Physics of the Solid State, Vol. 45, No. 9, 2003, pp. 1679–1682. Translated from Fizika Tverdogo Tela, Vol. 45, No. 9, 2003, pp. 1600–1602.
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DEFECTS, DISLOCATIONS, AND PHYSICS OF STRENGTH

Kinetics of Point Defects and Amorphization in Thin Films under Irradiation

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Received February 11, 2003

Abstract—A theoretical model is proposed for describing the evolution of an ensemble of point defects (vacancies and interstitial atoms) and its effect on the solid-phase amorphization in crystalline thin films under irradiation. Kinetic equations are derived for point defects in irradiated thin films in the absence of ion implantation. The temperature dependence of the radiation dose required for the onset of solid-phase amorphization is calculated using numerical solutions of the kinetic equations. The results obtained are compared with available experimental data. *© 2003 MAIK “Nauka/Interperiodica”.*

1. INTRODUCTION

Structural and phase transformations in solids under irradiation have been a subject of intensive investigation. Special interest has been expressed by researchers in radiation-induced amorphization (the crystal–glass phase transition) in initially crystalline solids [1–11], because this effect is of great technological importance. The radiation-induced amorphization is a multiparameter process, which, in particular, depends on the radiation dose, the nature and energy of incident particles, and the microstructure and chemical composition of irradiated solids. In this respect, the elucidation of the behavior of point defects that usually play a crucial role in radiation-induced amorphization is of particular interest for revealing the basic regularities in the amorphization.

The main objective of the present work was to construct a theoretical model describing the kinetics of an ensemble of point defects (vacancies and interstitial atoms) and its effect on the solid-phase amorphization in thin films under irradiation. Within the proposed model, we calculated the temperature dependence of the “dose of the onset of amorphization” (the radiation dose required for the onset of solid-phase amorphization) in irradiated films. The results obtained were compared with available experimental data [1] on the irradiation of an Al_2O_3 single-crystal film by Kr and Xe ions.

2. KINETICS OF AN ENSEMBLE OF VACANCIES AND INTERSTITIAL ATOMS IN IRRADIATED CRYSTALLINE FILMS

Let us consider a thin film exposed to irradiation by high-energy ions. In most cases, high-energy ions penetrate through thin films, which results in only a small number of implanted (under irradiation) ions [1]. Consequently, in this situation, the processes of amorphization in irradiated thin films substantially depend on the evolution of point defects, namely, vacancies and interstitial atoms, which are formed intensively under irradiation. Therefore, as a first approximation, we can restrict our consideration to the case of the evolution of the scalar densities of vacancies (ϕ) and interstitial atoms (ψ) in irradiated crystalline thin films.

Now, we analyze the behavior of point defects in irradiated films in terms of the kinetic theory of defects (see, for example, [12, 13]). According to the proposed model, the kinetics of an ensemble of point defects can be described by the following equations:

$$d\phi/dt = A - B\phi - C\phi\psi, \quad (1)$$

$$d\psi/dt = F - G\psi - C\phi\psi, \quad (2)$$

where t is the irradiation time and A, B, C, F, and G are positive time-independent parameters. The first term on the right-hand side of the kinetic equation (1) characterizes the generation of point defects under irradiation. The parameter A is defined as the rate (or intensity) of generation of point defects and is measured in units of dpa/s (“inelastic displacements per atom per second”), and the parameter $F = \alpha A$, where the coefficient $\alpha = 0.7$ accounts for the decrease in the density of just knocked-on interstitial atoms due to their sputtering (knocking out of the film).

The second term on the right-hand side of kinetic equation (1) accounts for the decrease in the density ϕ of migrating vacancies due to their escape from the bulk to the free surface of the film. In this case, the model parameter B is determined to be $B \approx 1/\tau_v^*$, where τ_v^* is the mean lifetime of a vacancy in the model situation where migrating vacancies are eliminated exclu-

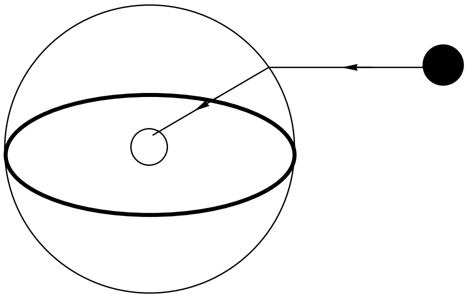

Fig. 1. A migrating interstitial atom (closed circle) and a vacancy (open circle) with the capture region (sphere of radius r).

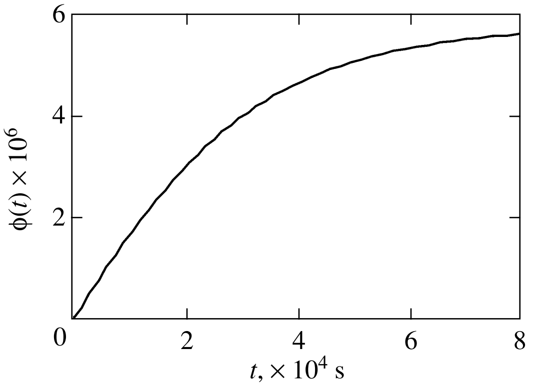

Fig. 2. Dependence $\phi(t)$.

sively through their escape from the bulk to the free surface. Similarly, the term $-G\psi$ in kinetic equation (2) characterizes the decrease in the density ψ of migrating interstitial atoms. In this equation, the model parameter G is estimated as $G \approx 1/\tau_i^*$, where τ_i^* is the mean lifetime of an interstitial atom. In the general case, we have the mean lifetime of the vacancy $\tau_v^* \approx l^*/\langle V_v \rangle$ and the mean lifetime of the interstitial atom $\tau_i^* \approx l^*/\langle V_i \rangle$, where l^* is the mean free path of the point defect and $\langle V_v \rangle$ and $\langle V_i \rangle$ are the mean velocities of migration of vacancies and interstitial atoms in the model situation, respectively. According to Vladimirov [14], the mean velocities of migration of point defects and the temperature T are related by the expressions

$$V_v = \tilde{V}\exp(-\varepsilon_{mv}/kT) \tag{3}$$

and

$$V_i = \tilde{V}\exp(-\varepsilon_{mi}/kT). \tag{4}$$

Here, $\tilde{V}$ is the velocity of migration of point defects at $T = 0$ K; ε_{mv} and ε_{mi} are the migration activation energies of the vacancy and the interstitial atom, respectively; and k is the Boltzmann constant. The mean free path l^* is assumed to be identical for the vacancies and interstitial atoms and, in the case of a single-crystal film is approximately equal to $3/2h$, where h is the film thickness.

The third term on the right-hand side of kinetic equations (1) and (2) describes the annihilation of the vacancies and interstitial atoms. In order to determine the dependence of the parameter C on the structural characteristics of the irradiated thin film, we consider a model situation in which point defects are eliminated exclusively due to their annihilation. Since the mean velocity of migration V_v of vacancies in this case is substantially less than the mean velocity of migration V_i of interstitial atoms (see, for example, [14]), it is assumed that the interstitial atoms are mobile point defects which collide with immobile vacancies when migrating over the crystal. Each collision leads to the annihilation of the vacancy and the interstitial atom. Within this approach, each vacancy is characterized by the so-called capture region, i.e., a spherical region of radius r (with the center at the vacancy position) where a migrating interstitial atom is attracted to the vacancy due to elastic interaction (Fig. 1), which is accompanied by their annihilation.

In the model situation under consideration, each annihilation event results in the elimination of a single vacancy and a single interstitial atom. Therefore, in each of the kinetic equations (1) and (2), the term characterizing the decrease in the density of point defects due to the annihilation can be represented as $-(\psi/\tau)$, where ψ is the density of interstitial atoms and τ is the mean lifetime of an interstitial atom. In turn, the mean lifetime of an interstitial atom is determined to be $\tau \approx l/V_i$, where l is the mean free path of the interstitial atom and V_i is the mean velocity of the interstitial atom. According to the concept of capture regions near the vacancies (Fig. 1), the mean free path of a migrating interstitial atom can be estimated as $l \approx 1/\pi r^2\phi$, where πr^2 is the capture area of a single vacancy and ϕ is the density of vacancies (and, consequently, capture regions) in the ensemble. On this basis, the model parameter C can be represented by the expression

$$C \approx \tilde{V}\pi r^2 \exp(-\varepsilon_{mi}/kT). \tag{5}$$

Let us return to the analysis of the kinetic equations (1) and (2). The solutions to these equations can be obtained only numerically. In this case, we use the initial conditions [15]:

$$\phi_0 \approx \rho\exp(-27T_m/T), \tag{6}$$

$$\psi_0 \approx \rho\exp(-9T_m/T), \tag{7}$$

where ρ is the density of atoms in the crystal and T_m is the melting temperature. Figure 2 depicts a typical curve $\phi(t)$, which was obtained from formulas (1)–(7) for the following parameters: $\varepsilon_{mi} \approx 4kT_m$, $\varepsilon_{mv} \approx 8kT_m$,

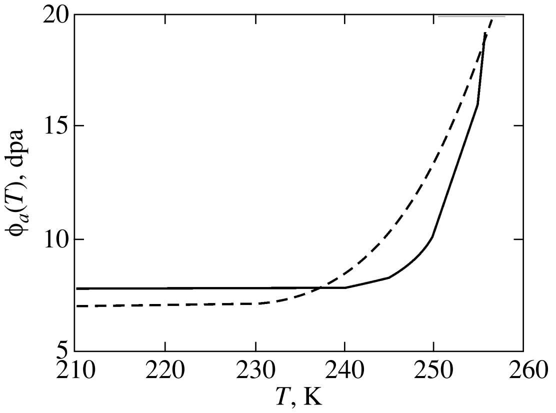

Fig. 3. Theoretical (solid line) and experimental (dashed line) temperature dependences of the dose of the onset of amorphization $\phi_a(T)$.

$r \approx 3a$ ($a = 3 \times 10^{-10}$ m), $\tilde{V} \approx n_k\omega_0 a \approx 3 \times 10^3$ ($n_k = 10$, $\omega_0 = 10^{12}$ s^{-1}) [14], $\rho = 1.17 \times 10^{29}$, $T \approx 0.2T_m$, $A = 0.0017$ dpa/s [1], and the film thickness (corresponding to the experiment performed in [1]) $h \approx 100$ nm.

3. TEMPERATURE DEPENDENCE OF THE DOSE OF THE ONSET OF AMORPHIZATION

Now, we elucidate the role played by point defects in radiation-induced amorphization. The accumulation of point defects in the irradiated crystal is accompanied by an increase in the density of the free energy (or another relevant thermodynamic potential) of the crystal phase. According to [9, 16–19], the nucleation of the amorphous phase (the crystal–glass phase transition) under irradiation and other actions takes place when the free energy density of the crystal phase with defects is comparable to the difference ε_{a-c} between the energy densities of the amorphous phase and defect-free crystal phase. In our case, the onset of the amorphization in the irradiated film with point defects is determined by the condition

$$\phi\varepsilon_v + \psi\varepsilon_i = \varepsilon_{a-c}. \qquad (8)$$

According to Friedel [20], we can write $\varepsilon_v = Ga^3/2$ and $\varepsilon_i = 3Ga^3$, where G is the shear modulus. In the case when the initial density of point defects is not very high, we obtain $\varepsilon_{a-c} \approx G/83 - G/63$ [21].

Within the proposed model, we calculated the temperature dependence of the dose required for the onset of the amorphization, i.e., the quantity frequently measured in experiments on radiation-induced amorphization (see, for example, [1]). In our interpretation, the dose required for the onset of the amorphization is determined as the density $\phi_a = At_a$ of vacancies nucleated in the crystalline film under irradiation during the period of irradiation $[0, t_a]$, where t_a is the instant of the onset of amorphization. Note that t_a can be approximately determined from condition (8) at $t = t_a$.

Figure 3 shows the temperature dependence of the dose of the onset of amorphization $\phi(T)$, which was numerically calculated according to formulas (1)–(8) for an Al_2O_3 single-crystal film irradiated with Kr and Xe ions at energies of 600 and 900 keV, respectively. In the experiment, the film thickness was equal to 100 nm, the ion flux was 10^{18} m^{-2} s^{-1}, and the irradiation temperature ranged from 90 to 300 K. The dependences $\phi(T)$ calculated in the framework of the theoretical model are in reasonable quantitative agreement with the experimental dependence $\phi_a(T)$ obtained in [1] for an Al_2O_3 film exposed to irradiation (Fig. 3).

4. CONCLUSIONS

Thus, we obtained a theoretical description of the influence of three basic processes (generation of point defects under irradiation, annihilation of point defects, and escape of point defects from the bulk to the free surface of the film) on the evolution of an ensemble of point defects, namely, vacancies and interstitial atoms, and on the solid-phase amorphization in irradiated thin films. The solution to kinetic equations (1) and (2), which account for the aforementioned processes, provides the basis for the calculation of the dose necessary for the onset of the amorphization (a quantity measured in the experiments). The temperature dependence of the dose of the onset of amorphization, which was calculated in the framework of the model proposed in this work, is in satisfactory quantitative agreement with the experimental data [1] obtained for Al_2O_3 films under irradiation.

ACKNOWLEDGMENTS

This work was supported in part by the Russian Foundation for Basic Research (project no. 01-02-16853) and by the Russian Federal Program "Integration" (project no. B0026).

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Translated by O. Moskalev