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Interlayer structure changes of graphite after hydrogen ion irradiation

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Abstract

Changes in graphite interlayer orderings due to keV energy hydrogen irradiation were investigated as a basic step for studies of plasma-wall interactions in fusion reactors. Distribution of interplanar spacings within a 0–45 nm deep implantation layer was measured using Fourier transforms of the (002) lattice fringe images from HRTEM taken at side facets of 700 nm diameter graphite whiskers after 1 keV H^+ irradiation. Discrete increases of the interplanar spacing from 0.34 nm to 0.38, 0.41 and 0.43 nm were observed, with other indications at 0.47, 0.56, 0.62 and 0.69 nm. A sub-peak formation at 0.376, and at 0.402 nm was also observed in (002) spectra of X-ray diffraction (XRD) of 200 nm diameter whiskers after 1–6 keV H^+ irradiations at 673 K, and at 623 K, respectively. The increases to 0.38 and 0.41–0.43 nm were explained through sp^3 type C–H bond formation in hexagonal carbon networks at the 'low' trapped H densities ($H/C < 0.4$), and the 'high' trapped H densities ($H/C > 0.4$), respectively, while those at 0.47–0.69 nm were attributed to interlayer, axial CH_3-bond formations and C_xH_y molecule insertions. © 1997 Elsevier Science B.V.

1. Introduction

Graphite is promising as a plasma-facing material for high-heat flux components of fusion experimental reactors, because of its excellent thermo–mechanical properties [1]. Drawbacks of graphite are its chemical sputtering and hydrogen recycling characteristics. In the last two decades, much study has been made in those aspects, yet with no definite data concerning trapping states of hydrogen in graphite under or after keV energy hydrogen ion irradiation [2].

Interplanar distance changes at graphite's basal faces after keV hydrogen ion irradiation have been investigated through high resolution transmission electron microscopy (HRTEM) [3], [4]. Due to the limited spatial resolution of the conventional selected area diffraction (SAD) technique, the distribution of d_{002} spacings within the ion implantation layer was directly measured at (002) lattice fringe images [4].

In the present study, depth profiles of d_{002} spacings within the hydrogen implantation layers were measured with Fourier transforms [5] of the (002) lattice fringe images. Also, a thin film analysis technique involving X-ray diffraction (XRD) was used for thin 200 nm diameter graphite whiskers, and changes in interplanar distance after hydrogen irradiation were measured. The H^+ irradiation temperatures were chosen in the 623–730 K range. These temperatures are below the chemical sputtering maximum at around 800 K [2], and are therefore considered to be suitable for observing the effects of C_xH_y formation on the interplanar spacings. Also, these temperatures, being close to the threshold for defect annealing at around 700 K [6], are considered to be suitable for XRD.

2. Experiment

2.1. HRTEM observation

Fig. 1 shows experimental schematics for hydrogen ion irradiation and HRTEM observation. Details of the experimental procedures are given elsewhere [3,4]. For the highly graphitized basal-face specimens, vapor-grown graphite whiskers (GWs) of mean diameters around 700 nm were used. The GWs are of 'growth ring' structure in which hexagonal carbon networks are stacking almost co-axially around the fiber axis, with facetted side faces. Prior to HRTEM observation, GWs, mounted on a Ni or Cu mesh,

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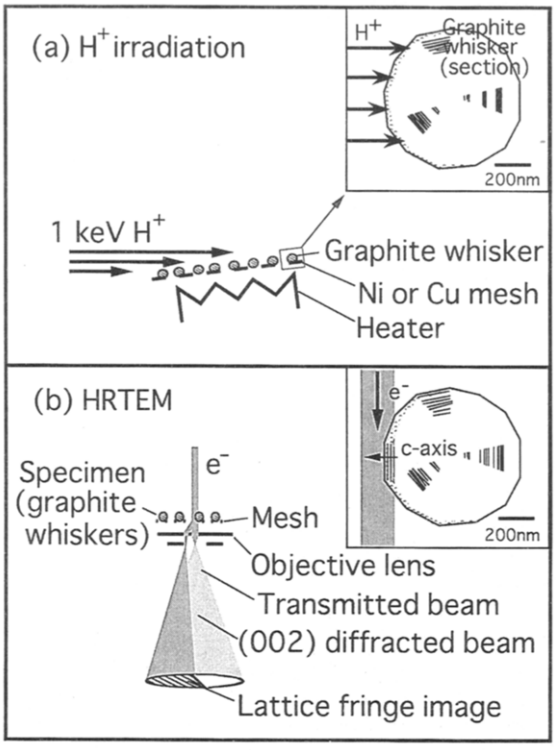

Fig. 1. Schematics of (a) the apparatus used for H^+ irradiation of graphite whiskers, and (b) the experimental setup for HRTEM observation.

were irradiated with a mass-separated 3 keV H_3^+ beam at 10° to the mesh plane (i.e., 10° to the normal of the side facets of the GWs), to a fluence of 1×10^{22} H/m^2 at 730 K.

HRTEM (type H-800, Hitachi) observations were made on the facets of GWs side faces, producing a tangential projection of three-dimensional (002) lattice structures of a nearly 50 nm deep subsurface layer just beneath the graphite basal face (see Fig. 1b). In the HRTEM observations, GWs, which fiber axes were oriented normal to the ion beam, were chosen.

SAD patterns were obtained through Fourier transform of the (002) lattice fringe images by means of a digital image analyzer (Ult Image). SAD patterns from two different size areas, 6.25×6.25 nm and 12.5×12.5 nm were compared. Interplanar spacings, d_{002}, were estimated from radial position of the (002) diffraction spots, R_D, relative to those of the un-diffracted beam, according to the inverse proportional relation between d_{002} spacing and R_D. The calculation of the d_{002} values was calibrated so that the R_D value of the outermost spots in the pattern obtained from the lattice image in the deepest bulk region of the GW, corresponds to the interplanar spacing 0.340 nm determined by XRD.

2.2. XRD

Schematics of both the hydrogen irradiation and XRD experimental arrangements are shown in Fig. 2. Vapor grown graphite whiskers of about 200 nm mean diameter, were used as specimens after heat-treatment at above 3100 K (Showadenko). Thin GWs layer was formed on a Si-single crystal substrate ($10 \times 10 \times 2$ mm) with a hole at a side face for insertion of a thermocouple element. A mass-separated hydrogen ion beam of about 7 mm diameter was used for irradiation of GWs which were supported on a Si substrate, the beam was incident normal to the substrate surface (see Fig. 2a). Irradiation temperatures were determined at 623 and 673 K. Irradiations were made with, first 6 keV H^+, then 6 keV H_2^+, and finally 3 keV H_3^+, at ion fluxes in the range 3.4×10^{18}–2.6×10^{19} H/m^2 s, to fluences in the range $(1.3–2.1) \times 10^{22}$ H/m^2 for irradiations at 623 K, and in the range $(2.4–3.4) \times 10^{22}$ H/m^2 for irradiations at 673 K. Immediately after the irradiation was stopped, the substrate temperature was decreased with an e-folding time constant of 240 s.

Bragg reflection angles were measured by using XRD (type RU-300, Rigaku) equipped with an optional goniometer for thin film analysis, on both hydrogen-irradiated and un-irradiated GWs. A parallel beam of Cu $K_{\alpha 1}$

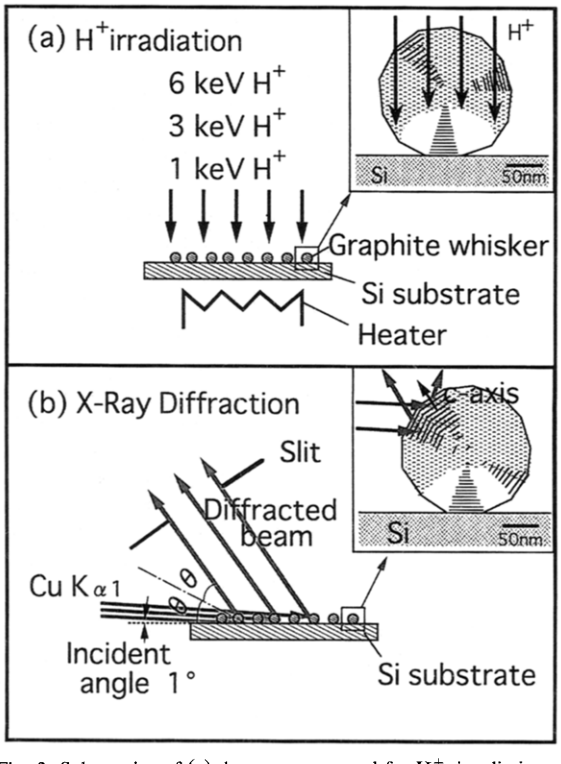

Fig. 2. Schematics of (a) the apparatus used for H^+ irradiation of graphite whiskers, and (b) the setup used for XRD spectroscopy.

was incident on the GWs (on the Si-substrate) with a fixed angle of 1.0° to the substrate's top surface. Instead of the usual θ–2θ scan, only 2θ scanning was used (Seemann–Bohlin type); which necessitate the use of randomly oriented polycrystalline specimens. Therefore, thin graphite whisker of 'growth ring' structure was chosen. The whiskers were composed of crystallites, the c-axes of which were oriented radially with respect to the fiber axis. The 2θ scan was made in steps of 0.05°, and with a 10 s accumulation time. A detector with a monochromator was used. Average interplanar spacings, d_{002} and d_{110}, were determined from Bragg angles of (002) and (110) diffraction lines by referring to a Si powder external standard.

3. Results

3.1. HRTEM

Fig. 3 shows a (002) lattice fringe image of a 45 nm deep subsurface layer of a GW after 1 keV H^+ irradiation

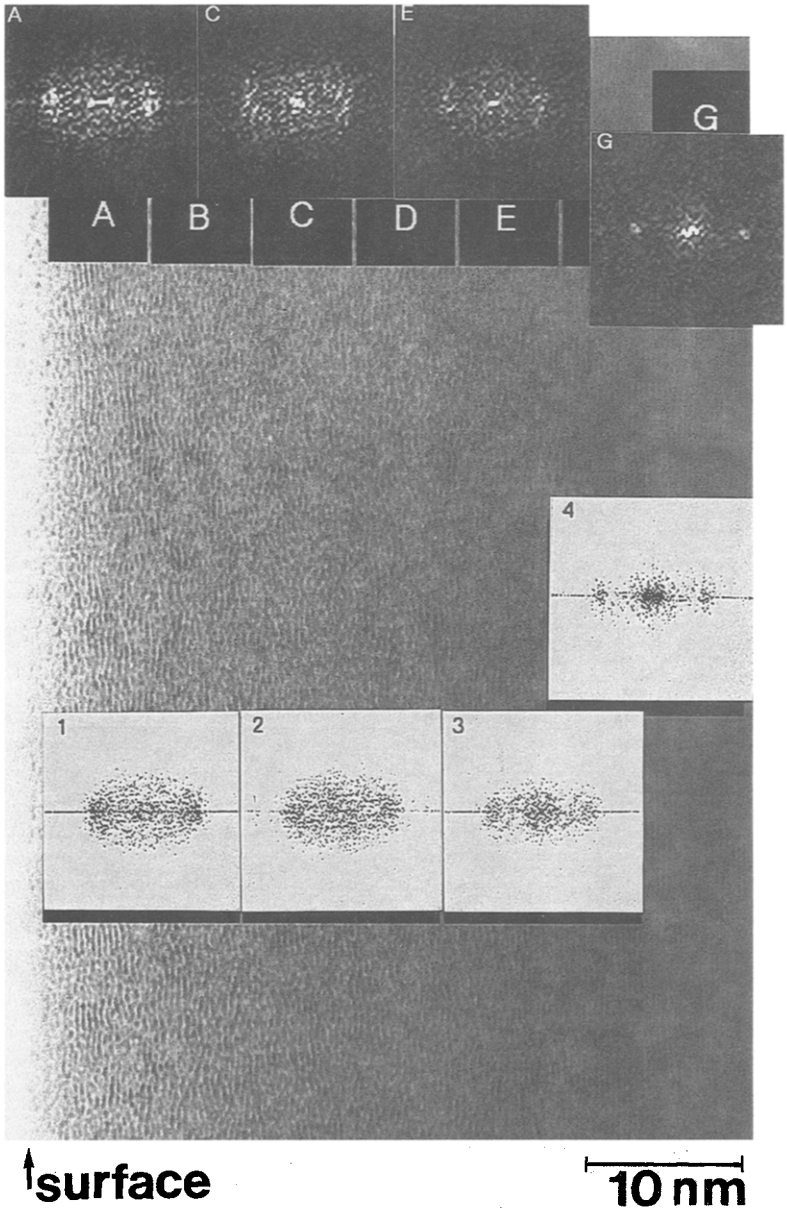

Fig. 3. (002) lattice fringe image at a side edge of a graphite whisker irradiated with 1 keV H^+ to a fluence of 1×10^{22} H/m^2 at 730 K. Insertions (A), (C), (E), (G) and (1)–(4) are Fourier transforms of lattice images at corresponding solid square insertions in the image.

to a fluence of 1×10^{22} H/m^2 at 730 K. Two series of Fourier transform patterns, (A)–(G) and (1)–(4), from different size areas, 6.25 and 12.5 nm squares, respectively, are shown as insertions with indications of their positions in the image with solid squares. As shown in the lattice image, (002) lattice fringes which are much shorter in length, slightly deflected in directions but still oriented almost parallel with the surface, are found within a subsurface layer of about 35 nm depths. Almost perfect parallel fringes are observed at depths beyond 35 nm. In the Fourier transformed pattern, (G), from an image area at 40 nm depth, a pair of rather sharp diffraction spots are found as bright spots on the horizontal axis, which correspond to the original parallel fringes of d_{002} spacings at 0.34 nm. As the depth of the analysis area goes shallower, the bright spots apparently appear to move inward along the horizontal axis, and to be scattered outward in the vertical directions, indicating deflections of the corresponding lattice fringes. In the pattern (A) from the outermost layer, again the $d_{002} = 0.34$ nm spots are found to be recovered, but with the larger bright spots of slightly smaller R_D. The qualities of the SAD patterns (1)–(4) are obviously higher than those of (A)–(G), because of the higher S/N ratio. Fig. 4(1)–(4) show magnified images of the insertions (1)–(4) in Fig. 3.

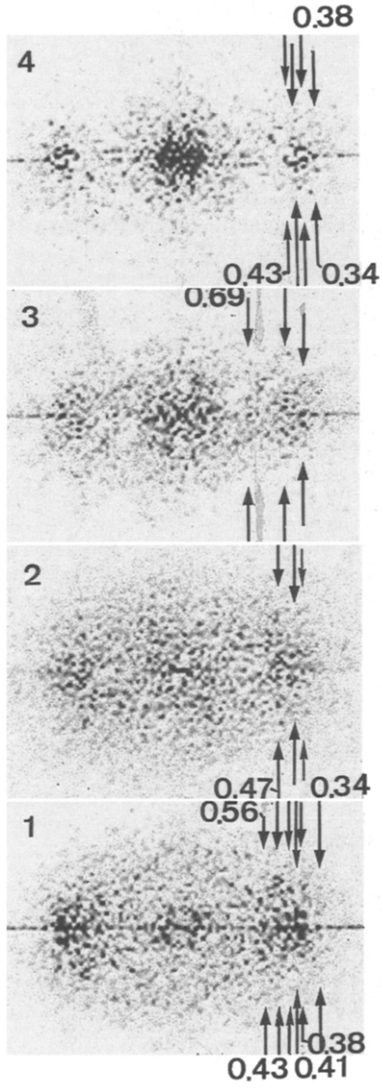

Fig. 4. Fourier transforms of the lattice fringe images at areas (1)–(4) indicated in Fig. 3.

Table 1
XRD results of graphite whiskers after 1–6 keV H^+ irradiation at 623, and 673 K

Line	623 K		673 K	
	2θ (°)	d (nm)	2θ (°)	d (nm)
C(002) sub-peak	22.07	0.4024	23.648	0.3759
C(002) main-peak	26.093	0.3412	26.158	0.3404
C (110)	77.967	0.1224	77.758	0.1227
Si (111)	28.342	0.3146	28.550	0.3129

Un-irradiated: C(002), $d_{002} = 0.3401$ nm ($2\theta = 26.178°$).

A pair of sharp spots are observed at the outermost positions on the horizontal line in both Fig. 4(1) and (4), corresponding to $d_{002} = 0.34$ nm (thin horizontal lines in the patterns are due to mismatch at the boundaries of the lattice images). Other than the 0.34 nm spots, for all of (1)–(4), at least a group of three spots of different R_Ds can be identified at just inside of the 0.34 nm spots, namely at d_{002} of 0.38, 0.41 and 0.43 nm. All of these spots are found somewhat split by $\pm(3–8°)$ off the horizontal axis, which means deflections of these fringes by a discrete amount of angle from the original parallel fringes. Faint spots corresponding to d_{002} at 0.47 (Fig. 4(1)–(2)) and 0.56 nm (Fig. 4(1)–(2)), and that to 0.69 nm (Fig. 4(3)) can be observed, whereas no remarkable corresponding spots can be found in Fig. 4(4).

The present Fourier transform analysis results of d_{002} spacing agree fairy well with the previous direct measurement results of lattice fringe spacings on the same HRTEM images [4].

3.2. XRD

Fig. 5(a) and (b) show (002) diffraction spectra of 200 nm diameter GWs after 1–6 keV H^+ irradiations to fluences in the range of $(1.3–3.4) \times 10^{22}$ H/m^2 range at (a) 623 K and (b) 673 K. Other than a main graphite (002) peak and a Si (111) peak from the Si substrate, small but isolated sub-peaks are found at the lower angle side of the main (002) peak for both of those spectra. The observed diffraction angles of the sub- and the main-C(002) peaks (Fig. 5) and the C(110) peaks, together with those for Si(111) peak (Fig. 5), are listed with the estimated d_{002} spacings, in Table 1. (The graphite interplanar spacing is

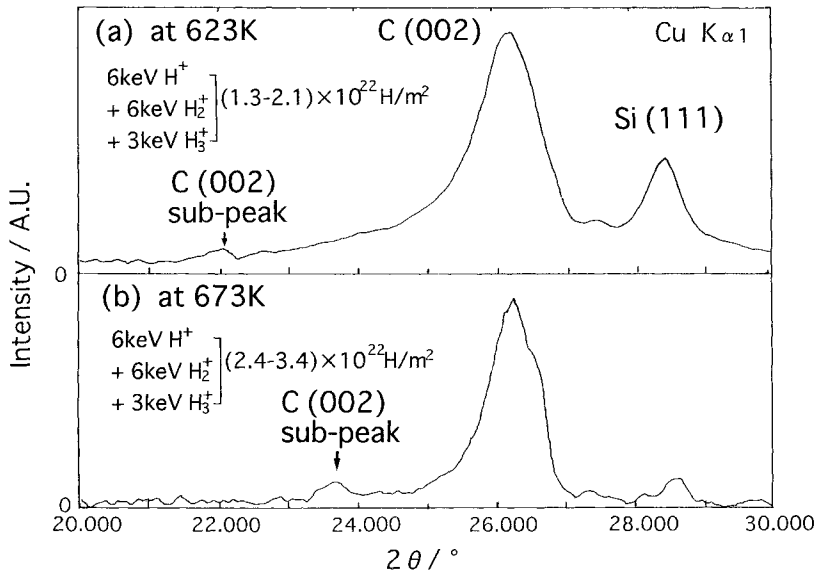

Fig. 5. (002) X-ray diffraction spectra from 1–6 keV H^+ irradiated graphite whiskers of 200 nm diameter, (a) irradiated at 623 K, and (b) irradiated at 673 K.

simply denoted with d_{002}, although rhombic structures might exist in the GWs.)

The observed much higher relative intensities of the main (002) line compared to those of the sub-peaks indicate that fairly large regions of the GWs may remain un-irradiated in the shadows of the irradiated ones. Even after taking this point into account, the present XRD results still show increases in d_{002} spacings, by discrete amounts, from 0.340 to 0.376 nm (at 673 K), and to 0.402 nm (at 623 K) due to hydrogen ion irradiation to fluences close to the saturation level.

4. Discussion

Among the increases of the interplanar spacing to 0.38, 0.41 and 0.43 nm, observed through both HRTEM and XRD, the smallest increase to 0.38 nm was found at relatively 'low' trapped hydrogen densities, namely, in the case of room temperature irradiations, at the earlier stage of irradiations, i.e., at H/C ratio of about 0.2 (for 1 keV H^+, at around 5×10^{20} H/m^2 [4]). The 0.41–0.43 nm spacings, on the other hand, appear to be at 'higher' trapped hydrogen densities, i.e., at H/C ratio ≥ 0.4. As the irradiation temperature is increased from room temperature, the average saturated hydrogen density within the ion-implantation zone decreases from H/C $\sim$ 0.4, to $\sim$ 0.2 at 700 K [7]. The present 730 K irradiation HRTEM results show that the diffraction spots corresponding to 0.38 nm are most clearly observed in the outermost subsurface layer, as shown in Fig. 4(1).

The d_{002} spacing observed at 0.38 nm is viewed as the spacing between a 'puckered' layer with sp^3 C–H bondings and its nearest-neighbor graphitic layers existing in the 'low' H/C ratio phases, while the spacings of 0.41–0.43 nm are to those between 'puckered' layers in the 'high' H/C ratio phases. With increasing H/C ratio, the d_{002} spacing is very likely to increase beyond 0.41 nm, up to 0.43 nm due to the increased interferences between the hydrogen-trapped neighboring layers. The observed d_{002} spacings of 0.38 nm and 0.41–0.43 nm can be reasonably compared with those estimated from the van der Waals radius (R_{vdW}) for graphitic layer, 0.17 nm, and that for CH_2- or CH_3-groups that might be formed at defects, 0.2 nm. It is also noted that the spacing of 0.69 nm found in Fig. 4(3) can be explained through a model that CH_4 molecules of $2R_{vdW} = 0.35$ nm are inserted between planar graphitic planes of $R_{vdW} = 0.17$ nm. Furthermore, the spacing at 0.47 nm is speculated to be due to formations of CH_3-groups axially bound at puckered lattices, and in between the puckered and the neighboring planar layer.

5. Conclusion

The present HRTEM and Fourier transform analyses of H^+ irradiated graphite whiskers show discrete amounts of increases in d_{002} spacing from 0.34 nm to 0.38, 0.41 and 0.43 nm, with additional indications at 0.47, 0.56, 0.62, and 0.69 nm. By means of XRD, the increases to 0.376 and 0.402 nm were found for GWs after 1–6 keV H^+ irradiations at 673 and 623 K, respectively. These increases to 0.38 and 0.41–0.43 nm are explainable through increases in R_{vdW} of hexagonal carbon networks due to

sp^3 C–H bond formations. Further increases beyond 0.47 nm can be explained through changes in the interplanar spacings due to interlayer CH_3-bondings to the hexagonal carbon network, and hydrocarbon molecule formations. The present results indicate large flexibility in the interlayer-ordering of graphite, thus possibilities for hydrocarbon molecule formation and diffusion, at and through the interlayer space under keV H^+ irradiation.

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