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Computer simulation of radiation-induced nanostructure formation in amorphous materials

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ABSTRACT

In this study, 3D simulations based on a theoretical model were developed to investigate radiation-induced nanostructure formation in amorphous materials. Model variables include vacancy production and recombination rates, ion sputtering effects, and redeposition of sputtered atoms. In addition, a phase field model was developed to predict vacancy diffusion as a function of free energies of mixing and interfacial energies. The distribution profile of the vacancy production rate along the depth of an irradiated matrix was considered as a near Gaussian approximation according to Monte-Carlo TRIM code calculations. Dynamic processes responsible for nanostructure evolution were simulated by updating the vacancy concentration profile over time. Simulated morphologies include cellular nanoholes, nanowalls, nanovoids, and nanofibers, with the resultant morphology dependant upon the incident ion species and ion fluence. These simulated morphologies are consistent with experimental observations achieved under comparable experimental conditions. Our model provides a distinct numerical approach to accurately predicting morphological results for ion-irradiation-induced nanostructures.

1. Introduction

Amorphous materials were initially thought to be ideal for use in radiation environments since no additional disorder could be induced by irradiation. However, over the past two decades, catastrophic irradiation-induced swelling has been observed in several amorphous materials, such as amorphous germanium [1] and GaSb [2,3], through ion beam irradiation experiments. In these materials, an irradiation effect is the development of a high density of cavities separated by nanowalls and nanofibers of ~10–20 nm in diameter. *In situ* transmission electron microscopy (TEM) has demonstrated that defect production and interactions, especially for vacancies, play an important role in the ultimate formation of these morphologies in the amorphous state [4,5]. One possible formation mechanism is that ion-irradiation creates excess vacancies in a material that then cluster to form voids, and growth of the voids continues as they act as sinks for vacancies produced thereafter. Since little is known about the nature and interactions of defects in amorphous materials, the problem is more complex than that which has been address by previous defect studies in semiconductors. Not only is a more complete understanding of formation mechanisms in the amorphous phase important due to fundamental limits of top-down processes based on lithography and ion etching but also because of the attractive applications of self-organized nano-patterns in irradiated amorphous semiconductors and in nanotechnologies such as solar cell fabrication [6–8].

In this study, 3D simulations developed through our theoretical model are proposed to investigate the dynamic formation processes for radiation induced-nanovoids, nanowalls and nanofiber structures in amorphous materials, with the resulting structures dependant on the ion species and fluence. In addition to defect production, elimination, and migration considered in traditional radiation damage theory, our model incorporates the effects of free energies of mixing and interfacial energies for phase separation. All concerned reactions are connected to the physics of radiation damage, while the driving force for vacancy clusters or precipitates is derived from the thermodynamics to reduce the total free energy of the system.

2. Phase field approach

Following the methodology in previous studies for irradiation-induced nanostructures [9,10], a phase field approach was adopted in this 3D model simulation. The microstructure of the system is described by a composition field [11]. The local vacancy concentration of a particular volume (ϕ) is expressed in terms of local reduction of atomic density with the range of $0 \leq \phi \leq 1$, and pores are treated as high vacancy concentration regions which represent

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the pseudo-phase of voids. The amorphous phase of the irradiated matrix consequently could be represented by low vacancy concentration regions $(1-\phi)$. Dynamic processes such as pore coalescence are captured by updating the vacancy concentration profile over time. A spatially continuous and time-dependent function of the vacancy concentration, $\phi(\mathbf{x}, t)$, includes the irradiation effects at position $\mathbf{x}$ (where $\mathbf{x}$ is the spatial coordinates) and was written as [12]:

$$\frac{\partial \phi}{\partial t} = \xi_0 - \xi_{rc}\phi(1-\phi) - \xi_{rd}\phi + \frac{M}{N^2}\nabla^2\left(\frac{\partial g(\phi)}{\partial \phi} - 2k\nabla^2\phi\right), \quad (1)$$

where ξ_0 is the source term for vacancy generation by incident radiation, ξ_{rc} is the rate constant for vacancy recovery reactions, ξ_{rd} is the rate constant for redeposition of sputtered atoms, M is the mobility, N is the number of atomic sites per unit volume, $g(\phi)$ is the free energy of mixing, and k is a gradient coefficient.

In general and especially in semiconductors, ion-irradiation generates a significant concentration of vacancies in the matrix, with displaced atoms turning into either sputtered atoms or interstitials in the matrix, and irradiation transforms a crystalline material into an amorphous one [13]. In Eq. (1), the first term describes the production of vacancies caused by the continuing irradiation that involves contributions of displaced and sputtered atoms. The second and third terms represent vacancy eliminations, including recombination with matrix atoms in the amorphous phase and redeposition of sputtered atoms. For an amorphous phase, such as Ge or GaSb after irradiation [1–3], vacancy and interstitial positions cannot be defined relative to a crystal lattice, and therefore the local vacancy concentration in this study is redefined as a local reduction of atomic density. In a disordered structure, it is difficult to identify specific interstitials in an amorphous matrix. Moreover, the amorphous matrix provides massive sinks for absorbing interstitials, and supplies matrix atoms to achieve the recovery reaction of vacancies from these sinks due to the high mobility of atoms (including interstitials) in the amorphous matrix. Thus, the interstitials are assumed to disperse in the low vacancy concentration regions to become matrix atoms in the amorphous phase. The recovery rate of vacancies takes the form of $\phi(1-\phi)\xi_{rc}$ [14]. The redeposition of sputtered atoms in the third term compensates for the hidden sputtering effect introduced by incident radiation in the source term. The effect of redeposition reactions is not obvious in materials with low defect concentrations or at early stages of irradiation, since a first order approximation ($\xi_{rd}\phi$) is taken [15]. The last two terms in the bracket represent the mixing energy of vacancies and atoms in the matrix, and the interfacial energy, respectively; $g(\phi)$ can be further analyzed by the form of a regular solution which has double wells in terms of concentration [10,16]:

$$g(\phi) = g_v\phi + g_a(1-\phi) + Nk_BT[\phi\ln\phi + (1-\phi)\ln(1-\phi)] + N\Omega\phi(1-\phi), \quad (2)$$

where g_v is the chemical energy of vacancies per unit volume and g_a is the chemical energy of matrix atoms per unit volume. N is the average number of atomic sites per unit volume, k_B is the Boltzmann constant, and T is the absolute temperature. The parameter Ω determines the shape of $g(\phi)$. When $\Omega > 2k_BT$, the function has double wells and drives phase separation. The free energy reduction of mixing system and interfacial energy provides the driving force for vacancy diffusion. For a high vacancy supersaturation, the corresponding total free energy is high. With a subsequent equilibration process, vacancies precipitate to form clusters or voids to reduce the free energy of the system. More details of model derivations are referred to Ref. [12].

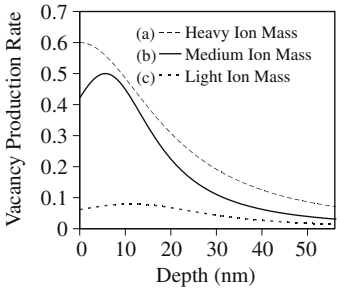

Fig. 1. Computer-simulated distributions of the vacancy production rate for various ion masses during ion irradiation according to TRIM code Monte-Carlo calculations.

Defining the length scale by $b = \sqrt{k/Nk_BT}$ and the time-scale by $\tau = k/M(k_BT)^2$, and normalizing the spatial coordinates by b and the time by τ, we obtain a dimensionless equation,

$$\frac{\partial \phi}{\partial t} = \xi_0^* - \xi_{rc}^*\phi(1-\phi) - \xi_{rd}^*\phi + \nabla^2\left(\frac{\partial g^*}{\partial \phi} - 2\nabla^2\phi\right). \quad (3)$$

Here t is the normalized time, ∇^2 is the normalized Laplace operator, $g^* = g/Nk_BT$, $\xi_0^* = \xi_0\tau$, $\xi_{rc}^* = \xi_{rc}\tau$, and $\xi_{rd}^* = \xi_{rd}\tau$.

3. Numerical calculation

We performed a series of 3D simulations with Eq. (3) to investigate the dynamic formation process for radiation-induced nanostructures in amorphous materials depending on the ion species and fluence. The initial vacancy concentration in the matrix was randomly distributed in the interval of [0, 0.1] to simulate the thermodynamic equilibrium concentration. According to Monte-Carlo calculations using the Transport of Ions in Matter (TRIM) code [17], the distribution profile of the vacancy production rate along the depth of an irradiated matrix is approximately Gaussian in shape. By increasing ion mass while all other parameters are held constant, the rate of vacancies produced increases and the depth of the peak vacancy concentration decreases. It should be noted that this profile of vacancy production rate is also a function of ion energy and substrate material with ion mass. These factors play important roles on the defect distribution profile. In this study, three TRIM simulated types of distribution profiles of the vacancy production rate (ξ_0^*) were considered, as shown in Fig. 1, to study the effect of ion species on irradiation-induced nanostructure formation. In Eq. (1), the gradient coefficient, k, depends on the lattice structure and the interatomic energy [18,19]. In this simulation, we take $k \sim 8\times10^{-19}$ J, $N \sim 2\times10^{19}$ m^{-2}, and $k_BT \sim 4.4\times10^{-21}$ J which corresponds to an irradiation temperature of 321 K [1]. Then, the length scale, b, can be calculated as ~ 3 nm. To elucidate the ion-irradiation effects we also used estimated values [10,12,14,15], e.g. $\Omega/k_BT = 3.75$, $\xi_{rc}^* = 0.14$, and $\xi_{rd}^* = 0.03$ to represent the ion-irradiation conditions corresponding to a certain temperature and material. A mesh size of $100\times100\times25$ with grid spacing of 0.75 and time step of 0.25 was used for the numerical calculation by a finite volume method [20]. The boundary condition is no flux at $x = 0$, $x = L_x$, $y = 0$, $y = L_y$, $z = 0$ and $z = L_z$, where L_x, L_y and L_z represent the size of the calculation units in the x, y and z directions, respectively.

4. Results and discussion

Fig. 2(a)–(f) shows the dynamic processes of formation and evolution of nanostructures with nanofibers calculated by Eq. (3) for heavy ion mass with a vacancy production rate based on the curve in Fig. 1(a). With heavy ion irradiation, a high vacancy production rate would be generated and defects would form close to the sur-