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Radiation-induced electrical and optical processes in materials based on Al_2O_3

O.A. Plasksin *, V.A. Stepanov, P.A. Stepanov, V.M. Chernov

SSC RF – Institute of Physics and Power Engineering, Obninsk 249020, Russian Federation

Abstract

Concentration inhomogeneities in the trap system have been shown to be responsible for radiation-induced electric charging of regions in the bulk of dielectrics under irradiation. Formation of electrically charged regions is caused by difference in hopping mobility of charge carriers over traps and does not violate general electric neutrality of the system. Formation of negatively charged regions during irradiation results in intensity increase for F-centres band (415 nm) in radiation-induced luminescence (RIL) spectra of single crystal Al_2O_3. In ceramic $Al_2O_3:Cr^{3+}$, the radiation-induced negative charging of grain boundaries with respect to grain bulk takes place which is revealed in the intensity increase of Cr^{3+} ion RIL band (690 nm), in spite of a constant intensity of this band in single crystal $Al_2O_3:Cr^{3+}$ under similar conditions. The idea of the radiation-induced electric charging due to concentration inhomogeneities in the trap system allows one, using the RIL method, estimating local charge density in grains of ceramic $Al_2O_3:Cr^{3+}$ and associated electric field. Under 8 MeV proton irradiation (dose rate up to 5×10^3 Gy/s), excessive positive charge in grains of ceramic $Al_2O_3:Cr^{3+}$ exceeds 10^4 Q/m^3, and associated electric field exceeds 10^6 V/m. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

Ability for application of dielectric materials in optical and electrical systems of radiation facilities depends on the occurrence of radiation-induced luminescence (RIL), optical absorption and electric charging. Radiation-induced optical phenomena are intensively studied; however, electric charge partitioning and accumulation in dielectrics under irradiation are not given enough attention. Nevertheless, these very processes, being the cause of radiation-induced electric break-down of dielectrics, induced EMF in metal–dielectric systems and other phenomena, often restrict ability for utilizing dielectrics in the diagnostic systems.

Charge states of impurities and self-defects in dielectrics influence optical activity of the defects, which is responsible for a strong relationship between electric charging during irradiation and radiation-induced optical properties. In this situation, a necessity of finding the mechanisms involving this relationship arises.

In this study, the attention is paid to a possibility of diagnostics of electric charging in dielectrics under irradiation by means of monitoring the radiation-induced optical phenomena.

2. Radiation-induced electrical processes in dielectrics

In dielectrics, the major part of the energy of ionizing irradiation is spent in production of free charge carriers, which recombine with each other and are captured by traps. In the uniform approximation the kinetics of these processes is described by the following equations:

$$\dot{c}_e = g_e \dot{D} - c_e c_h w_{eh} + v_e - c_e \eta_e, \quad (1)$$

$$\dot{c}_h = g_e \dot{D} - c_e c_h w_{eh} + v_h - c_h \eta_h, \quad (2)$$

where

$$\eta_e = \sum_j (N_{ej} - n_{ej}) w^t_{ej}, \quad \eta_h = \sum_j (N_{hj} - n_{hj}) w^t_{hj},$$
$$v_e = \sum_j n_{ej} w^a_{ej}, \quad v_h = \sum_j n_{hj} w^a_{hj},$$

* Corresponding author. Tel.: +7-08439 96870; fax: +7-095 230 23 26; e-mail: chernovv@icfrm.obninsk.su.

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c_e and c_h are electron and hole concentrations, n_e and n_h are concentrations of filled electron and hole traps (localized charge carriers), N_e and N_h are total trap concentrations (empty and filled), w^a_{ej} and w^a_{hj} are probabilities of thermally activated release of electrons and holes from traps, w^t_{ej} and w^t_{hj} are trapping coefficients of electrons and holes (typical values of w^t_{ej} and w^t_{hj} are about 10^{-14} m^3/s at room temperature), and w_{eh} is a coefficient of electron–hole recombination ($w_{eh} \sim 10^{-16}$ m^3/s [1,2]). Production of free electrons and holes, electron–hole recombination, free charge carrier trapping and thermally activated release of charge carriers from traps are considered in Eqs. (1) and (2). The production rate is proportional to the dose rate $\dot{D}$ with the proportionality coefficient

$$g_e \leqslant \frac{\rho}{E_g}, \tag{3}$$

where E_g is a band gap and ρ is a density of a material.

The results on radiation-induced conductivity measurements reported in Ref. [2] indicate that, for a dose rate exceeding 10 Gy/s, magnitudes of v_e and v_h at the room temperature are much smaller than the production rate $g_e\dot{D}$. According to Eqs. (1) and (2), in the steady state, the electron–hole recombination rate is lower than the rate of trapping as soon as the following condition is satisfied:

$$\dot{D} \leqslant \frac{2\eta_e\,\eta_h}{g_e\,w_{eh}}. \tag{4}$$

In materials with low trap content of 10^{23} m^{-3} (for single crystals of high purity) the condition in Eq. (4) is satisfied for a dose rate lower than 10^{12} Gy/s at the room temperature.

At the dose rate lower than 10^{12} Gy/s, the charge carrier trapping predominates the electron–hole recombination, and the free charge carrier concentrations reach steady-state values with the characteristic times $(\eta_e)^{-1}$ and $(\eta_h)^{-1}$ not exceeding 10^{-9} s for the trap concentrations exceeding 10^{23} m^{-3}. This statement is in agreement with the data on dielectric radiation-induced conductivity [3,4], according to which steady-state free charge carrier concentrations are reached in 10^{-9}–10^{-12} s. Characteristic times of reaching steady-state concentration for filled traps ($c_e w^t_e$ and $c_h w^t_h$) are much greater than those for free carriers. For example, at the dose rate of 10^3 Gy/s, these elapsed times are about 10^{-3} s.

Estimations performed show that for elapsed time exceeding 10^{-1} s, the electric charge density in the bulk of dielectrics under irradiation with the dose rate varying from 10 to 10^{12} Gy/s can be evaluated over difference of trapped electron and hole concentrations without taking into account free carriers. Let us show that the concentration inhomogeneities in the trap system can be the cause of charged region formation in the bulk of dielectrics under irradiation (besides accumulation of primary charged particles and secondary emission of charged particles from the surface under irradiation). Changes in trap concentrations in this case are described by the following equations:

$$\dot{n}_e = D_e\nabla^2 n_e + \nabla(\mu_e n_e \vec{E}\,), \tag{5}$$

$$\dot{n}_h = D_h\nabla^2 n_h - \nabla(\mu_h n_h \vec{E}\,), \tag{6}$$

where D_e and D_h are diffusion coefficients for filled traps, μ_e and μ_h are hopping mobility of electrons and holes over traps, and $\vec{E}$ is electric field.

The following equation is derived for local charge density $Q(x)$ in the single-dimensional case

$$\frac{\dot{Q}(x)}{e} = D_h\frac{\partial^2 n_h}{\partial x^2} - \frac{\partial(\mu_h n_h \vec{E}\,)}{\partial x} - D_e\frac{\partial^2 n_e}{\partial x^2} - \frac{\partial(\mu_e n_e \vec{E}\,)}{\partial x}, \tag{7}$$

where e is an elementary charge and x is a coordinate.

For inhomogeneous trap distribution over the volume $N_{e,h} = N_{e,h}(x)$ an expression for filled trap concentrations in the steady state is written as:

$$n_e(x) = \alpha N_e(x) - \frac{Q(x)}{2e},$$

$$n_h(x) = \beta N_h(x) + \frac{Q(x)}{2e} \tag{8}$$

$$\left(\frac{Q(x)}{2e} \ll N_{e,h}(x)\right),$$

where coefficients α and β are derived from the solution for the uniform distribution and depend on trapping coefficients. Substitution of Eq. (8) into Eq. (7) gives the equation for the steady state

$$\frac{1}{2}\frac{dQ}{dx}(D_e + D_h) - e\left(\alpha D_e\frac{dN_e}{dx} - \beta D_h\frac{dN_h}{dx}\right) = (\mu_h N_h + \mu_e N_e)\frac{e}{\varepsilon\varepsilon_0}\int_{x_0}^{x} Q\,dx. \tag{9}$$

The solution of Eq. (9) is the following:

$$Q(x) = \frac{2e\sqrt{2\pi}}{a(D_h + D_e)}\int_{-\infty}^{\infty}\left(\beta D_h\frac{d^2N_h(x-u)}{dx^2} - \alpha D_e\frac{d^2N_e(x-u)}{dx^2}\right)e^{-|au|}\,du, \tag{10}$$

where

$$a = \sqrt{\frac{2e(\mu_h\bar{N}_h + \mu_e\bar{N}_e)}{\varepsilon\varepsilon_0(D_e + D_h)}}, \tag{11}$$

$\bar{N}_e$ and $\bar{N}_h$ are mean trap concentrations.

Hence, the local charge density is determined by the second order derivative of the total trap concentration over coordinate. The sign and magnitude of the local charge depend on the ratio of trap concentration and

hopping mobility. According to this mechanism, the radiation-induced electric charging in dielectrics results in changing their optical properties at the elapsed time exceeding 10^{-1} s.

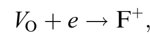
3. Origin of luminescence centres in Al_2O_3

To interpret the RIL spectra, it is necessary to refine the mechanism of alteration of charge states of luminescence-active centres and relationship of these states with electric charging. It is conventional that F^+ and F-centres are single positively charged and neutral oxygen vacancies in Al_2O_3 responsible for absorption bands at 205 nm (6.05 eV), 227 nm (5.4 eV) and 256 nm (4.8 eV) and also photoluminescence or RIL at 413 nm (3.0 eV) and 328 nm (3.78 eV) [5–7]. These centres can arise both under ionizing irradiation and as a result of special thermochemical treatment. However, high intensity of F^+-centre RIL at low doses of irradiation in different conditions indicates high initial oxygen vacancy concentration [8]. It is unclear why oxygen vacancies (V_O) with excess of positive charge are thermodynamically stable, for example, with respect to electrically neutral F-centres.

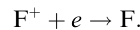
The model of in-centre transitions [9] does not explain several experimental results on kinetics of excitation, luminescence and reciprocal conversion of F^+ and F-centres. Under excitation into the absorption band associated with F^+-centres (4.8 eV), the increase of absorption band of F-centres was observed (6.1 eV) [6]. That is, the excitation of one electron centre results in formation of two electron ones. This process was explained by the charge transfer after photoionization of other centres [6].

The studies [7,10,11] on kinetics of luminescence of F^+ and F-centres indicate their substantially different nature. According to the results on photoluminescence kinetics, the relaxation of F-centres involves two prolonged stages, namely, transition with the lifetime of 3.6×10^{-2} s and charge transfer from neighbouring traps lasting for about 5 s [10], whereas F^+-centre lifetime in the excited state is equal to 7×10^{-9} s at 80 and 300 K [7]. With the elapsed time up to 10^{-6} s after a pulse of 200 keV electron irradiation (pulse duration 5 ns, flux 1.25×10^{24} e/m^2 s), F^+-centre RIL band was observed and F-centre RIL band was not revealed [11]. Obviously, the in-centre transition model is only useful for F^+-centre absorption spectra corresponding to a hydrogen-like system.

The most adequate model of F^+ and F-centres represents them with their neighbourhood, involving hole traps in the adjacent shells [9]. In a similar model, a stability of double charged oxygen vacancy is provided by a negative charge localized on the adjacent trap shell. Concentration of traps with energy from 0.7 to 2.7 eV in Al_2O_3 reaches 10^{27} m^{-3} [2]. This concentration of shallow traps corresponds to the observed radiation-induced electric conductivity. Since the oxygen vacancy concentration is 3–4 orders of magnitude as low, the system of shallow traps is a medium, the states of which determine electron configurations in oxygen vacancies. F^+-centre formation involves electron transfer from the neighbouring traps to the oxygen vacancy or electron delocalization within the range of the nearest vacancy neighbourhood. This model is in agreement with EPR measurement performed in Ref. [12] where EPR spectrum of F^+-centres has been reported to correspond to trapped holes rather than to trapped electrons. To explain EPR spectrum, a model considering the charge transfer following F^+-centre excitation has been introduced in [13]. Hence, F^+-centre appears to be an excited state of the 'oxygen vacancy – adjacent shell' system (VS-system). Formation of F-centre takes place in capturing an extra electron by VS-system. Being consistent with the above-mentioned studies, this consideration does not involve the two-stage process of F-centre formation resulting from the reactions

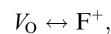


$$V_O + e \rightarrow F^+,$$

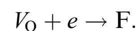


$$F^+ + e \rightarrow F.$$

Therefore, F^+ and F-centre luminescence under photoexcitation or ionizing irradiation appears to be caused by two-particle processes, luminescence intensity being proportional to the oxygen vacancy concentration. For this reason, the intensities of F^+ and F-centre RIL bands are comparable in several observations. F^+-centre excitation requires the perturbation of VS-system, whereas F-centre lighting results from relaxation of an extra electron in this system:



$$V_O \leftrightarrow F^+,$$



$$V_O + e \rightarrow F.$$

A substantial feature of this model is the total charge being negative for VS-system in the state corresponding to F-centre. So, the luminescence in the range of F-centre band indicates negatively charged regions in the material.

4. Effect of electrical charging on RIL of materials based on Al_2O_3

Let us consider the effect of local electric charging on RIL of pure and chromium-doped Al_2O_3. RIL spectra of Al_2O_3 single crystals under 8 MeV proton irradiation (dose rate up to 5×10^3 Gy/s) were obtained in the study [8]. With increasing the dose, the increase of intensity of F-centre RIL band (330 nm) was observed, the intensity of F^+-centre band (415 nm) being constant. Under

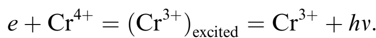
proton irradiation, the production of free electrons and holes in the bulk of the material occurs. Free charge carrier recombination in traps results in either excitation of VS-systems if the traps belong to the systems or lattice heating in other cases. Almost all the energy of ion irradiation is spent for free electron and hole production, whose rate can be estimated using Eq. (3). In the steady state this production rate is equal to the rate of recombination of free charge carriers on traps. The probability of VS-system excitation resulting from recombination on traps (formation and luminescence of F^+-centres) is equal to the ratio of the trap concentration in VS-systems and the total trap concentration. The luminescence intensity is determined by the product of this probability and the rate of free charge carrier production. Hence, efficiency η of conversion of the energy of ionizing constituent of irradiation into F^+-centre luminescence is determined by the ratio

$$\eta = \frac{c_v n}{N}, \tag{12}$$

where c_v is a vacancy concentration, n is a mean number of traps in VS-system, and N is a total trap concentration. This value is constant if the material structure does not change during irradiation.

Changing of F-centre RIL band intensity with the dose indicates changing of concentration of VS-systems, containing excess of a negative charge, probably, either localized in traps of VS-systems or delocalized in the ranges of VS-systems. F-centre concentration increase is a response to both total and local negative charging in the bulk of the material. Changing of RIL spectra features took place with the time (~10^3 s) much greater than the characteristic time of charging ϵ_0/σ_{RIC} (~10^{-3} s) due to accumulation of protons and secondary emission of electrons. Therefore, RIL features are not caused by these processes. The cause is the formation of charged regions in the bulk of the material, which resulted from the difference in total trap concentrations in these regions according to Eq. (10).

Estimation of a local charge, building up under irradiation, appears to be possible for $Al_2O_3{:}Cr^{3+}$, where elementary luminescence process takes place after an electron to be trapped by Cr^{4+} ion (with the trapping coefficient w_e^t)



$$e + Cr^{4+} = (Cr^{3+})_{excited} = Cr^{3+} + h\nu.$$

Cr^{4+} ion formation is controlled by the process of hole trapping in Cr^{3+} ions with trapping coefficient w_h^t. In the steady state, the rate of recharging of all traps, considering chromium ions also is equal to the free charge carrier production rate. Therefore, the efficiency of conversion of the energy of ionizing constituent of irradiation energy into RIL in the spectral range of Cr^{3+} band is determined by the ratio of the rate of electron trapping in Cr^{4+} ions to the rate of free charge carrier production

$$\eta = \frac{c_e n_{Cr^{4+}} w_e^t}{g_e \dot{D}}. \tag{13}$$

The ratio of steady-state Cr^{4+} and Cr^{3+} ion concentrations is determined by equality of the rates of electron and hole trapping in these ions, respectively,

$$n_{Cr^{4+}}/n_{Cr^{3+}} = \frac{c_h w_h^t}{c_e w_e^t}. \tag{14}$$

Chromium ions in Al_2O_3 are deep traps, and their concentration exceeds concentration of the rest deep traps (F-centres). Therefore, accumulation of the positive charge consists, for the most part, in increase of Cr^{4+} ion concentration

$$\Delta n_{Cr^{4+}} \leqslant \frac{Q}{2e}. \tag{15}$$

On charging, relative increase of intensity of Cr^{3+} ion luminescence $\Delta I/I$, caused by electron trapping in Cr^{4+} ions, is described by the expression

$$\Delta I/I = \frac{\Delta n_{Cr^{4+}}}{n_{Cr^{4+}}}. \tag{16}$$

Concentration inhomogeneities in the trap system, responsible for electric charging, according to Eq. (10), take place in ceramics, for example, due to existing grain boundaries. RIL spectra of $Al_2O_3{:}Cr^{3+}$ single crystal and ceramics (grain size of 1–10 μm) with the chromium content of 10^{-2} % mass under 8 MeV proton irradiation (ionizing dose rate up to 5×10^3 Gy/s) were registered in the study in Ref. [14]. On increasing the dose, the Cr^{3+} ion band (690 nm) intensity for $Al_2O_3{:}Cr^{3+}$ ceramics has been observed to increase (Fig. 1). The increase is equal to 11% at the end of irradiation, the intensity of the similar band in single crystal $Al_2O_3{:}Cr^{3+}$ being constant under similar conditions.

Chromium ions in the grain boundaries are inactive in the corresponding spectral range (690 nm) owing to changing the position symmetry. The difference in dose dependence of Cr^{3+} band in these materials is due to positive charging of the grain bulk with respect to grain boundaries in ceramics and total electrical neutrality of the bulk of $Al_2O_3{:}Cr^{3+}$ single crystal under irradiation. To estimate local charge density with the help of Eqs. (15) and (16), let us calculate a steady-state concentration of Cr^{4+} ions.

Taking the data on radiation-induced conductivity (RIC) in Al_2O_3 single crystals with chromium concentration of 10^{25} m^{-3} [2], one can estimate a steady-state concentration of mobile carriers of about 10^{16} m^{-3} for the dose rate of 5×10^3 Gy/s. Free charge carrier production rate is about 10^{25} m^{-3} s^{-1}, according to Eq. (3). Experimental value of RIL efficiency η is equal to 10^{-2}. Trapping coefficient w_h^t responsible for chromium ion

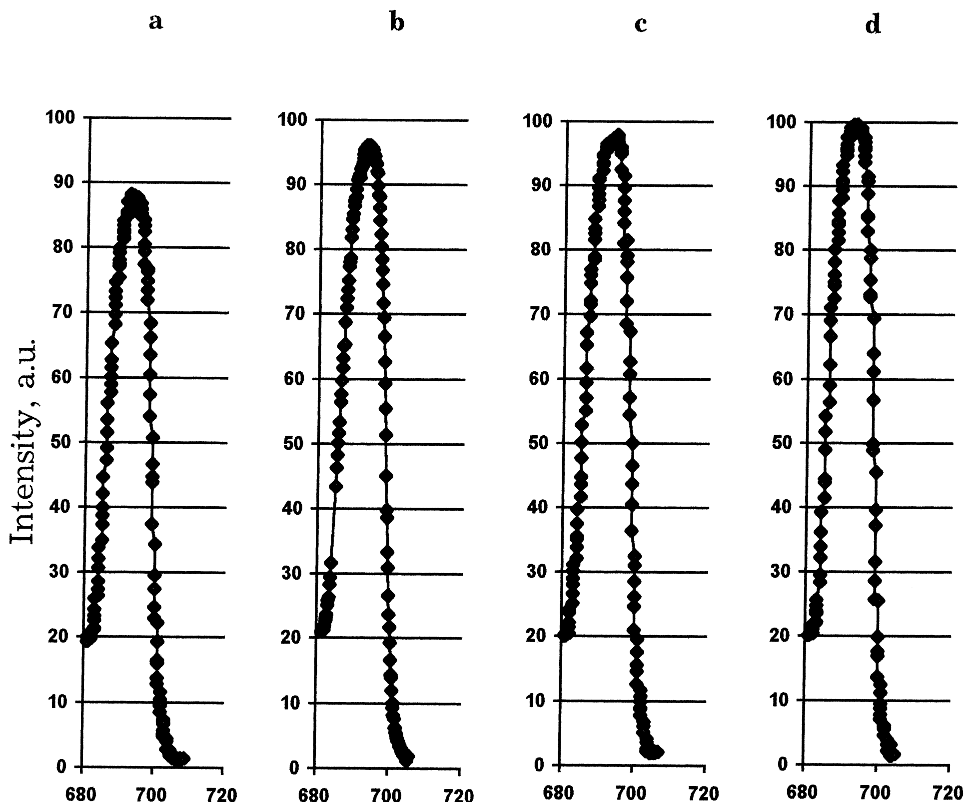


Fig. 1. Dose dependence of Cr^{3+}-band of RIL of ceramic Al_2O_3 under 8 MeV proton irradiation [14]: (a) 1.5×10^6 Gy; (b) 3×10^6 Gy; (c) 4.5×10^6 Gy; (d) 6×10^6 Gy.

conversion, according to Eqs. (13) and (14), is approximately equal to 10^{-18} m^3/s. For w_e^t 10^{-14} m^3/s (typical value for charged impurities [1,2]), the Cr^{4+} ion concentration is equal to 10^{21} m^{-3}, and its increment during irradiation is equal to 10^{20} m^{-3}. The magnitude of excessive positive charge Q, corresponding (Eq. (15)) to the calculated increase of Cr^{4+} ion concentration, exceeds the value of 10^4 Q/m^3. The associated electric field exceeds 10^6 V/m under the assumption that the positive charge in grains is recompensed by a negative charge in grain boundaries.

5. Conclusion

The results presented are evidence that radiation-induced electric charging in dielectrics, as well as RIL and RIC, is caused by free charge carrier relaxation by means of recombination in the electron and hole traps. Concentration inhomogeneities in the trap system has been shown to be responsible for radiation-induced electric charging of regions in the bulk of dielectrics under irradiation. Formation of electrically charged regions is caused by difference in hopping mobility of charge carriers over traps and does not violate general electric neutrality of the system. In ceramics, electric charging in grain bulk with respect to grain boundaries occurs.

Electric charging results in RIL intensity change. Formation of negatively charged regions during irradiation results in intensity increase for F-centre band (415 nm) in RIL spectra of single crystal Al_2O_3. In ceramic $Al_2O_3:Cr^{3+}$, the radiation-induced negative charging of grain boundaries with respect to grain bulk takes place, which is responsible for intensity increase of Cr^{3+} ion RIL band (690 nm) at a constant intensity of the similar band in single crystal $Al_2O_3:Cr^{3+}$.

The idea of the radiation-induced electric charging due to concentration inhomogeneities in the trap system allows one, using the RIL method, estimating local charge density in grains of ceramic $Al_2O_3:Cr^{3+}$ and associated electric field. Excessive positive charge in grains of ceramic $Al_2O_3:Cr^{3+}$ exceeds 10^4 Q/m^3 under 8 MeV proton irradiation (dose rate up to 5×10^3 Gy/s), and associated electric field exceeds 10^6 V/m.

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