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On the mechanism for dose rate dependence of stationary luminescence of F and F^+ centres excited by electron beam in α-Al_2O_3

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Abstract

We have examined the kinetic model proposed by Moroño and Hodgson for the dose rate dependence of stationary luminescence of colour centres under electron beam excitation. A set of kinetic balance equations based on their model is formulated and analytic solution is derived in terms of stationary concentrations of electrons and holes under irradiation. The solution shows that the ratio of F^+ to F luminescence intensities is proportional to the stationary concentration of holes. For high electron beam currents, the effect of saturation of the F centre emission is predicted. Possible mechanisms related to dose rate dependent quenching of the F centre are presented. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Aluminium oxide α-Al_2O_3 or sapphire is known as a radiation resistant material, which is able to be used under various radiation environments. Particularly, it can be used as an insulating material and as an optical transmission window in fusion energy devices [1,2]. The radiation-induced damage in sapphire can be monitored by means of optical absorption and luminescence measurements. The well known defects, so called F and F^+ centres produced by irradiation, have clearly resolved absorption bands in the aluminium oxide band gap and their excited states decay radiatively [3]. A. Moroño and E.R. Hodgson (referred as M&H hereafter) have made a systematic study of radioluminescence during electron irradiation and indicated complex changes of emission intensities of bands associated with both F and F^+ centres on dose rate, total dose, and temperature [2,4]. The luminescence can be affected by the history of irradiation and sample imperfection. M&H considered the case of stationary irradiation with 1.8 MeV electrons. Details of experimental setup and used materials are given in [2,4] and references therein. The total radiation dose was not enough to allow a segregation of radiation defects and impurities as evidenced by optical absorption before and after irradiation. Under these conditions, the quasi-equilibrium is established among the charged states of radiation defects and impurities. The stationary luminescence of F and F^+ centres is in marked contrast to impurity related luminescence (Sc^{3+}, Ga^{3+}, Cr^{3+} and other impurities), which increases linearly with the dose rate [2,5]. The observed dose rate dependence also does not correlate with exciton luminescence at low temperatures [5]. Moreover, the optical absorption measurements showed the existence of stable F centres only, while the F^+ related absorption bands were not resolved. To explain the observed dose rate

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dependence of stationary luminescence, a kinetic model was suggested by M&H [4]. According to Moroño and Hodgson model (M&H model), F and F^+ centres are excited through direct recombination of electrons and holes on these centres. Mechanisms related to transfer of excitation from impurities or excitons were neglected. They declared that their model is consistent with the experiment, though the solution and analyses of the model were not performed until now.

In this paper we have obtained an analytic solution for the M&H model [4] in terms of stationary concentrations of electrons and holes under irradiation. Comparison with the experiment evidenced that the dose rate dependent quenching of F centre should be taken into account in order to construct a more reliable model.

2. Kinetic model for radioluminescence

Under electron irradiation, the production rate of new colour centres via ion displacements is many orders of magnitude smaller than the generation rate of carriers (electrons and holes). Thus, the problem can be treated as quasistationary. Total colour centre concentration depends on the dose, but not on the dose rate.

Within the M&H model [4], an external irradiation produces electron-hole pairs at a rate Φ, proportional to the corresponding electron beam current. The charge carriers are rapidly relaxed towards thermal equilibrium and finally trapped or recombined. Colour centres act as radiative recombination centres. An F^* centre (excited state of F centre) is formed as a result of capture of one electron–hole pair: $F + h \to F^+$, $F^+ + e \to F^*$. One way of the F^* centre deexcitation is the emission of a photon with radiative decay probability $1/\tau_1$. On the other hand, it can be converted into an F^{+^*} (excited state of F^+ centre) by hole capture: $F^* + h \to F^{+^*}$. The F^{+^*} centre decays through the emission of a photon with rate $1/\tau_2$.

A set of kinetic balance equations corresponding to the above-considered excitation mechanisms is formulated in the following way:

$$\frac{dF}{dt} = -k_1 hF + \frac{1}{\tau_1}F^*, \tag{1}$$

$$\frac{dF^+}{dt} = -qeF^+ + k_1 hF + \frac{1}{\tau_2}F^{+^*}, \tag{2}$$

$$\frac{dF^*}{dt} = -\frac{1}{\tau_1}F^* - k_2 hF^* + qeF^+, \tag{3}$$

$$\frac{dF^{+^*}}{dt} = -\frac{1}{\tau_2}F^{+^*} + k_2 hF^*, \tag{4}$$

where F, F^+, F^*, and F^{+^*} denote the concentrations of colour centres in ground and excited states, respectively. e and h are the concentrations of thermal electrons in the conduction band and holes in the valence band. k_1, k_2, q are the corresponding chemical reaction rates for electron-hole recombination on the colour centres. The carriers evolution is determined by their capture and recombination on different kinds of defects related to impurities or formed as a result of radiation damage. For the case of stationary luminescence (the time derivatives are set to zero), Eqs. (1)–(4) can be considered as linear functions with respect to the concentration of colour centres. The solution can be easily obtained. We found

$$F = \frac{F_0}{R}, \quad F^+ = \frac{k_1 h}{qe}(1 + k_2 h\tau_1)\frac{F_0}{R}, \quad F^* = k_1 h\tau_1 \frac{F_0}{R},$$

$$F^{+^*} = k_2 h\tau_2 k_1 h\tau_1 \frac{F_0}{R},$$

$$R = 1 + k_1 h\tau_1 + k_2 h\tau_2 k_1 h\tau_1 + \frac{k_1 h}{qe}(1 + k_2 h\tau_1). \tag{5}$$

Here F_0 denotes the total colour centre concentration. The luminescence intensities I_F and I_{F^+} are related to the F^* and F^{+^*} concentrations, respectively:

$$I_F = \frac{1}{\tau_1}F^*, \quad I_{F^+} = \frac{1}{\tau_2}F^{+^*}. \tag{6}$$

From the Eq. (5), the ratio of I_{F^+} to I_F is given by a simple formula

$$\frac{I_{F^+}}{I_F} = k_2 h\tau_1. \tag{7}$$

Assuming linear dependence of the hole concentration on dose rate, this ratio must be proportional to the electron beam current. Fig. 1 illustrates the comparison with the experiment [2,4]. A qualitative agreement is achieved. The existing discrepancy may be caused by the deviation from linear relationship between the hole concentration and the dose rate. It is known that the radiation-induced conductivity σ is related to the dose rate according to $\sigma \propto \Phi^\delta$, $\delta < 1$ [6]. Applying similar relation $h \propto \Phi^{0.95}$, the agreement between the model and

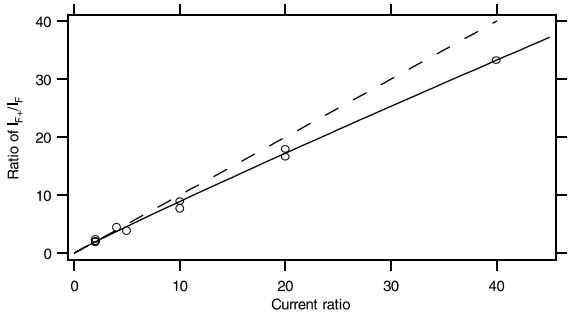

Fig. 1. The dependence of emission intensity ratio I_{F^+}/I_F on beam current ratio. The result of kinetic model with $h \propto \Phi$ is shown by the dashed curve, and with $h \propto \Phi^{0.95}$ by solid curve, respectively. Experimental points were taken from [2,4].

experiment becomes rather good. We note that hole dynamics cannot be observed from conductivity experiments because the contribution of holes to the conductivity is small compared to that of electrons [6].

Instead of examination of the results of the suggested model, the authors of [4] proposed an empirical formula that relates F^+ and F luminescence intensities:

$$I_{F^+} \propto \Phi\sqrt{I_F}. \tag{8}$$

Using the raw peak position data on the F^+ and F luminescence bands, qualitative agreement between this formula and experiment was found. One can see that Eq. (8) disagrees with the result of the kinetic model. For the comparison among Eq. (7), Eq. (8) and the experiment, we performed a refined analysis of the emission spectra in [2,4]. The broad component peaked at 250 nm (possibly related to Ga^{3+} and other defects) was subtracted implying that its shape stays unchanged under irradiation. We used its shape from luminescence data on small dose rate limit. The remaining two-band shaped graph was fitted with two gaussians having the same width for all beam currents. To allow comparison, we changed to dimensionless variables. The dimensionless dose rate ϕ and dimensionless luminescence intensities i_{F^+} and i_F were introduced by dividing the corresponding dimensional data on data for 0.5 $\mu A/cm^2$ current (1750 Gy dose rate). Fig. 2 shows a comparison with the experiment for the ratios $i_{F^+}/i_F h$ and $i_{F^+}/\phi\sqrt{i_F}$. The closer the ratio to 1, the better is the agreement with the experiment. One can see that the result of the kinetic model is in better agreement with the experiment than the empirical formula (8).

The optical absorption measurement showed the presence of F centre band only. Bands associated with F^+ centre were not observed. This fact can be explained within the kinetic model. Under quasistationary conditions, the F centre lifetime $\tau_F = 1/k_1 h$ substantially exceeds the F^+ centre lifetime $\tau_F = 1/qe$ (due to Coulomb attraction the reaction rate between charged particles is larger). Produced by ionising radiation the F^+ centre rapidly converts into F centre by electron capture. Taking it into account together with the small radiative lifetime of F^{+*} centre $\tau_2 \leqslant 7$ ns [3], the formulas for the stationary luminescence were simplified:

$$I_F \approx \frac{k_1 h F_0}{1 + k_1 h \tau_1}, \quad I_{F^+} \approx k_2 h \tau_1 I_F. \tag{9}$$

Formula (9) shows that the F centre luminescence increases approximately linearly with the dose rate at small beam currents and reaches saturation at large currents. The predicted saturation level $I_{FS} \approx \frac{F_0}{\tau_1}$ corresponds to conversion practically of all colour centres into F^* centre. In order to make a comparison with the experiment, luminescence intensities in absolute unit photons/cm^3s were calculated from those of [2] implying isotropic angular distribution of emitted photons and Gaussian-type band shape. The data on I_F are in qualitative agreement with saturation hypothesis as evidenced by Fig. 3. Using 10 $\mu A/cm^2$ data as a saturation level for F centre luminescence intensity, we found that it is approximately 7 times smaller than I_{FS}. The radiative lifetime τ_1 was taken to be 36 ms [3,7], and $F_0 \approx 1 \times 10^{16}$ cm^{-3}. This discrepancy is the main drawback of the M&H kinetic model. The effect of nonradiative losses within the system of F and F^+ centres was not taken into account.

The effect of F^* centre quenching at high excitation density is well established in heavy ion induced luminescence [8,9], but its nature is not understood at present. The non-radiative losses can be related to imperfect yield of excited states in recombination reactions. Trapping of electron by F^+ centre can results in formation of F centre both in excited (probability η_1) and ground state (probability $1 - \eta_1$). Hole recombination on F^* centre can produce F^+ centre in excited (probability η_2) and ground (probability $1 - \eta_2$) states. Parameters $\eta_1, \eta_2 \leqslant 1$ were not determined from an independent experiment.

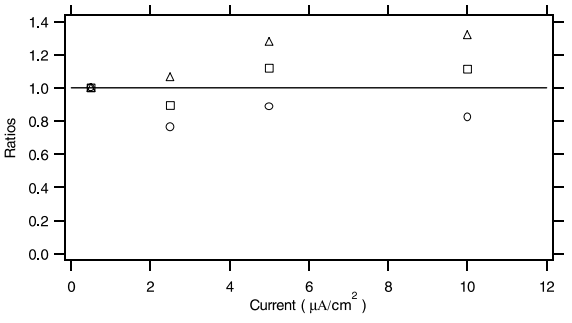

Fig. 2. The dependence on relative dose rate of the luminescence ratios. Data are plotted by triangles for $i_{F^+}/\phi\sqrt{i_F}$, by circles for $i_{F^+}/i_F\phi$, and by boxes for $i_{F^+}/i_F\phi^{0.95}$.

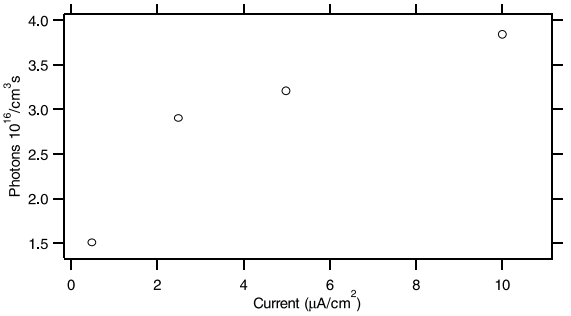

Fig. 3. The dependence of F centre luminescence intensity on beam current. Data in absolute unit were calculated from those of [2,4] assuming isotropic angular distribution and Gaussian band shape.

To account for the imperfect yield of excited states within the kinetic model, we modified the kinetic balance Eqs. (1)–(4). The procedure is simple and straightforward, so we report only the final result. The modified luminescence intensities are given by the formulas:

$$I_F \approx \frac{\eta_1 k_1 h F_0}{1+\eta_1 k_1 h\tau_1 + (1-\eta_1)k_2 h\tau_1}, \quad I_{F^+} \approx \eta_2 k_2 h\tau_1 I_F. \quad (10)$$

The saturation of F centre emission is reached at a lower level

$$I_{FS} \approx \frac{F_0}{\tau_1}\frac{\eta_1 k_1}{\eta_1 k_1 + (1-\eta_1)k_2}$$

compared to that of Eq. (9) and tends to improve an agreement between the model and the experiment. However, direct comparison was impossible because of parameters k_1, k_2 and η_1 are not known.

The other explanation for the dose rate dependent deexcitation of F^* centre can be related to superelastic collisions with thermal electrons $e + F^* \rightarrow F + e'$ (e' denotes the scattered electron). The effect of superelastic collision of slow electrons with excited atoms was observed in gaseous discharge [10], and was intensively studied by slow electron scattering on optically pumped atoms [11]. According to radiation induced conductivity model, the stationary electron concentration is not high (of order of 10^{-10} cm^3 at beam current of a few $\mu A/cm^2$) [6]. However, due to long radiative lifetime of F^* centre, the collisional de-excitation rate can be comparable with radiative deexcitation rate, if the cross section is of the order of 10^{-16} cm^2. This cross section value is not unrealistic, because in gases it is as large as 10^{-14} cm^2 [11–13].

We also investigated the alternative mechanisms for the F^+ centre excitation published in the literature. Direct hole recombination on F centre can result in formation of F^{+*} centre $F + h \rightarrow F^{+*}$, as suggested in thermally stimulated luminescence studies [14]. Electron capture by oxygen vacancy F^{2+} (pre-existed or formed due to F^+ centre ionisation) leads to formation of F^{+*} centre [8,9]. The account of these two excitation mechanisms into kinetic model leads to a constant (independent on dose rate) ratio of F^+ to F luminescence intensities at small electron beam currents, which strongly contradicts the experiment [2,4]. Thus, their contribution to F^+ centre excitation must be negligibly small.

3. Conclusions

According the M&H model for the dose rate dependence of stationary luminescence of colour centres under electron beam excitation, a set of kinetic balance equations based on their model is formulated and analytic solution is derived in terms of stationary concentrations of electrons and holes under irradiation.

We have found that the M&H model is consistent with the dose rate dependence of the emission intensities ratio I_{F^+}/I_F in electron irradiated α-Al_2O_3 and the model predicts a saturation of F centre emission at high electron beam currents. Nevertheless, the saturation level substantially exceeds the experimental one. In other words, the dose rate dependent quenching of F centre should be taken into account in order to construct a more reliable model. Possible explanations for the dose rate dependent quenching of F^* centre are the imperfect yield of excited states in chemical recombination reactions or collisional deexcitation of F^* centre by thermal electrons. The stationary luminescence originates from ionisation of F centres and can provide valuable information on hole dynamics under irradiation, which cannot be observed in conductivity measurements.

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