Formation of dislocation dipoles in irradiated graphite

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Abstract

Recently, we have proposed a dislocation dipole accumulation model to explain the irradiation-induced amorphization of graphite. However, the structure of dislocation dipole in the hexagonal networks is still an open question at the atomic-level. In this paper, we propose a possible formation process of the dislocation dipole. © 2001 Elsevier Science. All rights reserved

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1. Introduction

Disordering of graphite, occurring under high energy particle irradiation, is an interesting issue in terms of defect formation in graphite. An appearance of halo rings in the transmission electron microscope (TEM) diffraction pattern after a critical dose [1] and the related remarkable broadening of Raman spectrum [2] imply that graphite amorphizes under irradiation by the accumulation of defects. However, it was not clear what type of defect leads to the disordering of graphite. Then, assuming a transformation to a disordered region from the original graphite structure due to the introduction of vacancies in the hexagonal networks, we have proposed a semi-empirical model to explain the irradiation-induced amorphization [3]. The model can predict the temperature dependence of the critical dose for amorphization and give an insight into the mobilities of single interstitials and di-interstitials, but it cannot predict the change in the defect concentration under irradiation nor give information on the structure of the disordered region. Then, we have modified the “disordered region” model for a “dislocation accumulation” model by assigning the disordered region to a dislocation dipole [4]. The model well simulates the experimental results of the square-root dose dependence of the Raman intensity ratio [5] and the dose dependence of the c-axis expansion [6] under irradiation. However, the nucleation and growth processes of the dislocation dipole are still an open question at atomic-level. Here, briefly reviewing irradiation-induced amorphization and dislocation accumulation model, we propose the formation process of the dislocation dipoles.

2. Irradiation-induced amorphization

Disordering occurring in the basal plane of graphite under irradiation can be detected by TEM diffraction pattern observed along the c-axis. Halo pattern starts to appear and then the diffraction spots disappear.

Fig.1 TEM diffraction pattern of highly oriented pyrolytic graphite (HOPG) foil irradiated with 25 keV D+ ions at 473 K. (a) before irradiation; (b) 1.0x10^15 ions/m^2, (c) 2.5x10^16 ions/m^2. Observations were done along the c-axis.

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after a critical dose (Fig. 1). However, the layered sequence of the basal planes still remains in the initial stage of the amorphization process [7] in spite of the occurrence of the in-plane disordering. A remarkable broadening of the Raman spectra also appears in the disordering process (Fig. 2). The critical dose for amorphization increases with increasing the irradiation temperature.

3. Dislocation accumulation model

The dislocation accumulation model [4] is a kinetic model, taking account the point and defect clusters shown in Fig. 3. The reaction kinetics can be summarized as follows. An incident atom knocks a host atom, resulting in the formation of an interstitial and a vacancy (Frenkel pair). The fraction of atomic sites at which Frenkel pair production can take place gradually decreases with increasing concentration of vacancy and dislocation dipoles. Single interstitials move two-dimensionally parallel to the basal plane. Other movements of interstitials and vacancies parallel to the basal plane and along the c-axis are neglected owing to the high activation energies [8]. An interstitial in a recombination volume around a vacancy annihilates with the vacancy. A barrier exists for the mutual annihilation. A pair of interstitials is thermally stable once formed. We neglect the formation of interstitial clusters except for di-interstitials as we suppose that the interstitial clusters are not dominant for the total reaction kinetics at comparatively low temperatures. Di-vacancies formed by knock-ons, occurring at sites close to single vacancies, reconstruct to eliminate dangling bonds as shown in the left hand side area of Fig. 4. The reconstructed di-vacancies do not annihilate with interstitials and are the nucleus of the dislocation dipoles. Dislocation dipoles can grow by successive knock-ons close to the ends of dislocation dipoles as shown in the right hand side area of Fig. 4. The dislocation dipoles cannot annihilate with interstitials.

The irradiation-induced amorphization, which occurs in the basal plane at first, is attributed to the destruction of the topological long-range order due to the introduction of dislocation dipoles, leading to nanocrystalline structure connected by dislocation dipoles [4]. The simulations of the experimental results showing the square-root dose dependence of the Raman intensity ratio [5] and the dose dependence of the c-axis expansion [6] revealed the existence of a strong barrier to the annihilation of interstitials at vacancies. A relation is given

Fig. 2 Change in Raman spectra for HOPG foils irradiated with 25keV He⁺ at room temperature. Remarkable broadening of Raman spectra appears when the irradiated graphite amorphizes.

Fig. 3 Point defects, defect clusters and their reactions assumed in the dislocation dipole accumulation model [4]. A recombination barrier exists between an interstitial and vacancy.

Fig. 4 Nucleation and growth of dislocation dipole. Di-vacancies formed by knock-ons, occurring at sites close to single vacancies, reconstruct to eliminate dangling bonds as shown in the left hand side area. The reconstructed di-vacancies are the nucleus of the dislocation dipoles. Dislocation dipoles can grow by successive knock-ons close to the ends of dislocation dipoles as shown in the right hand side area.
for estimating the concentration of single vacancy quantitatively from the Raman intensity ratio [4]. However, the dislocation accumulation model does not give any information on the structure of dislocation as simply shown by broken lines in Figs. 3 and 4.

4. Formation of dislocation dipole

Figs. 5(a) and 5(b) show two possibilities of the nucleation process of dislocation dipole, i.e., the reconstruction of di-vacancies. The left one transforms to two eightfold rings, sitting opposite to each other, and the right one to eightfold ring and two fivefold rings. The right one may be energetically favorable [9]. If knock-on occurs at sites denoted by dark spots in Fig. 5(b), both of them would grow to the same structure consisting of eightfold, sevenfold and fivefold rings as shown in Fig. 5(c).

Successive knock-ons at the ends of the dislocation dipoles induce their growth along the zigzag line. A long dislocation dipole generated from 9 vacancies (Figs. 6(a)) is shown in 6(b), where a vacancy line reconstructs to a dislocation dipole to make an energetically favorable structure by eliminating dangling bonds. In the reconstructed structure of Fig. 6(b), one dangling bond remains at a site denoted by a circle. The dislocation dipole can grow by knock-on at the ends of dislocation dipole denoted by symbols in Fig. 6(b). Neighboring eightfold and sixfold rings at the left hand side end of the dislocation dipole in Fig. 6(b) transforms to neighboring sevenfold and fivefold rings in Fig. 6(c) after a knock-on of an atom denoted by a circle. On the other hand, the neighboring sevenfold and fivefold rings at the right hand side end of the dislocation dipole in Fig. 6(b) can grow into the neighboring eightfold and sixfold rings in Fig. 6(c) after a knock-on of an atom denoted by a triangle. The two processes can repeat alternately, leading the growth of the dislocation dipole. The contraction in the basal plane along the direction denoted by the broken line in Fig. 6(a) occurs.

We should note that the dislocation dipole grows just at the ends because lattice sites of the dislocation dipole between the ends consists of honeycomb structure and reconstruction does not occur by knock-on of neighboring lattice sites, just leaving single vacancy which can

Fig. 5 A possible nucleation process of dislocation dipole by the reconstruction of di-vacancy. The left one transforms to two eightfold rings, sitting opposite to each other, and the right one to eightfold ring and two fivefold rings. If knock-on occurs at sites denoted by circles in (b), both of them can transform to the same structure consisting of eightfold, sevenfold and fivefold rings as shown in (c).

Fig. 6 A long dislocation dipole generated from 9 vacancies (light spots). The dislocation dipole can grow by knock-on at the ends of dislocation dipole denoted by symbols in (b). Neighboring eightfold and sixfold rings at the left hand side end of the dislocation dipole in (b) transforms to neighboring sevenfold and fivefold rings in (c) after a knock-on of an atom denoted by a circle. The neighboring sevenfold and fivefold rings can grow into the neighboring eightfold and sixfold rings as shown at the right hand side area by knock-on an atom denoted by a triangle. The contraction in the basal plane along the directions denoted by the broken lines in (a) occurs.
annihilate with an interstitial.

One may have a question why the dislocation accumulation model, which is valid for a low temperature range where vacancies cannot move [4], omits the formation of vacancy loops. This is explained by annihilation of vacancy loops with interstitials, if loops were formed by knock-on process. One dimensional vacancy cluster of dislocation dipoles, on the other hand, cannot annihilate with interstitials due to the reconstruction but can grow by knock-ons as shown in Figs. 5 and 6. However, if we raise the irradiation temperature high enough to induce an aggregation of vacancy type defects, vacancy loops may be formed, as was observed on annealing above 923 K for a heavily irradiated graphite [10]. One should note that the lowest temperature of 923 K on the appearance of vacancy loops almost coincides with the highest temperature where the irradiation-induced amorphization occurs [11].

One should remember that the remarkable broadening of the Raman spectrum appears when disordering occurs under irradiation. This may be due to the life time broadening of phonons originated in the lattice distortion around the dislocation dipole. The remarkable broadening does not occur in the initial stage of irradiation where single vacancies are dominantly formed. This suggests that the lattice distortion around single vacancy is not so strong to induce the remarkable life time broadening.

In conclusion, we propose a probable process on the formation of dislocation dipole, which accumulation leads to the destruction of the long range order of graphite. The key process is the reconstruction of di-vacancies and dislocation dipoles at the ends after knock-ons. Theoretical and experimental works are awaited to confirm the processes.

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References