PHYSICAL REVIEW B VOLUME 54, NUMBER 1 1 JULY 1996-I

Model for radiation-induced electrical degradation of α-Al_2O_3 crystals

Xiang-Fu Zong, Cheng-Fu Shen, Song Liu, Yi Chen, and Renjun Zhang
Fudan University, Department of Materials Science and Engineering, Shanghai 200433, China

Y. Chen*
Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, ER 131,
Germantown, Maryland 20874-1290

Jane G. Zhu
Oak Ridge National Laboratory, Solid State Division, P.O. Box 2008, Oak Ridge, Tennessee 37831-6031

B. D. Evans
Edtek, Inc., 7082 South 220 Street, Kent, Washington 98032

R. Gonzalez
Universidad Carlos III, Departamento de Fisica, Escuela Politecnica Superior, Butarque, 15, 28911 Leganes, Madrid, Spain

(Received 16 January 1996)

When a ceramic oxide with an applied electric field is subjected to extended irradiation with energetic particles at elevated temperatures, the electrical conductivity has been reported to increase, a phenomenon termed radiation-induced electrical degradation (RIED). In the present study α-Al_2O_3 crystals were subjected to 1800 V/cm while irradiated with 1.8 MeV electrons at 773 K. Above a critical dose the conductivity increased. During the conductivity enhancement, the applied field was reversed, resulting in a decrease in the conductivity. This result demonstrates that RIED was caused by carriers injected from the electrodes, in concert with electrons and holes created during ionizing irradiation. A model for RIED is proposed: the injected carriers are trapped mainly at impurities near the electrodes, leading to formation of dislocations. These dislocations serve as traps for electrons and holes generated during ionizing radiation. A network of interconnecting dislocations is associated with the enhanced conductivity. [S0163-1829(96)00626-1]

I. INTRODUCTION

Radiation-induced electrical degradation (RIED) of ceramic oxides poses a serious problem in advanced energy devices, where electrical insulators are required in several components.[1,2] *Concurrent* application of radiation with energetic particles, electric field, and elevated temperature (Rad-**E**-T) to α-Al_2O_3 for an extended period has been reported to lead to an enhancement of the electrical conductivity.[3,4] In earlier Rad-**E**-T experiments involving energetic electrons, it was reported that at some critical dose the electrical conductivity began to increase and became irreversible.[3,4]

Hodgson[3] reported that concurrent ionization and elastic-collision events are necessary for RIED to occur, based on his observation that RIED depended on the bombarding electron energy. Subsequently Zong *et al.*[5,6] established the following: first, RIED is associated with dislocations generated during Rad-**E**-T, second, RIED was induced by electrons and holes from ionizing radiation and not from displacement damage by elastic collisions with energetic electrons.

In this paper we (i) demonstrate that point defects produced during Rad-**E**-T are negligible in concentration compared to impurities in virgin crystals; (ii) show that RIED was caused by carriers injected from the electrodes, in concert with electrons and holes created during ionizing radiation; (iii) propose a model for RIED; (iv) conclude that there are two types of electrical degradation—bulk conductivity (RIED) and radiation-enhanced surface conduction[7,8] (RESC)—and that field-reversal experiments permit a distinction between these two effects.

II. EXPERIMENTAL PROCEDURES

Optical-quality cylindrical disks of nominally pure ($\sim 10^2$ ppm) α-Al_2O_3, with the surface perpendicular to the c axis, were purchased from Union Carbide Corporation (UCC). The sample thickness was 1.0 mm and the diameter was 25 mm. Platinum contacts were deposited in the sample by sputtering from a Pt foil in vacuum. The procedure for processing the contacts has been reported.[5,6] With an applied electric field of 1800 V/cm (along the c axis), the central region of the sample was irradiated with 1.8 MeV electrons in air at a dose rate of 4 $\mu A/cm^2$ at 773 K. A two-terminal electrical technique was used for conductivity measurements. The electron irradiation was carried out with a vertical Van de Graaff. The electron beam was collimated such that the periphery of the sample was shielded from the beam.[5,6] Samples for transmission electron microscope (TEM) observations were cut ultrasonically to a diameter of about 50 μm by dimpler (Model D500) and were thinned by dual ion mill (Gatan Model 600) until a small hole appeared.

A Philips EM 430 electron microscope with an operating voltage of 300 kV was used for post-irradiation TEM obser-

0163-1829/96/54(1)/139(5)/$10.00

vations. Optical-absorption measurements were made with a Perkin-Elmer Lambda 9 spectrophotometer. Luminescence experiments were made with a calibrated Spex Fluorolog spectrofluorimeter. The emission was detected using a cooled Hamamatsu R928 photomultiplier tube.

III. RESULTS AND DISCUSSION

A. Defects

Both point defects and extended defects were characterized in two regions: the central region, which was subjected to Rad-**E**-T, and the (shielded) peripheral area, not subjected to Rad-**E**-T.

1. Point defects

Atomic displacements can occur either by elastic collision (knock-on) or photochemical (ionization) processes.[9] Displacements in oxide crystals,[10,11] metals, and semiconductors are known to occur by elastic collision, with the exception of hydrogenic impurities, which are readily displaced via an ionization mechanism.[12,13] In oxide crystals, 1.8 MeV electrons are energetic enough to displace single ions, resulting in F^+ and F centers (anion vacancies with one and two electrons, respectively). At 295 K the effective cross section for displacements is extremely low $\sim 5\times 10^{-3}$ b.[5] Oxygen interstitials are unstable at 573 K.[14,15] Therefore, at 773 K few anion vacancies can survive because the cross section for interstitial-vacancy recombination far exceeds that of production.[6]

Photochemical processes prevail primarily in alkali halides.[16] There has been no evidence that atomic displacement events of indigenous ions in α-Al_2O_3 and MgO occur via photochemical processes. In fact, the precursor of the F center in the alkali halides, the V_k center (self-trapped hole on a pair of anions), has never been observed in these oxide crystals.

Optical absorption and luminescence were used to determine the presence of F^+ and F centers. The procedure to obtain these data have been described elsewhere.[17] Figure 1 illustrates two optical absorption spectra: the bottom for the central region of the sample subjected to Rad-**E**-T and the top for the periphery of the sample not subjected to Rad-**E**-T. No F^+ or F absorption (at 258 and 214 nm, respectively) was observed. However, Ti^{4+} absorption was observed at 230 nm. Clearly, Rad-**E**-T *reduces this absorption*. The decrease is attributed to valence change from Ti^{4+} to Ti^{3+}.[18] Luminescence experiments, because of their high sensitivity, were performed to detect F^+ centers (Fig. 2). Both regions of the sample were excited with 250-nm photons, which overlap the F^+ and Ti^{4+} absorption bands. Emission at 420 nm (Ti^{4+}) was observed, but not the F^+ luminescence (326 nm). The central (irradiated) region had a lower intensity, consistent with the lower absorption. There were no detectable anion vacancies as a result of Rad-**E**-T, indicating that if anion vacancies were present, they were in concentrations of 10^{15} cm^{-3} or less. Impurities in nominally pure α-Al_2O_3 crystals typically are $\sim 10^{19}$ cm^{-3}. Clearly, *anion vacancies generated during Rad-***E***-T are negligible compared to impurity concentrations.* We conclude that *it is unlikely that RIED is caused by anion vacancies produced during Rad-***E***-T.*

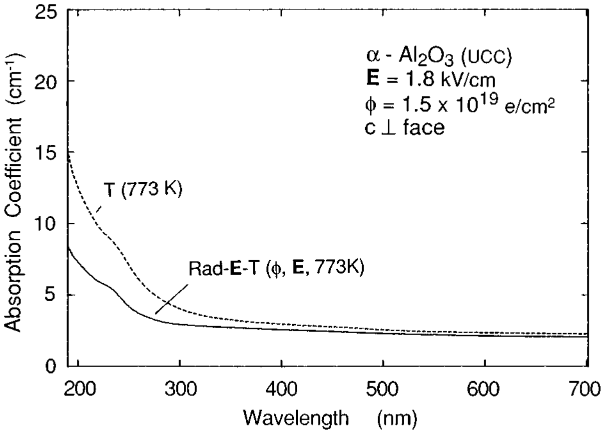

FIG. 1. Optical absorption spectra of two regions of an Al_2O_3 crystal: one region (upper curve) was shielded from the electron beam at 773 K, with no applied voltage; and the other region (lower curve) was subjected to electron irradiation and an applied field at 773 K. The measurements were made at 295 K.

2. Extended defects

A sample was subjected to Rad-**E**-T to a dose of 1×10^{19} e/cm^2. For TEM observations both regions were also characterized. The major difference was the disparity in dislocation density. The dislocation density in the central region averaged $\sim 10^9$ dislocations/cm^2; the distribution was highly non-uniform. In the peripheral region, dislocations were scarce and difficult to find; the density was estimated to be $\sim 10^4$ dislocations/cm^2, which is the magnitude expected in virgin crystals. Most of the dislocations in the central area were in the form of low-angle grain boundaries (Fig. 3, top). The orientation was determined to be $[02\bar{2}1]$. Figure 3 (bottom) illustrates the dislocation structure with respect to the different axis of the crystal lattice. No dislocations oriented in the direction of the applied electric field, i.e., the *c* axis, were observed. We also searched for precipitates in both regions. None was observed.

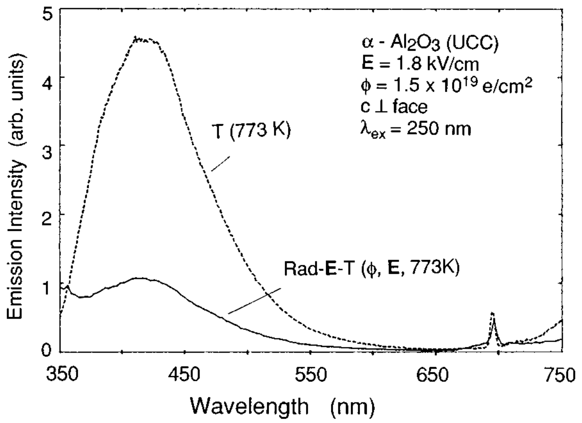

FIG. 2. Luminescence of two regions of the Al_2O_3 crystal during excitation with 250-nm light: one region (upper curve) was shielded from the electron beam at 773 K, with no applied voltage; and the other region (lower curve) was subjected to electron irradiation and an applied field at 773 K. The measurements were made at 295 K.

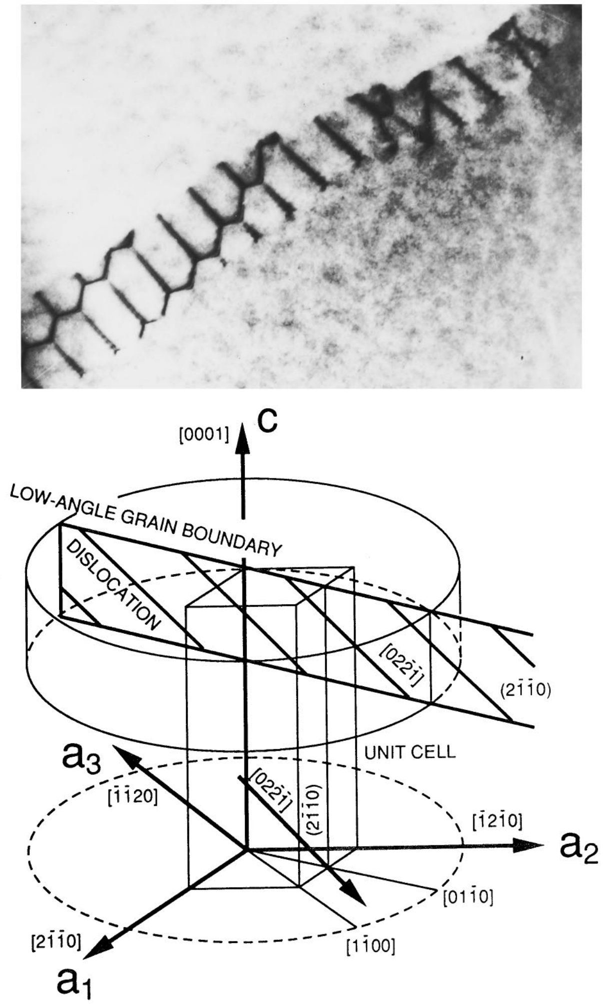

FIG. 3. Top: TEM of a low-angle boundary dislocation in an area previously subjected to Rad-**E**-T; the width of the micrograph corresponds to 4.4 μm. Bottom: dislocation orientation with respect to the different axis of the crystal lattice. The configuration of the observed [0221] dislocations is shown.

B. Injection of carriers

A magnitude of 10^9 dislocations/cm^2 is comparable to that observed in heavily deformed crystals. The dislocations were evidently formed efficiently. A possible mechanism involves carriers injected from the electrodes and subsequently trapped at lattice defects. A similar mechanism was identified with electrical breakdown in MgO single crystals at high temperatures without radiation.[19–22] A critical test for an injection model is field-reversal experiments during RIED.

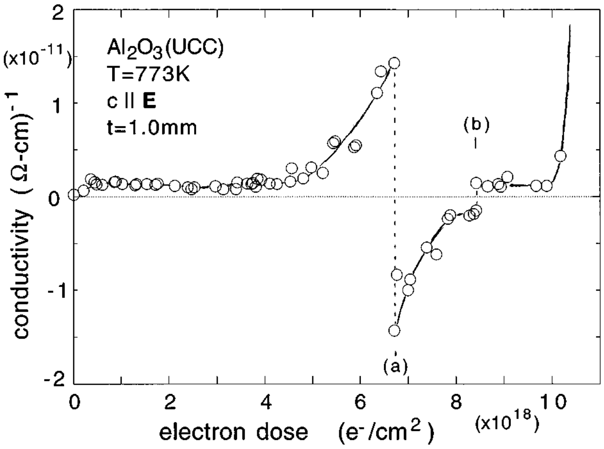

FIG. 4. Electrical conductivity at 773 K versus electron dose of an Al_2O_3 crystal after irradiation followed by stabilization of the current. Field reversals were applied at doses (a) and (b).

The result of such an experiment is shown in Fig. 4. The conductivity, measured at equilibrium (5 min after the electron beam was turned off), began to increase at a critical dose of 4×10^{18} e/cm^2. When the conductivity reached 1.4×10^{-10} (Ω cm)$^{-1}$, at a dose of 6.7×10^{18} e/cm^2 [represented by (a) in Fig. 4], the applied field was removed and the sample was cooled down. The cooling rates were 13 min from 773 to 593 K and 15 min from 593 to 493 K. The form of field reversal performed was sample rotation: after the field was removed, the sample was flipped over. The sample remained at 295 K for 116 h. Subsequently, the sample was reheated to 773 K, requiring about 30 min. The field was reapplied; the polarity of the field was effectively reversed. Prior to irradiation, the conductivity was remeasured and was found to be the same as prior to the cooling down of the sample (1.4×10^{-10} Ω^{-1} cm^{-1}). The cooling and reheating, the off-on of the electric field, and the flip over of the sample did *not* affect the conductivity. With further Rad-**E**-T, the conductivity *monotonically* declined over a period of 19 h of Rad-**E**-T until it reached a plateau at $\approx10^{-11}$ (Ω cm)$^{-1}$.

At a total dose of 8.3×10^{18} e/cm^2 [represented by (b) in Fig. 4] a second field reversal was applied. The procedure was the same as that in the first cycle. Continuing with Rad-**E**-T, the conductivity remained essentially constant until the dose reached 9.9×10^{18} e/cm^2, at which point the conductivity began to increase again. In effect, the experiment covered two field reversals leading to RIED. In the first, the critical dose required for RIED to initiate was 4×10^{18} e/cm^2. The second critical dose was 1.6×10^{18} e/cm^2 (from 8.3×10^{18} to 9.9×10^{18} e/cm^2), about half of that in the first cycle. The reason for the reduction will be given in Sec. III C.

In a previous study sapphire was the only oxide investigated that did not suffer electrical breakdown under a moderate electric field ($\approx$1500 V/cm) at 1473 K (no irradiation) within two weeks.[21] In the present study electrical degradation was observed at a lower temperature, but in the presence of electron irradiation. We deduce that electron irradiation induced the degradation process by supplying electrons and holes.

C. Proposed model

The essence of our model is as follows (i) RIED is initiated by injection of carriers, which are trapped mainly at impurities near the electrodes. (ii) An ample accumulation of trapped carriers leads to formation of dislocations. These dislocations are built up from the beginning, even when the conductivity remains low (a dose less than 4×10^{18} e/cm^2). (iii) These dislocations serve as traps for electrons and holes generated during ionizing radiation. Electrically charged dislocations are mobile under an applied electric field. Therefore, they respond to changes in polarity of the electrodes and redistribute accordingly. (iv) The trapped electrons and holes are metastable and will recombine with one another, rendering the dislocations immobile, unless replenished with more electrons and holes from the irradiation. (v) The network of dislocations can be compact (islandlike) or diffuse (interconnecting); the former corresponds to low conductivity and the latter to enhanced conductivity. (vi) Rad-**E**-T, if carried out sufficiently long, will result in a diffuse network of dislocations and enhanced conductivity. However, a reversal of the applied electric field during Rad-**E**-T will have the effect of compacting the dislocation network, thereby diminishing the conductivity. This proposed model explains why both ionizing radiation and electric field are necessary for RIED to occur.

In order for RIED to initiate, there must be traps for injected carriers. We have shown that impurity concentrations are much greater than defects produced by the radiation. We deduced that impurities are the main traps for carriers near the electrodes. Accumulation of charge carriers will result in ionic charge compensation in the region and drift of ions. There are two additional pieces of experimental evidence that lend credibility to impurity (or sample) dependence. First, under identical experimental conditions, the critical dose was 1.0×10^{18} e/cm^2 for a crystal from the Shanghai Institute of Optics and Fine Mechanics (Ref. 5) which is four times smaller than for a UCC crystal (present study). Second, it has been reported[23] that Vitox polycrystalline alumina gave rise to RIED, whereas those from Wesgo did not.

A model involving trapping of carriers is supported by the observation that conductivity diminished during RIED when the electric field was reversed. Injected carriers are trapped near the electrodes. (For a classic book on injection and electrical breakdown, see Ref. 24.) When the field is reversed, the same electrode injects opposite carriers that annihilate carriers trapped earlier or neutralizes previous injection effects. The important implication of this model is that *if field reversals are applied sufficiently frequently, such as in an ac field, there would be no RIED.*

The next step is to understand the interplay between the dislocation network and RIED. Once the dislocations are produced, their population is essentially conserved. Therefore, in subsequent field reversals, the critical dose required for RIED is reduced because most of the dislocations are already formed. The conductivity at any given time during Rad-**E**-T is governed not only by the dislocation density, but also how they are distributed. A large conductivity is associated with an overlapping network of dislocations and a low conductivity is associated with a nonoverlapping (compact) network of dislocations. During RIED the dislocation network becomes more diffuse, leading to enhanced conductivity. When the polarity of the electrodes is reversed, the dislocation network will move in the opposite direction and become compact, giving rise to lower conductivity. We believe that there are some similarities to the electrical breakdown in MgO (without irradiation). Analogies can be made. We refer to micrographs from early TEM studies[25,26] in MgO. When the electrical conductivity increased by a factor of 100 (approaching breakdown), the micrograph exhibited a large, diffuse, and overlapping network of dislocations. However, when the electrical field was subsequently reversed and the current density decreased, the dislocations did not vanish, but redistributed themselves in concentrated islandlike domains, with virtually no overlaps among the domains (see Fig. 4, Ref. 26).

D. Implications: Bulk vs surface effects

There exists a controversy concerning past experiments. Electrical degradations in Rad-**E**-T experiments using electrons,[3,4,27] neutrons,[28–31] and ions[32] were reported as due to bulk effects. On the other hand, Kesternich, Scheuermann, and Zinkle[7] and Jung, Zhu and Klein[8] reported that the increase in conductivity in their samples was *not* due to a bulk effect, but was a result of radiation-enhanced surface conduction (RESC). On the basis of our model, it is possible to reconcile and distinguish surface versus bulk effects using electrical measurements alone. A decrease in current density upon field reversal during RIED is indicative of a bulk effect, as shown in the present study. In contrast, surface conductivity should not be affected by field reversals. Based on this reasoning, an alternating electric field (rapid field reversals) during Rad-**E**-T can lead to RESC, but not RIED. In fact, in earlier **E**-T studies (without the radiation) in MgO there was no electrical breakdown when a dc field was replaced by an ac field.[19–21] Therefore, we conclude that electrical degradation with an applied alternating field is indicative of a surface phenomenon.

There were two previous Rad-**E**-T studies in $\mathrm{Al_2O_3}$ that utilized alternating electric fields. In Jung, Zhu, and Klein's study,[8] alternating fields contributed to electrical degradation; the authors attribute it to surface contamination. In contrast, Hodgson concluded[4,27] that RIED occurred equally well with an alternating field and that the effect showed little or no frequency dependence from 33 Hz to 126 MHz. On the basis of the present study, we conclude that in both experiments the degradation was due to surface effects.

IV. SUMMARY AND CONCLUSIONS

The experimental results are summarized as follows. (i) Optical absorption and luminescence techniques showed that in crystals subjected to Rad-**E**-T, the concentration of point defects was negligible in comparison with the impurity content. (ii) TEM observations demonstrate that the dislocation density was very high, 10^9 dislocations/cm^2. Most of these dislocations are in the form of low-angle grain boundaries with an $[0221]$ orientation. Precipitates were not observed. (iii) Field-reversal experiments during RIED showed that the electrical conductivity diminished when the electric field was reversed.

In conclusion, we demonstrated that RIED in $\mathrm{Al_2O_3}$ during Rad-**E**-T does not involve displacement events, as previously proposed.[3,4,27] The cross section for producing point defects is too small and the interstitials are too mobile at 773 K to sustain a measurable population. A model involving impurities, carrier injection, and dislocations is proposed. RIED has been identified primarily as a dielectric degradation process initiated by carriers injected from the electrodes. The main traps for the carriers are impurities near the electrodes. An ample accumulation of trapped carriers leads to formation of dislocations. These dislocations serve as traps for electrons and holes generated during ionizing radiation.

Electrically charged dislocations are mobile under an applied electric field. At any given time during Rad-**E**-T, the polarity of the electrodes determines whether the dislocation network is becoming more diffuse and conducting, or more compact and less conducting. Electrical degradation takes two forms: bulk effect (RIED) and surface effect (RESC, or the Kesternich-Jung effect). These two effects can be distinguished from one another by experiments using field reversals or alternating fields.

ACKNOWLEDGMENTS

Research at the Oak Ridge National Laboratory was sponsored by the Division of Materials Sciences, U.S. Department of Energy under Contract No. DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp., Inc. Research at the Universidad Carlos III was supported by the Comision Interministerial de Ciencia y Tecnologia of Spain and by the Comunidad Autonoma de Madrid.

---

[*] The research of this author is an outgrowth of past investigations performed at the Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831.

[1] F. W. Clinard, Jr., J. Nucl. Mater. **85&86**, 393 (1976).

[2] F. W. Clinard, Jr., Ceram. Int. **13**, 69 (1987).

[3] E. R. Hodgson, J. Nucl. Mater. **179-181**, 383 (1991).

[4] E. R. Hodgson, J. Nucl. Mater. **191-194**, 552 (1992).

[5] Xiang-Fu Zong, Cheng-Fu Shen, Song Liu, Zhong-chi Wu, Yi Chen, Y. Chen, B. D. Evans, R. Gonzalez, and C. H. Sellers, Phys. Rev. B **49**, 15 514 (1994).

[6] Xiang-Fu Zong, Cheng-Fu Shen, Song Liu, Zhong-chi Wu, Yi Chen, Renjun Zhang, Jane G. Zhu, Y. Chen, B. D. Evans, R. Gonzalez, and C. H. Sellers, J. Nucl. Mater. **219**, 176 (1995).

[7] W. Kesternich, F. Scheuermann, and S. J. Zinkle, J. Nucl. Mater. **206**, 68 (1993).

[8] P. Jung, Z. Zhu, and H. Klein, J. Nucl. Mater. **206**, 72 (1993).

[9] E. Sonder and W. A. Sibley, in *Defect in Crystalline Solids*, edited by J. H. Crawford, Jr. and L. M. Slifkin (Plenum, New York, 1972).

[10] B. D. Evans and M. Stapelbroek, Phys. Rev. B **18**, 7079 (1978).

[11] Y. Chen, D. L. Trueblood, O. E. Schow, and H. T. Tohver, J. Phys. C **3**, 2501 (1970).

[12] Y. Chen, R. Gonzalez, and K. L. Tsang, Phys. Rev. Lett. **53**, 1077 (1984).

[13] Y. Chen, M. M. Abraham, and H. T. Tohver, Phys. Rev. Lett. **37**, 1757 (1976).

[14] K. Atobe, N. Nishimoto, and M. Nakagawa, Phys. Status Solidi A **89**, 155 (1985).

[15] J. H. Crawford, Jr. and K. H. Lee, Phys. Rev. B **19**, 3217 (1979).

[16] R. T. Williams, B. Craig, and W. L. Faust, Phys. Rev. Lett. **52**, 1709 (1984).

[17] L. S. Cain, G. J. Pogatshnik, and Y. Chen, Phys. Rev. B **37**, 2645 (1988).

[18] B. D. Evans, J. Lumin. **55**, 6079 (1994).

[19] K. L. Tsang, Y. Chen, and H. T. Tohver, Phys. Rev. B **30**, 6093 (1984).

[20] K. L. Tsang, Y. Chen, and J. J. O'Dwyer, Phys. Rev. B **26**, 6909 (1982).

[21] K. L. Tsang and Y. Chen, J. Appl. Phys. **54**, 4531 (1983).

[22] K. L. Tsang, H. T. Tohver, and Y. Chen, in *Defect Properties and Processing of High-Technology Nonmetallic Materials*, edited by J. H. Crawford, Jr., Y. Chen, and W. A. Sibley, MRS Symposia Proceedings No. 24 (Elsevier, New York, 1984).

[23] A. Moslang, E. Daum, and R. Lindau, 18th *Symposium on Fusion Technology*, Karlsruhe, Aug. 22–26, 1994 (in press).

[24] J. J. O'Dwyer, *The Theory of Electrical Conduction and Breakdown in Solid-Dielectrics* (Oxford University Press, Oxford, 1973).

[25] J. Narayan, R. A. Weeks, and E. Sonder, J. Appl. Phys. **49**, 5977 (1978).

[26] R. A. Weeks, J. Narayan, and E. Sonder, Phys. Status Solidi A **70**, 631 (1982).

[27] E. R. Hodgson, in *Proceedings of the XII International Conference on Defects in Insulating Materials*, edited by O. Kanert and J. M. Spaeth (World Scientific, Singapore, 1993), p. 332.

[28] E. H. Farnum, J. C. Kennedy, F. W. Clinard, Jr., and H. M. Frost, J. Nucl. Mater. **191-194**, 548 (1992).

[29] E. H. Farnum, F. W. Clinard, Jr., W. F. Sommer, J. C. Kennedy III, and T. Shikama, J. Nucl. Mater. **212-215**, 1128 (1994).

[30] T. Shikama, M. Narui, Y. Endo, A. Ochiai, and H. Kayano, J. Nucl. Mater. **191-194**, 544 (1992).

[31] T. Shikama, M. Narui, Y. Endo, T. Sagawa, and H. Kayano, J. Nucl. Mater. **191-194**, 575 (1992).

[32] G. P. Pelis, J. Nucl. Mater. **184**, 177 (1991).