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On the origin of the F^+ centre radioluminescence in sapphire

A. Moroño, E.R. Hodgson *

Euratom / CIEMAT Fusion Association, Avenida Complutense 22, 28040 Madrid, Spain

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Abstract

Electron irradiation of sapphire produces primarily F centres, in marked contrast with neutron and ion irradiations where both F and F^+ centres are produced. However, radioluminescence studies during electron irradiation indicate bands associated with both F and F^+ centres. These emission bands show a complex dependence on dose rate and temperature. A systematic study of the radioluminescence spectra as a function of these two parameters together with optical absorption measurements indicate that the ionization of F centres is the cause of the F^+ centre radioluminescence. A model describing the way the F^+ emission occurs is proposed and compared with the results obtained. © 1997 Elsevier Science B.V.

1. Introduction

For many years α-Al_2O_3 has been considered a material of technological interest for diverse applications such as dielectric substrates for SOS structures, solid state lasers, UV windows, radiation dosimeters and, more recently, fusion energy devices. As a consequence of this interest numerous papers have been published concerning the defects in α-Al_2O_3. In these studies undoubtedly the point defects which have received most attention are the so-called F and F^+ centres (oxygen vacancies with two and one trapped electron, respectively).

Oxygen vacancies in α-Al_2O_3 result from either thermochemical reduction during vacuum heat treatment [1] or from lattice displacement events during particle irradiation [2–9]. Optical absorption measurements have shown that when sapphire (single crystal α-Al_2O_3) is irradiated with neutrons, protons, or other ions, both F and F^+ centres are produced [2–8]. However, when sapphire is irradiated with electrons essentially only F centres are produced, as evidenced by the single absorption band at 6.03 eV [2,3,9]. In apparent contradiction with the optical absorption results, radioluminescence measurements for electron irradiated sapphire show luminescence bands at 3.0 and 3.8 eV corresponding to both F and F^+ centres [9–11]. In view of the fact that radioluminescence measurements are now being employed as a tool to study oxygen vacancy production in sapphire it is essential that these differences be understood [10–16].

The aim of this paper is to clarify the origin of the F^+ centre radioluminescence in electron irradiated sapphire and to reconcile the above apparent contradiction. To achieve this objective a systematic study of the F and F^+ radioluminescence bands as a function of dose rate and temperature has been made. A model describing how the F^+ radioluminescence occurs is proposed and then used to explain the results obtained.

2. Experimental procedure

The work reported here has been performed in a chamber mounted in the beam line of a 2 MeV Van de Graaff accelerator, in which a Union Carbide UV grade sapphire sample has been irradiated with 1.8 MeV electrons. The sample, approximately $5 \times 5 \times 1$ mm^3 in size, was placed sandwich-like between the faces of a double oven and irradiated edge-on through a 3×1 mm^2 collimator on to one of the 5×1 mm^2 faces. Two 3×1 mm^2 windows cut in the oven enable in situ measurements of optical absorption and radioluminescence to be made perpendicular to the irradiation direction at a distance of 1 to 2 mm behind the irradiated face. The sample may be heated from 15 to 650°C and maintained at any temperature to within 1°C.

* Corresponding author.

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The sample was initially irradiated at 50°C, 3 μA cm^{-2} for 14 h to produce oxygen vacancies. During irradiation, radioluminescence spectra were taken to monitor the increase in the oxygen vacancy concentration. After 14 h the change with irradiation time in the radioluminescence spectra was slow enough to enable a study to be carried out as a function of dose rate (beam current) and irradiation temperature. In this study radioluminescence spectra at beam currents of between 0.025 and 10 μA cm^{-2} for temperatures between 50 and 200°C were taken. Each recorded spectrum took approximately 3 min and the total integrated dose was observed to have no measurable effect on the reference spectrum recorded following the initial 14 h of irradiation, as evidenced by a further reference spectrum taken at the end of the experiment. In addition, optical absorption spectra were recorded before and after irradiation.

3. Results

Fig. 1 shows radioluminescence spectra for the initial part of the experiment at 50°C, 3 μA cm^{-2} for different irradiation times in which one observes the growth of bands at about 410 (3.0 eV) and 329 nm (3.8 eV) corresponding to F and F^+ centres, respectively [17], together with a decrease in the Ga^{3+} emission at 250 nm [18]. Following 14 h of irradiation very little further change was observed for these bands. In Figs. 2 and 3 radioluminescence spectra at 50°C for 0.25 and 10 μA cm^{-2} following the initial 14 h irradiation are given. One observes that the relative amounts of F and F^+ emission depend on the beam current (dose rate). This dependence is more clearly seen in Fig. 4 where radioluminescence spectra for three different dose rates are presented, normalised to unit dose rate. We observed that the normalised F^+ emission increases and the normalised F emission decreases on increasing the dose rate. Exactly the reverse behaviour was

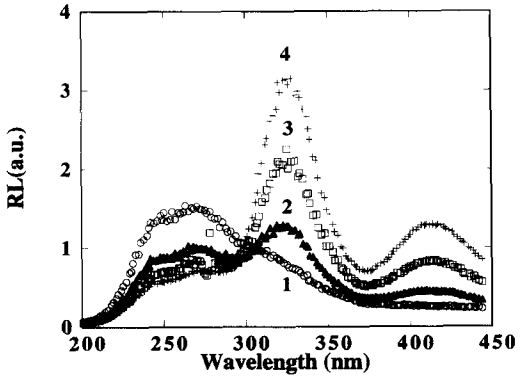

Fig. 1. Radioluminescence spectra for sapphire irradiated at 50°C, 3 μA cm^{-2} after irradiation for; 1 min (1), 30 min (2), 110 min (3) and 240 min (4).

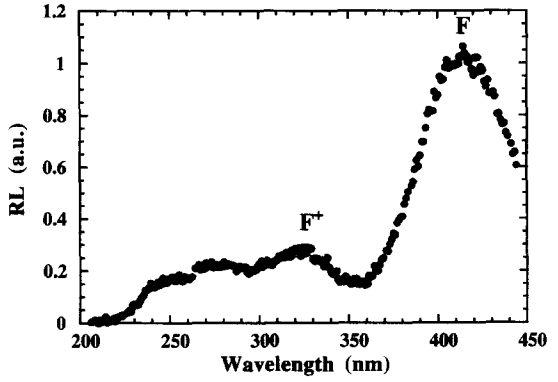

Fig. 2. Radioluminescence spectrum taken at 50°C and 0.25 μA cm^{-2} following 14 h of irradiation at 50°C, 3 μA cm^{-2}. The F radioluminescence band is much larger than the F^+ band.

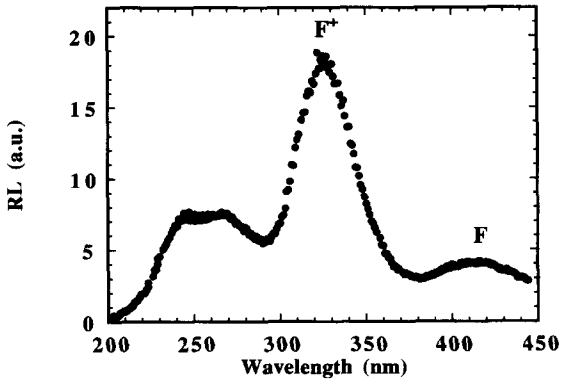

Fig. 3. Radioluminescence spectrum taken at 50°C and 10 μA cm^{-2} following 14 h of irradiation at 50°C, 3 μA cm^{-2}. The F radioluminescence band is much smaller than the F^+ band.

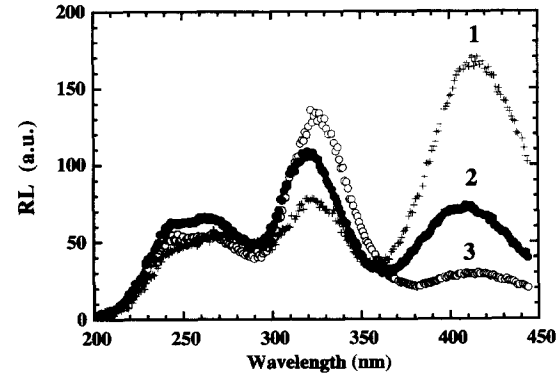

Fig. 4. Radioluminescence spectra normalized to dose rate (intensity divided by beam current), taken at 50°C for 0.5 (1), 2.5 (2) and 10 μA cm^{-2} (3) after 14 h irradiation at 50°C and 3 μA cm^{-2}.

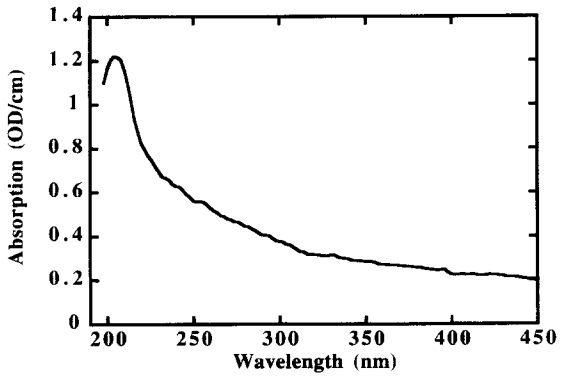

Fig. 5. Optical absorption spectrum for sapphire after 14 h irradiation at 50°C and 3 μA cm^{-2}. Only the F centre band at about 205 nm is visible.

observed on decreasing the dose rate. Very similar results were obtained for irradiations at 100, 150 and 200°C. These results clearly indicate that the F emission intensity depends sub-linearly on dose rate while the F^+ intensity has a superlinear dependence.

The optical absorption spectrum taken at the end of the experiment can be seen in Fig. 5. A band at 206 nm due to F centres is clearly observed [2] corresponding to a density of approximately 10^{16} centres/cm^3. But there is no indication above the background of optical absorption bands at about 229 or 256 nm associated with F^+ centres [2,4].

4. Discussion

The optical absorption measurements (Fig. 5) show that essentially only F centres are produced when sapphire is irradiated with electrons, in agreement with previous results [2,3,10]. However, as may be seen in Figs. 1–4, both F and F^+ radioluminescence bands are observed during irradiation. It is clear from Figs. 2–4 that these two emission bands show a complex dependence on dose rate, with the intensity of the F^+ emission increasing super-linearly with dose rate while the F centre emission increases sub-linearly with dose rate. This behaviour, together with the reversibility on decreasing dose rate and the absence of F^+ centres in the optical absorption, suggests that the origin of the F^+ centre radioluminescence is related to the ionization of F centres. One is at first tempted to envisage the F^+ radioluminescence as a simple three-step process in which; firstly one F centre is ionised becoming an F^+ centre, then this F^+ centre is excited and, finally, it de-excites emitting a 3.8 eV photon. However such a process is questionable as it requires two consecutive energy depositions at the oxygen vacancy to occur on a time scale less than the time between vacancy ionization and localization at the defect of an electron from the conduction band, which is known to be $< 10^{-12}$ s [19].

The above problem may be overcome if we take into account the mechanism for energy absorption by the lattice and the way F^+ to F centre conversion occurs. In insulating materials radiation is mainly absorbed by the excitation of electrons from the valence band into the conduction band producing electrons and holes [20]. These either recombine or migrate through the lattice where they interact with defects. The interaction of a hole with an F centre produces an F^+ centre. This F^+ centre rapidly ($< 10^{-12}$ s) traps an electron from the conduction band to form an F^* centre (excited F centre). The F^* centre will then de-excite emitting a 3.0 eV photon (F centre radioluminescence).

However the F^* centre has a lifetime of the order of tens of milliseconds related to the strongly forbidden triplet to singlet transition [9,17]. This long lifetime will increase the probability that a further hole may recombine at the F^* centre before the centre de-excites. Such an interaction between a hole and the ground state electron leaves an excited F^+ centre (F^{+*}). In this case the transition to the ground state is allowed and de-excitation occurs rapidly with a lifetime of less than 8 ns, emitting a 3.82 eV photon (F^+ centre radioluminescence) [5]. We can now use this model to obtain a relationship between the intensities of the radioluminescence bands associated with F and F^+ centres.

The processes involved are

(1) $F + h/e \rightarrow F^*$: Excitation of the F centre by electron and hole capture;

(2) $F^* \rightarrow F + h\nu_F$: De-excitation of the F^* giving F luminescence;

(3) $F^* + h \rightarrow F^{+*}$: Ionization of the F^* by hole capture giving F^{+*};

(4) $F^{+*} \rightarrow F^+ + h\nu_{F^+}$: De-excitation of the F^{+*} giving F^+ luminescence;

(5) $F^+ + e \rightarrow F^*$: Reconversion of F^+ to F^* by electron capture.

Fig. 6 gives a sequential flow diagram for these processes. We can see that the F^+ radioluminescence RL_{F^+} (steps 3 and 4) comes from the ionization of the F^* and is directly proportional to the number of F^{+*} and as all the F^{+*} de-excite to give F^+ we can write

$$RL_{F^+} = AN_{F^+}, \tag{1}$$

where A is a constant and N_{F^+} is the F^+ concentration.

In contrast, the F radioluminescence RL_F (step 2) which comes from the de-excitation of the F^* is not directly proportional to the number of F^* because these can either de-excite (step 2) or convert to F^{+*} (step 3). In this case RL_F is proportional to the number of F^* and inversely proportional to the probability of F^* to F^{+*} conversion, which is proportional to the hole production rate, i.e., the dose rate Φ. Hence we have

$$RL_F = BN_{F^*} 1/\Phi, \tag{2}$$

where B is a constant and N_{F^*} is the F^* concentration.

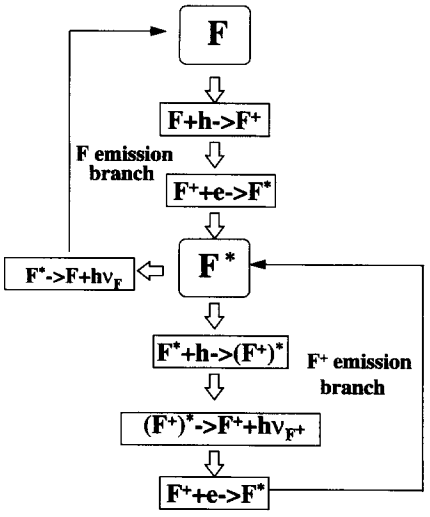

Fig. 6. Flow diagram for the F and F^+ luminescence processes.

Once steady state conditions are reached, which also requires that the oxygen vacancy concentration is constant or varies only very slowly with time, the numbers of F, F^*, F^+, and F^{+*} centres are constant. Under these conditions the number of F^* centres converted to F^{+*} centres per unit time (step 3) has to be equal to the number of F^{+*} centres reconverting via F^+ to F^* centres (steps 4 and 5). The former is proportional to the F^* centre concentration (N_{F^*}) and ionizing dose rate Φ, while the latter is proportional to the F^+ centre concentration (N_{F^+}) and the concentration of the unpaired electrons promoted to the conduction band during the conversion of F to F^+, which is also equal to N_{F^+}. Thus the steady state rate equation

$$N_{F^*}\cdot\Phi = C(N_{F^+})^2, \qquad (3)$$

where C is a constant.

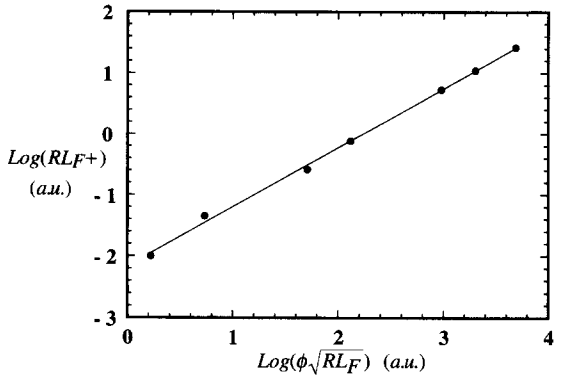

Fig. 7. Log–log plot of the height of the F^+ radioluminescence band versus the product of the dose rate (beam current) and the square root of the height of the F radioluminescence band at 50°C, for beam currents from 0.025 to 10 μA cm^{-2}. The straight line fit is of slope 1.

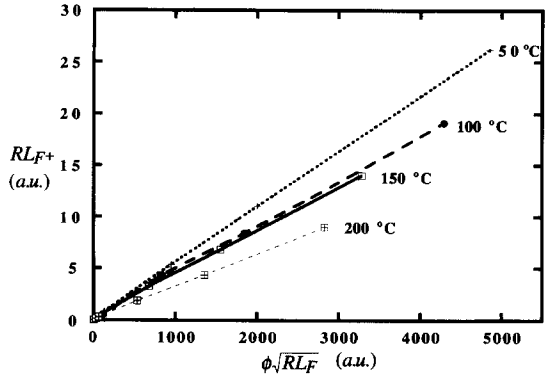

Fig. 8. Plot of the height of the F^+ radioluminescence band versus the product of the dose rate and the square root of the height of the F radioluminescence band at 50, 100, 150 and 200°C, for beam currents from 0.025 to 10 μA cm^{-2}.

If we now substitute for N_{F^*} and N_{F^+} from Eqs. (1) and (2) we obtain

$$RL_{F^+} = D\Phi\sqrt{RL_F} \text{ where } D = A/l(BC), \text{ a constant.} \qquad (4)$$

Hence we see from Eq. (4) that if the above model is essentially correct, a plot of the height of the F^+ radioluminescence band versus the product of the dose rate and the square root of the height of the F radioluminescence band should be a straight line. As may be seen in Figs. 7 and 8 this prediction is fulfilled over a wide dose rate range, and for various temperatures. The effect of the temperature on the slope (Fig. 8) may be due to a differential decrease in the F and F^+ band heights on increasing temperature [10], or a possible decrease in the F^* lifetime with increasing temperature [21].

It is therefore clear that the F^+ radioluminescence observed during the electron irradiation of sapphire is not a measure of stable F^+ centres, but is a consequence of the long lifetime of the F^* centre and its ionization to give F^+ centres. Furthermore, it is important to notice that the experimentally observed F radioluminescence intensity also cannot be used as an indication of the F centre concentration.

5. Conclusions

The results presented here show that F and F^+ radioluminescence depend in a complex way on the ionizing dose rate. The observation of F^+ luminescence does not indicate the presence of stable F^+ centres, and the F luminescence cannot be used as a direct indication of the F centre concentration. A model describing the way F and F^+ centre radioluminescence occurs has been developed. This model predicts a complex dependence with dose rate of the F and F^+ centre radioluminescence, which has been experimentally observed.

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