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A study of the critical factor determining the size of etched latent tracks formed on SiO_2 glass by swift-Cl-ion irradiation

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ABSTRACT

When a Cl ion with energy of the order of megaelectronvolts collides with SiO_2 glass, it penetrates the glass along a straight line. The region through which the ion passes and its vicinity, called the latent track, can be easily etched by hydrofluoric acid, resulting in the formation of a nanopore. With increasing ion energy, the nanopore radius first increases, reaches a maximum, and then decreases. In order to analyze this strange phenomenon, we investigated the radius of the region that melted upon ion irradiation, as one of the possible approaches. We calculated its radius using heat diffusion equations and compared it with the radius of nanopores. We found that both the radii depend on the ion energy in a similar manner.

1. Introduction

In order to apply "nanotechnology" to practical devices, further development of various element technologies is required. For example, the fabrication technique used for nanostructured insulators has to be further improved for fabricating advanced optical devices with various functions such as optical confinement by photonic crystals [1] and the antireflection effect of moth-eye structures [2]. A combination of lithography and subsequent reactive ion etching has been used widely for the fabrication of nanostructures [3,4]. However, trenches fabricated by reactive ion etching sometimes have rough sidewalls because of the use of corrosive gases [3,4], which can degrade the device performance.

As a solution to this problem, a novel fabrication method using heavy ions with energy of the order of megaelectronvolts has been proposed [5–13]. The swift-heavy-ion irradiation induces the formation of damaged regions; these regions are cylindrical in shape with diameters of a few nanometers and depths of a few micrometers, and one region is formed corresponding to each ion. These ion-induced damaged regions are called "latent tracks". For a given etchant, the etching rate at latent tracks is significantly higher than that at nonirradiated regions. As a result, nanopores can be fabricated in insulators using this method [5–13]. This method is quite useful since the fabricated sidewalls are very smooth as compared to those formed by reactive ion etching [3,4].

It is very important to elucidate the critical factor determining the pore size in order to apply nanopores to various applications. Dallanora et al. have introduced an interesting study on threshold energy loss necessary to form nanopores on the SiO_2 glass surface, through the analysis based on the thermal spike model [11]. Furthermore, it has been implied for rutile TiO_2 single crystal that the size of the melted region calculated using the thermal spike model, where the lattice temperature exceeds the melting point, seems to be correlated with the etched nanopore size [13]. Thus, in this study, we attempted to find the critical factor for SiO_2 glass, a typical insulator, through the analysis of heat diffusion using the thermal spike model, as one of the possible approaches [11–15]. For this, we estimated the radii of melted regions formed by swift-Cl-ion irradiation from the change in lattice temperature. We then compared the estimated radii with the experimentally obtained radii of nanopores formed by the immersion of the glass in hydrofluoric acid following the Cl-ion irradiation [16]. The nanopore radius was found to change in a complicated manner depending on the ion energy [16].

2. Calculation methods

First, electronic and nuclear stopping powers of Cl ions in SiO_2 glass were calculated using the SRIM 2008 code [17], assuming the density to be 2.2 g/cm^3 [18]. Fig. 1 shows the electronic and

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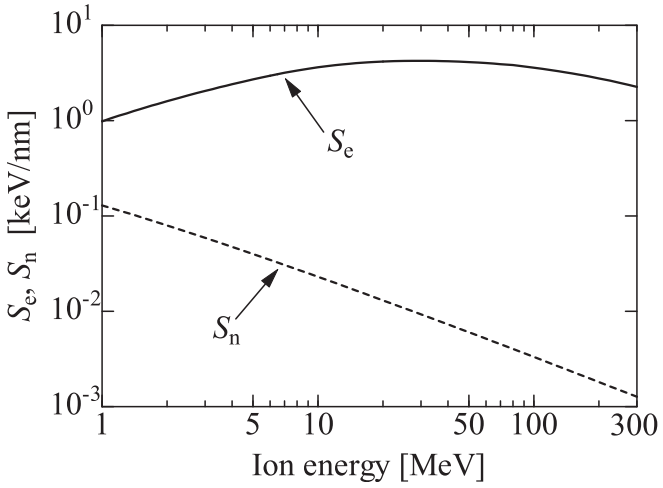

Fig. 1. Electronic and nuclear stopping powers, S_e (solid curve) and S_n (broken curve), respectively, as a function of energy of Cl ions.

nuclear stopping powers, S_e (solid curve) and S_n (broken curve), respectively, as a function of the energy of Cl ions. Calculations by the SRIM code may not be very reliable in an energy range where electronic as well as nuclear stopping processes contribute, and synergetic effects of nuclear and electronic stopping processes may occur. However, since S_e is significantly higher than S_n in the energy range of 1–300 MeV, in which the calculations were performed, it is assumed that the reliability of the SRIM code is high. Thus, the lattice temperature was calculated as a function of time elapsed from the ion collision by assuming that the energy of ions was transferred only to the electrons in SiO_2 glass. The electronic temperature T_e and lattice temperature T were calculated using the following heat diffusion equations by assuming that a single swift Cl ion collided with SiO_2 glass [12–15]:

$$C_e\frac{\partial T_e}{\partial t} = \nabla\cdot(K_e\nabla T_e) + A(r,t) - g(T_e - T), \quad (1)$$

$$C(T)\frac{\partial T}{\partial t} = \nabla\cdot(K(T)\nabla T) + g(T_e - T), \quad (2)$$

where C_e and K_e are the electronic specific heat per unit volume and electronic thermal conductivity, respectively, and $C(T)$ and $K(T)$ are the specific heat and thermal conductivity of the lattice, respectively. Furthermore, $A(r,t)$ is the energy density given to electrons in SiO_2 glass by a single swift Cl ion in a unit period of time at a distance r from the ion collision point, as a function of time t elapsed from the ion collision. It is expressed as follows:

$$A(r,t) = A_0 D(r)\exp(-t/\tau), \quad (3)$$

where $D(r)$ is the initial spatial distribution function of the energy density of electrons, estimated by Waligorski et al. [19], and τ is the mean flight time of δ-ray electrons. By introducing $D(r)$ that depends on ion species and ion velocity, the ion-velocity effect on the track formation can be estimated. In the present calculation, τ is assumed to be of the order of 10^{-15} s [12–15]. A_0 is a normalization constant related to S_e, which is given by the following equation:

$$S_e = A_0\int_{r=0}^{\infty} D(r)2\pi r\,dr\int_{t=0}^{\infty}\exp(-t/\tau)\,dt. \quad (4)$$

Further, g appearing in Eqs. (1) and (2) is the electron–phonon coupling constant. As expressed by Eqs. (1) and (2), it is assumed that the energy of a Cl ion is first transferred to electrons in SiO_2 glass and then to the lattice via the electron–phonon coupling process, resulting in an increase in lattice temperature.

In this study, the thermodynamic parameters of quartz, such as the melting point T_m, were employed [15], since those of SiO_2 glass are unknown. Further, T was assumed to be 300 K before the ion irradiation. For g, we used the value obtained from the mean energy-diffusion length fitted experimentally [14,15]. The latent heat was taken into account in the calculations. From the above equations, T was calculated at a point r as a function of t.

3. Results and discussion

The data reported in the literature [16] are replotted in Fig. 2. Namely, the open squares in Fig. 2 show the radius r_n of the nanopores formed on the SiO_2 glass surface by the irradiation of Cl ions with various energies and subsequent immersion in 4.8% hydrofluoric acid for 7 min at room temperature [16]. The solid circles in Fig. 2 show the radius r_m of the melted region, calculated as a function of ion energy, which will be discussed later. It is found that r_n changes in a complicated manner depending on the ion energy. It becomes maximum at 15 MeV and decreases with a further increase in energy [16].

A crucial parameter to govern the etching of latent tracks is generally known to be threshold energy loss. We have reported that rutile TiO_2 single crystal becomes soluble for hydrofluoric acid, when S_e of the ions exceeds 6.2 keV/nm, regardless of the ion species in the case of I, Br, Cu, and Ti ions [20]. However, in the present research, the Cl-ion energy where S_e becomes maximum is ~30 MeV as shown in Fig. 1, and this energy differs from 15 MeV at which r_n becomes maximum. Therefore, the dependence of r_n on the ion energy (Fig. 2) cannot be elucidated by investigating only S_e. We have also reported that the TiO_2 crystal was not etched in the case of fast Ca and Cl ions, with energies higher than ~72 MeV and ~77 MeV, respectively, even if S_e exceeded the value of 6.2 keV/nm [20]. Furthermore, Meftah et al. have also reported that the faster ions create smaller latent tracks on $Y_3Fe_5O_{12}$ than the slower ions having the same value of S_e [21]. These facts in turn indicate that the threshold energy loss necessary to form the nanopore (and the latent track) shifts to a larger value when the ion velocity increases, which is consistent with the result reported by Dallanora et al. [11]. Thus, the ion-velocity effect should play an important role in the nanopore formation. The ion-energy dependence of r_n, shown in Fig. 2, should be discussed taking the above-mentioned ion-velocity effect into account.

Therefore, in order to carry out a further analysis, we calculated the temporal change in the lattice temperature T upon the ion irradiation, using the heat diffusion equations, in which the ion-

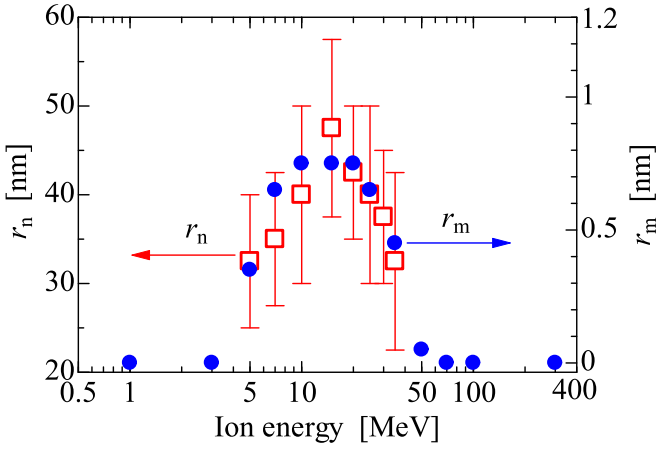

Fig. 2. Radius r_n of nanopores formed on SiO_2 glass surface by immersion in hydrofluoric acid, following irradiation of Cl ions, as a function of ion energy (open squares) [16]. The error bar on each square represents one standard deviation. The estimated radius r_m of the melted region formed on the SiO_2 glass surface by the collision of a Cl ion is also shown by solid circles.