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Desorption of positive and negative ions from SiO_2/Si surfaces by electron excitation of core levels

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Electron-stimulated desorption of positive and negative oxygen ions and positive, multiply charged silicon ions from thin SiO_2/Si films has been studied as a function of impact electron energy. Thresholds observed for O^+ are correlated with core-level binding energies of substrate atoms. Desorption of negative ions closely follows threshold behavior of positive ions; it is explained in terms of a charge-exchange process in which the outgoing positive ions (or neutrals) capture electrons in the surface region and desorb as negative ions. Desorption of multiply charged silicon ions is also related to creation of core holes, but requires some additional, multielectron excitations.

I. INTRODUCTION

The bombardment of a sample surface by low-energy electrons (typical energies range from 5 eV to 1 keV) can induce desorption of neutral and ionic species from the surface.[1] This effect, referred to as electron-stimulated desorption (ESD) and known for more than 20 years, is still attracting considerable interest because of both fundamental and practical considerations.[1] Several different models have been proposed for explanation of desorption from ionic and covalent surfaces by low-energy electrons.[1,2] Although these differ in detail, all models consider core or valence electronic excitations, followed by rapid electronic rearrangements to repulsive states, as the driving force for desorption.[3-6]

By far the bulk of ESD studies of positive ions have been performed in either the low- (up to 50–100 eV) or high- (above 50–100 eV) energy regime in order to determine whether valence- or core-initiated desorption is active as a mechanism for producing positive ions (Ref. 7 is one of only a few exceptions to this practice). It now appears that, in many cases, the valence excitation mechanism plays a minor role in positive-ion desorption, as a growing number of experiments show sharp and dominant onsets in positive-ion yields at energies related to the excitation of core levels.[8]

On the other hand, most of the work published on negative-ion desorption considers only low electron energies and points to the importance of valence excitations.[1,2] In this energy regime, dissociative attachment and/or polar dissociation mechanism has been shown to dominate formation of negative ions.[9] Recently, Lanzillotto, Madey, and Baragiola[10] have shown that negative-ion desorption can also be initiated by core-level excitations. In this paper we report on desorption of both positive and negative oxygen ions, as well as positive, multiply charged silicon ions, from SiO_2 films and focus the discussion on the role of core-level excitations in desorption process.

II. EXPERIMENT AND RESULTS

The SiO_2 layers used in this study were thermally grown on Si wafers at 900 °C in an oxygen (industrial grade, 99.5%) atmosphere for different times. The thickness of resulting oxide films (from 90 to 1000 Å) was checked by both the elipsometric measurements and the secondary-ion-mass spectrometry (SIMS) profiling. All ESD measurements were carried out in a high-sensitivity quadrupole SIMS instrument (Riber MIQ 256 Ion Microprobe) equipped with an electron source (Riber CER 306 Auger and LEED grazing angle electron gun). The base pressure in the analysis chamber during measurements was in the low 10^{-10}-Torr range. The electron beam, which impacts at 45° with respect to the sample surface, was focused to a spot of ~ 1 mm^2 and each desorption curve was taken from a "fresh" spot on the sample surface. The count rate for each ion type was maximized separately (by tuning the quadrupole filter and mass selector) and taken from the peak in the energy distribution (by biasing the sample holder to typically ± 20 V for negative and positive ions, respectively). The electron energy scale was corrected for both the bias voltage and the work function of the W filament (~ 5 eV).[11] The low ion yields of some elements often require the use of electron-beam current densities in the μA/mm^2 range.[12] For such ions, the electron gun and associated optics employed in our experiments are not suitable for desorption below about 40 eV as a result of very small currents in the nA range.[13] In the 100-eV range, however, typical currents of 1–10 μA into spot sizes of a few mm^2 can be routinely achieved.[13]

The ESD data are summarized in the next few figures. Typical ESD positive- and negative-ion mass spectra from a 150-Å-thick SiO_2 film are shown in Fig. 1. In the positive spectrum [Fig. 1(a)], we have observed many anion-related peaks, such as O^+, H^+, some molecular complexes, such as SiO^+, several multiply charged substrate (cation) ions (Si^{n+}), and the ever present F^+ and Cl^+. The negative-ion spectrum [Fig. 1(b)] is dominated

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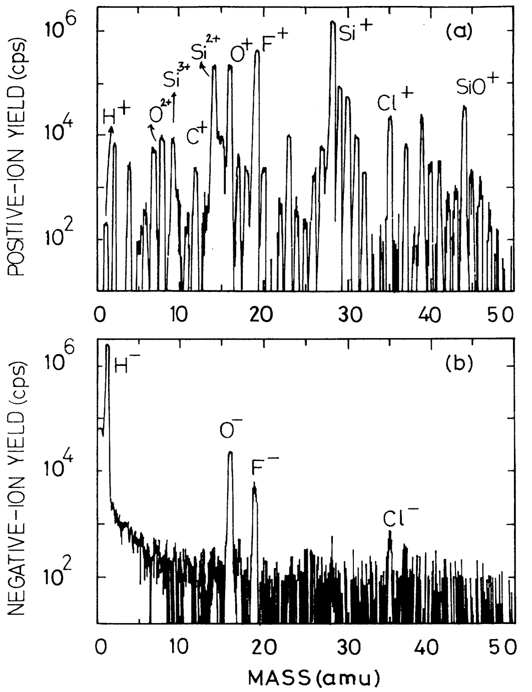

FIG. 1. (a) ESD positive-ion mass spectrum from a 150-Å-thick SiO_2/Si film, obtained by 1-keV electron bombardment. (b) Negative-ion mass spectrum from the same sample under 1-keV electron bombardment.

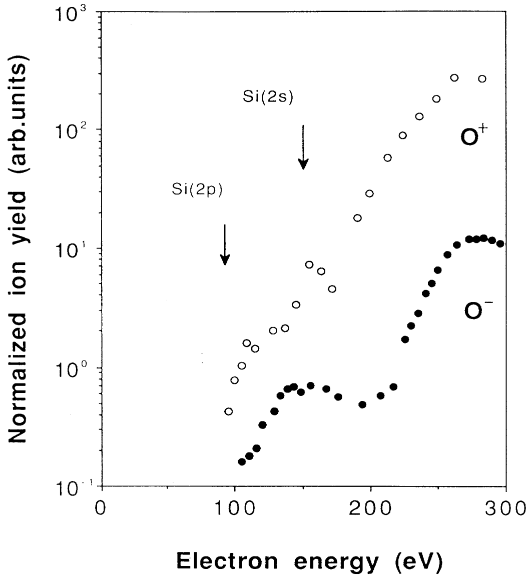

FIG. 2. Normalized desorption yields of O^+ and O^- from a 150-Å-thick SiO_2/Si film as a function of primary electron energy. Binding energies of Si(2*p*) and Si(2*s*) core levels (with respect to the Fermi level) are indicated by arrows.

by H^-, O^-, and F^- peaks. Note that a high background level in the negative spectrum for 1-keV electron bombardment may originate from both primary and secondary electrons entering the quadrupole. For impact electron energies higher than 1.5 keV we have also observed a peak at 28 amu, representing presumably Si^-.

Figure 2 shows representative O^+ and O^- desorption curves, $Y(E)$, obtained also from a 150-Å-thick SiO_2 film. Both $Y(E)$ curves exhibit thresholds at ~100 and ~180 eV, followed by maxima at ~155 and ~275 eV, respectively. We were not able to detect any signal below 100 eV due to the low ion yields and/or limitations of the source used for electron bombardment. The position of thresholds and the general shape of the desorption curves do not depend on electron dose and thickness of SiO_2 films. The only exception was a 1000-Å layer showing a shift of ~10 eV in the position of the lowest threshold, most probably due to sample charging. A similar effect was reported in Ref. 14. To avoid any artifact caused by surface charging, we used in this study only thin (<500 Å) SiO_2 films, which were showing only some changes in ion yield intensities, presumably as a result of local differences in oxygen surface coverage.[15]

Figure 3 shows the yield for Si^{n+} ($n=1,2,3$) as a function of electron energy. Si^{n+} peaks were identified from the correct ratios of the silicon isotopes and no silicon signal was observed from the sample holder. This time, threshold at ~100 eV is absent in all $Y(E)$ curves. The absolute (lowest) threshold for Si^+ occurs at ~150 eV, while these thresholds for multiply charged ions are shifted towards higher energies for about 20–30 eV. All three curves, however, exhibit a maximum at ~300 eV and a second (weak) threshold at 530–540 eV. We observed that the higher the charge state of Si, the more pronounced was the second threshold and the lower the ratio of peak intensities at ~300 and 600 eV. The increase in yield after the first threshold also decreases dramatically with increasing Si charge state. From a number of mea-

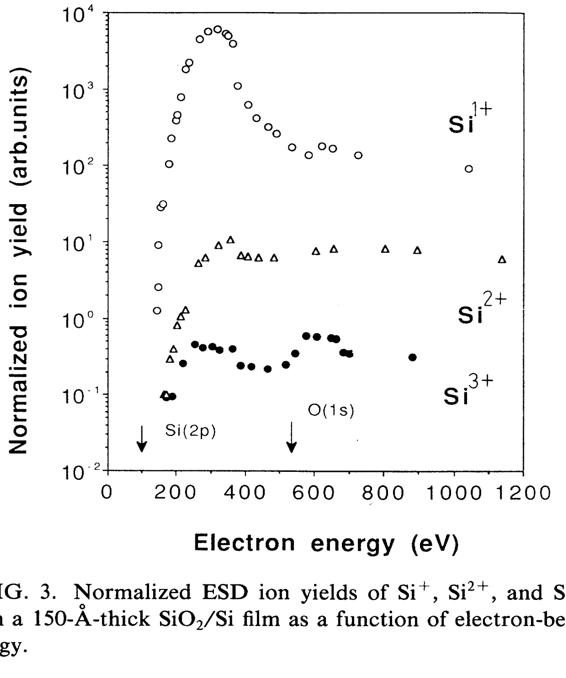

FIG. 3. Normalized ESD ion yields of Si^+, Si^{2+}, and Si^{3+} from a 150-Å-thick SiO_2/Si film as a function of electron-beam energy.

surements on different SiO_2/Si samples, we determined desorption thresholds at 150–160 eV for Si^+ and 170–190 eV for multiply charged ions. Intensities of latter ions at 300 eV are three to four orders of magnitude lower than the intensity of Si^+.

III. DISCUSSION

The most comprehensive ESD study of oxygen from SiO_2 surfaces was presented by Knotek and Houston.[16] However, only positive-ion yields under electron bombardment up to 100 eV were covered in that work. The thresholds observed in the 20–30-eV range have been explained in terms of the O(2s) core-level excitations followed by the Auger decay, as proposed in the Knotek-Feibelman (KF) model.[5] On the other hand, Lanzillotto, Madey, and Baragiola[10] have recently published results on O^- desorption from the SiO_2 surfaces for the electron energies in the 100–4500-eV range. They observed the threshold in negative-ion yield at the core-level binding energy of substrate atoms. This behavior was explained in terms of a charge-exchange process in which a positive oxygen ion or a neutral atom, desorbed after some multielectron excitations, captures electrons in the surface region and desorbs as a negative ion.[10] Surprisingly, the authors did not provide a comparison with the desorption of positive oxygen ions (although the mass spectrum in Ref. 10 exhibits an intensive O^+ peak), which would have verified their proposition. Indeed, if negative-ion formation originates from a charge-exchange process involving positive ions, the negative-ion yield curve should be determined to a large extent by the shape of the positive-ion yield curve.

The thresholds in Fig. 2 are most likely related to the Si(2*p*) (~100 eV) and Si(2*s*) (~150 eV) core-level binding energies, indicated by arrows in the figure. Such threshold behavior is indicative of a desorption mechanism involving Auger decay of core hole.[5] On the other hand, the similar threshold behavior of both $Y(E)$ curves strongly suggests that the same processes initiate desorption of both positive and negative oxygen ions.

Our threshold measurements for O^- (Fig. 2) differ, however, in some detail from those previously reported.[10] First of all, we have resolved both Si(2*p*) and Si(2*s*) thresholds, whereas, in Ref. 10, only one threshold, related to the Si(2*p*) level, was observed. Thresholds observed in our measurements are followed by broad maxima, which is essentially in agreement with the energy dependence of ionization cross sections.[12,17,18] The second important difference concerns the threshold itself. The lowest threshold observed in our measurements occurs at ~100 eV, while in Ref. 10 it appeared to be delayed by ~30 eV, which was interpreted as arising from some multielectronic excitations of adsorbate atoms.[7] In our case, it is the threshold related to the Si(2*s*) level, which is apparently shifted towards higher energies, but not the lower Si(2*p*) edge.

We suggest the following explanation for desorption of positive and negative oxygen ions. Core-hole formation in the Si *L* shell (2*s* and 2*p* levels) initiates an interatomic Auger decay process involving Si-O bonds. Auger decay of a core hole in a covalent Si-O bond may lead to a localized two-hole (2h) final state in the bonding orbital.[19] The lifetime of this state has been shown to be sufficiently long[6,19] that desorption of O^+ may occur via unscreened hole-hole (Coulombic) repulsion. On the other hand, the onset delayed from the Si(2*s*) threshold can be explained in terms of some additional electronic excitations as suggested in Refs. 10 and 14.

Since an Auger process produces, in general, two holes in the bonding orbital, it cannot by itself account for the direct formation of negative ions. Similar shapes of both positive and negative $Y(E)$ curves in Fig. 2 suggest, however, a correlation between positive- and negative-ion desorption. Thus, we speculate that negative ions originate from a charge-exchange process, as proposed previously by Lanzillotto, Madey, and Baragiola.[10]

Let us now turn to the interesting results on desorption of multiply charged substrate ions. In contrast to metal surfaces, emission of positively charged substrate ions is possible from insulators.[8] In the case of metals, quenching of excitations by electron transfer from valence states is extremely efficient: metal bonds are quickly reformed and no desorption of substrate ions occurs. In insulators, the valence electrons are tightly bound and their contribution to the quenching process is significantly lower. However, while many ESD studies on desorption of positively charged anions confirm this assumption, there are only a few reports of ESD of cations from insulators.[20,21] In addition, desorption studies of multiply charged ions have previously concentrated on adsorbate ions[7,21,22] rather than those from the substrate itself. Only recently have multiply charged substrate ions been observed in ESD from SiO_2 surfaces[23] and examined in some detail by Baragiola, Madey, and Lanzillotto.[14] Desorption of Si^{n+} ions ($n=1,2,3$) from that work is characterized by thresholds at ~140 and ~600 eV, with higher ion yields at higher primary energies. These were related to core excitations but showed delayed onsets with respect to Si(2*p*) and O(1*s*) thresholds. Core-level excitations were considered as necessary for desorption, but not a sufficient condition, and some additional shallow electronic excitations were proposed to account for delayed thresholds.[14]

Our threshold measurements (Fig. 3) differ in some details from the measurements published in Ref. 14. First of all, we have not observed as large an increase in desorption yield above the energy corresponding to the O(1*s*) binding energy. On the contrary, in the case of Si^+ we observed much larger yields at energies below the O(1*s*) threshold. The ratio of the yield at 300 eV [where *no* O(1*s*) excitation can occur] to that at 1000 eV is almost two orders of magnitude, just as expected from the ratio of the core ionization cross sections for Si *L* and O *K* edges in SiO_2.[19] However, the same yield ratio for multiply charged ions (Si^{2+} and Si^{3+}) is very much reduced. This indicates an increased importance of O-related excitations in the desorption of multiply charged silicon ions. It is important to mention here that the authors of Ref. 14 stated in a later publication[10] that their threshold measurements near the oxygen edge were probably in error and should be reexamined.

Let us now examine desorption of Si^+ ions in terms of partial ionic character of the Si-O bond [the large electronegativity difference between O and Si (Ref. 24) may give rise to charge separation between Si and O, thus giving rise to a large ionic component in the Si-O bond: configurations of $Si^{1.6+}$ and $O^{0.8-}$ or Si^{1+} and $O^{0.5-}$ have been reported in some publications[8]]. Desorption of Si^+ can be initiated by the ionization of the Si L shell, but only if followed by an interatomic Auger decay involving oxygen ions. Such a decay preserves positive charge on Si ions but converts negative oxygen ions into positive ones. Desorption of both Si^+ and O^+ can occur in this case due to Coulomb repulsion (KF mechanism). Indeed, we observed the onset in desorption of O^+ (Fig. 2) at an energy corresponding closely to the onset in Si^+ yield. In the case of O^+ desorption, this onset was related to the Si(2*s*) threshold.

Auger decay of Si(2*p*) holes or Si(2*s*) holes can produce multiply charged Si ions directly, but they will be even more attracted to adjacent O^- ions and have a lower probability for desorption. However, Si^{2+} and Si^{3+} *do* originate from some electronic transitions involving Si^+ ions because they do not reflect the initial charge state of silicon atoms in an unperturbed lattice.[14,25] Consequently, ESD of multiply charged ions can also be initiated by Auger decay of Si^+ holes but requires additional excitations which convert O^- into O^+. These additional excitations give rise to delayed onsets in $Y(E)$ measurements. Indeed, thresholds, delayed relative to core binding energies by tens of eV, have been observed in ESD of many covalently bound elements.[7,26] They have been explained in terms of multielectron excitations giving rise to repulsive, multihole final states. These are intrinsically localized and provide increased Coulombic repulsion as well as much longer lifetimes than one-electron excitations.[6,12,27]

The above picture is fully consistent with our measurements: we relate observed onsets in Si^+ desorption to core-level excitations, delayed from the Si(2*p*) thresholds for ~40 eV. The excitation of O(2*s*) electrons can account for this delay. Desorption of multiply charged ions requires additional valence-band electronic excitations to allow hole-hole (Coulombic) repulsion and desorption. Consequently, one expects even a larger shift of desorption onset for larger ionic charge and, possibly, a larger contribution from the O(1*s*) level. Such a tendency was observed in our measurements by comparing Si^+, Si^{2+}, and Si^{3+} onsets (see Fig. 3). One also expects the kinetic energy of ions desorbed with charges 2+ (3+) to be on average two (three) times higher than the kinetic energy of singly charged ions as a result of Coulombic repulsion.[22] Our energy distribution measurements (displaying the dependence of yield on bias potential[13,28]), as well as those reported in Ref. 14, support this picture. It is worth noting here that the kinetic energy of desorbing multiply charged ions does not necessarily increase proportionally to the ion charge. The energy of desorbing ion A depends on the position of all of the neighboring atoms B, as well as A-B and B-B interactions. The Coulombic part of the A-B interaction would be increased proportionally with charge, but not the contribution from B-B. These effects will contribute to small shifts in peak positions.

IV. CONCLUSION

We have examined desorption of positive and negative oxygen ions and multiply charged, positive silicon ions from SiO_2 surfaces for a broad range of impact electron energies. We have argued that for energies above 100 eV an Auger-related mechanism plays the dominant role in ion desorption. Desorption yields of positive ions are related to core-level excitations of substrate atoms. Auger decay of core holes may result in multiple-hole final states in bonding orbitals. These holes are intrinsically localized, give rise to increased repulsion, and have much longer lifetimes than one-electron excitations. Negative ions are shown to follow closely the desorption pattern of corresponding positive ions. This behavior is consistent with a charge-exchange mechanism for ESD of negative ions.

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