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Comparison of the *F*-type center thermal annealing in heavy-ion and neutron irradiated Al_2O_3 single crystals

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ABSTRACT

The optical absorption and thermally stimulated luminescence of Al_2O_3 (sapphire) single crystals irradiated with swift heavy ions (SHI) ^{238}U with energy 2.4 GeV is studied with the focus on the thermal annealing of the *F*-type centers in a wide temperature range of 400–1500 K. Its theoretical analysis allows us to obtain activation energies and pre-exponentials of the interstitial oxygen ion migration, which recombine with both types of immobile electron centers (*F* and F^+ centers). A comparison of these kinetics parameters with literature data for a neutron-irradiated sapphire shows their similarity and thus supports the use of SHI-irradiation for modeling the neutron irradiation.

1. Introduction

Insufficient resistance against prolonged irradiation is considered as a serious limitation for the use of different functional optical, dielectric and ceramic materials in future fusion reactors. In the framework of the research programs of the EUROfusion consortium, several binary and complex oxides (MgO, Al_2O_3, BeO, HfO_2/fused silica, etc.), nitrides (BN, AlN, Si_3N_4) as well as SiC, ZnSe, $MgAl_2O_4$ spinel, diamond and several other single crystals and transparent ceramics have been considered as attractive candidates for diagnostics/optical windows, insulating materials, fiber optics and mirrors in fusion devices [1–10].

It is generally accepted that the accumulation of radiation-induced structural defects strongly affects the functionality of various functional and especially optical components. In case of fission neutron irradiation, it is well known that elastic collisions of incident neutrons with atoms/ions of the crystal lattice result in the efficient formation of interstitial-vacancy pairs of Frenkel defects and, therefore, are the main reason of material radiation damage (see, e.g., [3,11–13] and references therein). Due to the limited availability of test reactors for neutron irradiation of materials and a high residual radioactivity, one can use swift heavy ion (SHI) irradiation to understand/simulate the effects of neutron irradiation in reactor components, and interest in this application of ion irradiation has intensified in recent years [14,15]. A critical review by Zinkle and Snead [14] on the applicability and limitations of ion beam irradiation provides useful guidance both for interpreting the already available experimental data as well as for the ideas of future experiments.

According to recent studies, several mechanisms are responsible for radiation damage under irradiation of the variety of functional materials by SHIs [16–27]. A SHI with the energy $E > 1$ MeV/u spends about 95% of its energy on ionization and excitation of an electron sublattice that is ionization losses. As a result, extremely high density of electronic excitations (EEs, LET > 20 keV/nm) is formed within a cylindrical ~GeV-ion track (see, e.g., [27]). Under such conditions, some additional nonimpact/impact mechanisms of radiation damage, such as hot electron-hole recombination or acoustic shock wave, should be considered as well [16,21,22,28].

There are many experimental and supporting theoretical studies on the radiation effects and defects induced by fast neutrons, SHIs and high-energy electrons in numerous oxides materials, like MgO, Al_2O_3, $MgAl_2O_4$ and more complex metal oxide single crystals and ceramics [1–9,12,16–34]. It has long been clear that, in general terms, the nature of point defects created by neutron, electron or ion radiation is the same, while their spatial-mutual distribution is quite different and depends on the fluence and type of incident radiation particles.

Recently, the appropriate comparative analysis of the diffusion-controlled kinetics of the *F* center annealing was performed on an example of an Al_2O_3 crystal for two different regimes. Firstly, neutron-

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irradiation-induced immobile *F* centers undergo annihilation with complementary defects – mobile interstitial oxygen ions, while in the second case, in thermochemically reduced (additively colored) crystals mobile *F* centers aggregate and cause the creation of metal colloids [35]. An appropriate comparison of the experimental and theoretical kinetics allowed to obtain the estimated values of the migration energies for *F* centers as well as for interstitial oxygen ions. The similar analysis for SHIs has not been performed yet.

In this paper we report the results on the optical absorption and thermally stimulated luminescence (TSL) of Al_2O_3 single crystals irradiated with SHIs. A special attention is paid to the thermal annealing of the *F*-type centers in a wide temperature range of 400–1500 K and a detailed comparison of the obtained kinetics parameters with the corresponding literature data.

2. Method

2.1. Experimental

The experiments have been performed with stoichiometric α-Al_2O_3 single crystals grown by the method of horizontal-oriented crystallization. The samples were irradiated at room temperature (RT) by SHIs at the UNILAC linear accelerator of the GSI Darmstadt. According to SRIM 2013 code [36], ion range of used ^{238}U ions with energy of 2.4 GeV [20] approximately equals 90 μm that is significantly smaller than the sample thickness. The irradiation fluence of 10^{12} ions/cm^2 corresponds to an average distance between ion tracks of about 11 nm, that means a relatively small overlapping of track halos – radial regions around ion pass where mainly simple point defects are formed ([27] and references therein).

The spectra of the radiation-induced optical absorption (density, RIOD) were measured in the spectral region of 6.5–1.5 eV using a high-absorbance spectrometer JASCO V-660 with a double monochromator and low level of scattered light (limit of optical density linearity up to OD = 3.5). Note that the difference between two absorption spectra measured at RT before and after irradiation, i.e. for the virgin and the same sample after irradiation, is considered as RIOD.

The annealing of radiation damage was performed in a stepwise regime: ion-irradiated samples were heated up from RT to a certain temperature T_i in an extra dry air atmosphere inside a quartz reactor of a furnace. The sample was kept for about 5 min at this T_i and then cooled down by moving the reactor out of the furnace. Several "heating-cooling-measuring" cycles were executed for the irradiated samples, while all optical absorption spectra were measured at RT. Spectrally integrated (1.7–3.7 eV) TSL was measured at the heating of the irradiated samples (300–750 K) with a constant rate of $\beta = 2.86\ \mathrm{K\,s^{-1}}$ in the atmosphere of flowing nitrogen, using a System 310 TLD reader. As is well known [37], the *F*-type centers are immobile in sapphire below 1500 K and thus their recombination observed in the temperature range of 400–1500 K results from the interaction with highly mobile complementary defects – interstitial oxygen ions. A similar situation was earlier observed and was analyzed in detail in MgO single crystals [38–41].

2.2. Theoretical

Our model of radiation defect annealing kinetics includes the following steps: (i) primary Frenkel defects (vacancies and interstitials) are produced by radiation in equal concentrations; (ii) mobile defects (interstitials) migrate with the diffusion coefficients determined by the migration energies E_a and pre-exponentials D_0; (iii) the *F*-type center annealing at intermediate temperatures is caused by the recombination of *immobile* electron centers with mobile interstitials; (iv) the dissimilar defects recombine upon mutual approach within a critical distance *R* via a bimolecular reaction; (v) the post-irradiation annealing occurs at the linear increase of the temperature.

The relevant phenomenological theory describing the diffusion-controlled kinetics of the Frenkel defect annealing in ionic solids was recently developed [35,42–45].

Changes of the *F*-type center and interstitial (hole, *H*) concentrations are described by the bimolecular reaction

$$\frac{dn_F(t)}{dt} = \frac{dn_H(t)}{dt} = -Kn_F(t)n_H(t),$$

where $n_F(t)$ and $n_H(t)$ are defect concentrations; $n_F(t)=n_H(t) = n(t)$. It is convenient to introduce the dimensionless defect concentration $C(t) = n(t)/n(0)$, $C(0) = 1$. The *F* centers are immobile at temperatures 400–1200 K, whereas oxygen interstitials migrate with the diffusion coefficients $D = D_0\exp(-E_a/k_BT)$. There E_a is the activation energy.

The reaction rate could be well approximated as $K = 4\pi DR$ [46], where R is recombination radius, typically of the $R{\sim}a_0$ (lattice unit).

The defect concentration decay reads

$$d\left(\frac{1}{C(t)}\right) = Kn_0dt,$$

where $n_0 = n(0)$. For the linear temperature increase with the rate $\beta = \frac{d}{dt}T(t) = const$, the solution of equation is [44,45]

$$1/C(T) = 1 + 4\pi X\int_{T_0}^{T}\exp\left(-\frac{E_a}{k_BT}\right)dT$$

where $X = n_0RD_0/\beta$ is a simple combination of basic parameters (initial defect concentration n_0, recombination radius R, diffusion pre-exponent D_0, heating rate β) and $T_0 = T(0)$. We used the last solution for the least square fitting to the experimental kinetics.

As a result, the analysis of experimental annealing kinetics for the *F* centers in neutron irradiated sapphire allowed us to extract two control parameters: the migration energy of the interstitial oxygen ions E_a and pre-factor *X*. In this paper, we applied this model to the sapphire after SHI irradiation and compare results of these studies.

3. Main results

3.1. Thermal annealing of ion-induced structural damage

Fig. 1 shows the absorption spectrum (actually, RIOD spectrum) measured for an α-Al_2O_3 single crystal irradiated with 2.4-GeV SHIs (RT, 10^{12} U/cm^2) as well as a set of spectra measured after additional preheating of the irradiated sample to depicted temperatures. All

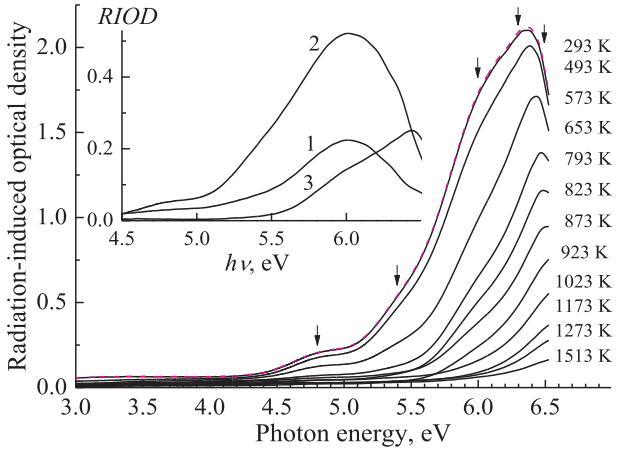

Fig. 1. The absorption (actually, RIOD) spectra of an α-Al_2O_3 single crystal measured after irradiation with 2.4-GeV SHIs (RT, 10^{12} U/cm^2) and after additional preheating of the irradiated sample to depicted temperatures. Insert depicts difference spectra representing the decreases of RIOD due to the preheating of the irradiated sample from 493 to 573 K (curve 1), 573 → 653 K (curve 2) and 823 → 873 K (curve 3). All spectra are measured at RT.