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Journal of Nuclear Materials 307–311 (2002) 1246–1249

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Oxygen interstitial trapping in electron irradiated sapphire

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Abstract

An existing model for first stage anion vacancy stabilization in irradiated alkali halides has been applied to sapphire. To monitor the F centre concentration growth during irradiation, radioluminescence instead of optical absorption measurements has been employed. The results indicate that the model is valid for sapphire and suggest that the F centre stabilization process depends on oxygen interstitial trapping. This implies that the resistance to radiation damage at low doses should depend on the impurity and dislocation content of the material. One presumes the model may be extended to other oxides.

1. Introduction

Refractory oxides including Al_2O_3, MgO and BeO are being considered as candidate insulators for use in different applications for future fusion devices. However, even in the case of Al_2O_3, the prime candidate insulating material, studies of basic radiation damage processes are scarce. In contrast the mechanisms are well studied and documented for the alkali halides. A now classical method for studying the formation of defects by radiation in the alkali halides is to obtain the so-called F colouring curve. This curve shows the variation of the F centre (anion vacancy) concentration with irradiation time or dose, and temperature. A generally accepted model for the first colouring stage for alkali halides assumes that the coloration is due to the production of Frenkel pairs, an F centre and interstitial halogen atom, and subsequent stabilization of interstitials in distinct traps [1,2]. The model thus equates the observed increase of the F centre concentration with the increase of trapped interstitials, and the actual growth rate of the observed F centres is determined by the rate at which interstitials are trapped and thermally released from different types of trapping centres such as impurities and dislocations. The difference in the cross-sections and activation energies of the traps gives rise to a component structure in the growth of the anion vacancy concentration. There is no obvious reason why this model cannot be extended to oxides. In the work to be presented the validity of the model for Al_2O_3 has been studied. To monitor the F centre (oxygen vacancy in this case) concentration growth, radioluminescence (RL) measurements have been made in the beam line of a 2 MeV Van de Graaff accelerator during electron irradiation at 50, 100, 150 and 200 °C. The results indicate that the model is also valid for Al_2O_3 and that the F centre stabilization process is governed by interstitial trapping, with the oxygen vacancy growth exhibiting a clear component structure. This implies that the resistance to radiation damage at low doses should depend on the impurity and dislocation content of the material.

The model [1,2] describes the growth of the F centre concentration n_F, by

$$n_F = \sum_{i=1}^{m} A_i (1 - e^{-a_i t}), \tag{1}$$

where

$$a_i = \sigma_i \phi + 1/\tau_i \tag{2}$$

and

$$A_i = (\sigma_i \phi N_{oi})/(\sigma_i \phi + 1/\tau_i). \tag{3}$$

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PII: S0022-3115(02)00977-7

N_{0i} is the concentration of trap type i, σ_i is the cross-section for capture of interstitials by these traps, τ_i the lifetime of the interstitial in trap i, and ϕ is the flux of interstitials during irradiation.

There is no obvious reason why this model cannot be extended to oxides. In the work reported here the validity of the model for Al_2O_3 has been studied. In this case, to monitor the F centre concentration growth, high sensitivity RL measurements rather than optical absorption have been made.

2. Experimental procedure

The experiments have been performed in a chamber mounted in the beam line of a 2 MeV Van de Graaff accelerator in which samples have been irradiated in high vacuum ($\approx 3 \times 10^{-6}$ mbar) with 1.8 MeV electrons. The samples, $\approx 1 \times 4 \times 4$ mm^3 in size, were mounted in a sandwich-like oven and irradiated through one of the 1×4 mm^2 faces. Two 3×1 mm^2 windows in the oven enable in situ optical absorption and RL measurements to be made perpendicular to the irradiation direction at a distance of 1–2 mm behind the irradiated face. The water or liquid nitrogen cooled oven permits irradiation at any temperature between about −200 and +900 °C maintained to within 1 °C, and linear heating if required.

Four high purity sapphire samples (Union Carbide UV grade, about 200 ppm total impurity content including optically active Cr and Ga trace impurities) have been irradiated at 50, 100, 150 and 200 °C with a beam current of 2 μA cm^{-2} (1400 Gy/s, 2×10^{-10} dpa/s on the oxygen sublattice) for up to 4 h. During irradiation RL spectra in the range between 200 and 450 nm were taken to monitor the F centre concentration growth [3].

3. Results

Fig. 1 shows the RL spectra for the sample irradiated at 100 °C at different irradiation times. One observes four bands present from the onset of irradiation. The two bands near 250 nm are associated with Ga^{3+} [4], the band at 330 nm (3.8 eV) is due to F^+ centres (an oxygen vacancy with one trapped electron) and that at 415 nm (3.0 eV) to F centres (an oxygen vacancy with two trapped electrons) [5]. With irradiation time the F and F^+ bands grow, whereas the bands associated with Ga^{3+} decrease.

Figs. 2–5 show the increase of the F centre RL band with irradiation time for each irradiation temperature. Expression (1) was fitted to the experimental data using the method of least squares. The results of the fittings are also shown in the figures, and the numerical values obtained for a_i and A_i are given in Table 1. In the case of irradiations at 50, 100, and 150 °C it was necessary to

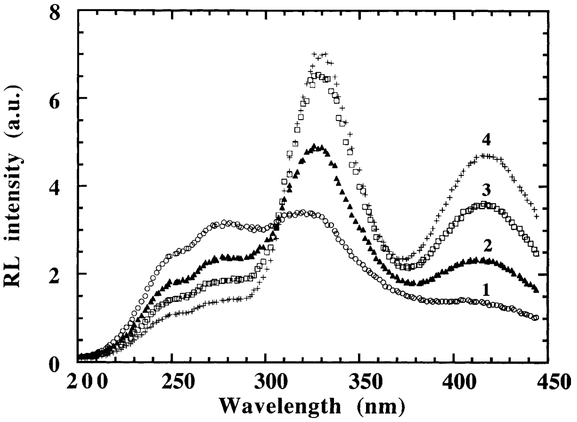

Fig. 1. RL spectra for sapphire irradiated at 100 °C, 2 μA cm^{-2} after 1 (circles 1), 30 (triangles 2), 120 (squares 3) and 240 (crosses 4) min of irradiation.

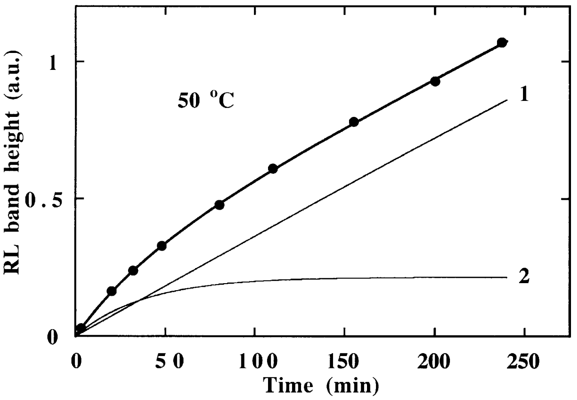

Fig. 2. F centre RL band height (dots) with irradiation time at 50 °C, together with the result of the two component fitting (lines).

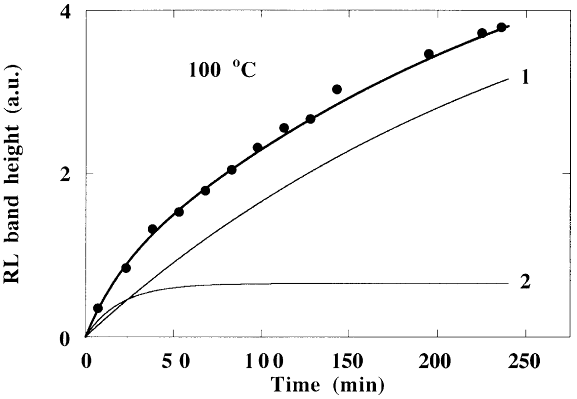

Fig. 3. F centre RL band height (dots) with irradiation time at 100 °C, together with the result of the two component fitting (lines).

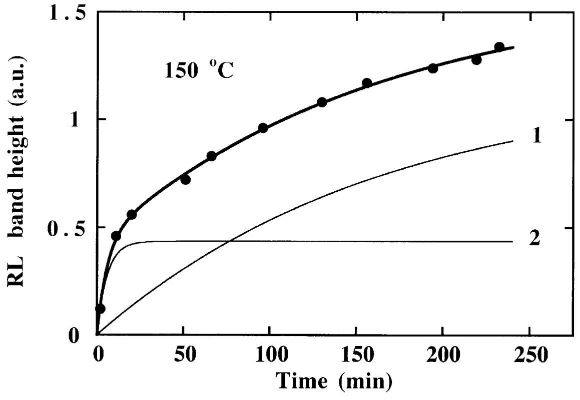

Fig. 4. F centre RL band height (dots) with irradiation time at 150 °C, together with the result of the two component fitting (lines).

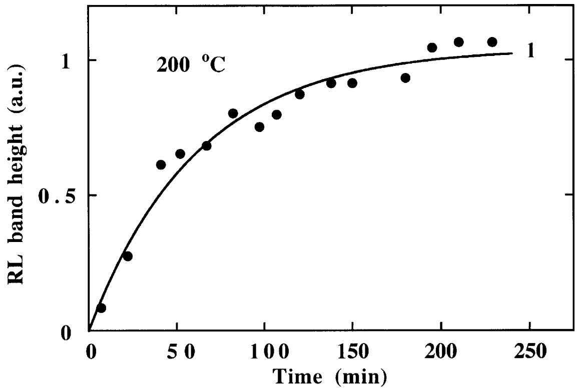

Fig. 5. F centre RL band height (dots) with irradiation time at 200 °C, together with the result of the single component fitting (lines).

Table 1
Values obtained from fits shown in Figs. 2–5

T (°C)	A_1 (a.u.)	a_1 (10^{-4} s^{-1})	A_2 (a.u.)	a_2 (10^{-4}s^{-1})
50	13 ± 62	0.05 ± 0.16	0.21 ± 0.01	4.3 ± 1.3
100	6 ± 2	0.66 ± 0.40	0.6 ± 0.5	8.3 ± 6.5
150	1.17 ± 0.07	1.0 ± 0.1	0.43 ± 0.03	28 ± 5
200	1.04 ± 0.06	2.6 ± 0.3		

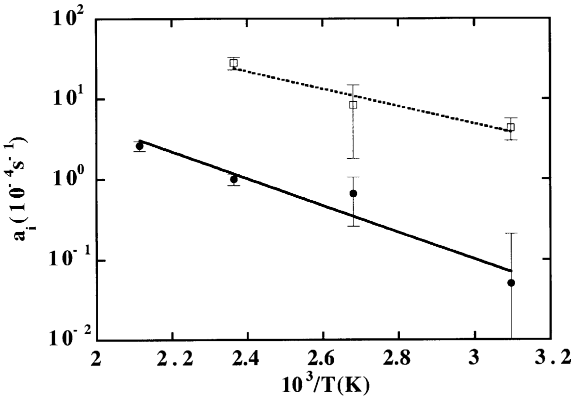

Fig. 6. Arrhenius plot for a_1 (circles) and a_2 (squares) obtained from fits in Figs. 2–5. The numerical values from these fits are given in Table 2.

Table 2
Values obtained from fits shown in Fig. 6

E_1 (eV)	$1/K_1$ (s^{-1})	E_2 (eV)	$1/K_2$ (s^{-1})
0.32 ± 0.04	0.7 ± 0.4	0.18 ± 0.05	0.4 ± 0.3

use two components, as may be seen in Figs. 2–4, but at 200 °C only one component is necessary, Fig. 5.

The expected temperature dependence of τ_i is [1,2]

$$\tau_i = K_i \exp(E_i/kT), \tag{4}$$

where E_i is the activation energy for detrapping the interstitial from trap type i. If we assume that $1/\tau_i \gg \sigma_i \phi$ (as the strong temperature dependence of a_i suggests) then from (2) we obtain

$$a_i \approx 1/\tau_i. \tag{5}$$

Hence for each component, $1/a_i$ should show an exponential variation with temperature with the same values of E_i and K_i.

In Fig. 6 an Arrhenius plot is given for a_1 and a_2. Both components are fitted by exponential functions in agreement with expressions (4) and (5). The values of E_i and K_i obtained from the fits for both components are shown in Table 2. The numerical values of both activation energies (0.32 and 0.18 eV) for the oxygen interstitial traps are very similar to the values obtained for the Cl traps in NaCl and consistent with thermally activated detrapping at moderate temperatures [2].

4. Discussion and conclusions

The results indicate that the growth of the oxygen vacancy concentration in sapphire shows a very similar behaviour to the growth of the concentration of anion vacancies in the alkali halides. This strongly suggests that an equivalent oxygen trapping mechanism is taking place, although the displacement processes are different for alkali halides and sapphire, radiolysis and elastic collisions, respectively [6,7]. Oxygen vacancies produced in MgO and Al_2O_3 by additive coloration, thermochemical or vacuum reduction are highly stable, and only anneal out at elevated temperatures (>1000 °C) due to the high activation energy for anion vacancy mobility [8,9]. However, in the case of radiation induced oxygen vacancies in MgO and Al_2O_3, some annealing is observed even below 200 °C [8,10]. This is consistent with interstitial trapping, and subsequent thermal release of oxygen interstitials from different trapping centres. Some evidence exists for the existence of oxygen interstitials in MgO [11,12] however not for Al_2O_3, due to the lack of associated optical absorption for such defect centres and the difficulty of interpreting magnetic resonance data for this more complex oxide. The results reported here strongly suggest that interstitial trapping does occur, and the observation of a small component (component 2) only for temperatures below 200 °C is in agreement with the thermal annealing data reported for neutron irradiated sapphire where F centre annealing is observed above about 150 °C [10]. The nature of the defects inducing the observed two types of trapping centres is unknown; however it is interesting to note that while the F centres increase the number of Ga^{3+} impurity centres decreases on a similar time scale, see Fig. 1. This might suggest that the Ga^{3+} is acting as an interstitial trap for, for example, O^- giving a (Ga^{2+}–O^0) complex. More work is required to clarify the nature of the traps, however the number and type of traps for interstitials will depend on the origin of the sample hence the F centre and corresponding interstitial concentration growths will be very different for different materials. This early stage of radiation damage stabilization is of paramount importance for the damage evolution and should be fully understood.

Acknowledgements

The authors are indebted to Mr Ernesto Sánchez-Cabezudo for his help in these experiments. The work forms part of the European Fusion Technology Programme.

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