Negative-Ion Desorption from Insulators by Electron Excitation of Core Levels

Ann-Marie Lanzillotto
David Sarnoff Research Center, CN 5300, Princeton, New Jersey 08543-5300

Theodore E. Madey
Department of Physics and Astronomy, Rutgers University, Piscataway, New Jersey 08855-0849

Raul A. Baragiola
Engineering Physics, University of Virginia, Charlottesville, Virginia 22901

(Received 5 February 1991)

We have observed the desorption of O^- and Si^- ions during the electron bombardment of SiO_2, and have determined ion yields and kinetic-energy distributions at electron energies > 100 eV. The threshold energy for the O^- yield corresponds to the excitation of Si-*L*-shell core levels. We propose that multielectron excitations cause the ejection of positive ions or neutral atoms from the surface, and that these species can capture electrons in the surface region to form negative ions. Alternatively, the creation of superexcited electronic states of an SiO_2 surface complex may lead to the ejection of O^-.

PACS numbers: 79.20.Kz

It is well known that the electron bombardment of oxide surfaces induces dissociation and ion emission leading to a depletion of oxygen at the surface [1-6]. Several investigations have focused exclusively on the desorption of positively charged ions from these surfaces [6-9]. Proposed mechanisms for positive-ion emission from oxides include the Knotek-Feibelman interatomic Auger decay model [6] and a process involving Auger decay from a core hole in the presence of additional electronic excitations leading to Coulomb repulsion [9].

We report the emission of negative substrate ions during electron-stimulated desorption (ESD) from thermally grown SiO_2 films on Si. Previously reported ESD measurements of negative-ion yields exhibit low-energy thresholds corresponding to valence-level excitations [10,11]. Those results are interpreted in terms of dissociative-attachment and dipolar-dissociation processes in which backscattered and secondary-electron effects [12] and image-charge effects [11] play a significant role. In our present work, we have investigated the electronic-excitation mechanisms for negative-ion formation during the bombardment of SiO_2 by electrons in the energy range above 100 eV. We have measured ion yields as a function of electron-beam energy and determined the kinetic energies of the ESD-produced O^- ions. The energy thresholds for O^- ions correspond to excitations involving a Si 2*p* core level. This is the first report of negative-ion ESD initiated by a core-level excitation.

The experiments were performed in an ultrahigh-vacuum chamber designed for high-sensitivity ion detection [13]. This system, equipped with an extranuclear quadrupole mass spectrometer (QMS), in-house-designed secondary-ion optics, a concentric hemispherical electrostatic analyzer, and an electron gun, maintains a base pressure of 1.0×10^{-10} Torr. The electron beam is incident at 70° with respect to the surface normal. The sample and extraction lens are kept at -20 V so the ions reaching the analyzer have an excess energy of (20 eV)$+eV_s$. V_s is the potential to which the sample charges with respect to the grounded sample holder. The measured ion-energy distribution curves are broadened by the 4% energy resolution of the electrostatic analyzer, 0.8 eV at a pass energy of 20 eV.

The electron-beam current was measured on a conducting surface biased to suppress secondary-electron emission. The electron-beam spot size was contained within the acceptance area of the ion extraction optics. The low yields of substrate ions required the use of electron-beam currents in the μA range. We obtained O^--ion count rates at a QMS mass setting of 16 amu and at the peak of the O^- energy distributions and normalized them by the incident electron current to obtain relative ion yields.

The experiments were carried out on samples of thermally grown SiO_2 films on Si. The ion signals are found to decrease monotonically with bombardment time until reaching a steady state. The position of the threshold does not depend on electron dose.

Figures 1(a) and 1(b) show ESD mass spectra from a 65-Å SiO_2/Si film bombarded with 2-keV electrons. Figure 1(a) depicts a positive-ion mass spectrum. We observe substrate ions (Si^+, Si^{2+}, Si^{3+}, SiO^+, O^+, O^{2+}) and impurity ions (H^+, F^+), as have been previously reported [8,9]. These ions are characteristic of different SiO_2 samples, and are not detected from the native oxide on the stainless-steel sample holder.

Figure 1(b) shows a negative-ion mass spectrum from a 65-Å SiO_2 film. The dominant ions are O^-, Si^-, and H^-, with smaller signals identified as C^-, F^-, Cl^-, and possibly C_2^-, $C_2H_2^-$. A substantially different negative-ion mass spectrum was observed from the stainless-steel sample holder; the ions include O^- (a factor-of-10 smaller signal than observed from SiO_2), C^-, O_2^-, and F^-. The background in Fig. 1(b) is due to electrons reaching the quadrupole. We observe linear behaviors for

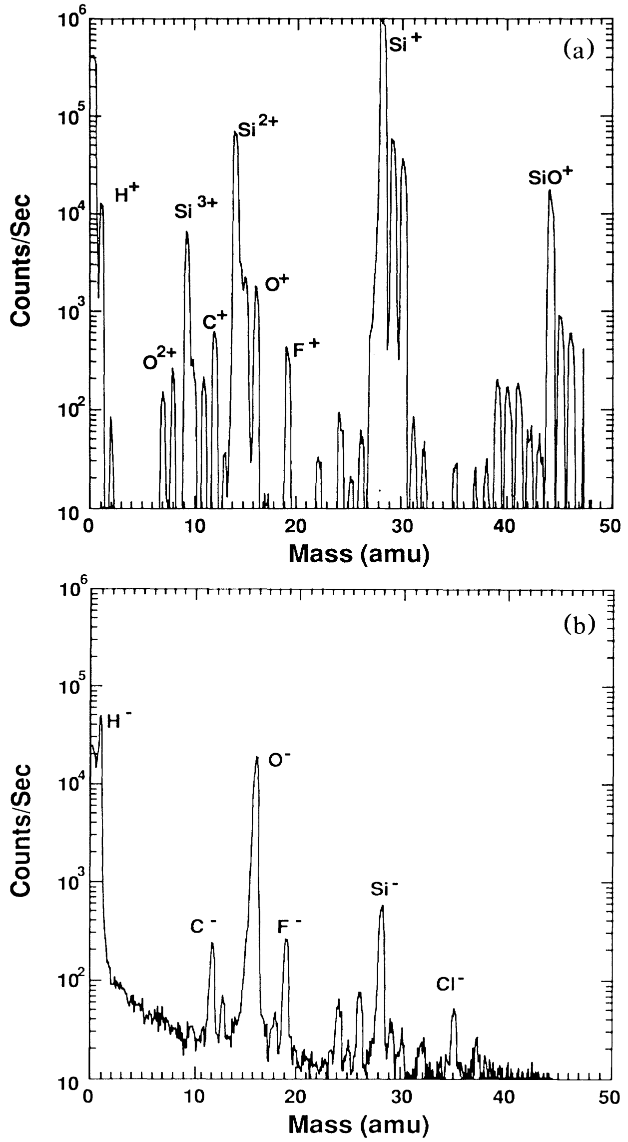

FIG. 1. (a) ESD positive-ion mass spectrum from a 65-Å SiO_2/Si film bombarded with 2-keV electrons: $I_e = 40\ \mu A$. (b) ESD negative-ion mass spectrum from a 65-Å SiO_2/Si film bombarded with 2-keV electrons: $I_e = 6\ \mu A$.

positive- and negative-ion signals as a function of bombardment electron current.

The relative ion signals (counts/secμA) for Si and O were determined from the mass spectra. The data indicate that the O^- signal is greater than the O^+ signal and the Si^+ signal is greater than the Si^- signal; whether the total yields are greater depends on (unknown) angular distributions and detector efficiencies. In the ESD of monolayers on metals, positive-ion signals are typically larger than negative-ion signals [14,15]. For example, Yu compared the ESD of positive and negative oxygen ions from O adsorbed on Mo [14]. He found that the O^- yield is 2 orders of magnitude smaller than O^+ at equal adsorbate coverages. In addition, Hock, Craig, and Lichtman observed that the O^- yield is 50 times smaller than the O^+ yield for ESD from CO adsorbed on W [15]. Negative-ion deexcitation at metal surfaces should be more efficient than at oxide surfaces, due to the availability of many vacant levels in the solid resonant with the affinity level of the negative ion.

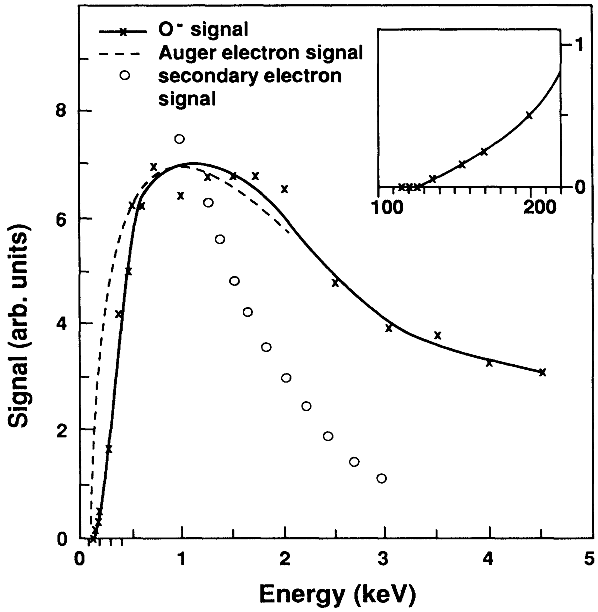

FIG. 2. ESD O^--ion yield from a 65-Å SiO_2/Si film vs electron bombardment energy; Auger electron yield for the $Si(L_{2,3}VV)$ transition vs electron bombardment energy (from Ref. [16]); and secondary-electron yield from a SiO_2 film vs primary electron energy (from Ref. [2]).

The solid curve with crosses in Fig. 2 is a representative $Y(E)$ curve for O^- ions. These measurements were performed in the electron energy range from 90 to 5000 eV. The observed threshold occurs at ~130 eV, corresponding to Si-L-shell ionization. There is no evidence that O 1s or Si 1s core excitations have a dominating effect. (Our previous report [9] of a threshold above the O 1s onset in positive-ion desorption is probably in error and is being reexamined.)

The dashed curve in Fig. 2 depicts the Auger electron yield for the $Si(L_{2,3}VV)$ transition in Si as a function of primary beam energy at 70° incidence [16]. This distribution is dominated by the core-hole ionization cross section and is also influenced by the energy distribution of the backscattered electrons. Our $Y(E)$ curve is delayed in energy but roughly follows the shape of the Auger yield curve at primary energies < 2.0 keV.

The open circles in Fig. 2 denote the secondary-electron yield versus primary beam energy for a SiO_2/Si thin film [2]. For SiO_2 films, the secondary-electron emission maximizes at ~380 eV [17]. This is well below the maximum in our $Y(E)$ curve. It is clear that the energy dependences for the O^- yield curve and the secondary-electron yield curve are different.

Figure 3 shows a kinetic-energy distribution (KED) for O^- that is somewhat narrower (i.e., less than 2 eV full width at half maximum, peak energy at 1.7 eV) than normally found in ESD for positive ions. The O^- KED's are unlike the KED's observed for O^+ ions from SiO_2 that extend from 0 to 25 eV [9]; this difference provides insight into possible mechanisms, as discussed below. The peaks and widths of the O^- KED's remain constant with a change in the primary energy from 0.5 to 2.0 keV. In contrast, Hock, Craig, and Lichtman [15] studied the ESD of O^- and O^+ ions from CO on a metal surface and found that the ion energy distribution for O^- is broader and peaks at a higher energy than the O^+-ion distribution.

The energy dependence of the yield exhibits a threshold (~130 eV) in the region of the Si L edges. We cannot resolve features due to the Si $2p$ and $2s$ core levels, whose maximum ionization cross sections are 8.4×10^{-18} and 1.0×10^{-18} cm^2, respectively [18]. Since the excitation of Si $2s$ is not possible at ~130 eV, this threshold is believed to be due to the Si $2p$ edge that is delayed in energy when compared with the Auger yield. This may be due to multielectronic excitations, as proposed previously [9].

The observation of negative ions with a threshold energy corresponding to a core excitation suggests that ions are emitted as a result of an Auger process leading to Coulomb repulsion. However, this process by itself should not account for the direct formation of negative ions, since Auger decay produces a two-hole final state in a bonding orbital which usually leads to the desorption of positive ions. Based on our previous studies [9], we believe that multielectronic excitations cause the ejection of positive ions or neutral atoms [19] from the surface. These species may recapture electrons in the surface region to form negative ions. Charge exchange between an SiO_2 surface and an outgoing O^+ to form O^0 is allowed because the O ionization energy (~13.6 eV) is below the valence-band edge of SiO_2 (~10.5 eV) [20]. Charge exchange to form O^- can occur because the affinity level is shifted downward by the surface image potential; there is a continuous shift from O^- in the gas phase to $O^{\delta-}$ bonded in the lattice. The electrons participating in the charge exchange may originate in the valence band or trap states [21] in the band gap of SiO_2.

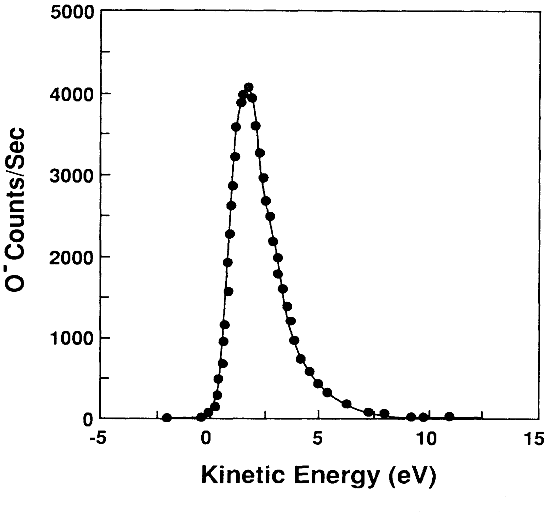

FIG. 3. Kinetic-energy-distribution curve for O^- ions ejected from a 65-Å SiO_2/Si film by 500-eV electrons.

The neutralization may also be thought of in terms of a recapture process localized to a molecular complex. For example, consider a SiO_2 surface complex in which a Si ($2p$) core-hole excitation leads to the formation of a highly excited molecular complex such as $(SiO_2)^*$ or $(SiO)^*$. For these excited neutral states to exist, the excited $2p$ electron must be trapped in a Rydberg-like orbital, analogous to the creation of an exciton in an insulating crystal. During dissociation of these excited complexes, the spectator electron may attach itself to the electronegative oxygen atom. The formation of O^- may be illustrated by the following sequence of events:

$$SiO_2+e^- \rightarrow (Si_{2p-1}O_2)^*+e^- \rightarrow SiO^+ + O^- + e^- .$$

This assumes that the lifetimes of these excited states are long enough to allow desorption to occur. Moreover, we observe a significant SiO^+ signal, as illustrated in Fig. 1(a).

Support for this mechanism comes from the work of Dujardin *et al.* who observed the formation of O^- ions by photon excitation of sulfur $2p$ core levels in gas-phase SO_2 molecules [22]. They propose the existence of superexcited electronic states of ${SO_2}^+$ that dissociate into negative ions as well as autoionize to produce SO^{++} ions. One aspect of our work which is not analogous to the work of Dujardin *et al.* is that our yield curve reveals a delayed onset of ~20 eV from the Si $2p$ edge. This may imply that a single core-hole excitation is not enough to cause desorption, but multielectronic excitations are necessary. One possibility is a short-lived superexcited state, e.g., $[(Si^+O^+)^{--}]^*$, resulting from the simultaneous excitation of a Si $2p$ core level and an O $2s$ level leaving two electrons in spectatorlike orbitals.

The ESD of negative ions is expected to contain contributions from true secondary-electron emission and backscattered primary electrons [12] when there are low-threshold-energy processes involved. We do not expect the secondary-electron yield to contribute to the initial core-level excitations because of their lower kinetic energies.

The Auger yield as a function of energy (which includes the backscattered-electron yield) has a shape and maximum similar to our $Y(E)$ curve. Because of their higher kinetic energies, we expect these backscattered electrons to contribute to the initial excitations, especially at glancing angles.

The measured kinetic-energy distributions of O^+ ranging from 0 to 25 eV support Coulomb repulsion in the final state. We observe lower kinetic energies for O^- ions ranging from 0 to 7.5 eV. This is consistent with both our ion-formation models, since only the lowest-energy positive ions or neutral atoms remain in the surface region long enough to be able to recapture electrons.

In summary, we have observed the desorption of O^- and Si^- ions during the electron bombardment of thermally grown SiO_2 films. We believe that multielectron excitations cause the ejection of positive ions or neutral atoms from the surface. These species can capture electrons in the surface region to form negative ions. Alternatively, the formation of a highly excited molecular complex, such as $(SiO_2)^*$, may lead to the ejection of O^-.

This work was supported in part by the New Jersey Advanced Technology Center for Surface Engineered Materials.

---

[1] B. Lang, Appl. Surf. Sci. **37**, 63 (1989), and references therein.

[2] J. S. Johannessen, W. E. Spicer, and Y. E. Strausser, J. Appl. Phys. **47**, 3028 (1976).

[3] V. V. Nikitin, K. F. Komolova, I. V. Razumovskaya, and N. F. Shevtsova, Izv. Akad. Nauk SSSR, Ser. Fiz. **48**, 2384 (1984).

[4] J. S. Johannessen, W. E. Spicer, and Y. E. Strausser, Appl. Phys. Lett. **27**, 452 (1975).

[5] V. E. Henrich, Rep. Prog. Phys. **48**, 1481 (1985).

[6] M. L. Knotek and P. J. Feibelman, Phys. Rev. Lett. **40**, 964 (1978).

[7] F. Ohuchi and P. H. Holloway, J. Vac. Sci. Technol. **21**, 863 (1982); Y. X. Wang, F. Ohuchi, and P. H. Holloway, J. Vac. Sci. Technol. A **2**, 732 (1984).

[8] A-M. Lanzillotto and C. W. Magee, J. Vac. Sci. Technol. A **8**, 983 (1990).

[9] R. A. Baragiola, T. E. Madey, and A-M. Lanzillotto, Phys. Rev. B **41**, 9541 (1990).

[10] Z. X. Liu and D. Lichtman, Surf. Sci. **114**, 287 (1982).

[11] H. Sambe, D. E. Ramaker, L. Parenteau, and L. Sanche, Phys. Rev. Lett. **59**, 236 (1987); **59**, 505 (1987).

[12] F. L. Hutson, D. E. Ramaker, V. M. Bermudez, and M. A. Hoffbauer, J. Vac. Sci. Technol. A **3**, 1657 (1985).

[13] C. W. Magee, W. L. Harrington, and R. E. Honig, Rev. Sci. Instrum. **49**, 477 (1978).

[14] M. L. Yu, Phys. Rev. B **19**, 5995 (1979); J. Vac. Sci. Technol. **16**, 518 (1979).

[15] J. L. Hock, J. H. Craig, Jr., and D. Lichtman, Surf. Sci. **87**, 31 (1979).

[16] J. H. Neave, C. T. Foxon, and B. A. Joyce, Surf. Sci. **29**, 411 (1972).

[17] D. J. Gibbons, in *Handbook in Vacuum Physics,* edited by A. H. Beck (Pergamon, New York, 1966), Vol. 2, p. 299.

[18] J. J. Vrakking and F. Meyer, Surf. Sci. **47**, 50 (1975); E. McGuire, Phys. Rev. A **16**, 73 (1977).

[19] L. Calliari, M. Dapor, L. Gonzo, and F. Marchetti, in *Desorption Induced by Electronic Transitions, DIET IV,* edited by G. Betz and P. Varga, Springer Series in Surface Sciences Vol. 19 (Springer-Verlag, Berlin, 1990).

[20] J. N. Chen and J. W. Rabalais, J. Am. Chem. Soc. **110**, 46 (1988).

[21] D. J. DiMaria, in *The Physics of SiO_2 and Its Interfaces,* edited by S. T. Pantelides (Pergamon, New York, 1978), p. 160.

[22] G. Dujardin, L. Heller, B. J. Olsson, M. J. Besnard-Ramage, and A. Dadouch, Phys. Rev. Lett. **62**, 745 (1989).