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TEM analyses of surface ridge network in an ion-irradiated graphite thin film

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Abstract

A ridge network induced by He^+-irradiation on a graphite surface was examined by in situ and ex situ transmission electron microscopy. It was found that the ridge structure appeared in a few seconds from the start of irradiation and developed to the full network structure within a minute, where the ion dose corresponds to less than 0.01 dpa. The analyses of electron diffraction patterns showed that the crystallographic relationship between the matrix and ridges was similar to those of twins as previously reported, but the ridges consisted of curled graphitic sheets rather than a pair of twin bands. We have to conclude from the present results that the formation was affected by collective electronic excitations associated with the high density of energy deposition near the surface, rather than the displacement damage or the accumulation of implanted gas.

1. Introduction

Radiation effects in carbon materials have been long investigated, but it is hard to say that the fundamental understanding of the elemental processes from the microscopic point of view is fully completed. It has been known among others that a network of straight ridges is formed on a graphite (irrespective of bulk or thin foil) surface by light gas ion irradiation [1–5]. It has been concluded that the ridge lines consisted of a pair of twin bands and the twinning has been ascribed to the dimensional changes produced by displacement effects which vary with depth because the twin density is increased with energy, dose and target temperature [6]. However, there is not at present, to the authors' knowledge, an explicit crystallographic analysis of the network.

In this paper we re-examine the crystallographic features and formation process of the network and propose a new mechanism for the formation process of the surface ridge network in graphite, inspired by the recent experimental results related to its structural modification induced by energetic particle bombardment [7–10].

2. Experimental procedure

Samples used in the present study were highly oriented pyrolytic graphite (HOPG) and natural graphite with larger crystal grain sizes and good crystallinity. Although both samples showed similar ridge formation, crystallographic directions of the ridge lines in HOPG were relatively ill-defined because of the grain boundaries and stacking faults. The large grain size and good crystallinity of natural graphite allowed us an unambiguous crystallographic analysis of the ridge lines. The original bulk crystals were repeatedly cleaved with an adhesive tape, followed by a dip in toluene to dissolve the adhesive material. Thus, obtained thin films were then transferred onto copper grid meshes for TEM observation.

Transmission electron microscope (TEM) observation of He^+-bombarded samples was done ex situ to

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characterize the crystallographic relationship between the formed network and matrix. He^+ irradiations at an accelerating voltage of 15 kV with a beam current of $\sim 5 \times 10^{13}$ cm^{-2} s^{-1} for 1 min, were made onto the freshly cleaved side of a natural graphite thin foil whose surface was covered by a fine grid copper mesh. This was used to see the difference in structure between the ion-bombarded and unbombarded areas.

In situ observation of the ridge formation was carried out in an electron microscope (operated at 200 kV) equipped with an ion gun, and the sequential change was recorded on a video tape. An HOPG thin film was irradiated at room temperature with He^+, where the ion gun was operated at an accelerating voltage of 20 kV with a beam current of $\sim 10^{13}$ cm^{-2} s^{-1}, at an angle of 30° to the sample surface normal. The damage rate was estimated to be about 0.001 dpa s^{-1} around the peak depth of the damage production.

3. Results

3.1. Crystallographic analysis of the ridge network

A SEM image of the ridge network is shown in Fig. 1, as a result of He^+ bombardment on the graphite surface. To take this micrograph the fine copper grid which had covered the sample front surface was removed. Nevertheless the sample was thin and transparent for electrons so that the supporting copper grid underneath is visible. The most important feature is that the straight lines constructing a triangular mesh are running over the whole area without any indication of the covered grid which is much finer than the supporting grid. Most of the ridge edges cross to make the network with a crossing angle of either 60° or 120°. One can accordingly imagine that the edges run along either the $\langle 1\ 0\ \bar{1}\ 0 \rangle$ or $\langle 1\ 1\ \bar{2}\ 0 \rangle$ directions. Such a clear crystallographic relationship is only observable for natural graphite with large crystal grains and few small angle grain boundaries.

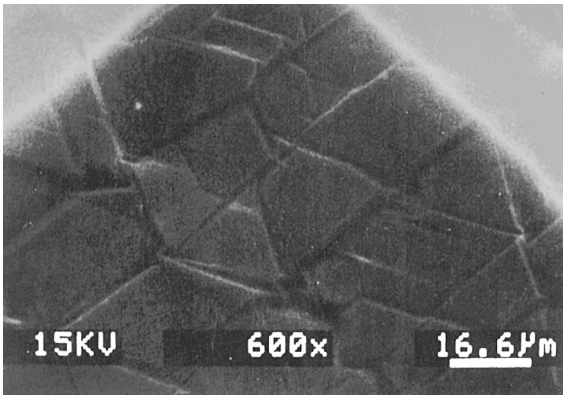

Fig. 1. SEM image of He^+-irradiated graphite showing the network structure formed by the irradiation. A portion of copper grid supporting the sample is seen as a bright contrast.

TEM micrographs of the same sample are shown in Fig. 2(a) and (b) with the corresponding diffraction patterns inset. A vague X-shape contrast is seen as a shadow of the fine grid which had covered the sample during the helium irradiation. This contrast is caused by the slight amorphization of the unshaded areas where the sharp contrast was lost due to slight structural disordering. As seen in the SEM micrograph on the other hand, the ridge lines are running through the unirradiated (shaded) area.

The inset diffraction pattern in (a) exhibits extra spots arranged in the $\langle 1\ 1\ \bar{2}\ 0 \rangle$ direction to the higher order side, which is perpendicular to the ridge lines. This diffraction pattern can be basically interpreted, except the fine structure of diffraction spots, as the superposition of the (0 0 0 1) and several other zone axis patterns obtained by the consecutive rotation about the $\langle 1\ 0\ \bar{1}\ 0 \rangle$ axis. The dark-field imaging confirmed that the (0 0 0 1) pattern is from the matrix and the other from the ridge

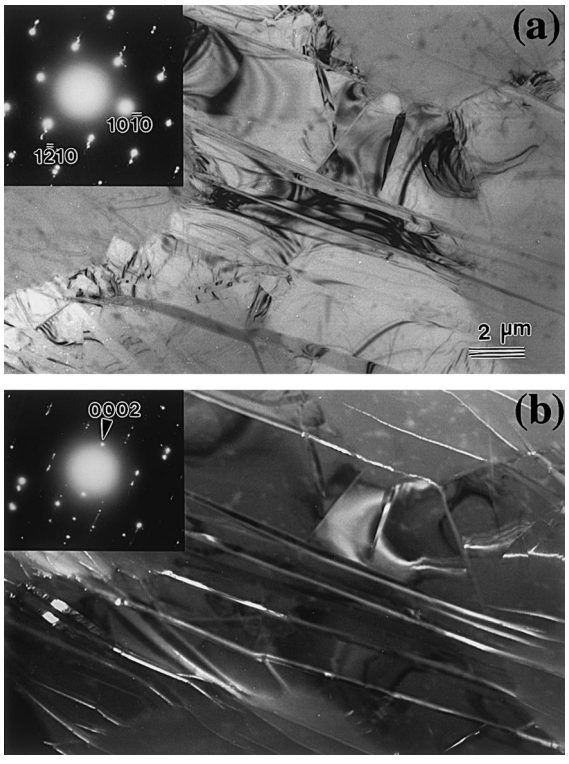

Fig. 2. TEM pictures and electron diffraction patterns of the He^+-irradiated graphite. (a) Bright field image with the incident beam parallel to the *c*-axis. (b) Dark field image taken by tilting ~35° from (a). The 002 reflection is marked with arrow head in the inset diffraction pattern.

lines. The shape of the Bragg spots is elongated in the $\langle 1\ \bar{2}\ 1\ 0\rangle$ except the $10\bar{1}0$ systematic row of reflection, which indicates that the ridges consist of thin graphitic sheets.

The sample was tilted until the 0002 reflection came into the Bragg condition as shown in the inset of Fig. 2(b). The ridge lines rise up in the picture by dark field imaging with the reflection, which again confirms that the ridge consists of the graphitic sheet inclined to the matrix. It is noted that the diffraction pattern exhibits the extra fine spots along with slight streaking for the fundamental Bragg spots except the 0002 systematic reflection row. This is probably due to the curled graphitic sheets losing their correct stacking relationship with the interplanar spacing maintained. A similar diffraction effect is observed under the electron irradiation [11], and the streaking of diffraction spots can be interpreted by the shape factor effect from the individual basal planes. All the above features can be explained by the continuous curling of the thin basal planes, rather than the formation of a pair of twin bands as previously reported [6].

3.2. In situ TEM observation of ridge formation

The formation process of the network was examined by in situ TEM observation and the result was recorded on a video tape. Sequential excerpts in every 6 s from the video recording are shown in Fig. 3(a)–(i). The time

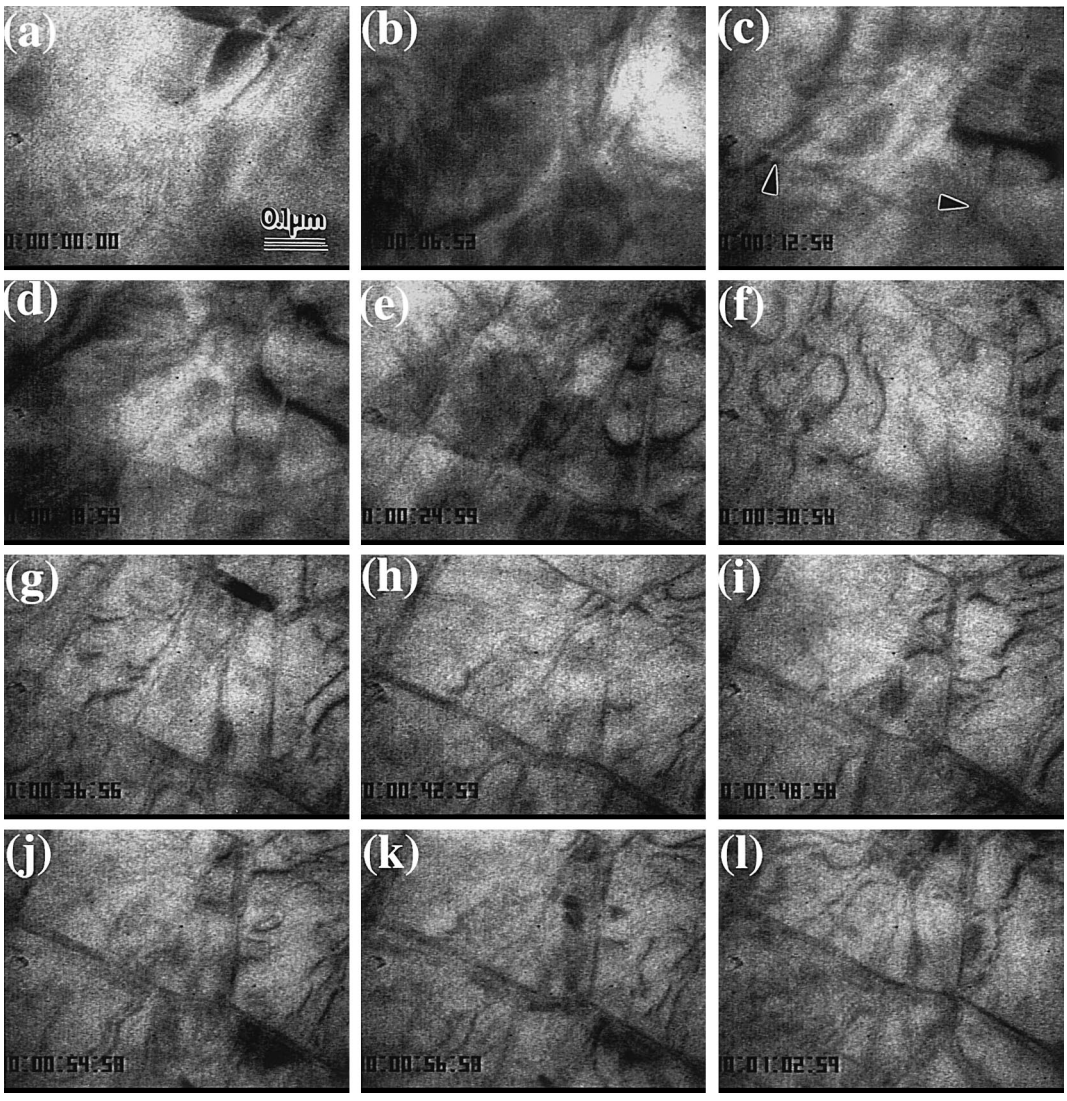

Fig. 3. Excerpts in every 6 s from the video recording of the network formation process under the He^+-irradiation in an electron microscope. Ridge lines appears in (c), as indicated by arrow heads.

from the start of helium irradiation is indicated at the lower left corner of each excerpt. It is seen that the ridge structure already started to appear at (c) (after 13 s), as marked by an arrow head. The network formation was almost completed within 1 min, though the widths or positions of ridge lines slightly varied by the prolonged irradiation.

It is very important to note that the dpa near the surface within a minute, considering the present dose rate, was too small to solely attribute the ridge formation to the displacement damage. This is discussed below in detail.

4. Discussion

The depth distributions of implanted He atoms and deposited energy by collision damage and ionization (electronic excitation) were calculated with the TRIM92 simulation code, the results of which are shown in Fig. 4. Since the present sample thickness was estimated as less than 100 nm, through which most of the helium ions penetrated, such quick formation of the network cannot be caused by the accumulation of implanted gas atoms. From Fig. 4 the dpa near the surface can be estimated as $\sim 10^{-3}$ dpa for the 1 min irradiation. It is therefore doubtful that the displacement damage plays a key role in the network formation. In the present in situ observation, however, electron irradiation might enhance the process.

The fact that the ridges were formed across the regions shaded by a fine grid suggests that the phenomenon starts at localized surface sites, which induces mechanical strains which propagate on the surface. A clue may be found in the folded graphitic sheets observed by atomic force microscopy [12]. According to the ab initio calculations reported there, it is claimed that the change from sp^2- to sp^3-like line defects may stabilize the π-orbital electronic energy by the introduction of bends into the originally strained graphitic sheet. The ridge lines are running along the $\langle 1\ 0\ \bar{1}\ 0\rangle$ and it follows that the graphitic sheets bend along the so-called arm chair lines (Fig. 5). This transition would give rise to additional strains because of different (longer) bond lengths for different (sp^3-like) bond characters.

We can now draw a rough scenario for the ridge network formation: the electronic transition is induced by a collective electronic excitation near the incident surface. This transition brings about the sp^3-like three-dimensional bond network with different bond lengths and angles in the graphitic sheet, which induces mechanical strains. Those strains can be released by the local curling of the graphitic sheets, and this propagates over the whole surface like a cooperative phenomenon such as martensitic transformations. This reasonably explains the fact that the observed morphology resembles a twinning network.

The idea can be naturally justified by recent experimental results [7–10]: the high energy electron irradiation can actually induce the microscopic structural modifications in graphite through an electronic excitation. The point is that the high density of energy deposition at the surface is indispensable for the ridge formation. This may be the reason why the phenomenon has been only observed for ion irradiation, and not for high-energy electron or neutron irradiation where the displacement effect is dominant.

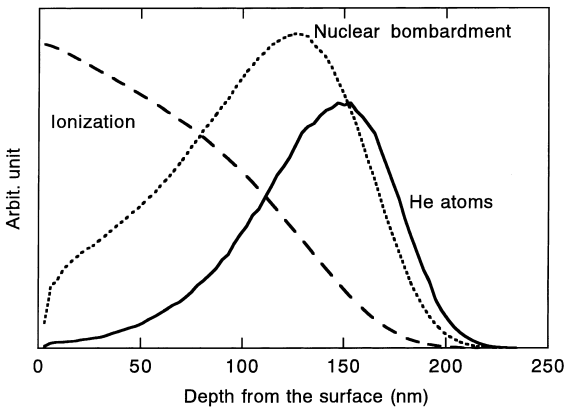

Fig. 4. Depth distribution of implanted atom (solid line), energy deposition of nuclear bombardment (dotted line) and ionization (dashed line) calculated by the TRIM92 simulation code.

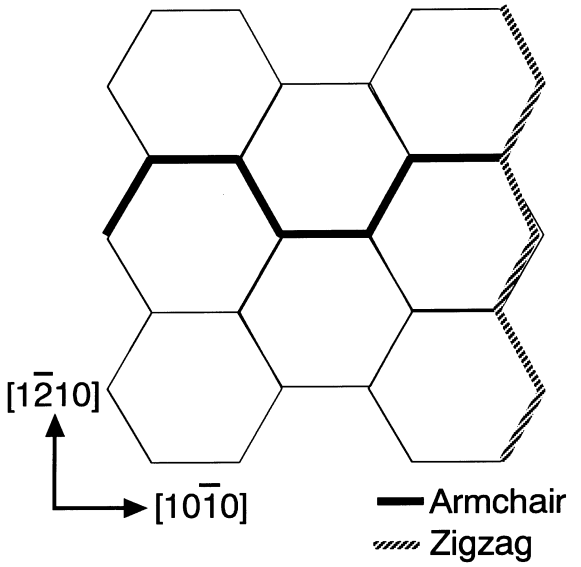

Fig. 5. Schematic drawing of armchair line and zig-zag line in a graphitc sheet.

5. Summary

The structure and the crystallographic orientation relation of the ridge network on the helium irradiated graphite surfaces were examined by TEM and electron diffraction. The ridges run along the $\langle 1\ 0\ \bar{1}\ 0\rangle$ direction, very similar to a pair of twin bands in their appearance, but in reality they consist of curled thin graphitic sheets. The in situ TEM observation of the formation process clearly indicated that the network started to form immediately after the irradiation. This suggests that the initial wrinkling of the graphite surface was induced by a collective electronic excitation rather than the displacement damage or accumulation of implanted gas atoms, and that the induced strains mechanically propagated over the sample surface to form the network. This is the first demonstration of the significance of electronic excitation by ion irradiation in the ridge network formation in graphite. The formation mechanism proposed here is, however, still rather speculative, and needs to be explored further, by defining amongst other things the critical energy deposition and nucleation sites.

Acknowledgements

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References

[1] G.J. Thomas, W. Bauer, P.L. Mattern, B. Granoff, Advan. Chem. Ser. 158 (1976) 97.
[2] S. Veprek, A. Portmann, A.P. Webb, H. Stuessi, Radiat. Eff. 34 (1977) 183.
[3] K. Sone, T. Abe, K. Obara, R. Yamada, H. Ohtsuka, J. Nucl. Mater. 71 (1977) 82.
[4] Y. Kazumata, J. Nucl. Mater. 68 (1977) 257.
[5] K. Niwase, T. Tanabe, Mater. Trans. Japan Inst. Metals. 34 (1993) 1111.
[6] D.J. Bacon, A.S. Rao, J. Nucl. Mater. 91 (1980) 178.
[7] S. Muto, M. Takeuchi, T. Tanabe, J. Surf. Anal. 3 (1997) 420.
[8] S. Muto, T. Tanabe, Philos. Mag. A 76 (1997) 679.
[9] M. Takeuchi, S. Muto, T. Tanabe, S. Arai, T. Kuroyanagi, Philos. Mag. A 76 (1997) 691.
[10] S. Muto, T. Tanabe, M. Takeuchi, S. Horiuchi, H. Kurata, K. Hojou, Proceedings of the 5th NIRIM International Symposium on Advanced Materials (ISAM'98), Tsukuba 1998, in press; S. Muto, M. Takeuchi, T. Tanabe, H. Kurata, K. Hojou, Phys. Rev. B, to be published.
[11] S. Muto, S. Horiuchi, T. Tanabe, unpublished.
[12] H. Hiura, T.W. Ebbesen, J. Fujita, K. Tanigaki, T. Tanaka, Nature 367 (1994) 148.