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Rapid Communications

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Multiply charged ions from electron bombardment of SiO_2

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We present the first systematic measurements of the emission of multiply charged substrate Si ions from SiO_2 under electron bombardment. The electron energy dependences of the ion yields show structure related to the Si $2p$ and O $1s$ thresholds, but delayed in energy. The ion yields do not follow core-ionization cross sections. The energy distributions of Si ions are a few eV wide, while those of O^+ extend to >25 eV. The results are consistent with a mechanism involving Auger decay from a core hole in the presence of additional electronic excitations.

Most oxide surfaces are not stable under irradiation with ionizing particles, but decompose with a loss of oxygen.[1] This type of radiation damage is particularly deleterious in uses of silica and silicate glasses in microelectronic circuits, and as a container for radioactive wastes. Decomposition occurs by mechanisms similar to those of electron-stimulated desorption (ESD) of adsorbed layers, where valence or core-level electronic excitations to repulsive states can lead to desorption of surface species if the excitation survives quenching by electron transfer from filled valence states.[2,3] In metals, no substrate ions are ejected since deexcitation inhibits desorption by bond reforming. Usually small yields of ions per incident electron can be obtained from light atoms or molecules adsorbed on metals, presumably because of a decreased neutralization rate caused, partially, by a small overlap with the filled valence band of the solid.

In the case of insulators, positive-ion emission from the substrate is expected, as in the case of secondary-ion emission by ion bombardment (SIMS), because of low neutralization rates from the tightly bound valence electrons in insulators to the ion escaping the surface.[4] Whereas, there are many reports of ESD of positively charged anions (O^+,F^+), there are few observations of ESD of cations from insulators.[5,6]

Recently, Lanzillotto and Magee[7] observed ESD of multiply charged substrate ions from BF_2-implanted SiO_2. The findings are surprising for substrate species, since numerous pathways for the dissipation of electronic excitations are expected to occur due to close interactions between the many neighboring atoms in the solid. In fact, doubly charged ions were previously observed only from adsorbates,[8,9] and following deep core ionization.

In this Rapid Communication we verify the ESD of multiply charged ions from SiO_2, present the first measurements of the energy thresholds and kinetic-energy distributions, and propose mechanisms for these interesting observations. We find that the onset of desorption of multiply charged ions is initiated by shallow core excitation (Si $2p$) coupled to an additional electronic excitation.

We use a high-sensitivity SIMS system[10] with an electron-beam incident at 70° with respect to the surface normal of thermally grown SiO_2 films on Si. The secondary-ions emitted normal to the surface are energy analyzed with a 180° electrostatic analyzer and filtered according to their mass-to-charge ratio by a quadrupole mass spectrometer (QMS). The sample and the extraction optics are kept at $+20$ V so the ions receive an excess energy of $q(20\ \mathrm{V}+V_s)$ before analysis. Here V_s is the potential at which the sample charges up with respect to the sample holder, and q the charge of the ion. The measured energy distributions curves (EDC's) have not been corrected for the transmission function of the energy analyzer, which increases proportionally to the pass energy, and that of the QMS which decreases with ion energy.[11] The EDC's are broadened by the finite resolution dE/E of the energy analyzer which is $\sim 4\%$, or ~ 0.8 eV at a pass energy of 20 eV. The broadening is the same for singly and multiply charged ions, therefore the actual energy broadening is $q\,dE$. EDC's were measured for oxides thinner than 65 Å, where charging effects are very small and cause little uncertainty in the origin of the EDC.

The electron-beam current is measured on a conducting surface biased to suppress secondary electrons. The electron-beam spot size is contained within the acceptance area of the secondary-ion extraction optics. We obtain ion count rates at a given mass setting of the QMS and at the peak of the energy distributions, and normalize them by the incident electron current to obtain ion yields *Y*. They are not corrected for the different efficiency of the QMS for different ions. During the measurements the pressure in the ultrahigh vacuum system is in the 10^{-11} Torr range.

Figure 1 shows a mass spectrum from a 5000-Å SiO_2/Si film bombarded with 2 keV electrons. We observe Si^+, Si^{2+}, Si^{3+}, SiO^+, O^+, O^{2+}, $O_2{}^+$, and the ubiquitous H^+ and F^+ impurities. The identification of Si^{q+} follows from the observation of the silicon isotopes in the correct ratios. We made several blank experiments to exclude experimental artifacts in the measured multiply charged ion signals. Multiply charged ions are observed from thermally grown oxides and also from crystalline quartz. They are not observed from the native oxide layer of the stainless-steel sample holder nor from a phosphor screen. When the electron beam is deflected by a small magnet, the signal drops several orders of magnitude and disappears into the background. This rules out desorption by negative ions which could conceivably be emitted by the filament in the electron gun. We also checked for the possibility that gas-phase ionization of previously desorbed atoms is the main source of multiply charged ions. The probability of this process should be proportional to the square of the current. We observed no deviation within experimental error from a linear behavior of the yields with electron current.

The very low yields of substrate ions requires the use of electron-beam currents in the μA range, over our ion collection area of a few mm^2. A few seconds exposure to such current densities are known to cause detectable damage in the oxide, consisting essentially of O vacancies and free Si.[12] Ion signals are found to decrease monotonically with bombarding time at about the same rate, except the Si^{2+} signal, which decreases more slowly with time. The positions of the thresholds and the main features in $Y(E)$ and the EDC's do not depend on electron dose or film thickness ranging from 17 to 5000 Å. No yield measurements could be made on the thicker films below 300 eV, due to sample charging. Figure 2 shows representative $Y(E)$ curves; the yields for Si^{n+}, SiO^+, and O^+ ions have the same general behavior with electron energy, but differ in detail. We observe that the higher the charge of the Si^{q+} ions, the slower the increase of $Y(E)$ near threshold.

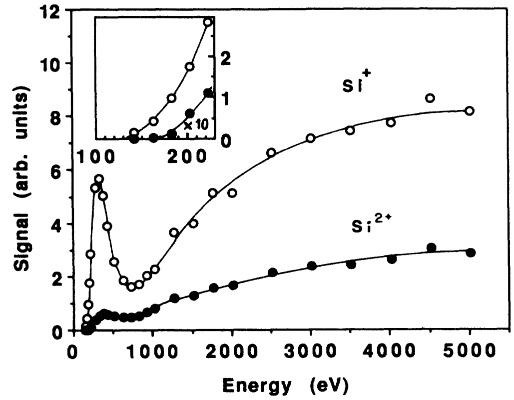

FIG. 2. ESD ion yields from a 65-Å SiO_2 film vs electron bombardment energy.

Figure 3 shows EDC's; they are narrow (i.e., a few eV full width at half maximum), as normally found in ESD. For O^+, there is a high-energy tail that extends to tens of eV. The peaks and widths of the Si^{q+} EDC's increase with the ion charge *q*, but not proportionally.[13] EDC's change when changing the primary energy from 0.5 to 1 keV and remain approximately constant at higher energies; the main change seen is a longer high-energy tail of the O^+ EDC's.

The energy dependence of the yields shows structure related to the Si 2*p* and O 1*s* edges, strongly suggesting that ions are emitted as a result of an Auger process.[14,15] Current models of core-hole initiated ESD propose that desorption occurs by the repulsion due to a two hole final state in a bonding orbital formed by the Auger decay of a core hole. Ramaker, White, and Murday[15] calculate that

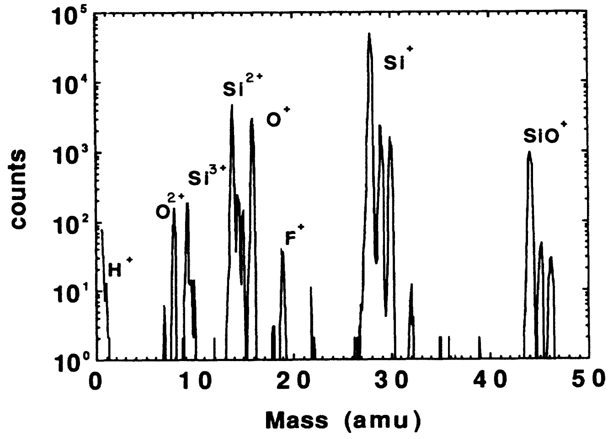

FIG. 1. ESD ion mass spectra from a 5000-Å SiO_2 film bombarded with 2 keV electrons.

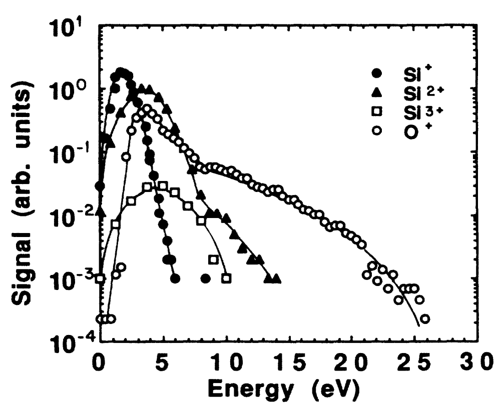

FIG. 3. Energy distribution curves for ions ejected from a 65-Å SiO_2 film by 2 keV electrons.

for 1 keV electrons in SiO_2, desorption should be more than 2 orders of magnitude more likely from Si 2*p* than from O 1*s* excitation. This is due to a much smaller core ionization cross section in the case of O 1*s*, and a smaller probability that the Auger decay results in two holes in a bonding orbital. These predictions contrast to our finding of larger ion yields at 2 keV than at 0.5 keV (where O 1*s* excitation is not possible). Contrary to theoretical predictions,[15] the shapes of $Y(E)$ are conspicuously different from the energy dependence of core excitation cross sections. Since theoretical predictions agree with recent results of the energy dependence of electron induced surface decomposition,[16] the difference with our results must be due to the ion desorption mechanism not included in the model.

It is then clear that core excitation is necessary, but not sufficient to produce *significant* ESD in our experiments. The more likely reason for the observation that ESD yields are not proportional to core ionization cross sections is that desorption requires additional excitations in shallow electronic levels. The multiple holes created by the decay of these double excitations should favor desorption by (i) increasing the lifetime of the repulsive final state[17] to make it comparable with ejection times, and by (ii) limiting the inhibiting effect on desorption caused by long-range lattice relaxation.[3]

Initial two electron excitations have been considered previously to be important only for *covalently* bonded adsorbates, not for partially ionic bonds as in SiO_2;[18] they cause a "delayed" onset of yields near core thresholds[8] in ESD and in photon stimulated desorption from adsorbates. The shapes of our $Y(E)$ curves show this effect also occurs in the partially ionic bonds in bulk silica: the Si 2*p* onset occurs at ~ 140 eV, delayed from the Si 2*p* threshold at 108 eV, and $Y(E)$ increases more slowly than reported Auger yields.[19] The second onset occurs several tens of eV delayed with respect to the O 1*s* threshold at 535 eV. Excitation of O 2*s* electrons is possibly responsible for the delayed onsets. The requirement of additional excitations for emission also provides insight into the low efficiency of Si 2*s* excitations to cause ESD, compared to O 1*s*. For short-lived (10^{-15}–10^{-14} s) outer-shell excitations to have any significant influence on desorption, core holes must decay fast, before valence excitations have extinguished. This is more likely the case for O 1*s*, whose lifetime is 4.5×10^{-15} s, than for Si 2*p*, with a lifetime of $\sim 10^{-13}$ s.[20] The highly excited final state thereby formed, must be repulsive with long enough lifetime ($\sim 10^{-14}$ s) against reneutralization or bond reforming.[18]

The high-energy tail of the O^+ EDC and the increase in the energies of Si^{q+} with ion charge also support Coulombic repulsion in the final state. To obtain repulsion energies of 25 eV, O^+ ions need to be repelled from a Si^{3+} ion, with little energy lost to the lattice,[21] possibly because these energetic ions come from adsorbed species. The fact that multiply charged Si have smaller energies than those observed in Coulomb explosions in the gas phase,[22] suggest that a substantial part of the repulsion energy of the bulk ions is spent in motion of other lattice ions, favored by long-range Coulomb forces, i.e., lattice relaxation accompanying desorption.[3] As a consequence, energetic events causing the emission of multiply charged ions may also result in an inordinate degree of radiation damage in the bulk of the material.

Regarding the origin of the multiply charged species, we recall that low-energy ions ejected from SiO_2 surfaces in SIMS are singly charged; a very small proportion of multiply charged ions are formed only when they carry a core excitation.[23] Thus, the observation of multiply charged ions from ESD does not reflect the initial charge state of the atoms in the unperturbed lattice, but rather multiple ionization results from excitations produced by the incident electrons. Three or four final holes in a bonding orbital, following the Auger decay of Si 2*p*–O 2*s* or O 1*s*–O 2*s* excitations, can readily produce the degree of ionization and the bond breaking required to explain our observations. Some of the ions produced can capture electrons during ejection: this process is unlikely for Si^+ since its hole state lies opposite the unoccupied band gap of the solid.

In summary, we have made the first observations on the energy dependence and EDC's for ESD of multiply charged substrate ions. The yields are related to core excitations but show delayed onsets and do not follow core excitation cross sections. The phenomenon is initiated by a core vacancy in a Si or O atom, accompanied by additional shallow electronic excitations. These excitations provide increased repulsion in the final state if the Auger decay occurs in times of the order of or shorter than lifetimes of shallow holes. Multiply charged substrate ions have low kinetic energies, probably due to energy loss to bulk atoms during emission. Oxygen ions have energies extending to a maximum which increases with primary electron energy.

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