Peculiarities of the diffusion-controlled radiation defect accumulation kinetics under high fluencies

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Abstract

Theory is developed for kinetics of the diffusion-controlled radiation defect accumulation in crystalline solids under high fluencies taking into account recently observed correlation between the defect diffusion energy and pre-exponential (known as the Meyer-Neldel rule in chemical kinetics) and their dependence on the radiation fluence (Kotomin et al, J Phys Chem A **122** (2018) 28). The predicted accumulation kinetics could be applied to all kinds of solids. It considerably differs from the commonly used, in particular, suggesting that concentration growth at high fluencies could be nonmonotonous and the saturation defect concentrations independent on the temperature.

Keywords: radiation defects; accumulation kinetics; diffusion; fluence effects

1. Introduction

As is well studied now, an irradiation of all kinds of solids results in formation of pairs of Frenkel defects - interstitials and vacancies [1, 2, 3, 4]. These defects are mobile above certain temperatures and participate in secondary diffusion-controlled reactions, including complementary defect recombination and aggregation of similar defects leading in oxides and halides to metal colloid or gas bubble formation [5, 6, 7, 8]. Since radiation defects considerably affect mechanical and optical properties of materials. Thus prediction and interpretation of the kinetics of defect accumulation upon irradiation is important, especially for optical materials [9, 10, 11, 12, 13, 14, 15] (such as MgO, Al_2O_3, MgF_2) used as lenses and windows for nuclear applications.

The simplest model [16, 17] of the process consists of creation of the Frenkel defect pairs $A - B$ with the rate p, their diffusion with the diffusion coefficients D_A and D_B, which exponentially depends on the activation energy E_c: $D_c = D_c^0 \exp(-E_c/k_B T)$, $c = A, B$. Typically, interstitials are much more mobile than vacancies which are practically immobile in oxides below 1000K [7, 8, 18, 19].

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The main point of this generally accepted model is that the diffusion energy and pre-exponential remain constants independent on the radiation fluencies, which implies that material structure under irradiation remains mostly undistorted.

This model allows us also to include mutual attraction and aggregation of similar defects (e.g. for description of colloid formation [7, 8, 18, 19, 20, 21, 22], where role of defect complexes as sinks for interstitials was in detail discussed). The effective diffusion coefficients of defects bound in these aggregates is considerably decreased. However, defects evaporated from these dynamical aggregates migrate again with their energies E_c.

2. Abnormal kinetics

Our recent analysis of the kinetics of the F type center (anion vacancies) annealing upon heating due to recombination with mobile complementary interstitial ions in several radiation-resistant ionic solids (MgO, Al_2O_3, MgF_2) performed in terms of bimolecular reactions have shown unexpected result [19, 23, 24, 25]: the migration energy E_a of interstitial and the corresponding pre-exponential factor X are correlated and considerably depend on the fluence. The parameter $X = N_0 R D_0/\beta$, where N_0 is initial defect concentration, R - recombination radius for dissimilar defects [16, 17], D_0 - diffusion pre-exponent for interstitials, and β heating rate.

Let's start our research with a brief overview of the abnormal behavior of radiation defect annealing kinetics. The work cycle [19, 23, 24, 25] is based on the assumption that recombination of F centers with interstitials is a simple diffusion-controlled recombination of defects with equal initial concentrations. If we use dimensionless concentrations $C(t)$ of defects (they are equal to unity at low temperatures), the law of decreasing concentrations over time is simple:

$$C(t) = \frac{1}{1 + N_0 \int_0^t K(t) dt},\qquad(1)$$

where the diffusion-controlled reaction rate $K = 4\pi DR$ is proportional to the mutual diffusion coefficient D [26] and, thus, depends exponentially on the defect migration energy E_a, $D = D_0 \exp(-E_a/k_B T)$. Assuming that the temperature increase with the heating rate $\beta(t)$, one gets the following relation for the concentration decay

$$C_i = \frac{1}{1 + 4\pi(N_0 R D_0) \int_{T_0}^{T_i} \exp(-E_a/k_B T)\beta^{-1}(T) dT}.\qquad(2)$$

Here we go from a continuous description (kinetics) to a set of temperature values T_i used in a specific experiment and corresponding concentration values C_i. Usually, the temperature in experiments is a linear function of time, $\beta(t) = \beta = const$, and we get two control parameters: the migration energy E_a, and pre-exponential factor $X = N_0 R D_0/\beta$ mentioned before. Finally, we fitted these two key parameters, E_a and X to the available experimental kinetics by means of the least square method.
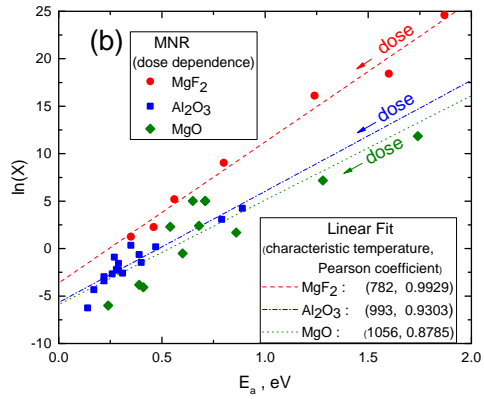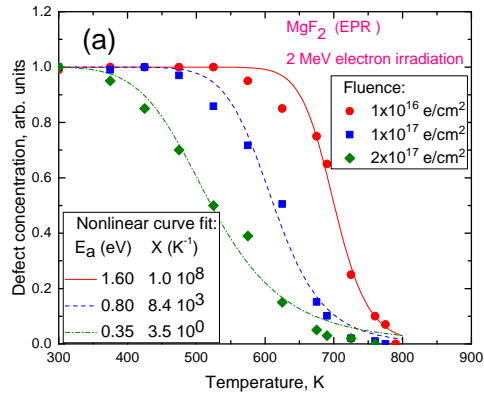
Figure 1: (a) Kinetics of the F^+ center annealing in electron irradiated MgF$_2$ [27] for dierent fluences. (b) Correlation of the effective energies and pre-exponents for MgF$_2$, sapphire, MgO [23].

Fig.1a shows fitting of theory to three F center annealing curves [27] from which we extract parameters E_a, X (see the legend in fig.1a) whereas fig.1b shows the result of the analysis for a wide range of experiments, not only for MgF_2 but also corundum and MgO [23]. As one can see, diffusion energies vary as the function of fluence by a factor of 4-5, whereas the pre-exponentials by 20 orders of magnitude! Typically, the diffusion energies at small fluencies are close to those theoretically predicted for perfect solid but then dramatically decrease with the fluence, very likely, due to migration in considerably radiation-distorted matrix.

The correlation $E_a - X$ (the level of this correlation is characterized by the standard Pearson correlation coeffcient very close to unity, see also the legend in fig.1b) is well described by the relation

$$\ln(X) = \ln(X_0) + \frac{E_a}{k_B T_0}. \tag{3}$$

This relation states that the pre-factor X depends on the activation energy, accordingly, which transforms into energy dependent pre-exponent $D_0 = D_0^* \exp(E_a/k_B T_0)$. That is the diffusion coefficient has more complicated as usual dependence on the migration energy [23]

$$D = D_0^* \exp\left(\frac{E_a}{k_B T_0} - \frac{E_a}{k_B T}\right). \tag{4}$$

This relation was observed for many disordered semiconductors and glasses. There T_0 is some characteristic temperature (a parameter particular to each material, often associated with the glass transition temperature [28]). The correlation, eq.(3), is known as Meyer-Neldel rule (MNR) [29, 30, 31]. The MNR, or compensation law, linearly relates the logarithm of the pre-exponential factors to the activation energy for any processes that are thermally driven in an Arrhenius manner. It was widely observed in many areas of materials science in physics, chemistry, biology and geology [30, 31], although the foundations of this *empirical* rule are still not fully understood (on the one hand, the theoretical explanation from statistical physics is lacking, but on the other side, the MNR can not relate directly to the microscopic details of the kinetic process [28]). The MNR was observed in many thermally activated phenomena such as solid-state diffusion. Surprisingly, in radiation physics, the correlation of kinetic parameters for diffusion has been established only recently [23]. This required studying the statistics of a large number of experimental observations (different authors, different materials, different sources of radiation).

As was shown [23], the fluence-dependence of the migration energy could be approximated in the simple way

$$E_a(\delta) = E_a(0) \exp(-\delta/\delta_0), \tag{5}$$

where $E_a(0)$ is the migration energy in defectless solid, δ_0 is characteristic parameter for material radiation-induced disordering. The parameter δ_0 has a simple meaning, it characterizes the radiation resistance of the material. At

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values $\delta \ll \delta_0$, the activation energy of the defect diffusion is not much different from that of a defect-free crystal. However at values $\delta > \delta_0$ the diffusion of defects in strongly disordered meterials is characterized by small activation barriers and in this sense is similar to the diffusion of atoms in a liquid [32, 33].

3. Theory and main results

We want to predict here, how the MNR affects the defect accumulation kinetics under prolonged irradiation. Let us introduce dimensionless parameters: displacements per atom (dpa) $\delta = pR^3t$ (the recombination radius R is of the order of the lattice constant), where p is defect concentration produced per unit volume and second (dose rate), t time. Characteristic dose rates in experiment vary from 10^{-7} dpa/s to 10^{-4} dpa/s. Assuming the irradiation time 24h (10^5 s), we estimate $\delta = 10^{-2} - 10^1$ dpa. Let us take the upper bound in our calculation, $\delta_{max} = 1$ dpa.

It is convenient to introduce the dimesionless parameter

$$\epsilon = E_a(0)/k_B T_0, \tag{6}$$

One can estimate from the data shown in the fig.1b and ref. [23] that $\epsilon = 30$ for MgF2, $\epsilon = 10$ in Al_2O_3 , and $\epsilon = 20$ in MgO. Let us fix $\epsilon = 20$ in further calculations. We employ the simple rate equation [16, 17] for defect concentrations $n(t)$ increase upon irradiation

$$\frac{dn}{dt} = p - Kn^2, \tag{7}$$

where $K = 4\pi DR$ is the Smoluchowski rate of diffusion controlled recombination [26] of vacancies and interstitials. The stead-state solution of eq.(7) in the high temperature limit $\tau = T/T_0 = 1$ reads

$$n_0^2 = \frac{p}{4\pi RD_0^*}. \tag{8}$$

The n_0 gives the *minimum* saturation concentration at any temperature $T < T_0$ but fixed parameters p and D_0^*. Let us introduce the dimensionless concentrations $\nu = nR^3$, $\nu_0 = n_0R^3$. Their meaning is average defect numbers in the unit cell volume. Now eq.(7) could be rewritten as

$$\frac{d\nu}{d\delta} = 1 - (\nu/\nu_0)^2 f(\tau, \delta), \tag{9}$$

where

$$f(\tau, \delta) = \exp(-\epsilon \frac{1 - \tau}{\tau} e^{-\delta/\delta_0}), \tag{10}$$

This equation could be numerically solved. Let us assume hereafter $n_0 = 10^{18}$ def/cm^3 and $\nu_0 = 10^{-3}$ (the choice is not fundamental and is related to the specification of calculations) and analyze how the accumulation kinetics depends
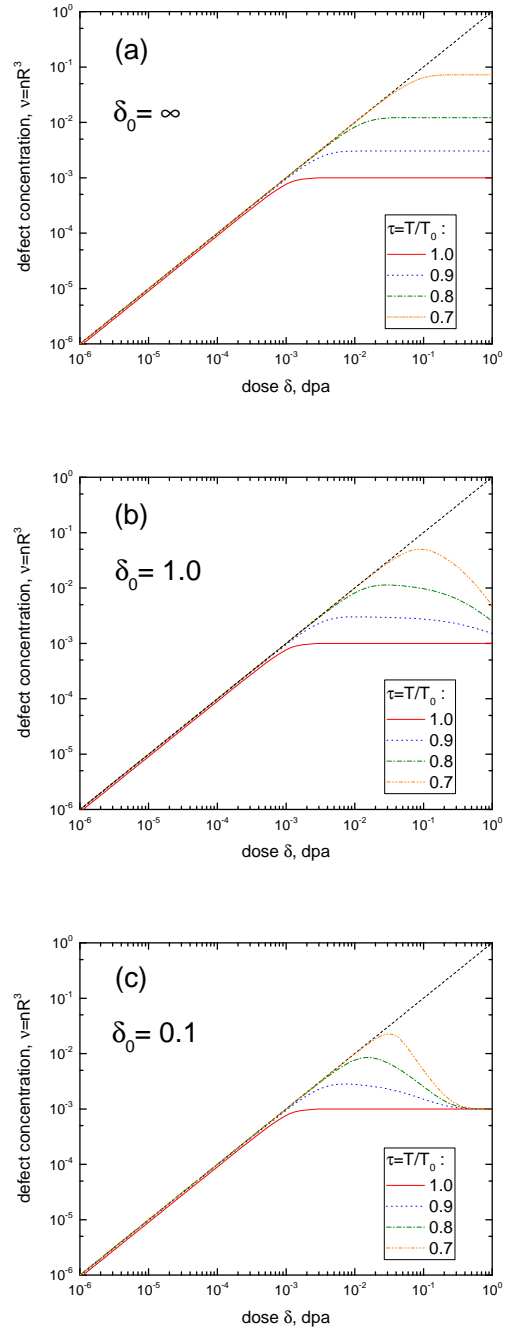
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Figure 2: The defect accumulation kinetics with migration energy depending on the fluence.

on the *two control parameters*: $\tau \leq 1$ (the relation eq.(3) is valid for $T < T_0$) and δ_0. In other words, we estimate the effect of the dose-dependence of migration energy in disordered solids.

Fig.2a shows the defect accumulation kinetics with constant migration energy (no MNR, formally $\delta_0 = \infty$). The saturation concentration is the lower, the higher temperature (and faster diffusion-controlled recombination). The minimum concentration corresponds to $\tau = 1$. Incorporation of the MNR in fig.2b shows new features: the kinetics becomes nonmonotonous with fluence and the saturation concentrations are close at all temperatures. In other words, fast defect migration in strongly disordered solids becomes similar to that in liquids [32, 33]. This effect is even better pronounced in fig.2b where the saturation concentration no longer depends on the temperature. We predict this effect to be observed, e.g. for prolonged high energy electron irradiation of MgF_2 [27]. Our calculations demonstrate the important effect of the MNR on the defect accumulation kinetics in strongly irradiated solids. Unfortunately, we did not find sufficient experimental data to apply our theory; the necessary experimental data (e.g. [12, 13, 15]) should show clear saturation and measured at different temperatures.

The accumulation of various color centers was most comprehensively studied in the alkali halides and some simple oxides. In particular, clear effects of temperature, crystal structure, impurities and the type of radiation [34, 35, 36, 37, 38, 39, 40, 41] were reported. Moreover, it has been more than once demonstrated that the saturation effects are most easily observed in case of ion irradiation.

4. Conclusions

Summing up, we demonstrated that dependence of the defect diffusion energy and pre-exponential on the radiation fluence is important for understanding and prediction of the defect accumulation kinetics and thus materials radiation stability stability at high fluencies. In particular, the saturation concentration could be independent on the temperature. We have shown here how defect annealing kinetics after irradiation with different fluencies could be used for prediction of the defect accumulation kinetics upon prolonged irradiation. Note that in order to predict qualitatively new effects, we used very simple model of the recombination kinetics, neglecting defect clustering and trapping. As was mentioned in Introduction, control of the defect concentrations is of a key importance for prediction of optical properties of materials in harsh radiation environment. Thus, our study could be useful for a wide class of optical materials, including nitrides, carbides and oxides, both crystals and ceramics (refs.[42, 43, 44, 45]).

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The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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