

Enhanced oxygen vacancy aggregation and colloid production in Al_2O_3

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Abstract

Optical luminescence and absorption measurements on Al_2O_3 (sapphire) electron irradiated at temperatures between 200 and 270°C with and without an applied electric field have been used to identify an oxygen vacancy aggregation process leading to the formation of aluminium colloids. This process, which is only observed when an electric field is applied during irradiation, occurs within the volume and is considered as a possible precursor for RIED. The results help to clarify the observed similarity between RIED and colloid production, and help to provide an explanation for the observation of gamma alumina in sapphire which has suffered RIED. © 1997 Elsevier Science B.V.

1. Introduction

Following the first report of radiation induced electrical degradation or RIED effect in electron irradiated sapphire (Al_2O_3) and MgO [1], numerous experiments have been carried out to assess its possible relevance to fusion insulator applications. These have been concerned with the effect of the applied electric field; dc or ac/RF [2] and voltage threshold [3], the irradiation temperature [4,5], the dose rate [5], the verification that, in addition to electrons, RIED occurs with protons [6], alphas [7], and neutrons [8], and the observation of RIED-like effects in other materials; MgAl_2O_4 [9] and AlN [10,11]. In addition further experiments have been carried out in which RIED-like effects have been observed in sapphire electrons irradiated in air [12] and in MgO insulated cable [13]. In contrast some experiments have not observed any RIED effect, or have observed enhanced surface conductivity [14–17]. This led to suggestions that the RIED degradation is not a real volume effect, but is caused by surface contamination [14,15]. This controversy was extensively discussed at an open IEA workshop [18] where no fault was found with the experimental techniques employed in the electron and proton irradiations to identify volume degradation. It was

furthermore pointed out that important factors such as dose rate, temperature, and/or material type differences which could cause RIED not to be observed were not being taken into account [5]. This was further clarified by later observations under identical conditions, of RIED in Vitox alumina but not in Wesgo AL995 alumina [7], strongly suggesting a material (possibly impurity and/or grain size) dependence, and by further observations showing that the low purity large grain size AL995 material was highly susceptible to surface degradation when irradiated in high vacuum [19].

In an attempt to clarify this confused situation further work was performed to try to identify the basic causes of RIED. These experiments detected specific volume effects in Al_2O_3 which occur only when irradiations are carried out with an applied electric field. The work involved the measurement of optical absorption and emission spectra in which a marked enhancement of the well characterized F^+ -centres (oxygen vacancy with one trapped electron) was observed [4], and TEM studies where large regions of gamma-alumina were identified within the bulk of RIED degraded Al_2O_3 [20]. It has been suggested that an increase in the production of F^+ -centre could give rise to an enhanced oxygen vacancy mobility through a lowering of the vacancy activation energy, and hence lead to vacancy aggregation and possible aluminium colloid formation [21]. This would explain the observed close similarity between

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the RIED effect and colloid production in the alkali halides [22,23], and furthermore help to explain the formation of gamma-alumina due to the removal of aluminium from the lattice, and the associated bulk electrical and mechanical degradation [20].

The work reported here is concerned with the evolution of the F^+ -centres during electron irradiation of high purity sapphire, at temperatures where both F^+ -centre enhancement and RIED have been observed [4,5]. The experiments demonstrate that in aluminium oxide a process of enhanced oxygen vacancy aggregation does occur when irradiating with an electric field applied. Optical absorption and emission measurements have been made in the early stages of irradiation where it has been possible to observe the aggregation of F^+ -centres to form F_2 type centres (two adjacent oxygen vacancies) and, of more importance, to identify the subsequent formation of aluminium colloids with increasing irradiation time.

2. Experimental procedure

The experiments described here have been performed in a sample chamber mounted in the beam line of a 2 MeV HVEC Van de Graaff electron accelerator. The system enables samples to be irradiated, with an electric field applied, at any temperature between about 15 and 600°C and maintained to within approximately 1°C. The chamber wall is water cooled, and liquid nitrogen traps are placed in the beam line at the entrance and exit of the chamber. In this way a clean high vacuum ($\approx 10^{-6}$ mbar) is obtained in the sample chamber. Samples of approximately $2 \times 3 \times 5$ mm³ were prepared with sputtered platinum electrodes on the two 2×3 mm² faces. One of these faces is in good electrical and thermal contact with a grounded oven, and the other is connected to a spring loaded electrode which enables an electric field to be applied to the sample. The samples are irradiated perpendicular to the electric field direction on a 2×5 mm² face. 3×1 mm² windows built on the oven enable in situ measurements of optical absorption and radioluminescence to be made perpendicular to both the electric field and the irradiation direction at a distance of approximately 1 to 2 mm. behind the irradiated face.

Al₂O₃ single crystal samples (Union Carbide UV grade sapphire) have been irradiated with 1.8 MeV electrons, 4×10^{-2} A m⁻², at 200, 240, and 270°C with and without an electric field applied (200 kV m⁻¹), and with 0.2 A m⁻² at 270°C with an electric field. In the high beam current case the temperature within the sample varied from 270°C at the oven electrode to approximately 310°C at the other electrode. Radioluminescence measurements, which serve as a way of monitoring the growth of the F^+ -centres, have been made during irradiation. For all the experiments absorption spectra were recorded at 15°C, before and after each irradiation. In addition following each experiment,

the samples were cleaned and polished to remove any possible surface contamination and absorption spectra recorded in a commercial Cary spectrometer. As mentioned in the introduction, the irradiation temperatures were chosen to cover the range where both enhanced F^+ -centre production ($> 150^\circ\text{C}$), and RIED ($\geq 250^\circ\text{C}$) have been observed. In addition the temperatures were restricted to the lower range in order to obtain clear unquenched luminescence spectra, and to ensure that any possible aggregation processes proceed as slowly as possible so as to be observable.

3. Results

Samples irradiated at and above approximately 200°C show that when the irradiation is carried out with an applied electric field a definite enhancement is observed in the F^+ production. This may be seen in Fig. 1 taken from Ref. [4] for a sample irradiated at 200°C. In order to search for possible aggregation processes a single sample was irradiated initially at 200°C for 10 h to 1.4×10^{-5} dpa, 1×10^8 Gy, then at 240°C for 8 h to 2.6×10^{-5} dpa, 1.8×10^8 Gy, and finally at 270°C for 11 h to 4.2×10^{-5} dpa, 2.9×10^8 Gy. The radioluminescence spectra for irradiations at 200 and 240°C are very similar and show in addition to the F^+ band at 3.76 eV, emissions due to F-centres (oxygen vacancies with two trapped electrons) at 3.02 eV, and Ga³⁺ emission at 4.61 and 5.15 eV [24,25]. These emission bands may be seen in Fig. 2 for the irradiation at 240°C. With irradiation time the emission spectrum showed no qualitative change apart from a slow monotonic increase in the F and F^+ emissions due to the increasing displacement damage (oxygen vacancy production). However, on increasing the irradiation temperature to 270°C, the form of the emission spectrum was observed to change with irradiation time and a further emission at about 3.5 eV becomes visible (Fig. 3). This additional emission is more clearly identified by taking the difference between spectra obtained at different times where, as may be seen in Fig. 4, the new emission is in fact due to two bands at 3.27 and 4.13 eV. These emissions correspond to the F_2^+ and F_2 centres, aggregates of two oxygen vacancies [26,27]. Following this final irradiation temperature an optical absorption spectrum was taken (Fig. 5). In this spectrum together with the well known F and F^+ bands [28,29], the four F_2 absorption band components [30,31] are visible indicating that stable oxygen vacancy aggregation has taken place. The spectra observed after removal and cleaning showed the same band structure. These results indicate that for irradiation at 270°C with an electric field applied, not only does enhanced F^+ center production take place but in addition aggregation of the oxygen vacancies occurs. For the irradiations performed without an electric field applied neither an enhancement of the F^+ centers nor vacancy aggregation were observed. It is also

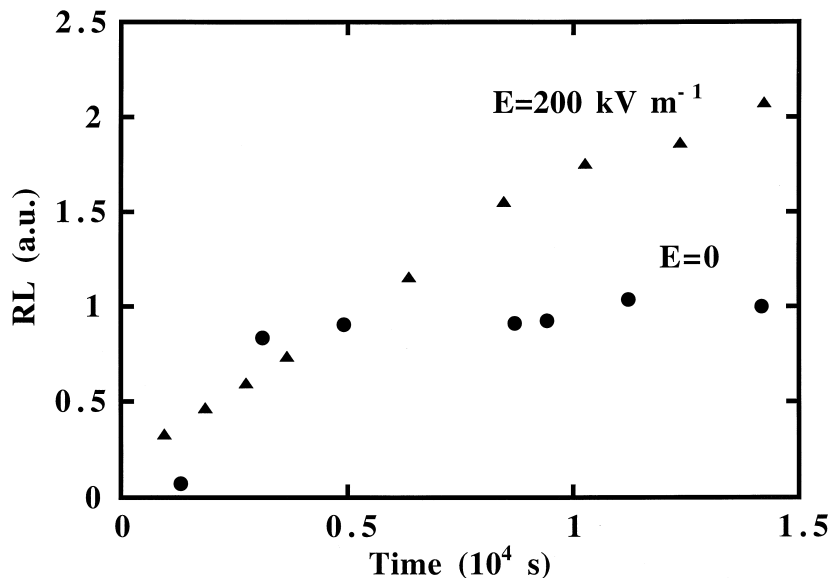


Fig. 1. F^+ radioluminescence band growth for samples irradiated at 200°C , 1400 Gy s^{-1} and $2 \times 10^{-10} \text{ dpa s}^{-1}$, with (triangles) and without (circles) an electric field applied.

clear in Fig. 5 that an underlying absorption increasing towards the high energy part of the spectrum is present. The existence of this underlying absorption, indicated in the figure, was also noted in attempts to fit the spectrum with the well characterized F and F_2 band components. This background absorption will be discussed later.

In order to confirm the above observation of vacancy aggregation, a further sample was irradiated at 270°C at a higher dose rate to reduce the necessary irradiation time. In this case the F_2 emission was visible within the first hour of irradiation, indicating that vacancy aggregation was taking place. With irradiation time the radioluminescence

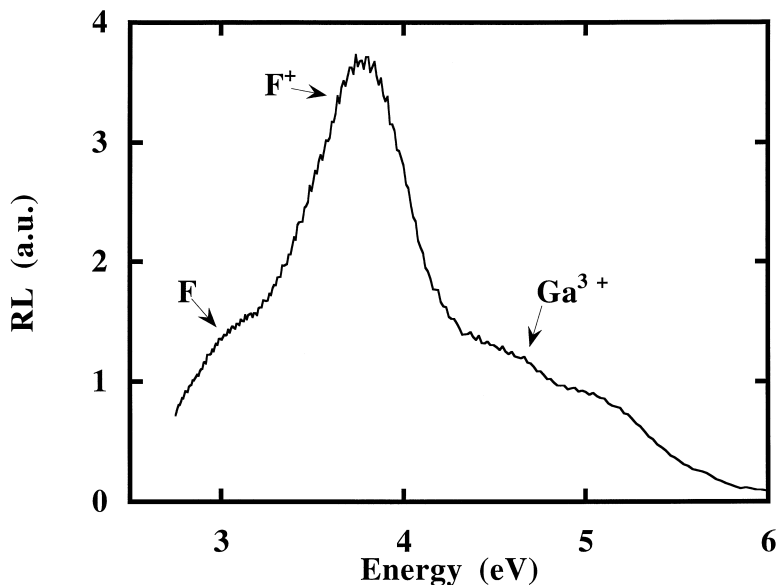


Fig. 2. Radioluminescence spectrum taken at 240°C , 2800 Gy s^{-1} and $4 \times 10^{-10} \text{ dpa s}^{-1}$, for a sample irradiated with an electric field applied, following 18 h of irradiation first at 200°C for 10 h and then at 240°C for 8 h.

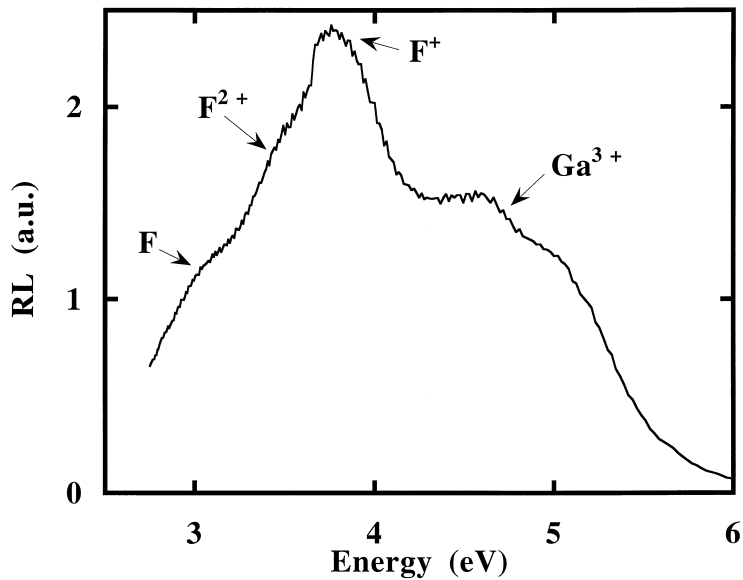


Fig. 3. Radioluminescence spectrum for the same sample in Fig. 2 irradiated for a further 3 h with an electric field applied at 270°C, 2800 Gy s⁻¹ and 4 × 10⁻¹⁰ dpa s⁻¹.

spectrum showed little further change. However following 3 h of irradiation to 2.1 × 10⁻⁵ dpa, 1.5 × 10⁸ Gy, the observed optical absorption spectrum had changed markedly as may be seen in Fig. 6 relative to that observed in the earlier experiment (Fig. 5). In Fig. 6 three spectra taken in the sample after it had been cleaned and polished, are shown for regions of the sample at different distances from the oven, corresponding to irradiation temperatures of approximately 270, 290, and 310°C. The large wide ab-

sorption band at approximately 5 eV clearly differs from the narrow F⁺ bands observed in Fig. 5, and does not correspond to any reported optical absorption band in Al₂O₃. However, the form of the spectra, with the 5 eV band increasing and becoming more narrow for higher temperature irradiation together with an associated band at about 6.4 eV decreasing and exhibiting an isosbestic point, is characteristic of metallic colloid extinction bands in equilibrium with the solute (anion vacancy) in the alkali

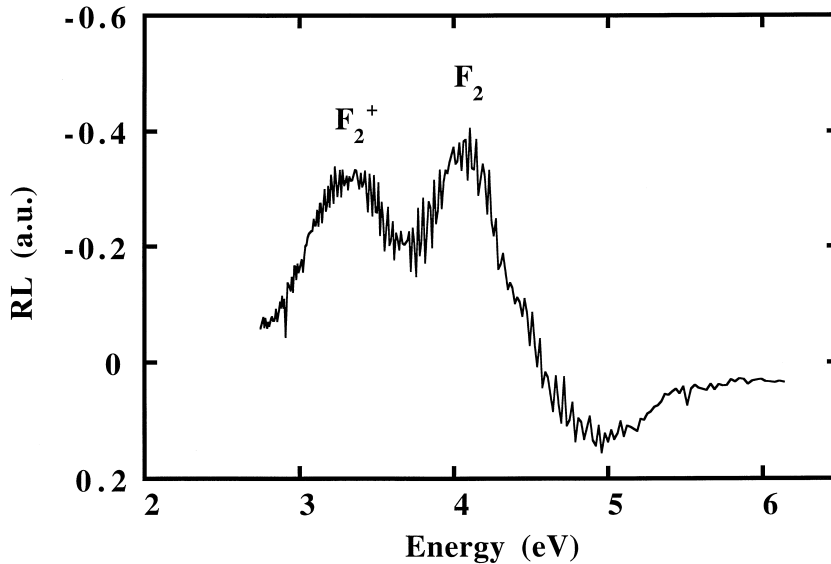


Fig. 4. Difference spectrum for the radioluminescence for the 270°C irradiation corresponding to the change in 11 h of irradiation.

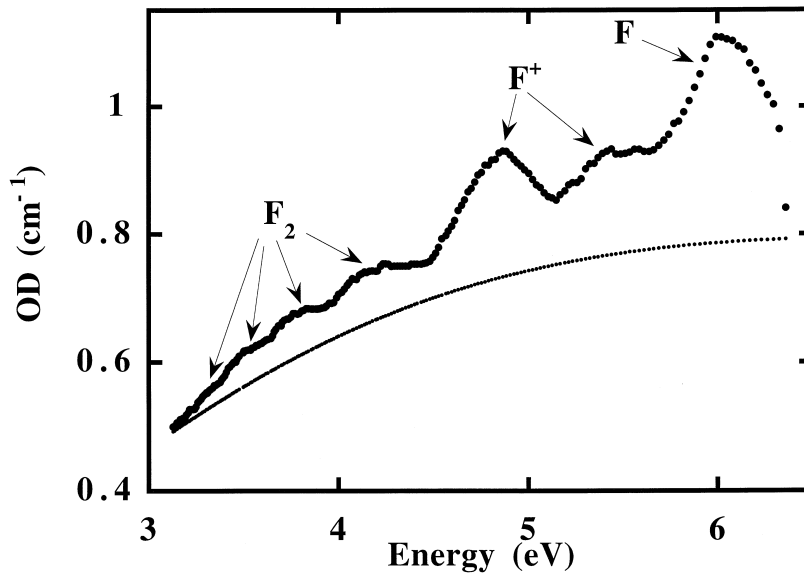


Fig. 5. Final optical absorption spectrum for irradiation at 2800 Gy s^{-1} and $4 \times 10^{-10} \text{ dpa s}^{-1}$, at 200°C for 10 h, then at 240°C for 8 h, and then at 270°C for 11 h. The underlying absorption is also shown.

halides [32]. Although to date unobserved in Al_2O_3 , a band due to small aluminium colloids has been predicted at between 4.59 and 5.64 eV [33–35]. To check this the three spectra have been fitted using the Mie theory for small colloids for the 5 eV absorption [36], and a Gaussian form for the 6.4 eV band, as shown in Fig. 6, and Tables 1 and 2. The parameters obtained for the 5 eV band correspond to aluminium colloids of about 1 nm in diameter with a total volumetric concentration of approximately 2.4×10^{-6} (see Table 1). This is consistent with the

estimated displacement damage on the oxygen sublattice ($2 \times 10^{-5} \text{ dpa}$). The parameters for the associated band (6.4 eV, 0.64 eV FWHH, see Table 2) agree very well with the high energy component of the F^+ center [37], i.e. an anion (oxygen) vacancy, the colloid solute. The fact that in this case the other components of the F^+ -center at 4.84 and 5.41 eV are not resolved is consistent with results obtained from ion irradiations in which the relative strength of the F^+ center components was observed to vary with the damage concentration [38]. With this observation of an

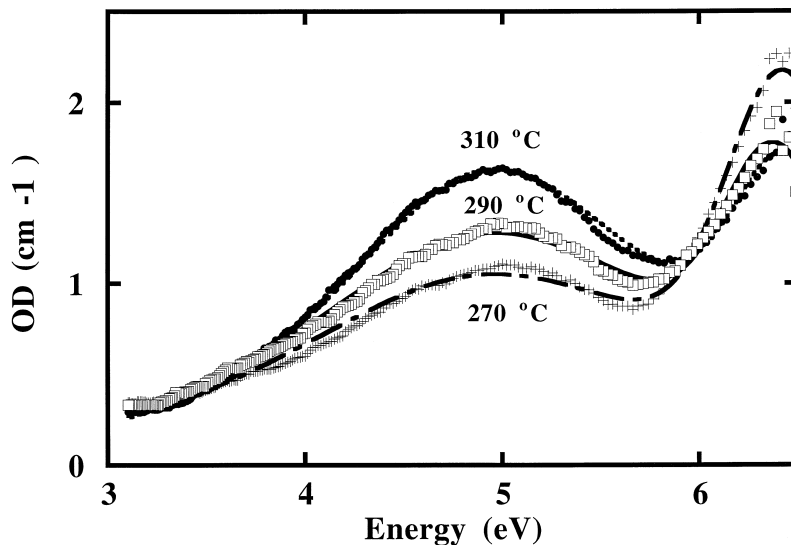


Fig. 6. Optical absorption for a sample irradiated at a nominal temperature of 270°C , 14000 Gy s^{-1} and $2 \times 10^{-9} \text{ dpa s}^{-1}$. The experimental points and the fitted curves are shown. The numerical values obtained from the fits are given in Tables 1 and 2.

Table 1
Colloid radius and volume fraction obtained from fits to the 5 eV band shown in Fig. 6

Temperature (°C)	R_c (nm)	NV (10^{-6})
270	0.487 ± 0.005	2.20 ± 0.02
290	0.534 ± 0.003	2.45 ± 0.01
310	0.653 ± 0.002	2.60 ± 0.01

Table 2
Positions and widths obtained from fits to the 6.4 eV band shown in Fig. 6

Temperature (°C)	Peak position (eV)	FWHM (eV)	Height (OD/cm)
270	6.43 ± 0.01	0.66 ± 0.02	1.60 ± 0.01
290	6.39 ± 0.01	0.62 ± 0.02	1.12 ± 0.01
310	6.45 ± 0.01	0.64 ± 0.02	1.07 ± 0.01

absorption band consistent with the presence of aluminium colloids, the results obtained at the lower dose rate (Fig. 5) were re-examined considering the possibility that the observed underlying absorption could be due to small (sub-nm) colloids. Wide colloid absorption (extinction) bands due to such small colloids are both predicted by theory and observed experimentally in the alkali halides [32,39]. With this assumption the absorption spectrum (Fig. 5) was fitted. The parameters obtained for the underlying colloid band give a colloid radius of about 0.15 nm and a volume fraction of 3.7×10^{-6} . The parameters for the oxygen vacancy centers are given in Table 3. The underlying broad absorption shown in the figure corresponds to a

Table 3
Positions and widths obtained from the gaussian band fit shown in Fig. 7

Defect	Peak position (eV)	FWHM (eV)	Height (OD/cm)		
F	6.05 ± 0.01	0.51 ± 0.01	0.324 ± 0.004		
F ⁺	4.83 ± 0.01	0.49 ± 0.02	0.189 ± 0.003		
F ⁺	5.45 ± 0.01	0.47 ± 0.04	0.154 ± 0.004		
F ₂	4.14 ± 0.01	0.49 ± 0.01	0.074 ± 0.001		
F ₂	3.77 ± 0.02	0.23 ± 0.01	0.048 ± 0.003		
F ₂	3.52 ± 0.02 </tr <tr> <td>F₂</td> <td>3.32 ± 0.03</td> <td>0.31 ± 0.05</td> <td>0.009 ± 0.002</td> </tr>	F ₂	3.32 ± 0.03	0.31 ± 0.05	0.009 ± 0.002
F ₂	3.32 ± 0.03	0.31 ± 0.05	0.009 ± 0.002		

colloid diameter of about 0.3 nm, i.e. a structure containing only four or five atoms. On subtraction of this broad band the remaining spectrum is fitted almost perfectly by the well known F, F⁺, and F₂ oxygen vacancy bands, as may be seen in Fig. 7.

4. Discussion

The results obtained in these experiments indicate that when Al₂O₃ in the form of sapphire is electron irradiated with an electric field applied at and above about 270°C, a sequential process of aggregation involving oxygen vacancies takes place, which leads to the formation of aluminium colloids in a way exactly analogous to the well established process in the alkali halides [40,41]. This is the first time that aluminium colloids have been observed optically in Al₂O₃, although the absorption band has been predicted theoretically [33–35] and their formation has

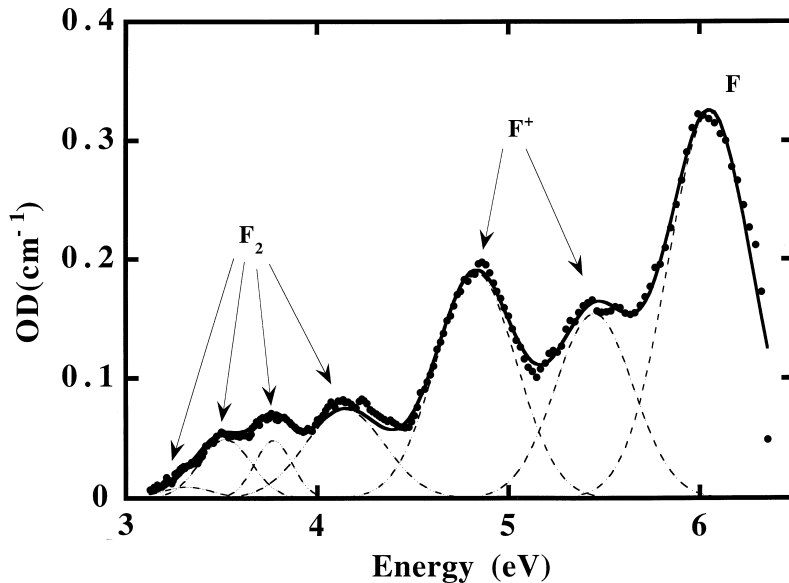


Fig. 7. The same spectrum shown in Fig. 5 with a colloidal background subtracted. The experimental points together with the different Gaussian bands used in the fit are shown. The values obtained from the colloid and Gaussian fits are given in Table 3 and in the text.

been identified during HVTEM irradiation [42,43]. It is important to point out two things. Firstly, the sequence of events leading to colloid production, i.e. enhanced F^+ and F_2 production, has only been observed in samples irradiated with an electric field applied. This is consistent with the HVTEM observations where large electric fields are known to be produced by the intense local electron beam. Secondly, these defects correspond to well known bulk defects, indicating that definite volume degradation is taking place.

It has been suggested that anion vacancy aggregation is unlikely to occur in Al_2O_3 at low temperatures [44] due to the high activation energy for mobility of the vacancies. This is clearly not the case as F_2 formation has been observed. However, this is in agreement with the extensive data for the alkali halides in particular NaCl where a marked reduction in the activation energy of the anion vacancies during irradiation causes vacancy aggregation and colloid production to occur as low as $\sim 90^\circ C$ [39–41].

The identification of colloid production under conditions known to produce RIED in electron irradiated sapphire is consistent with the observed similarity between RIED and colloid production in the alkali halides. Furthermore it helps to explain the formation of gamma-alumina recently identified in RIED degraded samples [20]. The production of oxygen vacancy aggregates will cause a local excess of oxygen in the form of interstitials, and the collapse of the aluminium ions to form metallic precipitates (colloids) will cause a similar deficiency of aluminium ions. These two processes provide the right conditions for the formation of a local gamma-alumina lattice within the main alpha-alumina lattice, i.e. an excess of oxygen and/or a deficiency of aluminium [45,46]. Theoretical work is now being carried out on the effect of small colloids together with gamma alumina on the electrical properties of sapphire in an attempt to explain in detail the degradation of the electrical conductivity of alumina (RIED). Initial results to be published indicate that the degradation of the electrical conductivity activation energy observed in various RIED experiments can be described, and that the vacancy aggregation process may be a precursor to RIED.

RIED like effects have also been observed in other insulators (MgO , BeO , $MgAl_2O_4$, AlN), however at the present time data is very limited and while similarities are noted with RIED in alumina, it is not known whether the degradation process is similar. Optical observations in at least some of these materials should help provide further information.

5. Conclusions

The results presented in this paper show that when high purity single crystal alumina (sapphire) is electron irradiated with an electric field applied, a process of oxygen

vacancy aggregation takes place which leads to the formation of aluminium colloids within the lattice. These results, together with the earlier observation of local gamma-alumina regions within RIED degraded sapphire, are now being examined as a possible precursor to the electrical degradation.

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