

## MICROSTRUCTURE OF $\text{Al}_2\text{O}_3$ IRRADIATED WITH AN APPLIED ELECTRIC FIELD - S. J. Zinkle, J.D. Hunn, and R.E. Stoller (Oak Ridge National Laboratory)

### OBJECTIVE

The objective of this study is to examine possible physical causes of permanent radiation-induced electrical degradation in ceramic insulators that are irradiated with an applied electric field.

### SUMMARY

A thin amorphous film of alumina was irradiated with 2-MeV  $\text{He}^+$  ions at  $\sim 400^\circ\text{C}$  up to a damage level of about 0.01 displacements per atom (dpa). The alumina films were sufficiently thin ( $\sim 1.8 \mu\text{m}$ ) to allow the ion beam to be completely transmitted through the specimen. An electric field of  $\sim 280 \text{ V/mm}$  (dc) was applied continuously during the irradiation. Radiation induced electrical degradation (RIED), i.e. a permanent increase in the conductance of the film, was observed in specimens irradiated at temperatures near  $400$  to  $450^\circ\text{C}$  but did not occur in a specimen irradiated above  $500^\circ\text{C}$ . An investigation by transmission electron microscopy found no evidence for colloid formation. The observed increase in the conductance of the alumina film may be due to radiation-induced microcracking.

### PROGRESS AND STATUS

#### Introduction

Ceramic insulators are used in magnetic fusion energy components for heating, control and diagnostic measurement of the plasma, and in nuclear thermionic devices under development for space propulsion. The electrical conductivity of the insulator must remain less than  $10^{-4} \text{ S/m}$  during exposure to a radiation field for the proper operation of most of these components [1]. There is a large data base on the electrical conductivity of irradiated ceramics [1,2]. It is generally observed that the prompt radiation induced conductivity (RIC) of insulators such as  $\text{Al}_2\text{O}_3$  is proportional to the ionizing radiation dose rate, with a typical room temperature conductivity of  $\sim 10^{-6} \text{ S/m}$  at a dose rate of  $10^4 \text{ Gy/s}$ . The RIC disappears promptly when the radiation source is turned off (typical prompt lifetime  $\sim 10^{-9} \text{ s}$ ).

Several recent studies have reported that ceramic insulators may suffer a dramatic permanent loss in their electrical resistivity if they are irradiated at moderate temperatures while an electric field is applied [1-10]. This radiation induced electrical degradation (RIED) has been reported to occur in  $\text{Al}_2\text{O}_3$  and other oxide ceramics following irradiation at relatively low displacement damage doses of 0.0001 to 0.1 displacements per atom (dpa) in the presence of an electric field  $> 50 \text{ V/mm}$  at temperatures between  $\sim 300$  to  $600^\circ\text{C}$ . The physical mechanisms responsible for this phenomenon have not yet been identified, due in part to a lack of microstructural analysis following electrical degradation. It was originally suggested that colloid formation (small metallic precipitates) may be responsible for RIED [5,6]. This suggestion was based on optical microscope observations and the similarity between the temperature dependence of RIED and colloid formation in alkali halides. However, colloid formation was not observed in a recent postirradiation transmission electron microscope (TEM) examination of electrically degraded  $\text{Al}_2\text{O}_3$  [9]. A recent spallation neutron irradiation experiment failed to find any evidence for RIED in alumina [11] and furthermore, several recent studies have questioned whether RIED may be an artifact associated with surface contamination by hydrocarbons [11-13]. Recent reviews of this emerging field of study have shown that the electrical degradation reported by different investigators cannot be correlated according to displacement damage or ionizing radiation dose, although it was noted that some of these discrepancies may be due to differences in the materials that were studied [2,14].

One objective of the present study was to verify that RIED occurs in thin films of ceramic insulators during ion irradiation at high vacuum conditions where surface contamination is not significant. Cross-section transmission electron microscopy was used to investigate possible microstructural origins of RIED in an electrically degraded alumina specimen.

## Experimental Procedure

An alumina film of thickness 1.8  $\mu\text{m}$  was rf-sputtered from a hot pressed  $\text{Al}_2\text{O}_3$  target onto a polished tantalum substrate using a planar magnetron in an Ar atmosphere of  $2 \times 10^{-3}$  torr [15]. This produced a dense film which was determined to be amorphous from Rutherford backscattering spectroscopy (RBS), electron diffraction and high resolution TEM analysis. The deposited film was determined to be stoichiometric and of uniform thickness by RBS analysis (within the experimental accuracy of  $\sim 10\%$ ). Tantalum was chosen as the substrate material due to its close match with alumina's coefficient of thermal expansion. This minimized tendencies for the film to crack or delaminate during thermal cycling. Platinum electrodes of 10 nm thickness were evaporated in a guard ring configuration on the surface of the alumina film. A center electrode of 3.1 mm diameter was surrounded by a concentric guard ring electrode with an inner diameter of 5.6 mm.

The target chamber used to measure the in-situ DC electrical conductivity of the alumina thin films is described in detail elsewhere [15]. The target chamber was enclosed within an electrically isolated thin Mo box which provided electrical suppression and also acted as a thermal radiation shield. The sample temperature was measured by a type K thermocouple that was placed on the guard ring electrode in a region that was exposed to the ion beam, in order to include beam heating effects. The Ta/ $\text{Al}_2\text{O}_3$  sample was mounted on a massive nickel block that contained resistive heater cartridges for controlling the temperature. Spring contact was made to the center electrode by a 250  $\mu\text{m}$  Mo wire. The outer periphery of the sample was covered by a Mo ring (9.5 mm inner diameter), which clamped the sample to the nickel block and provided electrical contact to the Pt guard electrode. The Mo ring shielded most of the guard electrode from the ion beam, but allowed the ion beam to strike the center electrode and part of the guard electrode. The back electrode (the Ta substrate) was in electrical contact with the nickel block. The entire experimental assembly was electrically shielded by a stainless steel vacuum chamber which was held at ground potential.

The conductivity measurements utilized a three electrode guarded configuration [15]. Voltage was applied and current was measured using a Keithley 617 electrometer. The voltage applied during the irradiation was 0.5 V, which corresponds to an electric field of 280 V/mm. The measured current at 20°C for an applied voltage of 0.5 V in the absence of irradiation was  $< 10^{-13}$  A (corresponding resistivity  $> 2 \times 10^{13}$   $\Omega\text{-m}$ ), which is near the resolution limit for our measuring system. Typical RIC currents under ion irradiation at 400°C were  $\sim 10^{-6}$  A. The current was periodically measured as a function of the applied voltage (-0.5 V to +0.5 V) in order to verify ohmic behavior.

Initial experiments on several specimens not analyzed by TEM showed that RIED occurred during He ion irradiation at 407°C with an applied electric field of  $\sim 300$  V/mm, but RIED did not occur in specimens irradiated without an electric field at 407°C or in specimens irradiated at 530°C [15]. The alumina film for the present study was irradiated at 400°C with 2-MeV  $\text{He}^+$  ions at a flux of 450 nA/cm<sup>2</sup> in the triple ion beam Van de Graaff accelerator facility at ORNL [16]. This produced a calculated [17] ionizing and displacement damage dose rate of 0.6 MGy/s and  $5 \times 10^{-7}$  dpa/s, respectively (an average displacement energy of 40 eV was assumed for the dpa calculation). The alumina thickness of 1.8  $\mu\text{m}$  allowed the radiation dose rate to be constant within  $\pm 10\%$  between the front and back surface of the ceramic, and ensured that all of the ions were transmitted through the specimen. The pressure was  $< 10^{-7}$  torr during the irradiation. Following irradiation the specimens were prepared for cross-section TEM examination using standard techniques [18], and were examined in a Philips CM-12 electron microscope (120 keV operating voltage) equipped with an EDAX 9900 energy dispersive X-ray spectrometer (EDS). Separate specimens corresponding to the center electrode, gap, and guard ring (unirradiated) regions were examined.

## Results and Discussion

The specimen was slowly heated to 400°C in the target chamber, and the electrical resistance was monitored with an applied electric field of 280 V/mm for 30 minutes prior to the start of the irradiation. A slight decrease ( $\sim 10\%$ ) in the film resistance was observed during the 30 minute anneal, indicating the presence of some imperfections in the alumina film (Fig. 1). The alumina resistance began to immediately

MICROSTRUCTURE OF UNIRRADIATED  $\text{Al}_2\text{O}_3$  FILM  
EXPOSED TO  $400^\circ\text{C}$  AND A DC ELECTRIC FIELD OF  $260 \text{ V/mm}$

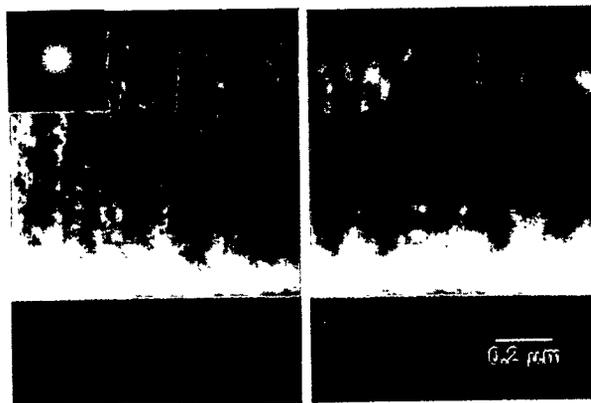


Fig. 1. Decrease in the resistance of the alumina film during annealing and irradiation at  $400^\circ\text{C}$  with an applied electric field of  $280 \text{ V/mm}$ .

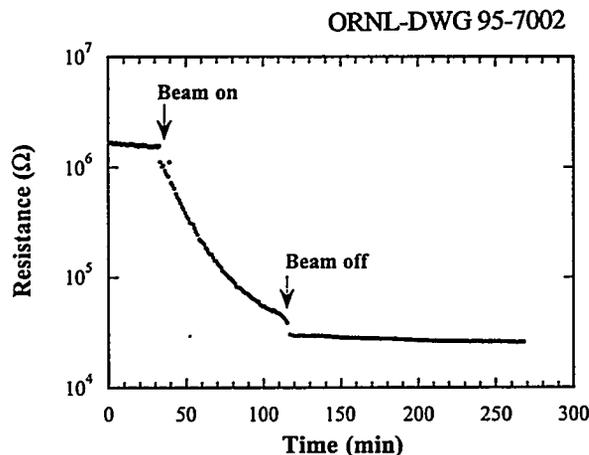


Fig. 2. Microstructure of unirradiated alumina film exposed to  $400^\circ\text{C}$  and a DC electric field of  $280 \text{ V/mm}$ . The left and right photos are underfocussed and overfocussed micrographs, respectively.

decrease at a rapid rate when the specimen was exposed to the  $2 \text{ MeV}$  He ion beam. The initial RIC in the alumina film at  $400^\circ\text{C}$  associated with the ionizing dose rate of  $0.6 \text{ MGy/s}$  was  $\sim 2 \times 10^{-7} \text{ S/m}$  ( $1.2 \text{ M}\Omega$  resistance), which was somewhat lower than published [2,15] RIC data obtained for bulk crystalline alumina specimens of  $10^{-6}$  to  $10^{-5} \text{ S/m}$ . As discussed elsewhere [15], this discrepancy is most likely due to the higher electron trap density in the amorphous film compared to crystalline specimens.

The specimen was irradiated for 85 minutes at  $400^\circ\text{C}$  with an applied electric field of  $280 \text{ V/mm}$ , which produced a cumulative damage level of  $0.0025 \text{ dpa}$ . The measured resistivity of the alumina film decreased dramatically during the irradiation to a value of  $1.2 \times 10^5 \Omega\text{-m}$  after  $0.0025 \text{ dpa}$ . Following the irradiation, the resistance of the film at  $400^\circ\text{C}$  was monitored for an additional 150 minutes with an applied dc electric field of  $280 \text{ V/mm}$ . A slight ( $\sim 10\%$ ) decrease in the film resistance was observed during this postirradiation anneal (Fig. 1). The room temperature resistance between the center and guard electrode was

$> 10^{12} \Omega$  following the irradiation, which shows that the measured resistance decrease in the center irradiated area cannot be attributed to surface contamination in the gap region. In addition, the high resistance in the gap region of the alumina film (which was not exposed to an electric field) provides further support for the original observation [3,4] that RIED requires the simultaneous application of an electric field and irradiation. The resistance between the guard and back electrodes decreased following irradiation in a manner similar to that observed for the center electrode. This may be due to the fact that part of the guard ring region was exposed to the ion beam, and hence would be subject to RIED similar to the center electrode region.

Figure 2 shows the typical microstructure of the alumina film in the guard ring region, which was exposed to the electric field and temperature but was not irradiated. The inset electron diffraction micrograph shows the apparent amorphous condition of the film. Small cavities were observed at the interface between the alumina film and the Ta substrate. The most significant microstructural feature in the alumina film was a moderate density of cavities that were elongated in the direction perpendicular to the Ta interface (i.e., along the electric field direction). A small amount of Ar ( $<1\%$ ) was detected in the alumina film by EDS, which may be associated with trapped argon from the sputter deposition process. The elongated cavities were also observed in the gap and center irradiated regions of the alumina film. Since the resistance of the gap region was relatively high, the elongated cavities and trapped argon apparently do not have a deleterious effect on the alumina film resistivity. Additional tests (including a RIED experiment where the guard ring is completely shielded from the irradiating beam) are needed to confirm this finding.

Figure 3 shows the typical microstructure of the alumina film from the center electrode region, which was exposed to temperature, electric field and irradiation. The microstructure of the center, gap and guard ring regions of the alumina film were generally found to be very similar. There was no evidence of colloid formation in the center irradiated region. Colloids larger than  $\sim 5$  nm diameter would have been easily detectable by the TEM observation.

Detailed examination of the center irradiated region of the alumina film revealed several isolated defect structures which were not observed in less detailed studies of the gap and guard electrode regions. A large cavity ( $\sim 0.1 \mu\text{m}$ ) was observed at the interface between the alumina film and Ta substrate in the center electrode region. However, since the size of this cavity was much less than the film thickness of  $1.8 \mu\text{m}$  it does not seem likely that it could be responsible for the observed RIED. A more plausible heterogeneous cause of the RIED in the center irradiated region is microcracking. Figure 4 shows a crack in the irradiated alumina film extending perpendicular to the Ta interface. Although it cannot be ruled out that the crack formation may have occurred during post-irradiation specimen preparation, this crack is the only significant microstructural difference observed so far between the electrically degraded center region and the insulating gap and guard ring regions of the alumina film.

A simple calculation demonstrates that microcracking could easily account for the large loss in electrical resistance in the center irradiated region of the alumina film. First, it is assumed that the total crack length (either one large crack or a number of small microcracks) completely penetrating the thin alumina film is  $\sim 1$  mm.

ORNL-PHOTO 10132-94

TYPICAL MICROSTRUCTURE OF IRRADIATED  $\text{Al}_2\text{O}_3$  FILM EXPOSED TO  $400^\circ\text{C}$  AND A DC ELECTRIC FIELD OF  $260 \text{ V/mm}$



Fig. 3. Typical microstructure of center irradiated region of the alumina film.

**CRACK OBSERVED IN THE IRRADIATED  $\text{Al}_2\text{O}_3$  FILM  
EXPOSED TO 400°C AND A DC ELECTRIC FIELD OF 260 V/mm**

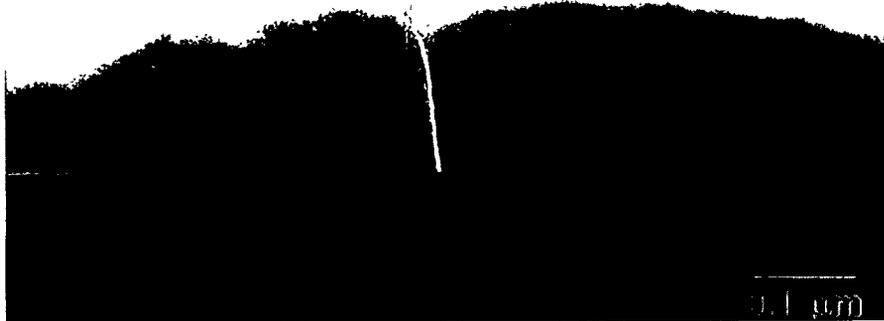


Fig. 4. Crack observed in center irradiated region of the alumina film.

This assumption would be consistent with the TEM observation of only one crack in the center irradiated region of the specimen (a total length of  $\sim 0.5$  mm along the irradiated Ta/alumina interface was examined by cross-section TEM). Second, it is assumed that radiation- and electric field-enhanced diffusion at a temperature of 400°C would eventually produce a monolayer coverage of Ta or Pt (the two electrode materials in this study) along the crack surface. For simplicity, surface scattering effects associated with the monolayer conducting film are ignored and the bulk resistivity of Ta and Pt ( $\sim 10^{-7}$   $\Omega\cdot\text{m}$ ) is used for the purposes of this simple calculation (Surface scattering could reduce the conductance of such a thin film by perhaps an order of magnitude). The total resistance associated with this 1 mm crack containing a monolayer of conducting electrode material would be only  $\sim 1$   $\Omega$  ( $0.2$   $\Omega\cdot\text{m}$ ), which is more than six orders of magnitude smaller than the initial resistance of the alumina film at 400°C and more than four orders of magnitude smaller than the measured resistance of the electrically degraded film (Fig. 1). Therefore, even partial coverage of the 1 mm crack surface by electrode material or else complete monolayer coverage of a crack only  $\sim 1$   $\mu\text{m}$  long would be sufficient to explain the RIED results in Fig. 1. It is apparent from this simple calculation that a few small cracks can produce a dramatic decrease in the resistance of insulators due to the low resistivity of the electrode material.

A recent study of RIED in a polycrystalline  $\text{Al}_2\text{O}_3$  specimen (produced by anodizing aluminum) found that the electrical degradation was due to radiation enhanced diffusion of the gold electrode material along the grain boundaries [19]. This mechanism for RIED is very similar to the present microcracking proposal. Another recent study suggested that the permanent electrical degradation in a single crystal alumina specimen was associated with an increased dislocation density [9]. However, it is not clear that the observed dislocation density of  $\sim 10^{13}/\text{m}^2$  in the electrically degraded specimen could account for the RIED without invoking diffusion of the electrode material. The present results are in agreement with another recent TEM study [9] that RIED in alumina is not associated with colloid formation.

Several studies have shown that large inhomogeneous electric fields can be induced in insulators during irradiation due to trapped space charge [20-27]. These studies suggest that the localized field is typically significantly different from the applied electric field and can exceed the dielectric breakdown strength of  $>10^7$  V/m in many cases [23,27]. Localized dielectric breakdown could produce microcracking and could eventually lead to significant permanent degradation of the electrical resistivity, particularly if electrode material diffused along the microcracks. Since the inhomogeneous electric fields in irradiated insulators are sensitive to numerous experimental parameters such as dose rate and chemical impurities, this proposed mechanism could explain why the RIED results obtained by different researchers on different grades of alumina are inconsistent with respect to displacement damage or ionizing radiation dose [2,14]. Further microstructural examination of polycrystal and single crystal RIED specimens is needed to confirm if microcracking is generally responsible for the electrical degradation in ceramic insulators. Radiation-induced microcracking would have severe consequences for electrical insulators in most fusion energy or nuclear thermionic applications since the surfaces of the insulator are typically in contact with highly conducting metallic materials.

## Conclusions

Radiation induced electrical degradation was confirmed to occur in an amorphous alumina film under conditions where surface contamination effects could not have compromised the measurements. Microstructural examination of the electrically degraded alumina film suggests that the RIED is associated with radiation-induced microcracking due to inhomogeneous internal electric fields. Colloid formation was not responsible for the electrical degradation.

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