Ionizing-irradiation-induced thermally stimulated currents in Al_2O_3:Mg

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The thermally stimulated currents (TSC) processes induced by ultraviolet light and x-ray irradiation at low temperature in oxidized magnesium-doped aluminum oxide single crystals has been studied between 80 and 300 K. It has been found that the main TSC process shows the same behavior as the main thermally stimulated polarization (TSP) process with respect to peak temperature, activation energy, and sample-thickness and thermal-treatment dependences. It is concluded that this TSC process, as it was also the case of the TSP one, arises from the thermally activated ionization of Mg^x_{Al} centers and is due to the existence of blocking contacts at the sample-electrode interfaces. The observed irradiation-induced decrease in the thermally stimulated depolarization (TSD) currents can also be explained in the frame of the stimulated dielectric-relaxation-currents theory previously applied to the TSP and TSD phenomena in such metal-insulator-metal systems with blocking contacts. [S0163-1829(99)02011-1]

I. INTRODUCTION

Developments in fusion technology have lead to the study of radiation effects in many types of materials. Insulators will be used in several parts of future reactors.[1] Irradiation with energetic particles (neutrons, ions, electrons) and with gamma rays will cause severe damage, thus the physical properties of materials will change. Besides this, transmutation products generated by nuclear reactions with 14-MeV fusion neutrons will increase the materials impurity content. All these effects must be carefully evaluated in order to ascertain which candidate materials are suitable for use in these applications.

Among others, Al_2O_3 is one of the main envisaged candidates for use as an insulator material or in the radio-frequency heating systems as transmitting windows. Magnesium is one of the most abundant transmutation products appearing as a result of nuclear reactions between fusion neutrons and aluminum ions.[1] The presence of magnesium ions in the host matrix has a strong effect on the permittivity and loss tangent of alumina.[2] It is therefore necessary to get a detailed knowledge about the effects of magnesium on the dielectric behavior of Al_2O_3. A basic understanding of part of the dielectric properties of an insulator can be achieved by means of the thermally stimulated polarization (TSP) and thermally stimulated depolarization (TSD) techniques.

In an extensive study published in a previous paper[3] it was shown that the TSP and TSD processes appearing in oxidized magnesium-doped aluminum oxide single crystals are related to the presence of Mg^x_{Al} centers, which consist of a substitutional Mg^{2+} ion with a trapped hole localized on one of the six oxygen ions surrounding the magnesium impurity.[4] The thermal stability of these centers (they anneal out above 800 K) is believed to be due to the formation of magnesium-rich inclusions, which behave in the same way as the ''microgalaxies'' postulated by Chen *et al.*[5] for MgO:Li. The TSP and TSD originate from the thermally activated ionization of these centers, which release holes. It was concluded that the dominant TSP (or TSD) peak at around 270 K (which was labelled peak *B*) is due to the formation of blocking contacts at the sample-electrode interfaces. Experimental findings such as the large current-density values in TSP and TSD measurements, the linear dependence of the total polarization related to this peak on the square root of the applied voltage, the independence of the capacitance on the sample thickness, and the current-voltage characteristics of Al_2O_3:Mg samples, support this conclusion, as predicted by the theory developed by Simmons and Taylor[6,7] to study TSP and TSD processes in metal-insulator-metal systems with blocking contacts. This theory is based on the changes in the width of the depletion regions, formed at the sample-electrode interfaces because of the blocking contacts, when connecting or disconnecting the voltage and in the subsequent heating runs. Other experimental results, including high-voltage TSP measurements, the first-order kinetics character of the 270-K peak, the sample thickness dependence of the peak position, and therefore of the relaxation time, and the observed hysteresis effects, are consistent with this conclusion. It is noteworthy to point out that the two TSD peaks found in oxidized MgO:Li single crystals also arise from these types of processes.[8]

The two other peaks (labelled peak *A* and *HT*) existing in the TSP and TSD spectra of Al_2O_3:Mg are closely related to peak *B*. Although nothing thoroughly conclusive has been proposed for them, the low-intensity peak *A* at around 245 K might be due to Maxwell-Wagner-type polarization of inclusions containing Mg^x_{Al} centers. These inclusions are produced by the oxidizing thermal quenching treatment from existing magnesium-aluminum-spinel precipitates inside the Al_2O_3 matrix.

The above processes are due to the thermal equilibrium charge carriers. On the other hand it is known that ionizing

irradiation can induce in insulators trapped charge carriers (nonequilibrium carriers), which are subsequently released from trapping states when the sample is heated, giving rise to a transitory electric-current enhancement known as a thermally stimulated current (TSC) and to thermoluminescence (TL) before recombining at some centers (see for example Ref. 9). It has been, in fact, shown that low-temperature ultraviolet-visible light irradiation induces Mg_{Al}^{x} centers and TL processes between 80 and 300 K due to hole release from these centers,[4,10] in which other impurities acting as donors, such as Cr and Fe undergo valence changes. This so-generated trapped charge may then have a strong influence on the TSP processes of Al_2O_3:Mg, so its study could contribute to have a better understanding of them. In this paper we present our results on the TSC processes induced in Al_2O_3:Mg single crystals by ultraviolet (UV) and visible light illumination and by x-ray irradiation. The observed TSC peaks are very closely related to the TSP peaks of unirradiated samples. The behavior of the irradiation-induced Mg_{Al}^{x} optical-absorption band and of the Cr^{3+} radioluminescence supports this conclusion.

II. EXPERIMENT

The same samples of Mg-doped Al_2O_3 single crystal used in our previous paper[3] have also been employed here. They were thermally quenched in air from temperatures above 1250 K by dropping them into liquid nitrogen. The electrodes were indium foils pressed on the sample surfaces. The same experimental setup used for TSP and TSD measurements has been used for the study of TSC induced by UV or visible light from either a 450 w xenon lamp or a Bausch and Lomb tungsten lamp. TSC induced by x-ray irradiation were measured in a continuous flow Oxford cryostat, model CF1204. Irradiations were performed with a Siemens AG W 66G tube (tungsten anode) operated at 60 kV and 30 mA. A Keithley 617 electrometer was employed for electric-current measurements. A voltage of 25 V was usually used in the TSP and TSC experiments and a voltage of 500 V in the TSD ones.

Optical-absorption and radioluminescence measurements were made in a chamber mounted in the beam line of a HVEC 2-MeV Van de Graaff accelerator, together with an on-line spectrophotometer system, which permits in-beam optical-absorption and emission spectra to be measured.[11] The samples were electron-irradiated edge on and the induced sample absorption or luminescence were measured perpendicular to the beam direction at a depth of 2 mm behind the irradiated face. At this depth no displacement damage occurs because of the energy loss of electrons in the sample, therefore only ionization effects are detected in the sample region where the measurements are done.

III. RESULTS

Figure 1 presents a TSP spectrum of a Al_2O_3:Mg sample quenched in air from 1520 K. As in our previous paper,[3] a peak labelled *B* at 278 K is clearly dominant. The *HT* region above 290 K is also observed. Peak *A* at around 245 K is hidden under the low-temperature tail of peak *B* because of its low intensity. Two TSC spectra induced by UV light irradiation at 170 K are also shown in this figure. One of them was obtained after the sample had been cooled from room temperature without any applied voltage (i.e., the same condition to take a TSP spectrum) and the other after cooling with 25 V applied to the sample faces. This is the same voltage that is applied at low temperature to measure the TSP and TSC spectra. It is worth remarking that no TSP current is observed after cooling the sample with an applied voltage equal to that applied during the subsequent heating run because the same polarization is maintained along the whole cycle. Both TSC curves are similar to the TSP curve, but they are higher in intensity, especially in the case of that obtained after cooling without voltage. Peak *B* in the TSC appears at 276 K. When illuminating the sample at temperatures below 170 K the TSC spectra are equal to that plotted in Fig. 1. Also, there is no difference in the TSC intensities whether or not the voltage is applied during irradiation.

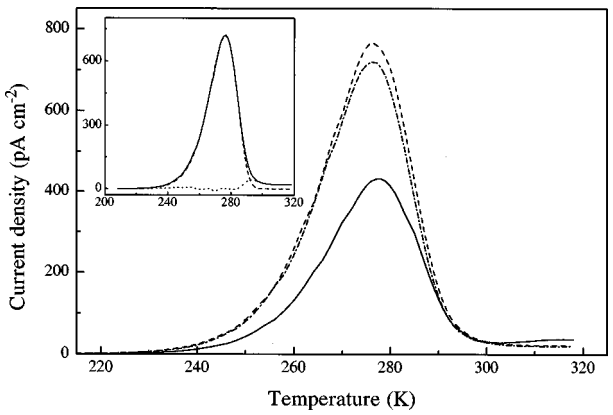

FIG. 1. TSP spectrum (——) of an Al_2O_3:Mg sample quenched in air from 1520 K. TSC spectra of the same sample after 10 min. xenon-lamp illumination at 170 K, previously cooled down from room temperature with (— . — . — . —) and without (— — —) applied electric field. The inset shows the result of fitting the main TSC peak to a first-order kinetics process (see text): experimental TSC curve (——), peak obtained for the calculated E_a and τ_0 values (— — —), and difference between both curves (· · · ·).

Since no TSP is seen when cooling and heating with the voltage on, it could be argued, in principle, that the difference in the area under the TSC curves obtained after cooling with and without the applied voltage should account for the charge released in a normal TSP measurement. Nevertheless, this is not the case because this difference is much lesser than the total TSP charge, as it can be easily deduced from Fig. 1. In other words, there is not a direct addition of TSP (polarization charge) and TSC (charge released by irradiation) processes when irradiating after cooling down without any voltage. All TSC measurements presented hereafter have been obtained after cooling and irradiating the sample with the voltage on.

X-ray irradiation at 80 K induces the TSC spectrum plotted in Fig. 2. Peak *B* and the *HT* region already observed in light-induced TSC spectra are also clearly seen. In addition, four very low-intensity peaks between 80 and 170 K appear. Their intensities are not affected by any sample thermal treatment (either oxidizing quenching or annealing in any atmosphere). They must thus be related to electric carrier release from some residual sample impurities or defects, and therefore they will not be studied anymore along this paper.

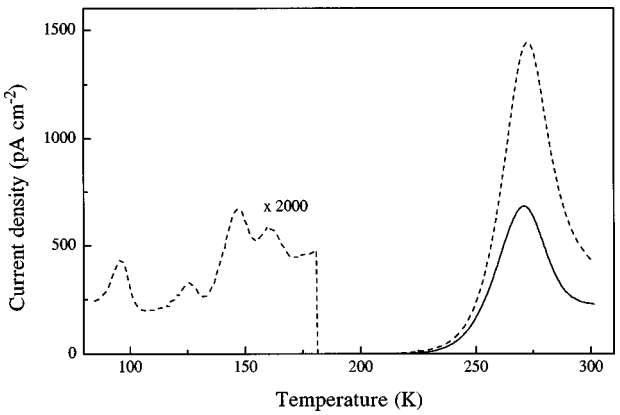

FIG. 2. TSP spectrum of Al_2O_3:Mg quenched in air from 1470 K (——). TSC spectrum of the same sample after x-ray irradiation for 30 min. at 80 K previously cooled down with an applied electric field (— — —).

The activation energy E_a and the preexponential factor τ_0 of TSC peak *B* have been calculated by using a fitting method for first-order processes.[12] As an example, the result of applying this method to the TSC curve obtained after cooling the sample with the electric field on, shown in Fig. 1, is plotted in the inset of this figure. It is seen that peak *B* can be very well fitted to a first-order peak with a high-temperature tail corresponding to the above-mentioned *HT* peak. The activation energy value is $E_a = 0.68 \pm 0.02$ eV, the order of magnitude of τ_0 being 10^{-11} s. These values are the same as those obtained for the TSP peak *B*.[3]

The excitation spectrum of TSC induced by UV and visible light illumination has been obtained by measuring the evolution of peak *B* height against the exciting light wave length for a constant illumination photon dose between 220 and 550 nm. The TSC response yield so obtained only shows a growth stage when decreasing the excitation wave length without any clear band.

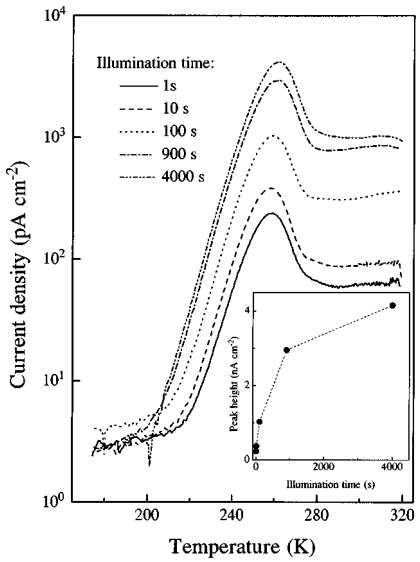

FIG. 3. Evolution with the illumination time of the TSC spectrum induced by Xenon-lamp illumination in a sample quenched from 1470 K. The inset shows the dependence of the TSC peak height on the illumination time.

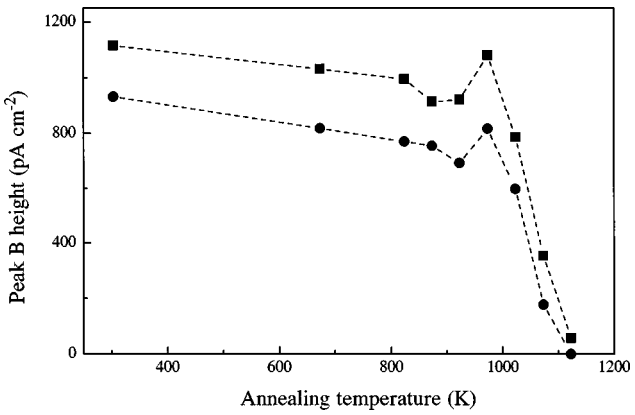

FIG. 4. Annealing curves for peak *B* in TSP (●) and TSC (■) measurements of a sample quenched in air from 1920 K.

The dependence of the TSC spectrum on the illumination time is shown in Fig. 3. With increasing this time only a slight shift (about 4 K between the lowest and the highest illumination time in the figure) to higher temperatures of the peak *B* maximum is observed. The current density of the whole spectrum grows with the illumination time showing a saturating trend, as it can be seen in the inset of this figure (this saturating trend is also observed when plotting the TSC area instead of the TSC peak height). When irradiating with x-rays, saturation is reached after about 30 min, which corresponds to an x-ray dose of around 700 Gy.

The TSC peak *B* evolves against the sample thickness in the same way as the TSP peak *B* (see Ref. 3). The peak temperature increases monotonically when increasing the sample thickness and the area under this peak depends linearly on it. There is also a parallel behavior of TSC and TSP peaks *B* with the thermal treatments given to the samples. Both peaks shift to lower temperature when the quenching temperature is increased, the amounts of these shifts being the same. Moreover, a pulsed thermal annealing experiment shows that the annealing curve for the TSC peak is identical to that of the TSP peak, as it can be seen in Fig. 4. During the pulsed-thermal annealing procedure, both peaks shift towards higher temperatures when increasing the annealing temperature (see Fig. 5 for the TSC peak; note that peak *B* appears here at about 250 K before the annealing procedure

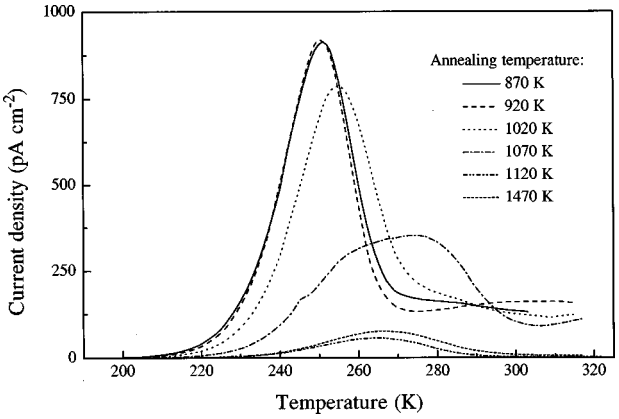

FIG. 5. Evolution with the annealing temperature of the TSC spectrum induced by Xenon-lamp illumination at 170 K in a sample quenched from 1920 K.

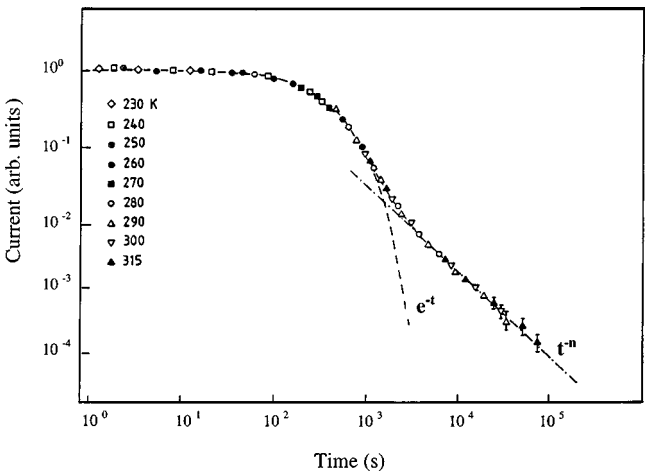

FIG. 6. Isothermal decay curves at several temperatures after Xenon-lamp illumination. The results for each temperature have been normalized by shifting laterally into coincidence.

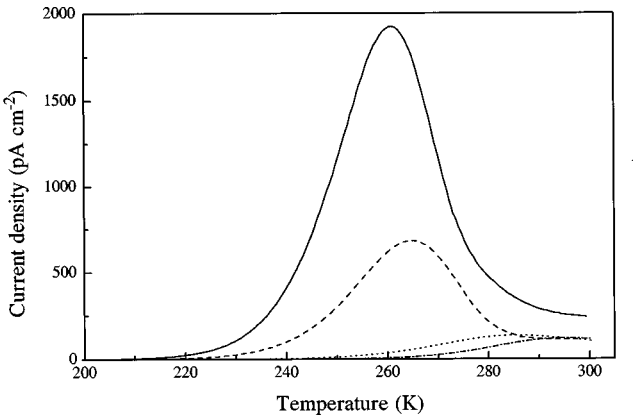

FIG. 7. TSD spectra of Al_2O_3:Mg quenched in air from 1470 K, after being polarized with 500 V for 10 min. at 290 K, cooled down with the field on, and x-ray irradiated at 60 kV and 30 mA at 80 K for 0 (——), 3 (— — —), 60 (· · · ·), and 1800 (—.—.—.—) s with the electric field off.

is started, instead of at 278 K as it was in Fig. 1; this is due to the high temperature 1920 K from which the sample used to study the thermal annealing was quenched).

After annealing the samples at temperatures higher than 1100 K, when the quenching-induced TSP spectrum and the Mg_{Al}^{x} centers have disappeared, there is a residual TSC peak at about 270 K, as it can be seen in this figure. It must be ascribed to a process other than peak *B* because its position does not vary with the temperature from which the quenching is made, unlike the case of peak *B* whose displacement to lower temperatures is about 25 K when the quenching temperature is increased from 1270 to 1920 K. A TSC peak around 270 K appears in x-irradiated pure Al_2O_3 single crystals.[13] It was ascribed to hole release from traps. It has been checked that its position and height do not change with high-temperature quenching, as the residual TSC peak of Al_2O_3:Mg.

The decay at a constant temperature of the UV light-induced processes has been studied between 230 and 320 K by performing current measurements after illuminating the sample for a given period of time at each temperature. The transitory phenomena so detected are related to detrapping processes of charge carriers in excess created by illumination. In the temperature range corresponding to the TSC peak *B* the electric current-density *J* follows an exponential decay function of time *t*, while at higher temperatures, when the *HT* region appears, *J* is proportional to $t^{-\alpha}$, α being a parameter whose value is near 1. This behavior is like that observed in studying the isothermal relaxation currents after applying a polarization voltage to the sample.[3] As in this case, all relaxation currents have been plotted together by displacing them along both *X* and *Y* axes in order for all of them to be superimposed in a unique ''master'' curve (Fig. 6).[14] The master curve obtained after light excitation is very similar to that obtained after applying a polarization voltage. Both show a clear transition from a time-exponential decay to a time-power decay.

The effect of x-irradiation on the TSD spectrum of quenched Al_2O_3:Mg has also been studied. Contrary to the TSP measurements, in a TSD experiment the sample is polarized at high temperature and cooled down with the electric field on, the depolarization currents being detected with the field off during the subsequent heating run. As it is known, the TSD spectrum of oxidized Al_2O_3:Mg consists of the same peaks that appear in the TSP spectrum.[3] A TSD spectrum of an Al_2O_3:Mg sample quenched from 1470 K is shown in Fig. 7. Peak *B* and part of the *HT* region are clearly seen. As it can be observed in this figure, an x-ray irradiation at low temperature (with the electric field removed) before starting the measurement leads to a decrease in the intensity of peak *B*. This completely disappears at approximately the same irradiation dose at which the TSC peak height reaches a saturation value, only the *HT* region remains. This very important result indicates that radiation-induced depolarization occurs in these samples.

Finally, some optical-absorption and radioluminescence measurements have been made in oxidized Al_2O_3:Mg to try to elucidate the possible role of some defects or impurities. Ionizing irradiation causes the Mg_{Al}^{x} optical-absorption band at 480 nm (Ref. 4) to grow with a saturating trend with dose. On heating after irradiation this band anneals out continuously between 200 and 280 K. The radioluminescence spectrum has a narrow band at 694 nm, which is due to the Cr^{3+} ion emission,[15] and a broad band at about 290 nm, which has been ascribed to the emission of F_{Mg} centers (F^{+} centers beside a Mg^{2+} impurity).[10] The Cr^{3+} emission decreases in intensity as the sample temperature is raised from 80 to 300 K.

IV. DISCUSSION

The experimental results presented along this paper lead to the conclusion that the main TSC process of oxidized Al_2O_3:Mg has the same origin as the TSP process already observed in this material:[3] both TSC and TSP curves are almost identical, both peaks labelled *B* have the same activation energy, the dependence of both types of processes on the sample thickness and on the thermal treatments (oxidizing quenchings and thermal annealing) are very similar, and the same behavior in studying the isothermal decays of either polarization- or irradiation-induced electric currents has been found. Moreover the occurrence of radiation-induced depo-

larization strongly supports this conclusion.

In our previous paper[3] it was shown that TSP and TSD processes in oxidizing-quenched Al_2O_3:Mg samples are related to thermally activated hole release from Mg_{Al}^{x} centers. From current-voltage measurements at room temperature it was concluded that any metal used as electrodes makes blocking contacts for holes with the sample. This implies the formation of a depletion region with a negative space charge (ionized acceptors) at the electrode-insulator interfaces due to hole escape from traps near the sample surfaces. According to the stimulated dielectric-relaxation-currents (SDRC) theory developed by Simmons and Taylor[6,7] to explain the TSP and TSD processes in metal-insulator-metal systems with blocking contacts, when a voltage is applied at a sufficiently high temperature the system relaxes to a steady state because of the growth of the anodic depletion region (ADR) caused by further hole escape, leading to a time-dependent current during relaxation. When an unpolarized sample is cooled down and the voltage is applied at low temperature, no current is observed because holes are not released from traps. As the temperature is raised hole release from traps (in our case the Mg_{Al}^{x} centers) leads to a peak-shaped electric current (the TSP peak). The electric current value goes back to zero when all the traps in the region corresponding to the steady-state ADR have been depleted of their holes.

Ionizing irradiation at low temperature creates additional Mg_{Al}^{x} centers in the bulk, as it is seen in our optical-absorption measurements. The formation of these centers by both light illumination and ionizing irradiation at low temperature has also been observed by other authors.[4,16] They arise from hole capture at isolated Mg_{Al}' centers, which are locally compensated by impurities (such as $Cr_{Al}^{\bullet}$ and $Fe_{Al}^{\bullet}$) or other defects. The radioluminescence measurements confirm the role played by Cr^{4+} ions in providing holes for Mg_{Al}^{x} formation. These centers become thermally unstable above 200 K, according to our optical-absorption measurements and to results by other authors.[4,10,17,18]

Taking the above conclusions into account the TSC processes in Al_2O_3:Mg can be explained as follows:

When the sample has been cooled from room temperature without any applied voltage the depletion region is still narrow. As seen before, irradiation induces excess Mg_{Al}^{x} centers. During the subsequent heating with the voltage on, holes released from both the Mg_{Al}^{x} centers near the sample surface and those excess Mg_{Al}^{x} centers contribute to the resulting current peak; so it must be higher in intensity than the TSP one measured with the same voltage, as it has been here observed. In parallel, the ADR width grows up to its polarized steady-state value at room temperature.

On the other hand, when the voltage is applied at 300 K and the temperature is lowered to 80 K, the room-temperature polarized steady state is frozen in. Therefore, no TSP peak would appear in a later heating run with the voltage on. Besides the isolated Mg_{Al}^{x} centers, irradiation at low temperature prior to this heating run causes partial refilling of the ionized acceptors (Mg_{Al}') in the frozen in ADR, hence reducing the sample polarization. In this way the total charge released during the heating run is less than that obtained when the sample is cooled down without any applied voltage. This explains the fact that the difference between the areas of the TSC measured after cooling the sample with and without the applied voltage does not give the TSP charge, in agreement with a theoretical work by Henish.[19]

The effect of x-ray irradiation on the TSD of Al_2O_3:Mg can also be understood in the frame of the SDRC theory. The main TSD peak arises from the relaxation of the frozen-in polarized steady state during heating.[3] X-ray irradiation at 80 K after cooling and before heating leads to hole capture at part of the ionized acceptors in the wide ADR, its width therefore decreasing to near its unpolarized equilibrium value. In the subsequent heating run the system relaxation is thus lesser than in the case of an unirradiated sample, so peak *B* is lowered in intensity. Although irradiation also creates isolated Mg_{Al}^{x} centers in the bulk, which anneal out when raising the temperature, no contribution of their released charge is detected in this experiment because no voltage is applied to the sample during heating. For a sufficiently high-irradiation dose the width of the ADR may diminish to the value corresponding to an unpolarized sample at room temperature, in this case no TSD peak *B* appears, as shown in Fig. 7. Note that this irradiation dose is approximately the same as that for which the TSC peak height reaches its saturation value. These TSD results lend then further support to our conclusion that TSP, TSD, and TSC processes in oxidized Al_2O_3:Mg with metal contacts have the same origin.

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