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ERD study of deuterium atoms implanted in edge-HOPG

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Abstract

The present study shows recent progress in the depth profiling of deuterium near the surface of basal oriented (BO) and edge oriented (EO) Highly Oriented Pyrolytic Graphite (HOPG) and the isotropic graphite, using the elastic recoil detection (ERD) analysis technique. The implantations were made at RT with 8 keV D_2^+ ions to the fluences up to $\sim 10^{22}$ D/m^2. The amounts of the trapped D atoms were measured as a function of fluence. It was shown in BO that the deuterium atoms lie in the depth range within 100 nm from the surface, agreeing with the depth profile computed using TRIM-code. However, the depth distribution for EO spreads over the depth beyond 700 nm. The depth profiles were also different from that in isotropic graphite. In this study, four types of EO classified according to mosaic spread have been investigated. The depth profiles obtained for EO samples were almost uniform, showing a constant concentration with depth. Careful determination of the saturation concentration yielded a value of 0.10–0.22 D atoms/C atoms.

1. Introduction

Graphite and carbon-based materials, in the last few years, have become important materials for the first wall of thermonuclear fusion reactors, because of their good thermal properties and low atomic number. In this environment, the surface material experiences high fluxes of energetic ions and electrons, resulting in severe near-surface damage. This damage leads to enormous surface erosion, amounting to 10 nm/s and more [1]. To optimize graphite for small surface erosion in this environment, a detailed understanding of the depth profiles of implanted hydrogen isotopes in several types of graphite is required.

Trapping and release of energetic hydrogen implanted in different types of carbon have been under investigation for two decades and a large amount of data has been reported. It is well known that the trapping efficiency at room temperature is close to 100% below doses of $\sim 3 \times 10^{21}$ D/m^2, with the depth distributions of the hydrogen atoms corresponding to the those expected from the implantation energies. The implantation builds up a saturated layer at the end of the range with the hydrogen atoms being chemically trapped into carbon atoms. The depth profiles of the implanted hydrogen isotopes in the isotropic graphite show an almost constant concentration of hydrogen isotopes around 0.4 H/C in the saturated layer at room temperature. Morita et al. [2–4] estimated various activation energies of hydrogen isotopes in graphite by using the ERD method. The binding energy of implanted hydrogen isotopes deduced from X-ray photoemission spectroscopy (XPS) and secondary ion mass spectroscopy (SIMS) [5,6] is almost 0.4 eV. Several authors [2,7–10] have studied the depth profiles of hydrogen in graphite. Scherzer et al. found that the saturation values of trapped deuterium are not different for basal and edge orientations of the targets. More recently Sone and McCracken [11] showed for 100 eV to 1 keV energy deuterium implantation that deuterium ions are trapped depending on the damage region. However, in some papers [9,12] it has been observed that hydrogen isotopes exist over large depths beyond the damage or ion range. Considering these results the behaviour of

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hydrogen isotopes implanted into graphite and their migration to the damage structure in graphite are not clearly understood.

In this study, we have mainly investigated ERD of D^+ irradiated edge oriented HOPG as a function of dose.

2. Experimental

Six types of graphites have been investigated:

(1) HOPG-basal (ZYA-grade from Union Carbide, USA) with the *c*-axis normal to the surface (denoted below as BO). Samples with clean surfaces were prepared by repeated stripping with adhesive tape.

(2)–(5) HOPG-edge (ZYA, ZYB, ZYD, ZYH grade from Union carbide, USA) cut parallel to the *c*-axis (denoted below as EO). Specimens were annealed under dry oxygen atmospheres by heating the sample at 1073 K in order to remove the damaged edge surface. The grades were classified according to mosaic spread.

(6) Fine grain isotropic graphite (2318-grade from Le Carbone-Lorrain, France) with a mean size grain of 4 μm. Sample surfaces were mechanically polished using superfine grinding papers and diamond paste, and were cleaned with acetone in an ultrasonic bath.

Before implantation, both HOPG and isotropic graphite samples were annealed in vacuum at a temperature of 1273 K for 10 min in order to remove the oxygen contamination or others. The characteristics of these materials are summarised in Table 1.

The implantation experiments were performed with 8 keV D_2^+ ions using 0.1–10 keV implantation plasma ion source. The beam had the spot size 10 mm in diameter and the flux was almost constant over the spot size. The current density was kept below 50 mA/cm^2 for all implantations. These were carried out perpendicular to the sample surfaces. Target heating by the implantation beam was almost negligible and target temperatures were kept at room temperature.

The ERD experimental set-up is shown in Fig. 1. After the implanted samples were transferred to the analyzing chamber devices, ERD measurements were carried out by using a 3 MeV $^4He^{2+}$ incident beam produced from a 1 MV tandem accelerator. The $^4He^{2+}$ beam was narrowed by a 1 mm diameter aperture. Detector geometries are as follows, that is, the incident angle $\alpha = 16°$ and recoil angle $\theta = (\alpha + \beta) = 30°$. Because these angles are small, the surface of the sample must be smooth to achieve a good depth resolution [13,14]. The depth profile of deuterium can be obtained through the conversion of the measured deuterium energy to the depth by estimating the energy losses of the particles along the trajectories in the target, where energy losses are computed using the known electronic stopping powers. Elastically scattered α-particles have to be stopped using an absorber in front of the detector. Furthermore, for quantitative profiling of the depth distribution, values of nuclear cross sections must be known as a function of incident α-particle energy. The differential cross section for deuterium recoils has been measured at ^4He energies between 1.5 and 3.0 MeV [15,16]. The ERD technique was found to be most suitable for profiling deuterium in the region of small depth (0.1–0.2 μm) below the surface. At the experimental conditions, the method yields a depth resoultion

Table 1
Graphite samples properties

HOPG (Highly Oriented Pyrolytic Graphite) Pseudo-single crystal			
Manufactured by Union Carbide Corp.			
	mosaic spread (°)		density (g/cm^3)
1. ZYA grade	0.4 ± 0.1		
2. ZYB grade	0.8 ± 0.2	↑ High	2.255 -
3. ZYD grade	1.2 ± 0.2	↑ Quality	2.265
4. ZYH grade	3.5 ± 1.5		
Isotropic graphite			
Manufactured by Lu Carbone-Lorraine Corp.			
	pore rate (%)		density (g/cm^3)
1. 2318 grade	9		1.90

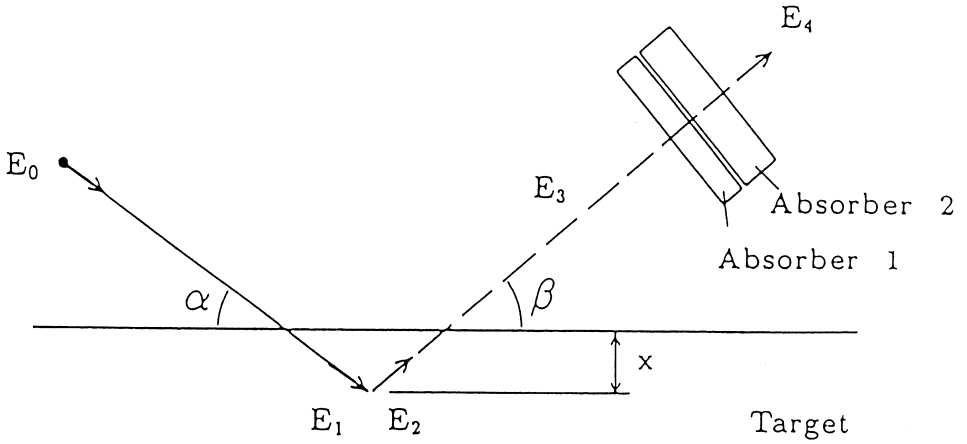

Fig. 1. Schematic drawing of the experimental setup: $E_0 = 3$ MeV ^{4}He, $\alpha = 16°$, $\beta = 14°$.

of <50 nm. In the region of large depth, both the signals from the implanted deuterium atoms and that from the pre-existing hydrogen contamination were measured in the overlapping channels. In order to get only signals from deuterium atoms, hydrogen contamination was subtracted by using the data obtained for the unirradiated samples.

3. Results and discussion

The deuterium distributions of 8 keV D_2^+ implant BO and isotropic graphite are shown in Fig. 2(a) and (b). The depth profiles of deuterium in BO samples [10] show that deuterium atoms remain in the depth range within 100 nm from the surface. It agrees with the depth profile

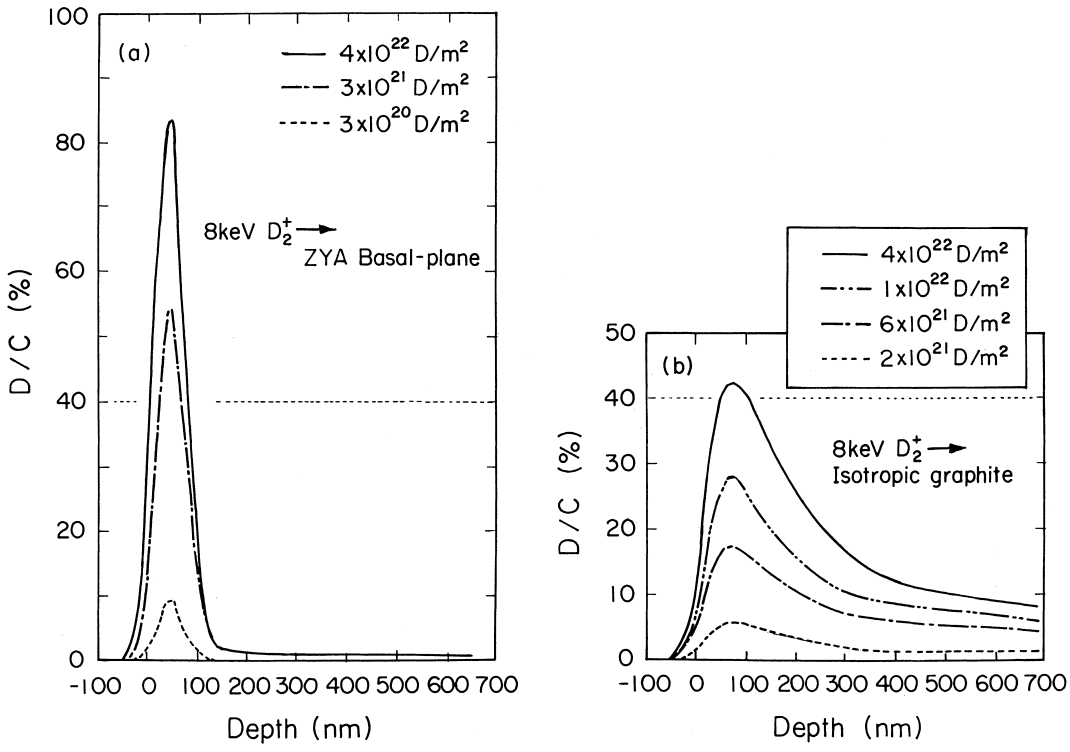

Fig. 2. ERD spectra of graphite implanted with deuterium at RT: (a) HOPG basal plane, (b) Isotropic graphite.

computed by using TRIM-code. Scherzer et al. [7] also have measured depth profiles and have obtained good agreement. On the other hand, in isotropic graphite there is considerable spreading of the deuterium distribution over the depth range beyond 700 nm. This result agrees well with that of nuclear reaction analysis in previous studies [12]. Some attempts have been made to explain this difference between these two specimens, taking into account the difference in the structure, which shows that in isotropic graphites the large penetration depth comes from the single-step detrapping and recombination mechanism of implanted deuterium ions (formation of D_2 molecules of high mobility) and the subsequent fast transgranular diffusion along basal planes towards grain boundaries and along the pores on the boundaries. The fraction of the retained deuterium atoms to carbon atoms is about 0.4 in isotropic graphites and about 0.8 for HOPG in the samples which reached a saturation state.

The depth profiles for EO samples are shown in Fig. 3(a)–(d). In comparison with BO and isotropic graphite, the deuterium concentrations for EO samples were not so high. The fraction of the retained deuterium atoms to carbon atoms in EO samples is about 0.10 (ZYA), 0.12 (ZYB), 0.15 (ZYD) and 0.22 (ZYH) which reached the saturation state. The depth profiles obtained for the EO samples were almost uniform, showing a constant concentration with depth. The saturation concentration depends on the mosaic spread of the edge samples. The more the mosaic spread extends, the more does the edge sample trap deuterium atoms, because a high mosaic spread means a higher concentration of latent defects in HOPG, such as crystallite boundaries and stacking disorders, which provide additional trapping sites for deuterium atoms along the basal plane. From earlier works [2–4,12], hydrogen atoms can be trapped at particle-induced defects, such as dangling bonds. From these EO samples cases, it can be inferred that deuterium atoms migrate from the surface to the bulk of the sample between the basal planes, and terminate the latent and particle-induced defects. Namely, the majority of the deuterium atoms trap latent defects over the ion range. The mechanism is, however, not clearly understood. In order to investigate the effect of channelling we carried out the oblique incidence of deuterium ions to the edge plane and confirmed that this deuterium migration is not affected by the channelling effect. Fig. 4 shows the total amount of deuterium versus incident fluence obtained in D_2^+ implantation at room temperature. The retained deuterium shows a linear

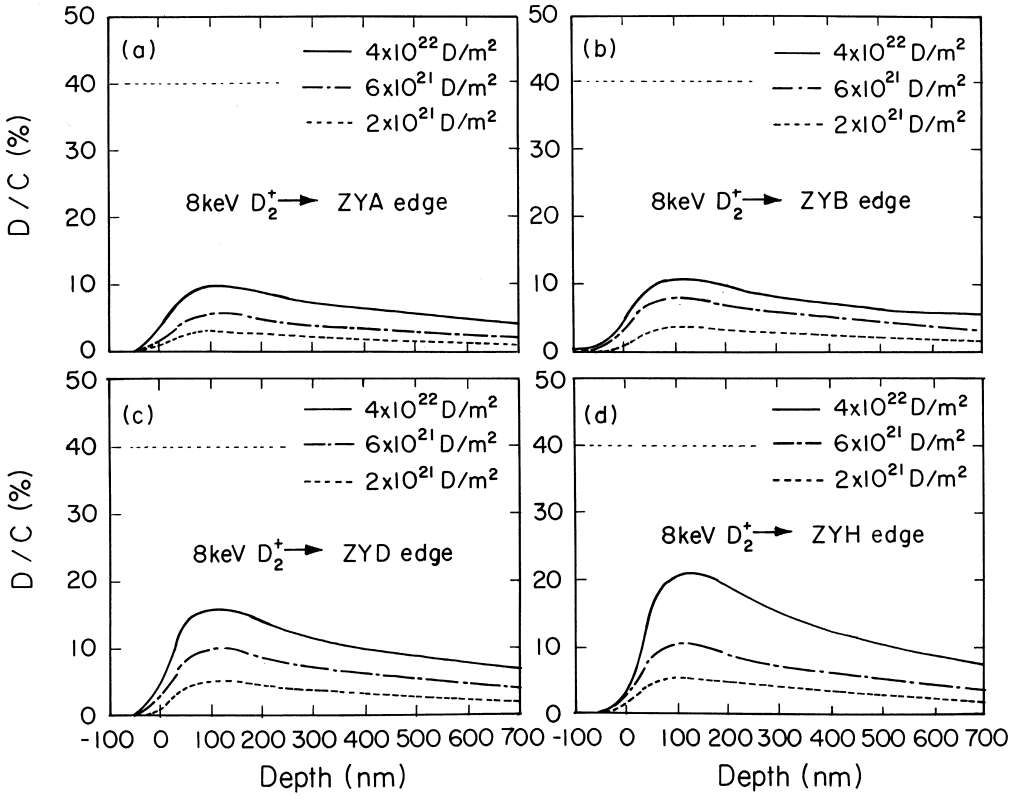

Fig. 3. ERD spectra of Edge-HOPG implanted with deuterium at RT: (a) ZYA, (b) ZYB, (c) ZYD, (d) ZYH.

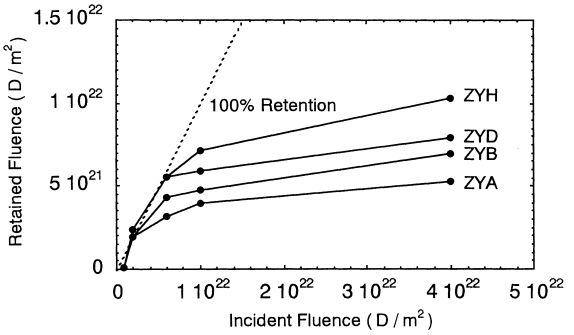

Fig. 4. ERD Measurements of retained total deuterium in Edge-HOPG exposed to 8 keV D_2^+ at room temperature, as a function of the deuterium fluence. 100% trapping is indicated by the dashed line.

dependence on fluence, with retention of deuterium close to 100%, from the very lowest fluences up to $\sim 10^{21}$ D/m^2. At higher fluences the amount of retained deuterium saturates. The saturated state agrees well with the earlier work of Scherzer et al. [7]. Tanabe et al. [16–18], Gotoh et al. [19,20] and Koike et al. [21] carried out in situ observations of damage structure of graphite with a high resolution transmission electron microscope (HRTEM) in order to investigate the mechanism of large volume expansion of graphite due to neutron, hydrogen and electron irradiation. In order to investigate the mechanism of migration of deuterium in edge-HOPG under irradiation, in situ observation of deuterium depth profiles with the ERD method is required.

4. Conclusions

From the above results, the following conclusions can be drawn:

In comparison with BO and isotropic graphite, the deuterium concentration of retained deuterium for EO samples was not so high. The fraction of the retained deuterium atoms to carbon atoms in EO samples is about 0.10 (ZYA), 0.12 (ZYB), 0.15 (ZYD) and 0.22 (ZYH) which reached the saturation state. The more the mosaic spread extended, the more was the edge sample trapped deuterium atoms. It was indicated that latent defects in HOPG, such as crystallite boundaries and stacking disorders provide trapping sites for deuterium atoms along the basal plane. The depth profiles obtained for EO samples were almost uniform, namely, showed constant concentration with depth.

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