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Multiphonon-induced charge trapping-detrapping and damage in insulators

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A model is presented that interprets both electron capture (trapping) and ionization (detrapping) processes in insulators. It emphasizes the importance of the electron-phonon interactions on the electronic transitions involving defect states. These electronic transitions are accompanied by multiphonon emission or absorption in the presence of a strong electron-phonon coupling. They are governed by the Meyer-Neldel compensation rule and display a departure from Franck-Condon-like transitions. It is shown, by using earlier thermodynamic measurements [G. Moya and G. Blaise, *Space Charge in Solid Dielectrics*, Proceeding of the Dielectric Society Meeting (Darwin College, University of Kent, Canterbury, U.K., 1997); G. Blaise and G. Moya, 3rd International Conference on Electric Charge in Solid Insulators (unpublished)] that the entropy associated with the electron trapping and detrapping processes in oxides and polymers increases with the activation energy as predicted by the model and that the activation energies can be derived directly from such measurements. Thus, atomic or ionic movements accompanying these multiphonon electronic transitions are shown to be the cause of insulator damage and aging.

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I. INTRODUCTION

Physical processes significant for damage and aging in insulators and their precursor phenomena have been widely investigated in several International Conferences.[3] From these studies it appeared that strong correlation exists between damage in insulators and storage of electric charges.[4] Various models had been developed to explain these phenomena.

At first, it was suggested that the principal cause of electrical damage in condensed systems should be impact ionization by electrons. Electronic collisions initiated by electron bombardment or by field emission have been considered. A cumulative effect should result in successive impact ionizations giving avalanches of electrons and positive ions and regenerating the electrons needed for the maintenance of the incident particle flow.[5–7] Elaborated models have been developed to describe the dielectric response to an electric field[8,9] and from these studies, space charge and polarization appeared to be the prevailing factors leading to a lattice perturbation. This model, valid for a perfect crystal, has been widely used. However, it does not interpret the entire experimental data because it does not take into account the role of defects and of temperature.

Another process extensively invoked to explain the damage is charge trapping. It was known that, as a free charge carrier present in the conduction band moves through a polar solid, its Coulomb field displaces the positive and negative ions with respect to one another. The resulting polarization modifies the motion of the charge that moves through the crystal accompanied by a cloud of phonons.[10] The electron and its polarization cloud, known as a polaron, are free to move in the crystal.[9,11,12] According to the size of the disturbed region around the electron with respect to the distance between first neighbor atoms, small or large polarons are formed and a continuous transition from the one to the other is possible without activation energy being necessary. The well known results of the polaron theory have been obtained from an adiabatic treatment of the carrier ground state in interaction with a defect-free deformable continuous medium, representing the electron-lattice interaction.[13] This interaction is long ranged and the probability that it induces a local change in the crystal is small. Self-trapped polarons have been suggested to be present. The charge carriers should be then localized leading to energy localization[14] but this effect is weak.

In real crystals another mode of trapping exists, namely, the condensation of charges from the conduction band into traps associated with the crystal imperfections. It is known that the damage depends strongly on the microstructure of the dielectric, including punctual defects, impurities, grain size and boundaries, dislocations, disorder, as well as on surface treatment, such as polishing and annealing.[15] Then it appears that the trapping of charges in the defects intervenes on the damage. Each trap is associated with a Coulomb field, thus a bound state, characterized by discrete energy levels located in the band gap of the insulator. Charges are trapped in these bound states.

Experiments have shown that ionization, or charge detrapping, plays also a dominant role in the damage of insulators[16] In the previous models, these processes were explained by the presence of hot electrons and polarization effects; an external energy, due to electric field, temperature or pressure influence, was considered necessary to induce the detrapping. The treatment of the charge transfers was based on adiabatic models,[5–8] assuming that the motion of an electron is sufficiently rapid compared to the motion of the lattice atoms so that the kinetic energy of these last can be neglected. Then the electron trapping and detrapping transitions were treated in the Franck-Condon approximation and the electron-phonon interactions were not taken into account. It was known that these models did not explain the whole of the experimental results.[17]

It is evidence that damage and aging phenomena are associated with changes in the positions of atoms or ions and

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bond breaking, that is to say with local processes.[18] To treat the damage, it is thus necessary to consider the interactions on an atomic scale and to investigate the effect of the charge transfer on the atomic motions. A model that takes into account the energy involved at ruptures of binding and that fits the experimental results for materials as varied as oxides or polymers was, therefore, needed.

The defects are known to have large vibration modes with specific high frequencies. After the trapping of a charge, a defect relaxes to accommodate the new charge configuration.[19,20] Consequently, a large perturbation of the lattice generally accompanies charge trapping and detrapping by the defects and the interaction between electronic transitions and lattice vibrations must be taken into account. One expects the multiphonon transitions to play an important role in these processes.

In this paper, the principle of the multiexcitation processes is reported. A model describing charge trapping and detrapping with the help of multiphonon transitions is presented. In this nonadiabatic model, the energy associated with the localization of the charge is transferred to the lattice vibrations and it is available for the detrapping or eventually for modifications of the system. Information concerning the damage is deduced. These processes are discussed by taking into account thermodynamic[1,2] and desorption results.[21]

II. MULTIEXCITATION PROCESSES

Many various processes including electron hopping in crystalline and amorphous semiconductors,[22] electrical properties of deep levels in semiconductors,[23] dielectric relaxation and conduction in polymers,[24] aging of insulating polymers,[25] are known to obey the Meyer-Neldel (M-N) rule, or compensation law.[26] Let us consider a process characterized by the activation energy E_a and the measured quantity x, with x varying according to the equation

$$x = x_0 \exp(-E_a/k_B T). \tag{1}$$

Here, k_B is the Boltzmann constant and T the temperature. From the *M*-*N* rule, the prefactor x_0 and the energy E_a satisfy the equation

$$\ln x_0 = a + bE_a \tag{2}$$

where a and b are positive constants. The constant b is the reverse of a characteristic energy, noted $1/k_B T_0$. T_0 is named the isokinetic temperature.

The *M*-*N* rule has initially been used in a phenomenological approach to treat the rate of chemical reactions. Let us consider a transition from an initial state over a potential barrier to a final state. The transition up to the top of the barrier governs the reaction rate. From the Eyring theory of the activated state,[27] the reaction rate depends on the variation in the Gibbs free energy ΔG between the initial state and the top of the activation barrier, named activated state. The free energy variation ΔG is equal to $\Delta H - T\Delta S$, where ΔH and ΔS are respectively the enthalpy and the entropy variations. The enthalpy variation ΔH is equivalent to the activation energy E_a and the reaction rate, v is

$$v = v_0 \exp(-\Delta G/k_B T) = v_0 \exp(\Delta S/k_B)\exp(-E_a/k_B T), \tag{3}$$

where v_0 is a constant. Thus, the *M*-*N* rule is verified only if the entropy increases with the activation energy increase.

In the processes where the *M*-*N* rule is obeyed, the activation energy is generally much greater than both $k_B T$ and the highest typical excitation energy of the system.[28,29] Consequently, it is necessary to add up many excitations to provide the activation energy. This implies the presence of multiexcitation processes. From Eq. (2), the *M*-*N* rule connects the activation energy of thermally activated processes with the prefactor x_0. This term varies exponentially with the activation energy. In the case of multiexcitation processes, a large number of excitations are present together at a particular site in the solid to make possible a thermally activated jump over the barrier and this assembly of excitations is associated with a large entropy variation. Consequently, the entropy term readily explains the wide variation in the prefactor and substantial fluctuations of the system are necessary for the *M*-*N* rule to hold.

The characteristic excitation energies can be the optical-phonon energies, the Debye energy or the energy associated to any elementary excitation. In a process with activation energy E_a (or enthalpy ΔH) much larger than the energy of exciting particles, as this is the case for phonon-assisted electronic excitations, the number of ways of assembling the exciting particles increases with the activation energy. In order to explain the compensation law, it is necessary to confirm that this increase is exponential.

This has been made from a microscopic point of view for the phonons, by coupling a two-level system to a multimode Bose field representing the phonon field.[30] When the activation energy E_a is small, the behavior of the system is dominated by one-phonon processes. However, when the activation energy is large, it has been demonstrated that the number of different paths to the final state, via multiphonon processes, increases exponentially with E_a. Then, the *M*-*N* rule concerns levels localized at least one or two electron volts below the conduction band, named deep levels. In a general point of view, the transition rate for a particle in a localized state coupled to a phonon bath is determined by a thermal factor $\exp(-E_a/k_B T)$ multiplied by an entropy term; this last term measures the number of ways in which the phonons furnish the energy required to surmount the activation barrier.

The *M*-*N* rule applies to numerous different properties. Among the properties satisfying this rule, mention can be made of the conductivity.[31] Thus, for ionic crystals, it has been shown that the logarithm of the conductivity prefactor varies linearly as a function of the activation energy above 0.9 eV. Below this limit, the rule breaks down. In a general point of view, by plotting the logarithm of the prefactor as a function of the activation energy, either for different properties of a same material or for the same property in a series of materials presenting equivalent characteristics, it is remarkable that all the data fall on the same *M*-*N* plot. Example is presented for the conductivity of two polymers in Fig. 1: the variation in the prefactor σ_0 as a function of activation en-

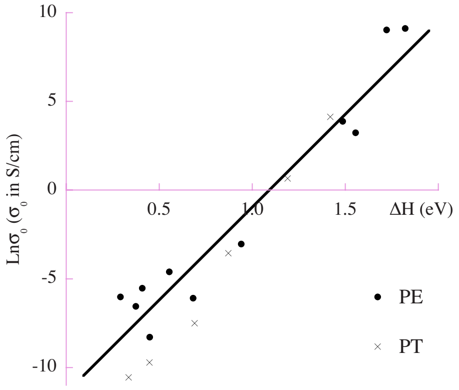

FIG. 1. (Color online) Log$_{10}$ conductivity prefactor vs activation energy for polyethylene (PE) and thermoplastic polymer (PT) (Ref. 32).

ergy ΔH is the same for both materials.[32] In amorphous hydrogenated silica, a-Si:H, many electronic phenomena have been studied and the data of the logarithm of the prefactor against the activation energy for each different experiment fit the M-N plot. The values of $k_B T_0$ deduced from these data vary between 35 and 55 meV while the activation energy is between 1 and 2 eV. The activation energy is about two orders of magnitude larger than the excitation energies.

A. Multiphonon process energy

The existence of the M-N rule in multiphonon processes has been demonstrated with the help of a simple model of phonon spectrum where each quantum has the same energy ϕ.[29] The number of phonons necessary for the excitation over the barrier occurs, is $n = \Delta H/\phi$. If N phonons lie within the interaction volume, the entropy change ΔS associated with the excitation is the logarithm of the number of ways of assembling n out of N interacting phonons. For $n \ll N$,

$$\Delta S/k_B = \ln[N!/n!(N-n)!] \sim n \ln(N/n) \sim (\Delta H/\phi)\ln N.$$

From this, the entropy variation is proportional to the enthalpy variation. The M-N rule applies to systems exhibiting both localization and strong electron-phonon coupling. Indeed the number of ways of assembling n out of N interacting phonons depends on the local electron-phonon coupling strength.

The energy of interaction between an electron and a vibration quantum is due mainly to the adiabatic adjustment of the electronic density in the potential field of the lattice vibration while the term due to the dynamic interaction may be neglected.[33–35] In contrast, in electron-multiphonon interactions the dynamic term cannot be neglected. It is known that the dynamic interaction alters the densities of energy levels and leads to anomalies. Among the first observed anomalies, one can mention the "infrared catastrophy" seen in the soft x-ray emissions of metals as Na. This process corresponds to the response of free electrons to the sudden application of a local scattering potential.[36] This response involves low-energy excitations of valence electrons into the continuum simultaneously with the creation of an inner hole in the metal.[37]

The first study of the desorption process by using the multiexcitation model concerns H_2 desorbed from a-Si:H.[22] Variation in the prefactor by about 14 orders of magnitude has been interpreted by the compensation effect with the help of a new kinetic many-body theory of thermally activated processes. It has been shown that desorption is induced by rapid energy fluctuations of the surface atoms so that the energy acquired during these fluctuations is much larger than $k_B T$ and sufficient to initiate the reaction. More recently, it has been demonstrated that in the absence of external action, desorption of Br adatoms from Br-saturated Si (100) is induced by thermally activated internal electrons.[38] The excitation energies needed to the desorption of Br from different Si samples are between 0.50 and 1.23 eV. Multiphonon processes provide the energy for the electronic excitation and the process follows the M-N rule with a characteristic energy $k_B T_0$ equal to about 60 meV. Such a transition is possible only if the electron is captured by a state strongly coupled to the lattice.

In summary, the M-N rule arises when the activation energy for a process is considerably larger than both $k_B T$ and the characteristic excitation energy of the system, for example the optical-phonon energy. It concerns deep levels that can be higher than two electron volts and not shallow levels. It accompanies the multiphonon processes. Unlike the adiabatic approach in which the electron-phonon interaction leads only to a modification of the electron wave function and does not give rise to specific transitions between different electron states, in the nonadiabatic approach, the phonons receive the energy emitted during the electron capture and provide the free energy needed for its excitation. This will be verified from thermodynamic and desorption results in paragraph IV.

B. Multiphonon process probability

The transition rates between electronic states are generally calculated by assuming the Condon approximation, i.e., by supposing the electronic matrix element to be independent of the lattice coordinates.[39,40] This representation is not convenient for nonradiative multiphonon electronic transitions.[40,41] In the quantum-mechanical framework, these processes are generally considered as due to the nonadiabatic parts of the electron-lattice Hamiltonian. However, the electron-lattice interaction being taken in the linear approximation, that leads to treating the electronic transition matrix element in Condon approximation in analogy with the theory of optical transitions. Calculations in a non-Condon approach had lead to transition rates by some orders of magnitude larger than the previous calculations.[41] The explanation is found in Ref. 42 where it was shown that this discrepancy disappears when the adiabatic results are derived rigorously. The agreement between the different versions is then due to the fact that the electron-lattice interaction is treated in the first order of the perturbation theory.

In order to reproduce the values observed experimentally for multiphonon charge capture cross sections in impurity levels of III-V semiconductors, Henry and Lang (HL) (Ref. 19) used a semiclassical model. The cross section σ of

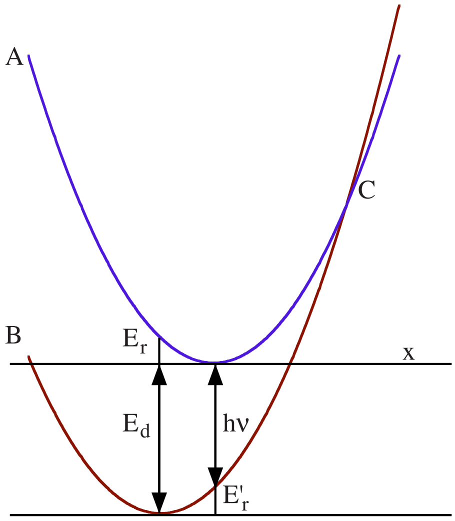

FIG. 2. (Color online) Configurational potential curves: C is the point of crossing of the potential curves associated with a conduction state (curve A) and a defect state (curve B) of binding energy E_d; $h\nu$ is the energy of a luminescence quantum; E_d+E_r is the optical ionization energy; E_r and E'_r are the relaxation energies.

charge capture by a defect is very sensitive to the configuration coordinate diagram and depends on the nonlinearity of the electron-lattice interaction. The defect levels move up and down in the energy gap as the lattice vibrates and for sufficiently large vibrations the defect level can cross into the conduction band and capture an electron (Fig. 2). HL take into account the breakdown of the adiabatic approximation near the level crossing and use the theory developed by Landau-Zener in the crossing region.[43] The electron capture cross sections are predicted to be thermally activated; Thus $\sigma=\sigma_{\text{limit}}\exp(-E_{\text{limit}}/k_BT)$. Multiphonon captures can have large cross sections. As an example, the different cross sections observed for a variety of impurity centers in III-V semiconductors have nearly the same limit value, i.e., $\sigma_{\text{limit}} \approx 10^{-14}-10^{-15}$ cm^2 at a temperature of the order of 1000 K.

The strength of electron-phonon coupling is generally described by the Huang-Rhys factor $S_{HR}=E_r/\hbar\omega$, where E_r is the relaxation energy, i.e., the energy released by an electron transiting from a vibration level n to the zero vibration level (cf. Figure 2) and $\hbar\omega$ is the phonon energy. The condition $S_{HR}\gg 1$ implicates a strong coupling and the condition $S_{HR} \ll 1$ a weak coupling. The value of S_{HR} depends on the respective position of the potential energy surfaces associated with the electronic states. HL showed that large cross sections are only possible if the lattice relaxation associated with the transition, and therefore the electron-phonon coupling, is substantial. One expects this condition to be satisfied at a defect site because the energy level of the defect strongly depends on the lattice. Despite the fact that the HL theory is cited as a reference in numerous reviews, it involves some limitations. Among these, the defect is neutral before trapping and only a single vibration mode is considered in the crossing of the free and bound states.

Another semiclassical calculation of the nonradiative charge capture and emission rates has been developed by Mandelis[44] and also tested in the case of III-V semiconductors. The expression obtained for the capture cross section is similar to that derived by HL, multiplied by a factor equal to $2(p\text{-}S_{HR})$, where p is the number of phonons. Consequently the cross section increases rapidly in the case of strong electron-phonon coupling because p increases more rapidly than S_{HR}. In the thermodynamic limit, the predicted cross sections are found to be in agreement with experiment. But large approximations are also present in this calculation.

HL used their model to determine the multiphonon emission rates of trapped carriers.[19] From this work, the probability for the captured electron to be reemitted to continuum states immediately after capture is about 1/2. These authors underlined that the dominant emission process is toward the conduction band and the ionization energies of the states are always a little larger than their bonding energies.

The radiative electron capture transitions are known to present a strong asymmetric broadening.[45] The line shape $f(h\nu)$ depends on complex interaction between broadening due to phonons and broadening due to the lattice relaxation, which increases with the temperature. Consequently it is difficult to account for the influence of these different phenomena on the line widths. However, it has been shown that the nonradiative capture cross section σ is equal to $Af(h\nu)$. Since the coefficient A does not depend on the lattice, the dependence of σ on the lattice and the temperature may be determined from $f(h\nu)$. Moreover, from the width of luminescence lines, information can be deduced on the importance of the nonradiative multiphonon transitions.

III. TRAPPING AND DETRAPPING

Charge trapping in a defect state induces the localization of the charge and an energy transfer. The trapping of a conduction electron has a strong probability to take place in a level located immediately below the conduction band. It could be either the ground level of a shallow trap or an excited level of a deeper trap. The energy transfer involving these levels is of the order of the thermal energy at room temperature.

Similarly, the thermal energy makes possible the excitation of the charge from a highly excited level of a defect. Thus, an electron trapped in such a level can be ejected into the conduction band, i.e., detrapped. The system returns to a state close to the initial state. The electron detrapped in the conduction band has a very small kinetic energy; it remains in the vicinity of the trap and can be trapped again. Trapping-detrapping processes involving highly excited states are quasi reversible and induce no relaxation in the crystal. More generally, the thermal energy at room temperature can generate hopping processes taking place between excited levels of various defect sites. Then, an electron trapped in a highly excited level can jump to another excited level of the same trap or to an excited level of another trap. These processes induce no perturbation of the system.

An electron trapped in one of the excited levels of a deep trap can decay to the ground level of the trap. The energy lost by the electron during its stabilization is dissipated by luminescence emission or by a nonradiative process like Auger emission or multiphonon transition.[46] In the last case, many phonons are involved in the process.[39] During the multiphonon transition the electronic energy is transferred to the vibration modes of the defect and of their immediate neighbors. With respect to the electronic transitions with energy dissipation by radiation or Auger emission, it is possible to say that the electronic energy is "gained" by the system during multiphonon transitions.

Immediately after the electron capture, the multiphonon transition gives rise to strong, rapid lattice vibrations and induces a large lattice relaxation localized at the defect and around it. As already mentioned, these transitions are caused by the crossings of free, or weakly bound, electronic states with bound electronic states (Fig. 2). The crossings occur for sufficiently large lattice displacements. The broadening of the levels favors their overlap and increases the multiphonon transition probability.

There is strong evidence that a nonradiative multiphonon transition occurs if a strong coupling exists between electrons and phonons. Moreover the displacement amplitude of the phonons is limited when the coupling between phonons is strong.[47] Consequently, large amount of the energy associated with the trapped charge remains concentrated in the disordered lattice around the trap. The free energy variation is weak because enthalpy and entropy are partially compensated, leaving the system in a metastable state. From this state, electron detrapping to the conduction band is possible by multiphonon transition. It is suggested here that the energy necessary to delocalize the charge from the trap is obtained from the vibration energy stored in its neighboring.

Then, the motion of charges, their trapping and detrapping, are controlled by the electron-lattice coupling. If the defect states are strongly coupled to the lattice, the characteristic time of the coupling is short enough for the lattice to follow the changes of the electronic state dynamically.[48] The significant electronic frequencies are comparable to the vibration frequencies of the ionic waves, making the adiabatic approximation invalid. In this model, after a charge is trapped into a solid, metastable state is established within a time interval of very few lattice vibrations and the potential energy associated with this state can induce detrapping. The associated phonon bath provides the energy for the electronic excitation as seen in the hot-electron stimulated desorption process.[38] The electron-phonon interaction is the coupling mechanism and this model is valid independently of the chemical bonding.

In contrast, when the electron-phonon interactions are weak, the probability of the multiphonon transitions is small and the electronic transitions perturb the lattice only slightly. The electron remains in the ground state of the trap and if the number of traps is small, the system is not perturbed.

From cathodoluminescence experiments of α-Al_2O_3 single crystal,[49] it has been shown that the density of trapped charges cannot exceed a threshold value characteristic of the material and that the value of the threshold increases inversely with the temperature. In the regions of the crystal where an excess of defects is present, mainly in the vicinity of dislocations, trapped charges interact each other, so that the detrapping can take place.

On the other hand, in a disordered material, the larger the lattice distortion and the electron-lattice interactions, the deeper the defect states. Just after the capture, significant amount of energy associated with the trapped charge is concentrated on few atoms, greatly enhancing the amplitude of their motion. These motions can lead to modifications or ruptures of bonds and cause nonlinear changes and local instabilities in the lattice, especially because the energy remains near the defects and their presence weakens the interatomic bonds. From a general point of view, the multiphonon electronic transitions associated with rapid lattice vibrations enhance the motion of the defect and neighboring atoms and can induce perturbation in a closed system without external contribution.

Electric effects must also be taken into account. In fact, the presence of charge carriers creates a space charge, inducing a local polarization field distributed in different crystal points in a nonhomogeneous manner. This field has two effects: it decreases the binding energies of the levels making their excitation more probable; it accelerates the detrapped charges. If the acceleration is sufficient, charges can induce ionizations and the detrapping process is amplified.

The damage inside an insulator takes place in the presence of defects, disorder or inhomogeneity and it is strongly connected with the breaking of chemical bonds. A binding rupture is a local process that induces changes in the distribution of bound electrons, in the interactions of electrons with the vibrations of their proper atom and with the vibration modes of the first neighbors.

Consequently, damage results from several processes, the first one being the charge trapping in the ground level of traps characteristic to the material imperfections. In the case of a nonradiative multiphonon transition, the vibration energy transferred to the insulator can operate directly on a bond between two atoms until these are pulled far enough apart that the bond breaks. Second, the sudden increase in electron detrapping in one or several microscopic regions of the material, controlled by the coupling with phonons, can perturb the bonds and the motions of atoms or ions in the lattice, increasing the number of free electrons, the electric conductivity, the polarization and the intensity of local fields, as well. If the number of these processes is high enough, an irreversible deformation of the insulator is induced. The polarization associated with the moving charges can largely amplify the processes.

It is thus evidence that electronic transitions with charge transfer play an important role in the damage of insulators. It must be underlined that the detailed description of the damage phenomena is complex owing to the interference of many factors. Extensive studies of damage and aging phenomena have been carried out.[50]

IV. EXPERIMENTS ON CHARGED INSULATORS

A. Thermodynamic analysis

An interesting and original analysis of the calorimetric properties of charged insulators has been performed by Blaise and Moya.[1,2] As the charged sample is heated from room temperature up to about 150 °C, exothermic peaks are observed. An endothermic peak is observed by cooling the sample (Fig. 3). The same behavior has been observed for

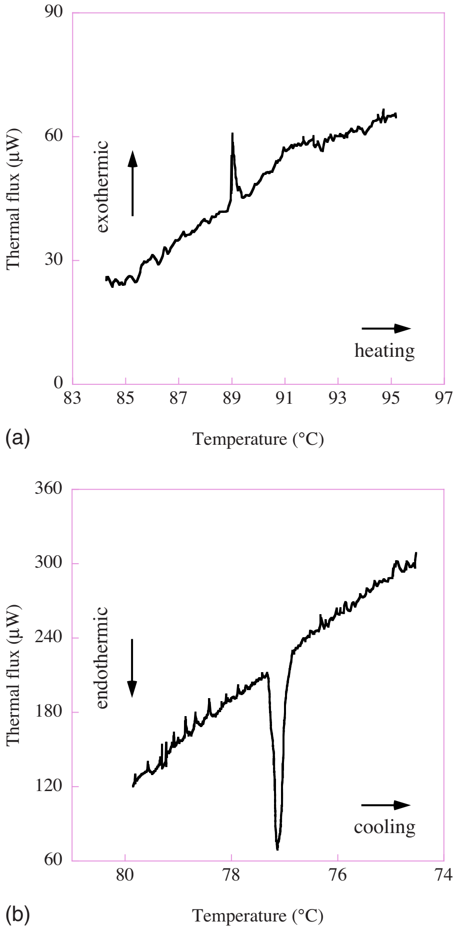

FIG. 3. (Color online) Thermograms obtained for Ag/Al_2O_3: (a) heating: charge of 2000 pC; (b) cooling: charge of 40 000 pC (Ref. 1 and 2).

doped and undoped Al_2O_3 and for polymers. It has been shown that in each experiment the areas under the endothermic and exothermic peaks are equal and proportional to the amount of the injected charges.

These peaks have been attributed to first order chemical reactions whose rate is given by Eq. (1). The values of the prefactors x_0 and the energies E_a have been determined. As an example, for the Ag/Al_2O_3 charged sample (40 000 pC), the prefactor x_0 and the energy E_a are 7.5×10^{20} s^{-1} and 1.6 eV for the exothermic peaks and 2.4×10^{20} s^{-1} and 1.5 eV for the endothermic peaks, respectively. As noted by the authors, the magnitude of the prefactors can be explained only by the presence of an entropy term.

These observations can be interpreted as follow: the exothermic peaks correspond to the charge detrapping while the endothermic peaks reveal the trapping. The traps are the impurity states associated with Ag. The energy of 1.6 eV is the energy necessary to excite an electron from the ground level of the trap to the bottom of the conduction band; the energy of 1.5 eV is the energy emitted by an electron present in an excited level of the trap when it decays back to the ground level of the trap. This last energy is smaller than the excitation energy because it corresponds to an electronic transition from a highly excited level to the ground level while the excitation takes place from the ground level directly to a level of the conduction band.

For undoped Al_2O_3, E_a is equal to 1.2 eV. The involved electronic processes are the trapping by a center F^+ giving a center F and the reverse process. The energies of optical bands associated to F^+ and F are 3.8 and 3.0 eV, respectively.[49] A large relaxation accompanies these trapping and detrapping processes, putting E_a 0.4 eV above the energy difference between both emissions.

The prefactors are characteristic of multiphonon transitions connected with large changes in the entropy. The energy gained by the system during the electron trapping is communicated to the phonons and inversely the random statistical motion of the phonons is the energy source to detrap an electron into the conduction band.

In summary, the kinetics of the thermal reactions in charged insulators proves the importance of phonons in controlling the trapping and detrapping processes. These processes follow the *M-N* rule. Consequently, there is a correlation between activation energy and entropy: the entropy term increases with the activation energy.

B. Desorption analysis

Similar multiphonon processes can also explain the oxide degradation of metal-oxide-semiconductor (MOS) systems.[21] In this reference it is underlined that the SiO_2 degradation is not due to polarization effects but to desorption of hydrogen; this desorption, considered as initiating the breakdown, should be possible from the energy gained by the carriers traversing the dielectric. Indeed, as discussed in 38, desorption can involve an electronic excitation controlled by the coupling of electrons with the phonons, thus showing the importance of considering the multiphonon transitions in this process.

V. CONCLUSION

The action of an electric field and associated ionization processes were considered as the predominant factors leading to damage of insulators. Models based on the charge motions in a polarized material have been developed and commonly used. Polarization effects due to the presence of trapped charges have been studied and in these models radiative and only nonradiative Auger transitions were considered to accompany the charge capture processes.[51]

The aim of the paper is to show the primary role played by multiphonon electronic transitions with charge transfer in the insulator damage. Indeed these transitions induce a strong relaxation of the lattice around the trapped charge. During the trapping into a localized defect state, energy is transferred to the lattice vibrations causing the weakening of the bonds. On the other hand, the energy concentrated in the vicinity of the defect can induce the charge detrapping. If defect states strongly coupled to the lattice are highly populated and if sudden trapping-detrapping occurs, large movements of atoms or ions are produced. This causes change of the lattice, making the detrapping a precursor process of the damage.

The complexity of these processes and the numerous parameters involved explain the problematics of the models treating nonradiative multiphonon electronic processes and the difficulties to develop an “exact” theory.

Multiphonon transitions are known to be present in many physicochemical processes accompanied by atom motions and bond rupture. The large change in entropy, the temperature dependence of the capture cross sections, the shape of luminescence lines and the variation in energy levels with the temperature as deduced from the radiative transitions, all point to the measurements of these different quantities can be used to validate the multiphonon model and its ability to explain the trapping and detrapping processes.

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