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Section 8. Ceramics and diagnostic materials

# An initial model for the RIED effect

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**Abstract**

A simple model based on electron acceleration in the conduction band giving rise to an increased $F^+$ oxygen vacancy lifetime provides an explanation for several radiation induced electrical degradation (RIED) associated observations in $Al_2O_3$. The increased $F^+$ radioluminescence noted during RIED is a direct consequence of the lifetime increase. The model predicts the observed electric field threshold for RIED, and an increase in the field threshold with increasing impurity content. RIED for RF electric fields is also explained. In addition the lifetime increase provides an explanation for the enhanced oxygen vacancy aggregation including colloid and gamma alumina production observed under RIED conditions. 

## 1. Introduction

At the present time, there are numerous conflicting results for radiation induced electrical degradation (RIED) in sapphire and aluminas. Some observations indicate that the degradation takes place in the volume of the material, while other experiments either observe no effect or report that surface degradation and sample cracking may lead to an apparent volume degradation. This situation has been recently reviewed, and also extensively discussed [1–3]. To date most of the reported experiments concerned with RIED have been performed in order to evaluate the technological limitation this phenomenon imposes on the use of electrical insulators in future fusion devices. Attention paid to the fundamental aspects has been scarce [4–8] and consequently at the present time little is known as to possible basic causes for the reported electrical degradation. However some research has shown that the application of a small electric field during electron irradiation in sapphire causes a notable increase in the $F^+$ radioluminescence [4], induces an enhanced oxygen vacancy aggregation process leading to aluminium colloid formation [7], as well as an alpha to gamma phase transition [5]. All these are volume effects. Hence although the discussion as to the bulk nature of RIED continues, it is necessary to seek an explanation as to why the application of a relatively small electric field during irradiation can substantially modify the damage production. At considerably higher temperatures and voltages, but without an irradiation field, or for irradiations performed without an applied electric field, no comparable damage is induced.

In the work to be presented a model has been developed, in which the above mentioned volume effects observed under RIED conditions are explained. It has been demonstrated through radioluminescence measurements during electron irradiation that oxygen vacancies in sapphire spend some time as F centres (oxygen vacancies with two trapped electrons) and some time as $F^+$ centres (oxygen vacancies with one trapped electron) [8]. The influence of an applied electric field is observable even in the early stage of irradiation as an increase in the $F^+$ concentration, see Fig. 1. The model explains this as a consequence of an increase in the $F^+$ centre lifetime, which in turn enhances the oxygen vacancy mobility and hence the probability of vacancy aggregation. The $F^+$ centre lifetime as a function of applied electric field intensity has been numerically calculated. A close correlation between previous experimental results on the field threshold for RIED and the $F^+$ lifetime has been found. In particular the model predicts that the electric field threshold for RIED increases with impurity content.

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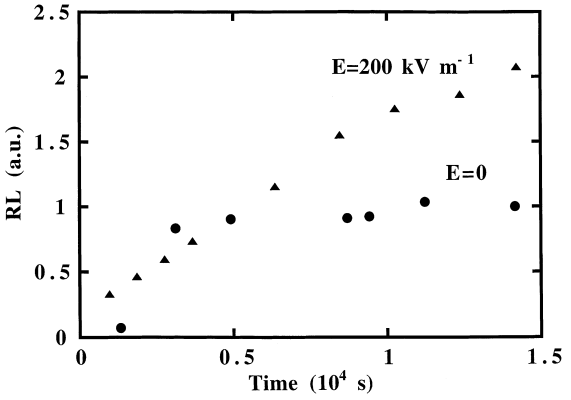


Fig. 1. Growth of the $F^+$ radioluminescence band for UV grade sapphire electron irradiated at 200°C, 1400 Gy/s and $2 \times 10^{-10}$ dpa/s with (triangles) and without (circles) an electric field applied.

Previous experiments have shown that Wesgo AL995 alumina is not susceptible to electrical degradation in the volume (RIED), whereas UV grade sapphire and Vitox high purity alumina have been observed to exhibit volume electrical degradation (see [1,2] and references therein). The model indicates that the reason for this discrepancy or difference is due to the higher impurity content of the Wesgo AL995 material. Taking this into account Wesgo AL995 alumina has been electron irradiated and has been found to be susceptible to RIED for irradiation conditions predicted by the theoretical model.

## 2. Theoretical model

Most of the oxygen vacancies produced by irradiation in $Al_2O_3$ are in the form of F centres. However during irradiation the ionizing component produces a small concentration of $F^+$ centres and electrons in the conduction band [8]. Radiation induced conductivity for $Al_2O_3$ at 700 Gy/s is of the order of $10^{-6}$ to $10^{-7}$ S/m [9] and the conduction band electron mobility $\mu$ is $3 \times 10^{-4}$ m$^2$/(V s) [10]. Electrical conductivity is given by $\sigma = qn\mu$, which implies that $n$ (density of electrons in the conduction band) is of the order of $10^9$ to $10^{10}$ electrons/cm$^3$. This value is much lower than the density required for themalization of electrons in the conduction band to occur [11]. Then these electrons will be accelerated by the electric field and during this acceleration process the electrons lose energy to the crystal lattice mainly through electron–phonon interactions. In addition they may be trapped by defects present in the material. As will be seen, this acceleration results in an increase of the lifetime of the electron in the conduction band, which in turn leads to an increase in the $F^+$ lifetime.

The energy transferred to the lattice by an accelerated electron due to an electron–phonon collision is of the order of $Km/M_i$ where $K$ is the electron kinetic energy, $m$ is the electron mass, and $M_i$ is the lattice ion mass. The increase in the electron energy after moving through a differential distance d$x$ is given by

$$\mathrm{d}K = \left[ -\frac{mK}{M_i \delta_{e\text{–}p}} + qE \right] \mathrm{d}x, \tag{1}$$

where $q$ is the electron charge, $E$ the electric field, and $\delta_{e\text{–}p}$ the average distance between two consecutive electron–phonon collisions which at and above room temperature is of the order of the interatomic distance [12]. Integrating (1) we obtain

$$K(x) = \frac{qEM_i\delta_{e\text{–}p}}{m}\left[1 - \exp\left(-\frac{mx}{M_i\delta_{e\text{–}p}}\right)\right], \tag{2}$$

where $x$ is the distance through which the electron has been accelerated in the conduction band. After travelling a distance of the order of $(M_i\ \delta_{e\text{–}p})/m$ the electron velocity reaches saturation when the energy taken from the electric field equals the energy given to the lattice through electron–phonon interactions.

This acceleration process will terminate before or after saturation is reached if the electron is trapped by a defect present in the material. Later on the electron may be detrapped and the acceleration process starts again. Probable traps are positively charged defects such as the $F^+$ centres themselves and cation impurities, in particular transition metals such as Fe and Cr. Taking into account the Coulomb interaction between the accelerated electron and the positively charged defect the cross-section $\sigma$ for the trapping of the electron by one of these traps is of the order of

$$\sigma(K) = \pi\left(\frac{q^2}{\varepsilon K(x)}\right)^2, \tag{3}$$

where $\varepsilon$ is the $Al_2O_3$ dielectric constant. If the average distance between two traps is $d$, then the probability of the electron being trapped after being accelerated through a distance $x$ is

$$T(x) = \frac{\sigma(K)}{d^2}. \tag{4}$$

The acceleration distance is determined by the trapping and detrapping process. Hence the probability of an electron being accelerated over a distance $z$ is the probability that the electron will not be trapped by any of the $j$ traps ($j = z/d$) it passes near. This is expressed mathematically by

$$P_j = \begin{cases} 1 - \sum_{i=1}^{j} T_i & \text{if } \sum_{i=1}^{j} T_i \leqslant 1, \\ 0 & \text{if } \sum_{i=1}^{j} T_i > 1. \end{cases} \tag{5}$$

where $P_j$ is the probability of an electron not being trapped after passing near by $j$ traps and $T_i = T(x = id)$.

When an F centre is converted to an $F^+$ centre, the $F^+$ lifetime $\tau$ will be given by the inverse of the frequency at which $F^+$ centres trap electrons becoming F centres

$$\tau = \left\langle \frac{1}{\omega T(x)} \right\rangle, \tag{6}$$

where $\omega$ is the frequency at which electrons pass near by and $T(x)$ is the probability that the electrons with energy $K(x)$ are trapped. The brackets mean the average over all the possible electron kinetic energies $K(x)$. The maximum electron velocity is limited by the electron–phonon interaction which corresponds to acceleration distances of about $(M_i\ \delta_{e-p})$/m then (6) may be expressed as

$$\tau = \frac{\sum_{j=1}^{n} \left(P_j / T_j \omega\right)}{\sum_{j=1}^{n} \left(P_j\right)}, \tag{7}$$

where $P_j$ is given by (4), $T_j = T(x = jd)$ and $n$ is

$$n = \left| \frac{M_i \delta_{e-p}}{md} \right|. \tag{8}$$

In the case of Union Carbide UV grade sapphire the content of likely electron trapping impurities is between approximately 20 and 100 ppm [13]. This corresponds to an average distance between trapping centres of 50 to 100 Å. Using these values the $F^+$ lifetime in Eq. (7) was numerically calculated as a function of the electric field using Eqs. (2)–(5). This is shown in Fig. 2 together with RIED values taken from [14]. It is clear that the electric field markedly increases the $F^+$ lifetime and hence explains the experimentally observed increase in the $F^+$ radioluminescence. However of more importance is the close similarity between the $F^+$ lifetime as a function of electric field and the two step function observed in RIED experiments performed on sapphire to study the role of the electric field. In view of this correlation, the lifetime calculation has also been made for Wesgo AL995 using an estimated impurity content of 5000 ppm [15]. This calculation is also shown in Fig. 2 and indicates that the threshold for RIED in Wesgo AL995 should be about 1 MV/m, over an order of magnitude greater than that for sapphire.

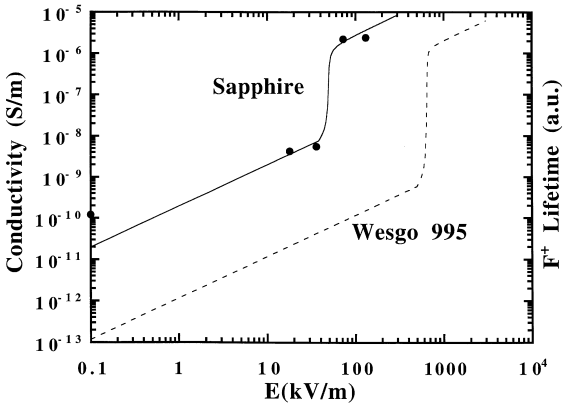


Fig. 2. Electrical conductivity degradation of UV grade sapphire samples electron irradiated at 450°C with different applied electric fields (points) together with the calculated $F^+$ centre lifetime for both UV grade sapphire and Wesgo AL995 alumina.

## 3. Experimental work

Previous work carried out within the IEA round robin experiment on Wesgo AL995 has shown that this alumina is not susceptible to RIED ([2] and references therein), but at field strengths of 100–350 kV/m. To check the electric field threshold prediction given by the model, three Wesgo AL995 alumina $25 \times 25 \times 1$ mm$^3$ samples with guard and central sputtered gold electrodes were irradiated with 1.8 MeV electrons in the beam line of a 2 MeV Van de Graaff accelerator. The beam was perpendicular to one of the $25 \times 25$ mm$^2$ faces where the guard and central electrodes were deposited. The irradiations were performed using a defocused beam on a 10 mm thick collimator in order to uniformly irradiate only the central electrode, for up to 170 h in vacuum at 450°C, 700 Gy/s and $10^{-10}$ dpa/s (1 μA/cm$^2$). In all cases the electrode resistances were of the order of 0.5 Ω and the use of a guard electrode permitted one to clearly separate surface from volume conductivity. The electric field applied during irradiation was 100, 500 and 1000 kV/m, respectively. Further experimental details are given elsewhere [15].

On initial heating to 450°C, the samples showed high volume conductivity (Fig. 3). At this temperature the volume conductivity was observed to slowly decrease

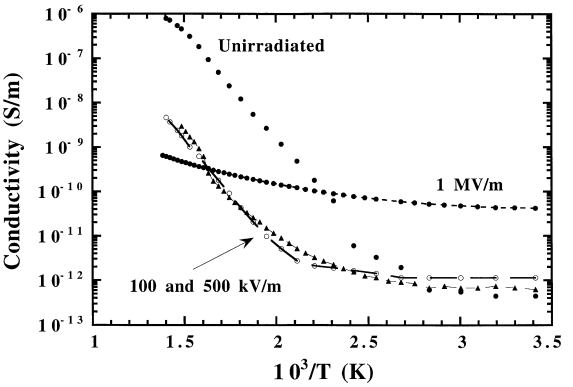


Fig. 3. Electrical conductivity as a function of temperature for Wesgo AL995 alumina unirradiated and irradiated with different applied electric fields.

reaching about $10^{-7}$ S/m after 2 h. On irradiation all three samples showed a more rapid decrease in their volume conductivities due to radiation enhanced electrolysis [16]. At 100 and 500 kV/m the conductivities saturated at about $5 \times 10^{-9}$ S/m, and on reheating following irradiation showed very similar activation energy curves (Fig. 3). A very similar behaviour has been observed in Wesgo and AlN for alpha particle irradiations with 100 kV/m [17]. However, at 1 MV/m while the high temperature conductivity showed a further decrease, following about 60 h the lower temperature conductivity began to increase, and by 170 h the activation energy is markedly reduced, consistent with electrical degradation.

## 4. Discussion

Initial attempts by the authors to explain the influence of an applied electric field on the radiation induced processes in $Al_2O_3$, examined the problem at an ionic level. However, the enormous difference between the externally applied electric field and the interionic field proved insurmountable. In contrast, this simple model in which the acceleration of an electron in the conduction band leads to a many order magnitude increase in the $F^+$ lifetime shows how a relatively small field can influence the radiation induced processes. The theoretical model not only indicates that an applied electric field increases the $F^+$ centre lifetime in agreement with experimental observations, but that this increase is also closely related to the observed thresholds for electrical degradation in both sapphire and Wesgo AL995.

RIED has been observed in electron irradiated sapphire not only with DC but also with AC/RF applied fields up to 126 MHz [14]. From these measurements it was suggested that the timescale for the basic mechanism involved in RIED must be $<10^{-9}$ s. The model presented here permits one to calculate this time. The timescale is determined by the time required to accelerate an electron to its saturation velocity. This may be obtained from the acceleration distance ($M_i\ \delta_{e-p}$)/m, Eq. (2).

$$t \approx \left(\frac{2M_i\delta_{e-p}}{qE}\right)^{1/2}. \tag{9}$$

For an electric field of 100 kV/m this gives a characteristic time of $10^{-11}$ s, consistent with the experimental value. This contrasts with the model of Zong et al. [6] based on charge injection which is only valid for dc fields, and where the authors suggest that degradation under an ac field would be due to surface effects.

An increase in the $F^+$ lifetime is not sufficient on its own to explain the electrical degradation observed in some RIED experiments; this will require extensive modification of the bulk material. However such an increase in the lifetime will enhance the oxygen vacancy mobility by increasing not only the number of $F^+$ centres during irradiation but also as a consequence the number of excited and ionized $F^+$ centres. The increased mobility of such vacancy centres is well documented for the alkali halides [18,19] and has been observed to cause radiation enhanced impurity aggregation in MgO [20]. An increase in the oxygen vacancy mobility will give rise to an increased vacancy aggregation. Such an enhanced aggregation effect has been observed in the early stages of RIED [7], as may be seen in Fig. 4, where optical absorption bands due to $F_2$ centres are clearly visible. Furthermore, this enhanced aggregation process has been observed to lead to aluminium colloid [7] and gamma alumina [5] production within electrically degraded sapphire.

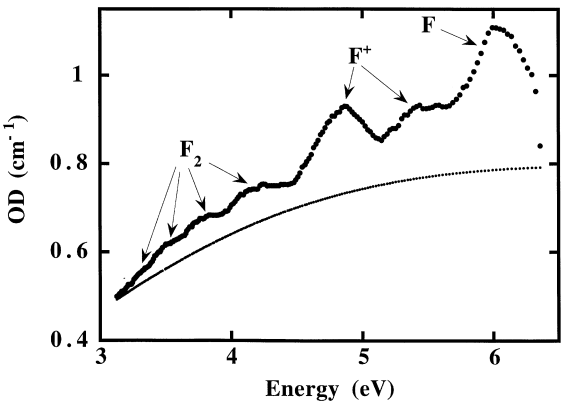


Fig. 4. Optical absorption spectrum for a UV grade sapphire sample irradiated with 1.8 MeV electrons at 2800 Gy/s and $4 \times 10^{-10}$ dpa/s, at 200°C for 10 h, then at 240°C for 8 h, and then at 270°C for 11 h. The irradiation was performed with an applied electric field of 200 kV/m. The underlying absorption is due to aluminium colloids.

Work is now in progress to bridge the gap between the production of extended defects, in particular colloids and gamma alumina, formed as a consequence of the increased $F^+$ lifetime, and the degradation of the electrical conductivity. Initial results indicate that the change in the electrical conductivity activation energy, as seen in Fig. 3 and reported in several RIED experiments, can be modelled [21].

## 5. Conclusions

A simple model based on electron acceleration in the conduction band giving rise to an increased $F^+$ oxygen vacancy lifetime provides an explanation for several RIED associated observations:

1. Increased $F^+$ radioluminescence.
2. Enhanced oxygen vacancy aggregation including colloid and gamma alumina production.
3. Electric field threshold for RIED.
4. Increase in the field threshold with increasing impurity content.
5. RIED for RF electric fields.

Further work is now in progress to extend the model to cover the electrical degradation.

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