. Asato, T. Iwano, Y. Ouchi, H. Shinobara, K. Seki, K. Umishita, S. Hino, S. Nagase, K. Kikuchi, Y. Achiba, UVSOR Activity Report, April 1996, BL2B1.
[10] R.F. Egerton, Electron Energy-Loss Spectroscopy in the Electron Microscope, Plenum, New York, 1986, p. 224.
[11] B.K. Teo, EXAFS: Basic Principles and Data Analysis, Springer, Berlin, 1986.
[12] A.E. Kaloyeros, W.S. Williams, F.C. Brown, A.E. Greene, J.B. Woodhouse, Phys. Rev. B 37 (1988) 771.
[13] G.E. Scuseria, Chem. Phys. Lett. 180 (1991) 451.
[14] W. Andreoni, F.G. Gygi, M. Parrinello, Chem. Phys. Lett. 189 (1992) 241.