Mechanisms of Charge Trapping at a Dielectric Surface: Resonance Stabilization and Dissociative Attachment

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A solid Kr film partially covered with O_2 molecules is charged by a 0- to 10-eV electron beam. The electron energy dependence of the trapping cross section indicates that surface charging in the 0–2-eV range is due to stabilization via the $^2\Pi_g$ O_2^- resonance, whereas in the 4–10-eV region, it is due to $O^-(^2P)$ formed by dissociation of the intermediate $^2\Pi_u$ state of O_2^-.

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Charge accumulation in dielectric solids and at their surfaces is of major interest in such diverse fields as radiation chemistry[1] and semiconductor,[2] electret,[3] and spacecraft technology.[4] *Negative charge* storage induced by dielectric breakdown,[5] electric discharges,[6] beam injection,[6] or ionizing radiation[1,6] is usually due to *electrons* which are trapped into long-lived localized states. Although it is generally understood that the electron localization occurs via thermalization of low-energy electrons,[1,6] the dynamics of the process, which leads to energy losses and subsequently immobilization at a particular site, cannot yet be described in detail.

With the present method, we measure charge accumulation at the surface of a thin dielectric film caused by *very low-energy* (0–10 eV) electron bombardments. We are therefore able to provide information in the critical energy region where attachment, dissociation, and energy-loss processes can lead to electron localization and trapping. As a first measurement, we report the electron energy dependence of the trapping cross section of Kr films partially covered by oxygen molecules. With this information, we can describe the *specific phenomena* causing the surface charges, namely, *resonance stabilization* and *dissociative attachment* (DA) at the O_2 site.

The new method of charge measurement[7] is derived from low-energy electron transmission (LEET) spectroscopy.[8] In a LEET experiment, a magnetically collimated *high-resolution* ($\cong$60 meV) electron beam impinges on a multilayer-dielectric solid-film vacuum deposited on a metal substrate. A LEET spectrum is obtained by recording the current arriving at the substrate as a function of a potential V applied between the substrate and the electron source.[8] When electrons have just enough energy to enter into the film from vacuum, a sharp rise, termed the "injection curve" (IC), is seen in LEET spectra.[8] The IC for an uncharged film is represented by the upper curve of Fig. 1. When the same film is charged at the surface by the electron beam, the IC is shifted by ΔV to a higher accelerating potential since the incoming electrons must possess additional kinetic energy to overcome the negative potential barrier. The IC is also broadened as a result of the spatial current-density distribution.[7] Treating the dielectric film as a charged capacitor, the potential barrier ΔV is related to the surface charge density $\sigma(t)$, which has accumulated after bombardment time t, by the relation[6]

$$\Delta V(t) = \sigma(t) h/\epsilon , \qquad (1)$$

where $\sigma(t) = \sigma_0(1 - e^{-\beta t})$ and $\beta = \mu J_0/e$; ϵ is the dielectric constant of the film, h is its thickness, σ_0 is the initial ($t = 0$) trap density, μ is the trapping cross section, J_0 is the incident current density, and e is the unit charge. *In the limit $t \to 0$ we can define a charging coefficient $A = d\Delta V/dt$ which is directly proportional to the trapping cross section* [i.e., $d\Delta V/dt\,|_{t=0} = (h\sigma_0 J_0/\epsilon e)\mu = A$].

The IC of a freshly deposited multilayer film is first recorded rapidly (i.e., 0.1 sec) to avoid any significant

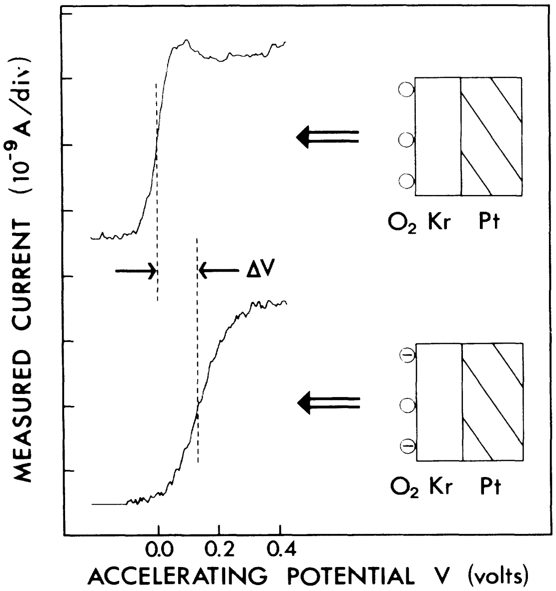

FIG. 1. Current transmitted through an uncharged (top) and a charged (bottom) Kr film covered with a 0.1 layer (L) of O_2 (0.1-L-O_2/Kr) as a function of the accelerating potential V of the incident electron beam.

charging. The film is then bombarded at a given V for a much longer period (i.e., 25 sec) with the same incident current (i.e., $I_0 \cong 5\times10^{-9}$ A). Afterwards, the IC is again rapidly recorded and the shift ΔV determined by comparison with the initial IC. Such a cycle can be repeated many times on the same film with the same V to obtain the time dependence of the process. To measure the thickness and energy dependence, a new film has to be deposited for each data point.

In the present experiments, 99.995% pure Kr was condensed on a Pt ribbon held at 20 K.[8] Film thicknesses were estimated within 15% accuracy by monitoring quantum-size interference structures in LEET spectra as previously described.[8] The amount of molecular oxygen (99.997% pure) leaked on the Kr film surface could be calibrated against the amount of Kr introduced into vacuum.[7] Unless otherwise stated the data were recorded with 20-layer (L) Kr films having an O_2 surface coverage corresponding to 0.1 layer (0.1-L-O_2/Kr).

The shift $\Delta V = 130$ meV of the IC in Fig. 1 was obtained after a 7.3-eV bombardment of a 0.1-L-O_2/Kr film. By recording another IC, 5–10 min later the charge leak rate was found to be smaller than 2% ΔV/min. By repeating the bombardment and IC-recording sequence of Fig. 1 6 times, Eq. (1) was verified within experimental error (i.e., 20%), and could therefore be fitted to the data in order to obtain the value of the coefficient A. Similar experiments with no O_2 at the surface produced shifts ΔV smaller than 10% of those obtained with 0.1-L-O_2/Kr films. In all subsequent experiments, the charging coefficient A_f of the pure Kr film was subtracted from A in order to obtain the surface-charging coefficient A_s due to O_2 (i.e., $A_s = A - A_f$). A_s was found to be directly proportional to the incident current intensity and surface coverage below 0.5-L O_2. The capacitance behavior of the films [i.e., Eq. (1)] was verified by measurement of the thickness (h) dependence of A_s for 7.3 and 1.0 eV electrons which was found to be linear for $h > 15$ L. Finally, the electron energy dependence of A_s was investigated between 0–10 eV. The result obtained [Fig. 2(c)] is comparable to the energy dependence of the anion yields derived from the gas-phase attachment rate coefficient for stable $O_2{}^-$ production[9] [Fig. 2(a)] and the DA cross section[10] [Fig. 2(b)]. No signal has been reported between 1.2 and 4.5 eV in the gas phase.[10] Figure 2(d) represents the electron-stimulated desorption (ESD) signal from a 0.1-L-O_2/Kr film.[11]

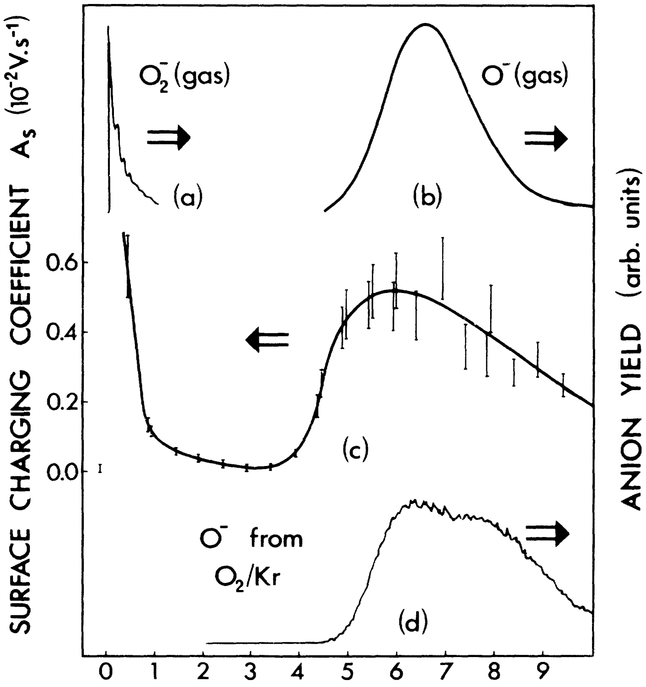

FIG. 2. Anion yields produced by 0–10-eV electron impact on (a) and (b) gaseous O_2 and on (d) a 0.1-L-O_2/Kr film. (b) Electron energy dependence of the surface-charging coefficient A_s for a 0.1-L-O_2/Kr film.

Surface charging as a result of the presence of molecular oxygen can be understood in terms of the potential-energy diagram of the two lowest ${}^2\Pi_g$ and ${}^2\Pi_u$ states of $O_2{}^-$ (Refs. 10 and 11) shown in Fig. 3. In the 0–1.2-eV range, temporary electron attachment to gaseous O_2 leads to the formation[10] of the ${}^2\Pi_g$ resonance state of $O_2{}^-$. This occurs in vibrational levels $v \geq 4$, since the $v < 4$ levels lie below the ground state of O_2. However, during the lifetime of the ${}^2\Pi_g$ anion when vibrational energy is transferred to another molecule in a third-body collision,[10,12] the $v < 4$ levels can be reached and the

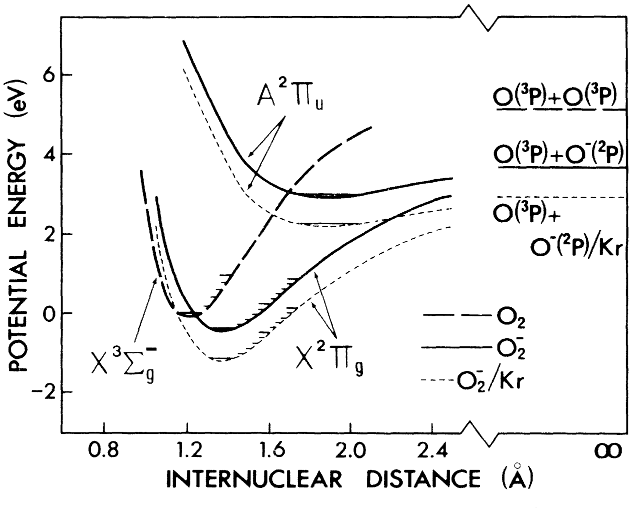

FIG. 3. Potential-energy curves of the ${}^2\Pi_g$ and ${}^2\Pi_u$ states (Refs. 10 and 11) of isolated (solid lines) and physisorbed (dashed lines) $O_2{}^-$ referenced to the ground state of $O_2({}^3\Sigma_g{}^-)$. The energy of physisorbed $O_2{}^-$ is shifted down by 0.7 eV to account for electronic polarization at a Kr surface. In the $O({}^3P) + O^-({}^2P)$/Kr limit, O^- remains bound to the surface.

electron becomes permanently attached to the molecule. Vibrational energy transfer may also occur when the O_2^- ($^2\Pi_g$) ions are formed within van der Waals clusters[12,13] which coexist with monomers at high pressures. Märk *et al.*[14] have recently shown in crossed-electron-molecular-beam experiments that the $^2\Pi_g$ state is formed in $(O_2)_n$ $(2 \le n \le 15)$ clusters and leads to the production of stable $[(O_2)_{n-p}]^-$ $(p<n)$ ions in the range 0-2 eV. The *resonance stabilization process* involves vibrational energy transfers to molecules within the the cluster,[14] causing evaporation of p O_2 molecules from this latter which leaves behind the anion $[(O_2)_{n-p}]^-$. The comparison in Fig. 2 strongly suggests that a similar stabilization process is effective at the Kr surface and responsible for surface charge accumulation in the range 0-2 eV. The electron can either lose energy to vibrationally excited O_2 via the $^2\Pi_g$ O_2^- state and afterwards stabilize at a Kr trapping site or the $^2\Pi_g$ state may itself stabilize by energy transfer to phonons. The estimated lifetime of the $^2\Pi_g$ O_2^- state within clusters is of the order of 10^{-12} sec (Ref. 13) which is comparable to the phonon vibrational period of the Kr lattice (5×10^{-13} sec).[15] *Hence, the additional electron resides a sufficiently long time at an* O_2 *site to polarize the phonon modes of the Kr lattice and thereby transfer energy to lattice vibrations.* According to the potential energy curve of the surface $^2\Pi_g$ state (Fig. 3), initial attachment of electrons arriving from vacuum would occur in vibrational levels $v \ge 10$.

At higher energies, anion production by electron impact on isolated O_2 molecules is dominated by decay of the $^2\Pi_u$ state into the DA channel[10] yielding the products $O(^3P)+O^-(^2P)$. This reaction has also been observed in O_2 clusters[14] and in O^- ESD from multilayer pure O_2 films[16] and O_2-covered rare-gas surfaces.[11] It is responsible for the O^- signal in Figs. 2(b) and 2(d). *We therefore ascribe surface charging in the 4-10-eV region to the dissociation of the* $^2\Pi_u$ *surface state into the limit* $O(^3P)+O^-(^2P)/Kr$. Accordingly, *the* O^- *ESD and the charging signal are of the same nature* and derived from the same O_2^- $^2\Pi_u$ surface state (Fig. 3). Since that state lies at lower energy than its gas-phase counter part, the maximum around 6 eV in Fig. 2(c) is found about 0.7 eV below the maximum in the gas-phase DA signal. Although the DA maximum in the ESD yield arises from the same O_2^- surface state as that in the charging signal, it is much less shifted in energy since, in order to overcome the polarization force of the Kr film, desorbing O^- ions must arise from O_2^- $^2\Pi_u$ states formed at higher electron energy in the Frank-Condon region.

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