Search for radiation-induced electrical degradation in ion irradiated sapphire and polycrystalline Al_2O_3

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An international discussion is being carried out on whether radiation-induced electrical degradation in ceramic insulators does or does not exist. In the present experiments on radiation-induced conductivity and radiation-induced electrical degradation in high purity polycrystalline Al_2O_3 and sapphire all interfering effects resulting from surface conductances have been eliminated. The results have not confirmed a permanent degradation of the volume conductivity. Radiation-induced conductivity values were observed to decrease with dose. A transient in the electrical conductivity after ion beam off was discovered.
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I. INTRODUCTION

As a result of irradiation, permanent losses in electrical resistivity of ceramic insulators by up to ten orders of magnitude have been observed. Such a decline of the insulating properties of oxide ceramics would be of severe consequences for fusion reactor design. The effect has been called radiation-induced electrical degradation (RIED). It had been observed after electron, ion, and neutron irradiation.[1–8] However, later the question was raised whether RIED may be an artefact only.[9] Many articles on RIED have since been published,[10–36] and a dispute is still continuing on whether RIED does exist or not. Reviews on the phenomenon of RIED, on the irradiation conditions where RIED should occur, and on the distinction of RIED (permanent conductivity increase) from radiation-induced conductivity (RIC) (transient conductivity increase) are found in Refs. 37–40.

As a compromise between the contradicting results it has been suggested that RIED might possibly exist in certain grades of Al_2O_3, and not in others. The present experiments in search for RIED have been carried out in order to clarify the suggested dependence on impurity atom content and on the possible influence of grain boundaries apparent from the different behaviors of single crystals and polycrystals.[40]

II. EXPERIMENTAL DETAILS

The specimen materials were an ⟨0001⟩ oriented single crystal and a Vitox-type (Deranox grade) polycrystal of Al_2O_3. The chemical composition is given in Table I (together with the composition of Rubalit and Wesgo-type alumina from previous RIED investigations). Specimens of 7.5 $\times$7.5 mm^2 area and 0.16$\pm$0.02 mm thickness were prepared from both materials. A circular electrode of 5 mm diam surrounded by a concentric ring (about 0.7 mm distance from the center electrode) as guard electrode, both consisting of subsequent Ti and Au layers, were sputter deposited onto the front side of each specimen. The back sides were soldered to metallic holders of alloy Vacon70.[22] No microcracks were detected while scanning the specimens in a scanning electron microscope equipped with field emitting electron source.[41] The specimen temperature was controlled via a thermocouple inserted into the holder 1 mm below the specimen. The specimens were irradiated in vacuum of between 5 $\times 10^{-7}$ and 2×10^{-6} Torr by 28 MeV alpha particles which have a range of about 210 μm in Al_2O_3. Further details on the specimen preparation and irradiation conditions can be found in Refs. 22 and 41.

Periodically during the irradiations, the volume conductivity of the specimens was measured with beam off (σ_P), in search for RIED, and with beam on (σ_i), for investigation of RIC (σ_{RIC}), where $\sigma_i = \sigma_P + \sigma_{RIC}$. The conductivity with beam off, σ_P, was always measured 4 min after the irradiation source had been turned off. Both measured conductivities in both materials revealed an almost linear (i.e., ohmic) behavior as a function of applied voltage between -50 and $+50$ V. A suppressor voltage of -50 V between target and beam aperture was used to eliminate erroneous secondary electron contributions in σ_{RIC}. For consistent three terminal guarding, triaxial cables and triaxial feedthroughs out of the irradiation chamber have been used.

III. RESULTS

The sapphire specimen was irradiated at 450$\pm$10 °C in an electric field of 280 V/mm with α-particle current density of 0.07 A/m^2 (corresponding to dose rates of 4.8 $\times 10^{-7}$ dpa/s and 8.7×10^5 Gy/s, after TRIM89 assuming a sublattice-averaged displacement energy of 40 eV) up to a final dose of 0.030 dpa. In Fig. 1 the electrical conductivity σ_i, which is practically identical to σ_{RIC}, is shown as a function of dose. The value at half the final dose is 5 $\times 10^{-7}$ S/m. A decrease by a factor of 3 during a dose increase by one order of magnitude has been observed. Higher RIC values than in Fig. 1 have been measured at lower doses. They were not included, however, because of their

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TABLE I. Chemical composition (in wppm) of Al_2O_3 grades: Wesgo Al-995, Hoechst Rubalit 710, Vitox (Deranox), and sapphire by Commercial Crystal Laboratories (CCL).

	Wesgo	Rubalit	Vitox	CCL Single crystal
B	<30	<30	<17	⋯
Ba	22±6	30±8	1.3	⋯
Ca	480±50	270±30	<10	⋯
Cu	<15	<15	⋯	⋯
Fe	500±70	250±50	<21	<21
Li	20±10	<10	<5	⋯
Mg	2000±300	2200±300	225	8.3
Mn	<10	<10	⋯	⋯
Na	350±100	100±40	<25	⋯
Ni	<30	<30	⋯	3
Si	1400±170	1100±150	150	65
Ti	80±20	25±10	⋯	⋯
Zn	10±3	16±4	⋯	⋯
Zr	40±20	45±20	2	4.8
Pb	⋯	⋯	⋯	5.0
	~5000	~4000	~500	~100

uncertainty from insufficient times of electrification (see below). In RIC, which originates from the formation of electron–hole pairs under ionizing irradiation, decreases with irradiation dose are caused by the creation of charge carrier traps and recombination centers.[42,43]

The measured preirradiation conductivity σ_0 at 450 °C was $2.0\times10^{-13}\,\mathrm{S\,m^{-1}}$. The conductivity during the irradiation σ_P, measured with beam off at 450 °C, is shown in Fig. 2 as a function of dose. The values are significantly higher than σ_0 due to the following effect. Polarization or space charge buildup close to the electrodes caused the measured electrical conductivities to pass through transients whenever the voltage was altered in discrete steps. Stationary conductivity was always reached, however, within the present electrification times of 4 min. A transient in conductivity, however, was observed to occur also after the irradiation beam was turned off. The transient was observed to be dose rate (linear increase) and dose dependent (decreasing with dose) in almost the same way as the RIC.

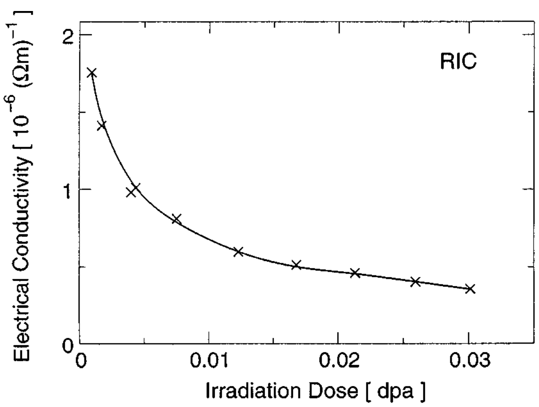

FIG. 1. Radiation-induced conductivity of single crystalline Al_2O_3 (measured with ion beam on) at 450 °C as a function of displacement dose.

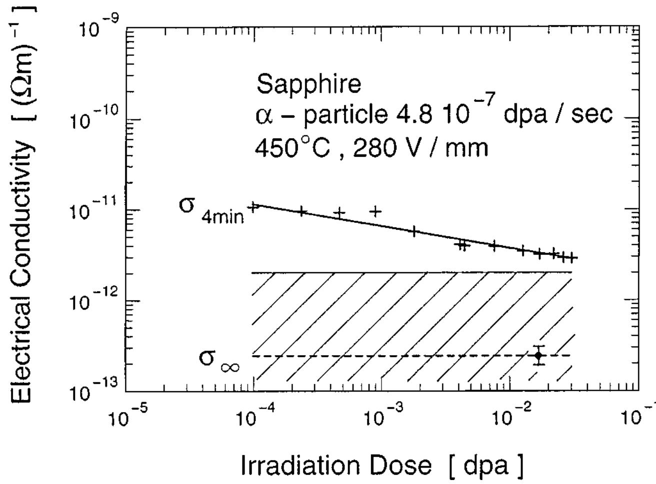

FIG. 2. Electrical conductivity of single crystalline Al_2O_3 (measured with ion beam off) as a function of displacement dose. The measured values ($\sigma_{4\mathrm{min}}$) are raised above the steady state conductivity (σ_∞) owing to insufficient time of electrification.

The corresponding time dependence was measured during an intermission of the irradiation (at 1.7×10^{-2} dpa) as shown in Fig. 3. Two hours after beam off the current had not yet reached its stationary value, but was approaching the preirradiation value. That σ_P values in Fig. 2 are larger than σ_0 is mainly an effect of the time of electrification. (To use electrification times of several hours, however, through the irradiation experiment was impracticable.) The estimated extrapolation to stationary conductivity values (basing on the observed dose dependence and the long-time measurement at 1.7×10^{-2} dpa) is indicated in Fig. 2 by σ_∞. That the transient effect is observed here for the first time, is possibly due to the present high measuring accuracy in combination with the low conductivity value of the single crystal material.

In Fig. 2 an error bar is included for the σ_∞ value at 1.7×10^{-2} dpa. For the remaining dose region a range of uncertainty (shaded) is included which is estimated from extrapolations measured between 1 and 20 min electrification times. The preirradiation conductivity value agrees with the value at 1.7×10^{-2} dpa within the error bar of 5

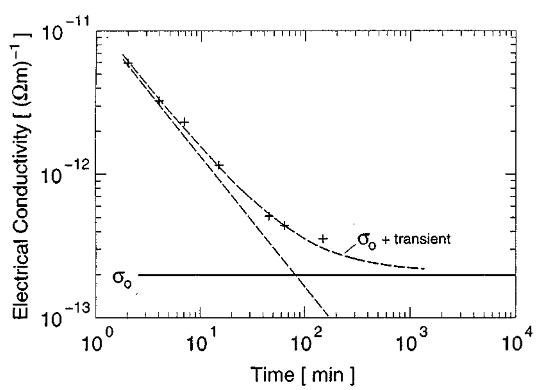

FIG. 3. Electrical conductivity of the single crystal specimen measured at 1.7×10^{-2} dpa as a function of time after beam off. After the common electrification time of 4 min the transient conductivity is still one order of magnitude higher than the asymptotic value σ_0.

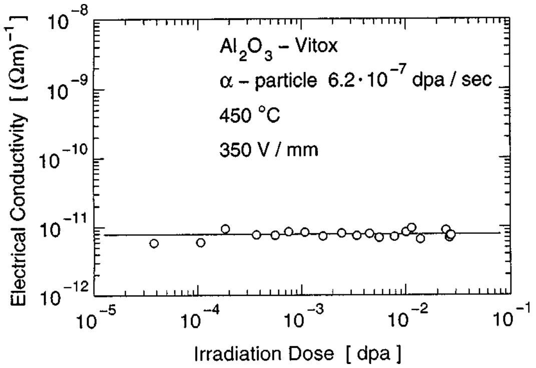

FIG. 4. Electrical conductivity of polycrystalline Al_2O_3 (measured with ion beam off) as a function of displacement dose.

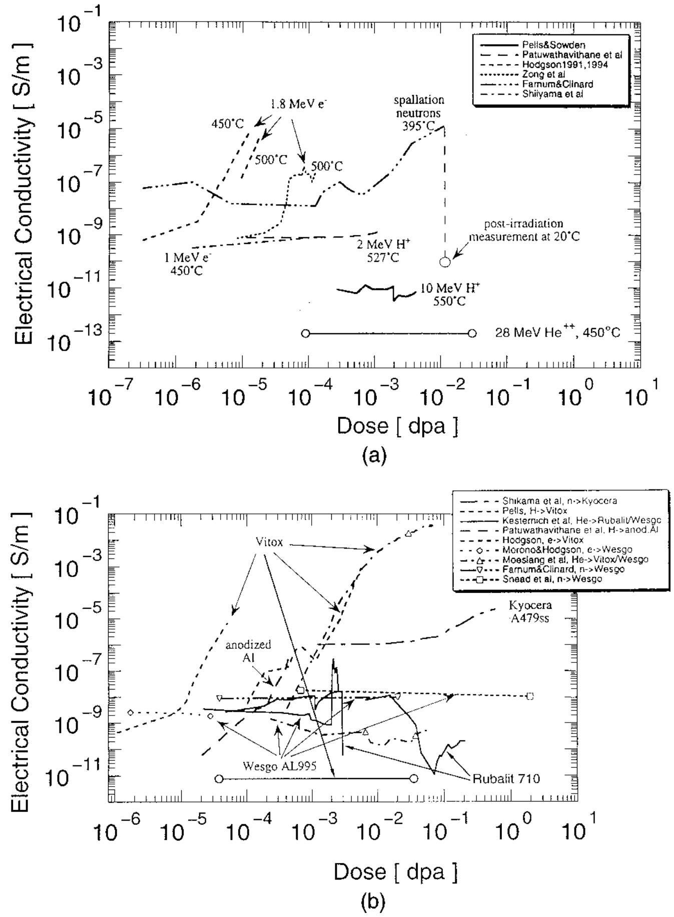

FIG. 5. RIED measurements on (a) single crystalline (Refs. 2, 11, 13, 17, 20, 29, 31) and (b) polycrystalline (Refs. 7, 8, 11, 17, 22, 25, 28, 29, 30) grades of α- Al_2O_3 as summarized in Ref. 40 with the present results (o—o) added.

$\times 10^{-14}$ S/m. Thus no RIED was observed within this error margin up to a dose of 1.7×10^{-2} dpa and within an error margin of 2×10^{-12} S/m up to the dose of 3×10^{-2} dpa.

The polycrystalline specimen was irradiated at 450 $\pm$20 °C in an electric field of 350 V/mm with a dose rate of 6.2×10^{-7} dpa/s (1.13×10^{6} Gy/s) up to a final dose of 2.6 $\times 10^{-2}$ dpa. The σ_{RIC} value at half the final dose was 3.1 $\times 10^{-7}$ S/m. In Fig. 4 σ_P, measured 4 min after beam off, is shown as a function of dose. The electrical conductivity was approximately 7.6×10^{-12} S/m, independent of irradiation dose. The same value was also measured before irradiation. The transient conductivity after beam off was small in the polycrystalline specimen and thus difficult to observe due to the higher intrinsic conductivity of the polycrystal than of the single crystal. As revealed in Fig. 4, again no RIED was observed.

In both irradiation experiments surface resistance values between guard and center electrode R_{PG} and between guard and back electrode R_G were periodically measured and were found to be always $>2\ G\Omega$, and the contact resistances to the guard electrode R_{cG} remained at their initial values of about 4 Ω during both irradiations. Thus the error due to surface leakage conductance, given by $\Delta\sigma/\sigma = R_P R_{cG}/R_{PG} R_G$,[22] where R_P is the volume resistance of the specimen, was always below 10^{-5}. This means that for the first time in our RIED studies,[9,22,23,41] surface leakage conductances could be kept lower than the volume conductance during the whole course of the irradiations. The achievement of an improved accuracy of the bulk conductivity measurement under the restricting conditions of an irradiation experiment were the result of a number of special efforts: (1) using a turbomolecular pump with oil-free magnetic bearings at the specimen chamber (diminishing hydrocarbon contaminants) and irradiating only the specimen area in the region of the center electrode (limiting radiation-enhanced contamination effects), and (2) susceptibility of crack formation was reduced by a thick and soft soldering foil as compliant layer (low temperature dislocation mobility) used between the specimen having a polished surface (in order to avoid stress concentration at surface grooves) and the specimen holder consisting of Vacon70 (for minimization of differential thermal stresses).

IV. DISCUSSION AND CONCLUSIONS

A strong transient electrical conductivity was observed in the single crystal as a result of changes in ion beam intensity. The transient appeared to scale with RIC in dose and dose rate dependence. It is assumed to be caused by creation and recovery of donors and acceptors during irradiation and by trapping and detrapping at radiation-induced charge carrier traps. The charging and decharging times were very slow in the present single crystalline material.

While our previous experiments in search for RIED have been carried out on polycrystalline specimens with moderate impurity contents, the present results were obtained on a single crystal and a high purity polycrystal (see Table I for impurity contents). Typical preirradiation and postirradiation electrical conductivity values were $\sigma_0 = 6\times 10^{-11}$ S/m in the medium purity Rubalit-type Al_2O_3,[22] $\sigma_0 = 7.6\times 10^{-12}$ S/m in the high purity Vitox, and $\sigma_0 = 2\times 10^{-13}$ S/m in the sapphire (at temperatures of 500, 450, and 450 °C, respectively). These conductivity values increase from single to polycrystal and from low to high impurity content.

Figure 5 shows two graphs on RIED results (differentiating between single crystals and polycrystals) from the review by Kinoshita and Zinkle[40] into which the present data have been added. In both graphs the present conductivity values are the lowest ones. That in RIED experiments the starting ''beam-off'' conductivities are already higher than expected for high to medium purity alumina and sapphire (see Refs. 44 and 45 and present σ_0 values) remains unexplained in most cases (neutron irradiation experiments are excepted, since specimens located inside a nuclear reactor are subject to RIC). This discrepancy points to the difficulties existing in electrical conductivity measurements in Al_2O_3.[45] The difficulties in measuring true conductivity values in highly insulating materials in irradiation environments are further increased and have been described in Refs. 22 and 41. The main difficulty in the present type of experiments are surface leakage conductances (along the specimen surface and through microcracks). Surface leakage currents have been unduly neglected in many previous RIED studies. In response to these difficulties, measurement and report of the surface resistances R_{PG} and R_G and (depending on type of contact) of the contact resistance R_{cG}, which enable the calculation of the surface leakage conductance in electrically guarded experiments,[22] has been demanded for all future RIED experiments at the 1993 International Energy Agency workshop on irradiation effects in ceramics. Nevertheless, only in few experiments (including recent RIED studies) this important rule has been followed. In our previous experiments on RIED, included in Fig. 5(b), the true conductivity was only reached occasionally after special irradiation procedures or heating in air. Finally in the present experiment we have accomplished a true conductivity measurement throughout the whole irradiation experiments, and the numerous precautions to reach this accomplishment have been described in Sec. III.

In addition to the difficulties normally existing in electrical conductivity measurements in Al_2O_3, surface leakage conductances along outer surfaces and through microcracks can be strongly enhanced under irradiation.[9,41] Also the chances of such possible radiation enhancements of conducting contamination layers have not been considered in most RIED experiments. The puzzling variety of measured RIED results as expressed in Figs. 5(a) and 5(b) is possibly a result of leakage conductance and its enhancement under irradiation, and it still remains to be checked whether any of the measured conductance increases represent a true RIED effect. With respect to radiation-enhanced surface conductances, it should be noted that in neutron irradiation not only electrically guarded specimens but also guarded electrical feedthroughs out of the irradiation capsules are essential and need to be carefully controlled, since also the feedthroughs are exposed to the full irradiation power.

The present experiment responds to the proposal that RIED might possibly exist in certain grades of Al_2O_3 (mostly the ones with low impurity contents and preferably the single crystalline ones), while it does not exist in others. Of the grades, on which more than one RIED experiment has been reported (cf. Fig. 5), Wesgo and Rubalit appeared to be free of RIED (within the investigated dose region), while Vitox appeared to reveal strong RIED effects (compare impurity atom listing in Table I). The present experimental result on Vitox Al_2O_3 is in contradiction to this view [see Fig. 5(b)], and also Möslang *et al.* have meanwhile withdrawn their result on Vitox Al_2O_3 after they found, following our suggestion,[23] cracks in their Vitox specimen and after a repeat experiment on Vitox (Deranox grade) Al_2O_3 did not show any sign of RIED.[34]

Regarding single crystal Al_2O_3, Patuwathawithane *et al.* have pointed out[29] that, in contrast to the RIED results by Hodgson, the susceptibility for RIED was higher in their polycrystal than in the single crystal Al_2O_3, that the latter however, was not supporting an intrinsic RIED effect but was caused by increased conductance via radiation-enhanced Au diffusion (from electric contacts) into the grain boundaries. This effect resembles the observation of surface conduction along microcracks[27,41] where the nature of the conducting layers inside the microcracks has not, however, been studied. Also in neutron irradiation experiments no RIED has been found so far in sapphire.[18,33,46] The very low electrical conductivity through the whole dose range of the present sapphire experiment is a further indication that also single crystallinity is not effectively advancing a susceptibility for RIED.

As a possibility, alternative to the effect of impurity content and grain structure, another parameter might be decisive for the existence of RIED, i.e., the type of irradiating particle. None of the many recent ion and neutron irradiation results (see, e.g., neutron irradiation on a large variety of Al_2O_3 grades in Ref. 33) does confirm RIED. Therefore it has to be assumed that the early RIED-like results in ion and neutron irradiations are caused by leakage conductances along outer surfaces or through undiscovered cracks. The situation is less clear in the case of electron irradiations where the existence of RIED is sustained on the basis of a large number of experiments. Several recent electron irradiation experiments have been published.[30–32,35] They do not exhibit RIED, but they have been performed on different Al_2O_3 grades than the various earlier electron irradiation experiments that revealed RIED behavior. These latter experiments need to be repeated with the knowledge which now exists on the danger of leakage conductances in irradiation experiments before the question for RIED can be resolved.

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