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Formation of ion tracks in amorphous silicon nitride films with MeV C_{60} ions

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Amorphous silicon nitride (a-SiN) films (thickness 5–100 nm) were irradiated with 0.12–5 MeV C_{60}, 100 MeV Xe, 200 MeV Kr, and 200 and 420 MeV Au ions. Ion tracks were clearly observed using high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) except for 100 MeV Xe and 200 MeV Kr. The observed HAADF-STEM images showed that the ion tracks consist of a low density core (0.5–2 nm in radius) and a high density shell (several nm in radius). The observed core and shell radii are not simply correlated with the electronic energy loss indicating that the nuclear energy loss plays an important role in the both core and shell formations. The observed track radii were well reproduced by the unified thermal spike model with two thresholds for shell and core formations.

1. Introduction

Passage of swift heavy ions may lead to permanent material changes, so-called ion tracks, along the ion path when the electronic energy loss is larger than a material dependent threshold value [1,2]. Beyond the threshold value, the radius of ion track increases with the electronic energy loss. After discovery of the ion track more than 50 years ago [3], a large number of studies has been conducted to reveal the structure and the formation mechanism of ion tracks in various materials [4]. With increasing number of the accumulated experimental data it has been recognized that the radius of ion track, produced in some materials, depends on the observation technique. In the case of CaF_2, the track radii deduced from measurements of channeling Rutherford backscattering spectrometry (C-RBS) are in good agreement with those extracted from the peak width analysis of X-ray diffraction (XRD), while the radii deduced from the peak area analysis of XRD are much smaller but in good agreement with the observation of transmission electron microscopy (TEM) [5]. Similar results were also observed for LiF [6], and pyrochlores [7]. These results suggest that the ion tracks consist of a heavily damaged cylindrical core region and a less damaged shell (halo) region. For crystalline materials, such core–shell structures may be directly observed using TEM [7]. For amorphous materials, the direct TEM observation of ion tracks is difficult due to a lack of sufficient contrast. There had been only a few studies on the ion tracks using TEM [8,9] and no core–shell structure was observed.

The first direct observation of the core–shell structure in amorphous materials has been performed for amorphous SiO_2 (a-SiO_2) irradiated with swift heavy ions using small angle X-ray scattering (SAXS) [10]. The observed SAXS spectra were analyzed assuming a simple model structure of the ion track, *i.e.* a step-function-like radial density distribution. The analysis showed that the observed ion tracks consist of a low density core surrounded by a high density shell. The observed core and shell radii were reproduced by the inelastic thermal spike (i-TS) model assuming two temperature thresholds [10]. The deduced densities of the core and shell are 40% and 120% of the bulk density, respectively. Such a large density change may be easily observed using TEM. Because TEM directly provides more detailed information about the fine structures of ion tracks, the TEM observation can shed more light onto the formation mechanism of the core–shell structure. Actually ion tracks produced in a-SiO_2 irradiated with 420 MeV Au ions were observed using high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) [11]. The derived radial density

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distribution is not a simple step-function-like distribution but is very similar to that predicted by MD simulations [10,12].

Recently, we have observed ion tracks produced in amorphous silicon nitride (a-SiN) films irradiated with 0.36–0.72 MeV C_{60} ions using HAADF-STEM [13,14]. In this energy region, the nuclear energy loss is larger than the electronic energy loss. The observed HAADF-STEM images suggested a core–shell structure. Although the image of the density-reduced core showed a strong contrast, the contrast of the density-enhanced shell was not strong enough for convincing the existence of shell. The energy dependence of the observed core radius showed a strange behavior, suggesting the cluster effect and/or the effect of the nuclear energy loss in the track formation. In the present paper, we report a more comprehensive study. We extend the study to a wider energy region (from 0.12 up to 5 MeV C_{60} ions) and also to monatomic swift heavy ions, such as 420 MeV Au ions. The a-SiN films irradiated with these ions were observed using TEM and HAADF-STEM. The observed core and shell radii are compared with the results of the calculation using the unified thermal spike (u-TS) model [15]. The role of the nuclear energy loss and the cluster effect in the formation of the core–shell structure are discussed.

2. Experimental

Self-supporting a-SiN films of thicknesses 5–100 nm were purchased from Silson Ltd, which were prepared by chemical vapor deposition on Si wafers. The nominal density of the a-SiN film was 3 g/cm^3, which is slightly smaller than that of the crystalline Si_3N_4 (3.44 g/cm^3). The composition of the a-SiN film was measured using high-resolution Rutherford backscattering spectrometry [16]. The obtained composition $Si_{0.47}N_{0.53}$ is slightly Si rich compared to the stoichiometric Si_3N_4. The a-SiN films were irradiated with 0.12–5 MeV $C_{60}^{+}$$^{2+}$ ions to fluences $1–20 \times 10^{10}$ ions/cm^2 at JAEA/Takasaki. The films were also irradiated with 100 MeV Xe ions, 200 MeV Kr ions, and 200 and 420 MeV Au ions to fluences about 1×10^{11} ions/cm^2 at JAEA/Tokai. In the irradiation of 200 MeV Au ions, a thin carbon foil was installed upstream of the beam line and the most probable charge state (32+) was selected by a dipole magnet for the irradiation. In the irradiation of other swift heavy ions, a carbon foil of 20 μg/cm^2 was installed in front of the a-SiN film to acquire equilibrium charge states.

After the ion irradiation, TEM observations were performed using a JEOL JEM-2200FS equipped with a field emission gun operating at 200 kV. The sample was held at the specimen tilting holder with a tilt angle from −30 to 30 degrees. The images were taken by GATAN Ultrascan 1000 CCD camera with a 2 k × 2 k pixel. In addition to the observation with the electron beam perpendicular to the film surface, observations at a tilt angle of 25° were also performed to determine the length of the ion tracks. For quantitative analysis of the density change inside the ion tracks, the samples were also observed using HAADF-STEM. In the HAADF-STEM, the size of the electron beam was 0.2 nm, the convergence angle was 12 mrad and an annular dark detector covering over 120 mrad were used. Differently from the conventional TEM, the image of HAADF-STEM is not sensitive to the focusing conditions and precise measurements of track radii can be easily performed.

3. Results

Fig. 1(a) shows an example of a bright field TEM images of a 30-nm a-SiN film irradiated with 5 MeV C_{60}^{+} ions. An ion track is clearly observed as a bright spot of several nm surrounded by a dark shell. Similar images of ion tracks were also observed for other ions except for 200 MeV Kr. The observed image suggests that the ion track consists of a density-reduced core and a density-enhanced shell. However, because the TEM image strongly depends on the focusing conditions, quantitative analysis is rather difficult. For the quantitative analysis, the samples were also observed using HAADF-STEM. Examples of the observed HAADF-STEM images of the a-SiN films irradiated with 5 MeV C_{60}^{+} and 200 MeV Au^{32+} are shown in Fig. 1(b) and 1(c), respectively. Ion tracks produced by these ions are also clearly seen in the HAADF-STEM images. The ion tracks produced by 5 MeV C_{60}^{+} ions are larger and have a stronger contrast compared to those produced by 200 MeV Au^{32+} ions although the electronic energy loss of the 5 MeV C_{60} (21.9 keV/nm) is smaller than that of the 200 MeV Au (23.8 keV/nm). The dark contrast of the ion track indicates that the density is reduced in the track interior. These cores are surrounded by a slightly bright shell. Similar images of ion tracks were also observed for other ions except for 200 MeV Kr. For 100 MeV Xe ions, the ion tracks were clearly observed using TEM but clear contrast could not be observed using HAADF-STEM probably due to its relatively poor resolution (0.5 nm) compared to TEM.

The contrast of the HAADF-STEM image is proportional to the areal density of the sample integrated along the observation direction. The density profiles of the ion tracks were derived from the observed HAADF-STEM images. Fig. 2 shows examples of the obtained radial density profiles of the ion tracks. The vertical axis shows the areal density (density integrated along the ion track) normalized to the nonirradiated areal density. All observed profiles are similar irrespective of the ion species and energy. It can be seen that the density is reduced by ∼20% at the track center. In the outer shell region, the density is slightly enhanced by ∼2%. Each profile was fitted by a straight line in the core region (shown by thin dashed lines) and the radius of the ion track core was determined by the crossing point of the fitting line with the bulk density (shown by arrows). The radius of the shell was also determined by the similar procedure. The inset of Fig. 2 shows the magnified density profile for 5 MeV C_{60}^{+}. The profile was fitted by a straight line in the outer part of the shell region (dot-dashed line). The shell radius was determined by the crossing point of the fitting line with the bulk density (shown by the arrow).

The obtained core and shell radii are summarized in Table 1 together with the electronic and nuclear energy losses estimated using SRIM2011 [17]. It is seen that the observed track radii does not depend on the thickness of the a-SiN film. Note that the shown core radius for 100 MeV Xe was deduced from the observed TEM images because no clear image of the ion track was observed using HAADF-STEM. In the estimation of the energy loss of C_{60} ions, cluster effects were neglected, namely the energy loss of the monoatomic carbon ion of the same velocity was multiplied by 60.

Figs. 3 and 4 show respectively the observed core and shell radii as a function of the electronic energy loss. The behavior of the core radius produced by the C_{60} ions is very different from that of the monoatomic ions (see Fig. 3). Although the core radius increases with the electronic energy loss for monoatomic ions, the radius for the C_{60} ions is almost independent of the electronic energy loss. On the other hand, the observed shell radius seems to follow a universal curve (dashed line in Fig. 4) but is almost independent of the electronic energy loss. This is also very different from the well-known trend, *i.e.* generally the track radius increases with the electronic energy loss.

Fig. 5 shows an example of the TEM bright field images observed at a tilt angle of 25° for the 100-nm a-SiN films irradiated with 5 MeV C_{60}^{+} ions. The ion tracks are elongated along the tilt direction. The observed image of the ion track is continuous and almost uniform along the length of the track. The average track length was determined to be 44 nm from the observed images. This is much smaller than the projected range (186 nm) calculated using SRIM2011. The observed track lengths of C_{60} ions with