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Nuclear Instruments and Methods in Physics Research B 245 (2006) 126–129
NIM B
Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

Temperature annealing of tracks induced by ion irradiation of graphite ☆

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Available online 26 January 2006

Abstract

Highly oriented pyrolytic graphite (HOPG) samples were irradiated by Xe ions of initial kinetic energy of 3 MeV/u. The irradiations were performed at temperatures of 500 and 800 K. Scanning tunneling microscopy (STM) images show that the tracks occasionally have elongated structures under high-temperature irradiation. The track creation yield at 800 K is by three orders of magnitude smaller compared to that obtained during room-temperature irradiation. STM and Raman spectra show that amorphization occurs in graphite samples irradiated at 500 K to higher fluences, but not at 800 K. The obtained experimental results clearly reveal that the irradiation under high temperature causes track annealing.

PACS: 61.80.Jh; 68.37.Ef; 87.64.Je

Keywords: Graphite; Heavy ions; Scanning tunneling microscopy; Raman spectroscopy

1. Introduction

The tracks induced by heavy-ion irradiation on graphite have been systematically investigated over many years mainly motivated by the usage of graphite as a moderating and shielding material for nuclear reactors [1–3]. More recent interest in radiation damage of ion-irradiated graphite emerged because graphite will serve as a target for fragment separators in future high-energy high-intensity beam facilities. In the past, defects and structural disorders induced when exposing HOPG to various ion beams with projectiles in the eV to keV energy regime and swift heavy ions of several MeV per nucleon were investigated by STM and Raman spectroscopy [2–12]. It was shown that ions at relatively high energies from MeV to GeV create surface hillocks of 2–3.5 nm in diameter. The probability that each projectile forms a hillock depends strongly on the electronic energy loss. The tracks do not consist of a continuous cylindrical damage trail along its projectile but of a discontinuous sequence of perturbed zones, in which the lattice is destroyed. In addition, it should be mentioned that graphite can be transformed into nano-diamond by ion irradiation in the electronic stopping regime [13,14].

However, in all these studies HOPG samples were exposed to the ion beams at ambient conditions and the effect of high irradiation temperatures on track formation is not clear. The purpose of this work is to understand the behavior of the thermal properties of graphite irradiated by energetic ions at elevated temperatures. We present the results of STM and Raman spectroscopy studies on HOPG exposed to energetic Xe ions of fluences between 10^{13} and 10^{15} ions/cm^2 at temperatures of 500 and 800 K.

☆ Project supported by National Natural Science Foundation of China (10375079) and the West-Project of Chinese Academy of Sciences.
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0168-583X/$ - see front matter © 2006 Published by Elsevier B.V.
doi:10.1016/j.nimb.2005.11.162

2. Experimental

HOPG crystals (Advanced Ceramics Co., USA) were freshly cleaved and then irradiated with defocused Xe ion beam of 3 MeV/u at the sector focused cyclotron (SFC) of IMP, Lanzhou. The beam spot was 20×20 mm^2 and the beam was uniform across this area. The irradiations were performed at temperatures of 500 and 800 K by contacting the samples with a Button Heater (HeatWave Labs. Inc., USA). The temperature was measured by a sensor close to the samples. The beam intensity was monitored by a secondary-electron emitting Al-foils detector. Fluences between 10^{13} and 10^{15} ions/cm^2 were applied. All irradiations were performed under normal incidence with respect to the *c*-planes of HOPG.

After irradiation the original sample surfaces were investigated in air using a commercial STM (Solver P47 SPM, NT-MDT Company) with mechanically prepared Pt/Ir tips. The microscope was operated in the constant-current mode in air. Tip voltage and tunneling current were fixed at +100 mV and 1 nA, respectively.

Pristine and ion-irradiated graphite samples were analyzed by a confocal micro-Raman spectroscopy using a triple grating spectrometer (ISA-JY T64000). The excitation source was a 514.5 nm Ar-ion laser with power 200 mW. A 100× microscope objective lens was used for focusing the laser beam. The measurements were performed in the backscattering configuration on a spot of around 2 μm in diameter.

3. Results and discussion

Fig. 1 shows STM images of the HOPG surface after 390-MeV Xe ion irradiation at an ion fluence of 2×10^{14} ions/cm^2 and 800 K. The 12×12 nm^2 images show hillocks on the initially flat surface. The protrusions are surrounded by the unperturbed crystal with a lattice constant 0.246 nm, typical of the hexagonal graphite structure. The cross sections of the hillocks formed at high irradiation temperature are predominantly circular but about 10% exhibit an elongated shape. The mean values of the track diameters are 2.2 ± 0.7 and 2.0 ± 0.4 nm at temperatures of 500 and 800 K, respectively. These are in agreement with earlier work, i.e. the mean track diameters are in the range of 2–2.5 nm for Xe ions of energies between 300 and 500 MeV under room-temperature irradiation [9]. A quantitative analysis of the number of observed surface tracks compared to the applied ion fluence (1×10^{14} ions/cm^2) gives a track creation yield (ξ) of $(1.0 \pm 0.2) \times 10^{-2}$ and $(0.8 \pm 0.2) \times 10^{-3}$ for the samples irradiated at 500 and 800 K, respectively. For room-temperature irradiation, the track creation yield for Xe ions of energy 482 MeV was 0.6 and thus by 2–3 orders of magnitude larger.

Fig. 2 shows STM images obtained on HOPG irradiated with 390-MeV Xe ions of 1×10^{15} ions/cm^2 at 500 and 800 K. It is obvious that at this high fluence the surface is damaged in such a way that the non-irradiated areas can no longer be observed with atomic resolution. As shown in Fig. 2(a), the surface irradiated at 500 K is obviously amorphized with the small grains of 6.3 ± 1.8 nm in diameter. Such kind of surface topography was observed at a fluence of 2×10^{14} ions/cm^2 and temperature 500 K. For 800 K irradiation, the total area of damages and the roughness of damaged surfaces increased with increasing ion fluence. In Fig. 2(b), the surface was drastically damaged and a large percentage of the surface covered with hillocks and flaked craters caused by overlapping of ion impacts at a fluence of 1×10^{15} ions/cm^2. This induced partly the lost of structural arrangement of carbon atoms on the first graphite layers, whereas the original basal-plane orientation was still maintained on the surface. No surface amorphization was observed up to a fluence of 1×10^{15} ions/cm^2 at 800 K. We found that the fluences required for such major surface modifications increased with rising irradiation temperature. Our observation agrees with the results that the critical amorphization dose increases with irradiation temperature and no amorphization was detected

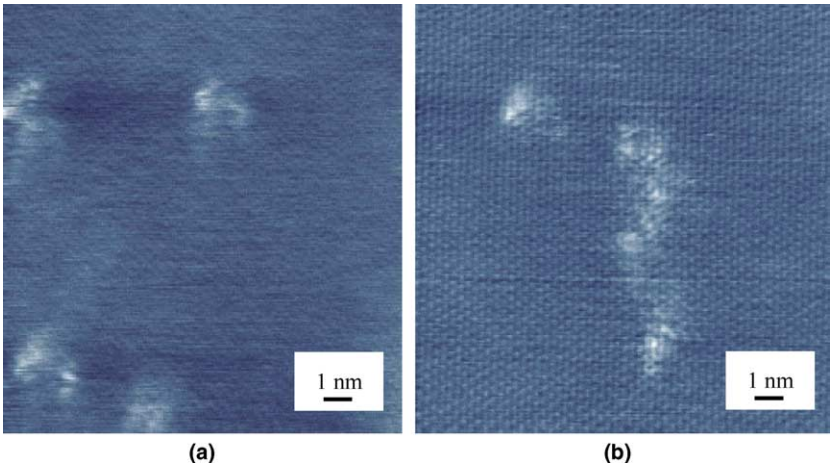

Fig. 1. STM images of HOPG surface irradiated with 390-MeV Xe ions of 2×10^{14} ions/cm^2 at normal incidence and 800 K.

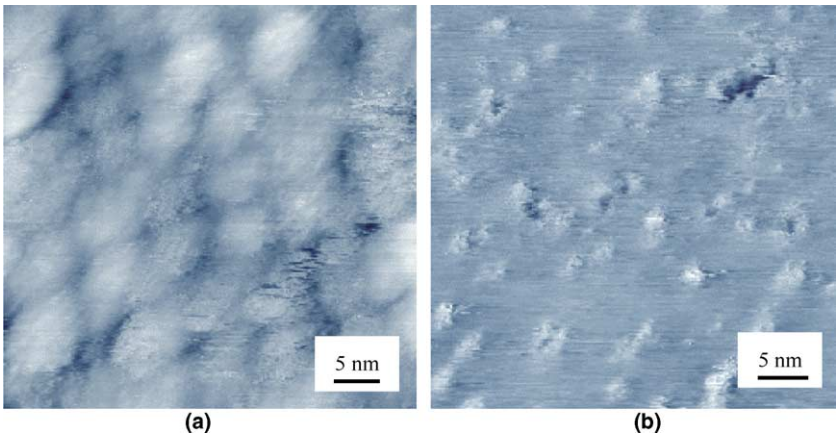

Fig. 2. STM images of HOPG irradiated with 390-MeV Xe ions at a fluence of 1×10^{15} ions/cm^2 and temperatures of (a) 500 K and (b) 800 K, respectively.

above 860 K in HOPG under irradiations of various ions of energy hundreds keV [15].

The first- and second-order Raman spectra of HOPG before and after Xe ion irradiations at 500 and 800 K are presented in Fig. 3. Except for the ordered Raman-active E_{2g} peak at 1580 cm^{-1} (G mode) in the Raman spectra of graphite, three additional extra first-order lines at 1346 (D_1), 1367 (D_2) and 1622 (D') cm^{-1} designated as D modes were originated from the onset of disorder after ion irradiation. The region of second-order Raman spectra show four distinct lines at 2442, 2686 ($2D_1$), 2727 ($2D_2$), 3248 ($2D'$) cm^{-1} appeared in the pristine and ion irradiated HOPG samples. It was shown that the D:G peak intensity ratio was enhanced by disorder [16]. The radiation-induced D_2 line became wider compared to the G line. From the magnitude of the relative intensity R of D_2 line to G line, $R = I_{D_2}/I_G$, the size of the ordered crystallite domains L_a can be determined by $L_a = 4.4/R$ (nm) for laser light of 514.5 nm [17]. In Fig. 4, the data of R and L_a as a function of ion fluence at temperatures of 500 and 800 K are presented. At a given irradiation temperature, the relative intensity R increases and the size of the ordered crystalline domain L_a decreases with increasing ion fluence, indicating an increase of damage with ion irradiation. However, for a given ion fluence, R was larger and L_a was smaller at 500 K than that at 800 K. For instance, L_a was 20 nm at 500 K compared to 30 nm at 800 K at a

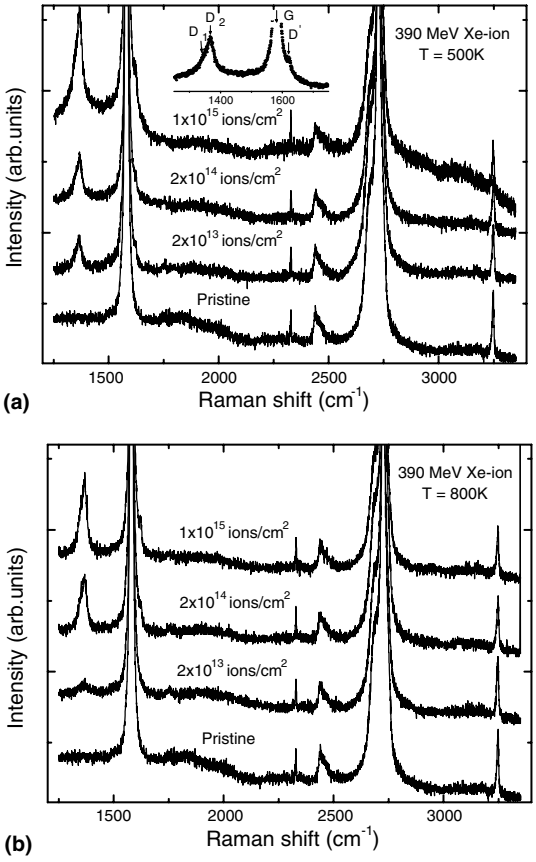

Fig. 3. Raman spectra of HOPG irradiated with 390-MeV Xe ion to different fluences at temperatures of (a) 500 K and (b) 800 K. The inset shows G, D_1, D_2 and D' peaks in the first-order spectrum of HOPG irradiated at 500 K and fluence 1×10^{15} ions/cm^2.

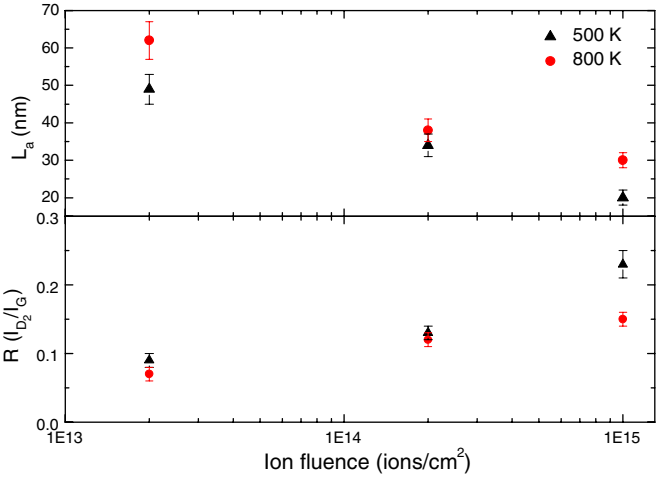

Fig. 4. The relative intensity R and the size of the ordered crystallite domains L_a change as a function of Xe ion fluence at 500 and 800 K, respectively.

fluence of 1×10^{15} ions/cm^2. So damage induced at low temperature was more serious than that at high temperature. In addition, the second-order spectrum showed a distinct band at 2727 ($2D_2$) cm^{-1}, the intensity ratio of the $2D_2$ line and the G line was insensitive to ion irradiation.

Swift heavy ions disturb or destroy the atomic order of HOPG both on the surface and in the bulk. The amorphization of graphite is related to the disordering of the two-dimensional structure, promoting bridging and bonding between the layers. It can be considered that the disordering of the lattice is followed in time by a rapid recrystallization occurring in particular in the bulk. High irradiation temperatures enhance recrystallization, the lattice damage relaxes and the crystal structure recovers by thermal annealing. Niwase [18] reported a temperature of 773 K at which vacancies become mobile in graphite. After reaching such a temperature, the bond breaking and reconstruction would dynamically occur, the apparent structure does not change significantly by further irradiation. Therefore, temperature is one parameter that influences the material modification under swift heavy ion irradiation. It should be mentioned that after ion implantation, no annealing effect in graphite was observed for temperature treatments in vacuum up to 1370 K, and it was found that high pressure plays an important role in the defect annealing which accelerating the graphitization process [19].

4. Conclusion

When swift heavy ions penetrate HOPG crystals, they create hillock-like surface tracks, which occasionally exhibit an elongated structure under high-temperature irradiation. The track creation yield at high temperature is much lower compared to at room-temperature irradiation. STM images and Raman spectra show that amorphization occurred when graphite samples are irradiated at 500 K to a fluence of 1×10^{15} ions/cm^2, but not at 800 K. This reveals the effect of high temperature on the annealing of surface and the bulk disorder induced by heavy ion irradiation on graphite.

Acknowledgements

We would like to thank C. Trautmann, R. Neumann, U.A. Glasmacher and M. Lang for many fruitful discussions, and the accelerator staff of the HIRFL for help during irradiation experiments.

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