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Letter to the Editors

Observation of relaxation processes of disorder in ion-irradiated graphite using Raman spectroscopy

E. Asari [a,b], K.G. Nakamura [b], T. Kawabe [a], M. Kitajima [b,*]

[a] *Institute of Physics, University of Tsukuba, Tennodai, 1-1-1, Tsukuba-shi, Ibaraki 305, Japan*
[b] *National Research Institute for Metals, 1-2-1 Sengen, Tsukuba-shi, Ibaraki 305, Japan*

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Abstract

Real-time Raman measurement has been applied to monitor the thermal relaxation processes in graphite at 411–463 K under 5 keV deuterium ion irradiation. The observed time dependence of density of defects revealed that the thermal relaxation process consists of three distinct stages. Dominant processes have been discussed for each stage.

1. Introduction

Ion irradiation of graphite has been extensively studied for graphite intercalation compounds [1–3] and plasma/surface interactions in fusion experiments [4,5]. It is expected that lattice damage can be relaxed and the crystal structure recovered by thermal annealing. Venkatesan et al. [6] have investigated a crystallization process of disordered surface layers of highly oriented pyrolytic graphite (HOPG) implanted with ions such as C, P and As by Rutherford backscattering and ion channeling techniques. Their isochronal annealing experiments in the temperature range of 573–3273 K indicate two clear regrowths depending on ion fluence: (1) the rapid regrowth with an activation energy of about 0.15 eV, proceeds where the disorder is sufficient to prevent ion channeling but not to cause a complete structural destruction; (2) another regrowth occurs with a higher activation energy of 1.2 eV, when the lattice disordering is almost saturated.

Raman spectroscopy is a powerful technique to study lattice disordering in graphite, because it is highly sensitive to both lattice disorder and radiation damage. The quantitative estimate of lattice disorder can be made based on the intensity ratio of the disorder-induced peak at ~ 1360 cm^{-1} to the Raman active E_{2g2} mode at ~ 1580 cm^{-1}; it is shown that this peak intensity ratio is inversely proportional to an in-plane phonon correlation length and/or microcrystalline size of graphite [7,8]. Niwase et al. [9] have conducted an isochronal annealing for HOPG irradiated to 1.3×10^{19}–1×10^{20} ions/m^2 with 25 keV deuterium ions and monitored the recovery of lattice disordering at temperatures below 873 K by Raman scattering. They have found that stable and/or unstable defects are present depending on the fluence of ions. Their result suggests that the thermal relaxation process of lattice disorder is composed of two or more stages for ion-irradiated graphite. In fact, our recent investigation [10], using real-time Raman measurements for 5000 s experiments, has revealed existence of two distinct stages in the thermal relaxation process at temperatures above 373 K under 3 keV helium ion irradiation. In this study, we have performed a real-time Raman spectroscopic study of graphite under deuterium ion irradiation, and monitored the thermal relaxation process over longer period of times up to ~ 40 ks and found the third stage of the thermal relaxation.

2. Experiment

A sample of HOPG with $12 \times 12 \times 2$ mm^3 in size (grade ZYA; Union Carbide) was used in the present work. In order to obtain a clean crystalline surface, the sample

* Corresponding author. Tel.: +81-298 53 1026; fax: +81-298 53 1087.

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was cleaved before each measurement by an adhesive tape technique. Ion irradiation of deuterium was carried out at 5 keV in an ultra-high-vacuum (UHV) chamber at a base pressure $< 10^{-8}$ Pa. The incident angle of ion beam was set to 55° from the normal to the sample c-plane to avoid ion channeling. Sample current was monitored with a digital multimeter (TR6848 ADVANTEST) and the flux of each irradiation was evaluated to be 2.7×10^{15} ions/m^2 s for deuterium ion after correcting the secondary electron emission [11]. For real-time Raman spectroscopy, the incident light of 514.5 nm was supplied by a cw-Ar-ion laser (Model INNOVA 70, Coherent) with a laser power 120 mW at the sample position. The power density was estimated to be 12 W/mm^2 at a beam size of 100 μm in diameter. The sample was attached to the sample holder with a Ni heater plate and its temperature was controlled from 411–463 K. The scattered radiation was collected through a sapphire window of the vacuum chamber in backscattering configuration; the collected radiation was analyzed by a triple-grating monochromator (TRS-660 JASCO), in combination with a spectrometric multichannel analyzer (SMA; D/DISA 700 Princeton Instruments). The SMA has 700 channels and allows to detect a width range of 400 cm^{-1}. The gate time of SMA was set to 48–333 s to obtain high-quality spectra with better signal-to-noise ratios. Ion irradiation was performed for 300 s. Raman spectra were numerically analyzed by Lorentzian curve fitting [1] in two peaks observed between 1300 and 1700 cm^{-1}.

3. Results and discussion

Fig. 1 shows typical first-order Raman spectra of HOPG before and during deuterium ion irradiation and subsequent thermal relaxation process at 433 K after stopping of irradiation; results of the Lorentzian curve fitting are shown as well. In the Raman spectrum prior to ion-irradiation (a), the Raman-active E_{2g2} mode (G peak) is observed around 1580 cm^{-1}. Upon ion irradiation for 150 s (b), a disorder-induced peak appears around 1360 cm^{-1} (D peak); this peak stems from a maximum in the phonon density of states and is observed due to the breakdown of wave-vector conservation rule. The D peak increases in intensity as the irradiation time elapses ((c); 300 s), whereupon Raman spectra were monitored after stopping of ion irradiation. At 5 ks and 40 ks ((d) and (e)), the D peak decreases in intensity as compared with the case for the irradiation time of 300 s.

It has been shown that the peak intensity ratio R of D to G in the first-order Raman spectra of graphite is related

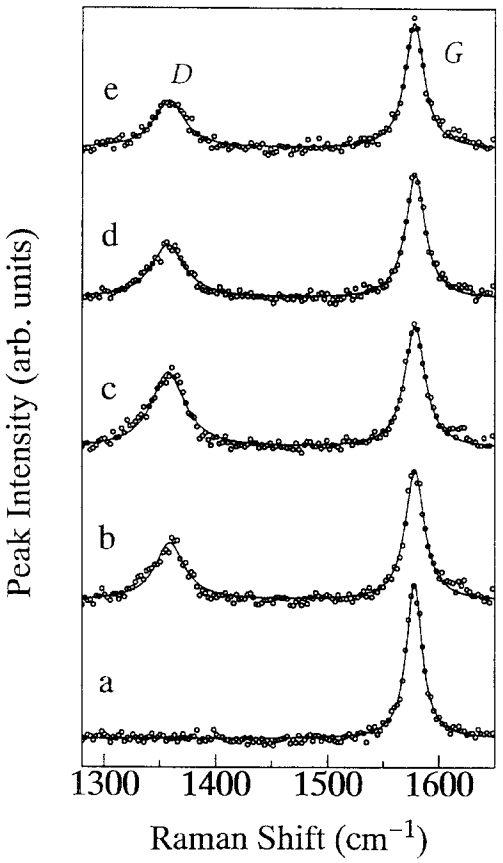

Fig. 1. Raman spectra of HOPG at 433 K: (a) before ion irradiation, (b) and (c) after 150 and 300 s upon irradiation to a flux of 2.7×10^{15} ions/m^{2}s with 5 keV deuterium ions, (d) and (e) at 5 and 40 ks after stopping ion irradiation. Solid lines represent the results due to Lorentzian curve fitting.

to the in-plane microcrystalline size and/or in-plane phonon correlation length (L_a) by an empirical relation; $R = C/L_a$, where C is 4.4 nm when L_a is expressed in units of nm [7,8]. The density of defects can be estimated using a relation $N_d = 1/fL_a^2$, where f is the distance between graphite layers [12–14].

Time dependence of the density of defects (N_d) at 433 K is shown in Fig. 2. It is well reproduced with a combination of three exponential decays, $\exp(-kt)$ where t is time, with relaxation rate constants k of 6.6×10^{-3}, 3.1×10^{-4} and 4.6×10^{-6} s^{-1}. This suggests that the thermal relaxation of lattice disorder consists of three relaxation stages (stage I, stage II and stage III) with different rate constants.

Previously we have studied the thermal relaxation process of disorder of graphite irradiated with 3 keV He^+ using real-time Raman measurement within time period of 5 ks and found that there are two stages for thermal relaxation process with fast and slow rates. The present measurements spanning a longer time period of 40 ks

[1] The Breit–Wigner–Fano function is in some case used for asymmetric spectrum. But the peak of 1580 cm^{-1} has little skewness. So we have used the Lorentzian function.

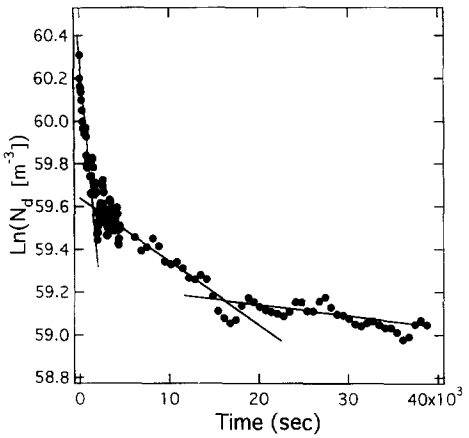

Fig. 2. Plot of $\ln N_d$ versus time at 433 K for HOPG after irradiated 2.7×10^{15} ions/m^{2}s for 300 s at 5 keV deuterium ions, to assure us of the third stage in addition to the previous two stages. The solid lines are only to guide the eye.

made clear that the slow rate process obtained in the previous work is further composed with two stages (stage II and stage III).

Ion-irradiation induced lattice disorder is considered to be mainly due to single defects in an early stage of ion irradiation, since the phonon correlation length of the disordered graphite corresponds to the interdefect distance [12–14]. Then the relaxation of the disorder of ion-irradiated graphite would be due to annihilation of single defects. We found previously that the annihilation of defects occurs by recombination between single-vacancies and single-interstitials via diffusion of single-interstitials for the fast relaxation process [10]. Since the relaxation rate in stage *I* is about the same for our previous work, the stage *I* is dominated by the recombination of single-vacancies and single-interstitials through the diffusion of single-interstitials. The single-interstitials (single-vacancies) migrate easier than the interstitials cluster (vacancy clusters) and the activation energies for in-plane migration for single-interstitial and di-interstitial are 0.14 and 0.86 eV [15], respectively, being much smaller than that of the vacancy (3.1 eV) [16]. Iwata et al. have reported that the single-interstitials start to migrate around 10 K and the di-interstitials recombine with vacancies via di-interstitial diffusion around 473 K [17]. The latter temperature, 473 K, is comparable to the present experimental conditions, therefore it is possible to occur the annihilation process of vacancies through the diffusion of di-interstitials in our experiment. Then we suppose that stage II is dominated by the recombination process of single-vacancies and di-interstitials proposed by Iwata et al., and stage III is dominated by combination of other slower processes which are like clustering of single-vacancies and/or related process of migration of larger interstitial clusters and vacancies clusters.

In summary, real-time Raman spectroscopy has been applied to study the thermal relaxation process at 411–463 K for graphite irradiated to 2.7×10^{15} ions/m^{2}s with 5 keV deuterium ion. It is shown that there exist three distinct stages of the thermal relaxation process in graphite under ion irradiation.

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