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Ion-stimulated desorption of positive halogen ions

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The ejection of F^+ ions from fluorinated silicon by Ar^+ or $O_2{}^+$ impact at 2–10 keV is shown to result from noncollisional processes which follow core-hole creation by the primary ion impact. The ejection mechanism is shown to be closely similar to electron-stimulated desorption, and can be explained using the model of Knotek and Feibelman. Cl^+ ejection from chlorinated aluminum appears to result from a similar mechanism, whereas O^+ ejection from oxygen-sputtered silicon appears to be purely collisional. The latter observation is shown to be consistent with the Knotek-Feibelman model.

Electron-stimulated and photon-stimulated desorption (ESD, PSD) of positive ions from ionic surfaces has recently been shown by Knotek and Feibelman (KF) to be initiated by core-level ionization of surface atoms. Auger decay of the core hole can lead to multiple electron loss from a negatively charged adsorbate atom, leaving it positively charged and subject to ejection by Coulomb repulsion.[1] Jennison *et al.* have generalized this mechanism to discuss desorption from covalently bonded surfaces,[2] and have pointed out that there exist localized two-hole states, accessible through Auger decay, which, by hole-hole repulsion, lead to ion desorption. Because energetic ion impact can produce secondary electrons of high energy by Auger processes, it has seemed reasonable to suppose that electron-stimulated processes, due to secondary electrons, play a role in sputtered ion emission.[3] The possibility also exists that positive ion ejection might also result directly from an Auger decay following core-hole creation in an energetic ion-surface collision. Such processes might be termed *ion-stimulated desorption* (ISD). To identify such processes is not straightforward because sputtered ions are also produced efficiently by collisional processes, by mechanisms which are incompletely understood. Empirically it is found that sputtered ion yields scale with the inverse exponential of the free-atom ionization potential.[4] This suggests that the most favorable species to investigate is F^+, which should have a low collisional ion yield due to its high ionization potential, but which is electron desorbed with high efficiency. To distinguish electron-mediated from collisional events, it is productive to examine the initial kinetic energy distributions of the ejected ions. Collisionally sputtered ions typically exhibit broad skewed energy distributions which peak at 5–10 eV and have tails extending up to several hundred eV, whereas ions resulting from ESD have narrow, approximately Gaussian, energy distributions peaking at a few eV.[5] We report here energy distribution data which suggest that $> 95\%$ of the F^+ ions ejected from a fluorinated silicon surface by energetic Ar^+ or $O_2{}^+$ bombardment appear to result from electron-mediated (noncollisional) events. Evidence is presented to support a model in which F^+ ejection is stimulated by a collisionally produced silicon *LVV* electron from a silicon atom which was not the nearest neighbor of the ejected F^+. This model also accounts for the observation of a low-yield ISD signal of Cl^+ from a chlorinated aluminum sample, and for the fact that the O^+ signal from oxygen-sputtered silicon appears to be purely collisional.

Experiments were performed in commercially available ion microanalyzers (CAMECA ims 3f and AEI IM20). Base pressure in the sample chambers of both instruments was $2-4 \times 10^{-8}$ torr. The samples studied were a fluorinated amorphous silicon film (8 at.% F), $BF_2{}^+$-implanted silicon (peak F concentration about 2 at.%), and a chlorinated aluminum sample made by codeposition of Al and Cl_2 onto a cooled substrate (Cl concentration was about 10 at.%). Energy distributions were determined in the CAMECA instrument by ramping the sample accelerating voltage while measuring the mass-analyzed current of the chosen ion species passing through a spherical electrostatic analyzer which formed the first stage of the secondary ion mass spectrometer.[6] It was possible in this instrument to distinguish ions ejected from the surface from those formed in gas-phase processes because an accelerating field of 10^6 V/m exists at the sample surface. Ions formed in the gas phase are formed some way down the accelerating potential gradient. Such ions could clearly be identified because they would appear in the energy spectrum with negative energies.[7] In fact, as the energy distributions shown below demonstrate, gas-phase ions were not observed in significant amounts in this work.

Figure 1(a) shows the energy distributions of F^+ and Si^+ from the fluorinated amorphous silicon sample under Ar^+ bombardment. The two distributions differ significantly. The near absence of a high-

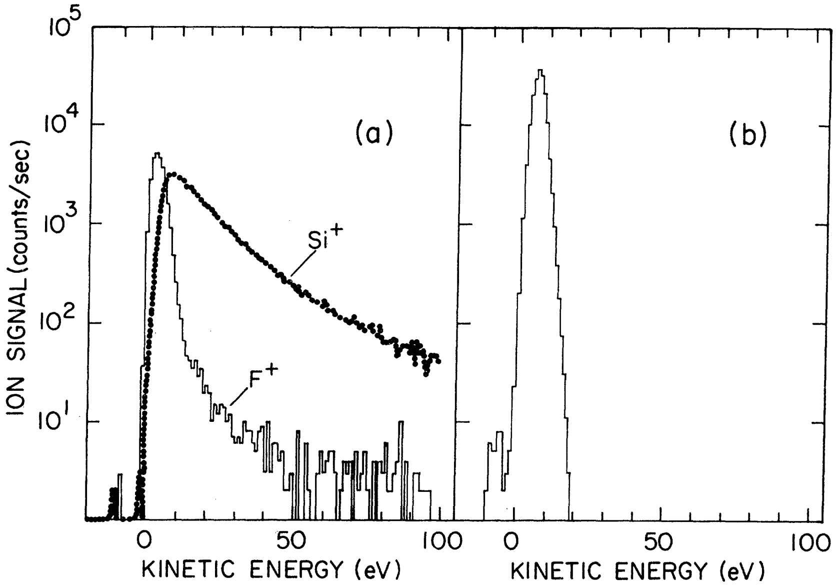

FIG. 1. (a) Energy distributions of F^+ and $^{30}Si^+$ ejected from a fluorinated amorphous silicon sample by the impact of 8-keV Ar^+. Primary current approximately 500 nA. (b) Energy distribution of F^+ ejected from the same sample by the impact of 14.5-keV electrons. Primary current approximately 1000 nA.

energy tail on the F^+ distribution is quite anomalous for a sputtered atomic ion, and particularly so for a species of high ionization potential. The systematics of sputtered ion energy distributions suggest that the intensity of the high-energy tail relative to the peak *increases* with increasing ionization potential. That the narrow F^+ distribution does not reflect anomalies in the sputtering process for fluorine is demonstrated by the negative ion energy distribution (Fig. 2) which is quite normal. Using the ion-implanted sample, in which the fluorine level is too low to enhance appreciably the Si^+ yield, it was determined that the F^+ ionization probability *exceeded* the Si^+ ionization probability by a factor of > 30 although the ionization potential of fluorine is more than twice that of silicon.

Figure 1(b) shows the energy distribution for F^+ ejected by the impact of 14.5-keV electrons (extracted from the duoplasmatron ion source) on the fluorinated amorphous silicon sample. The close similarity of the electron-stimulated and ion-stimulated energy distributions for F^+ from this sample is striking. The conclusion seems inescapable that F^+ is ejected in both instances by processes which are energetically identical. In order to identify the initiating event in the ISD process, the variation of ion yields with primary ion energy was studied for the fluorinated amorphous silicon sample (Fig. 3). The Si^+ curve is clearly distinct from the F^+ curve, which instead parallels the behavior of Si^{++}. The latter species is felt to result from the gas-phase Auger decay of a silicon atom sputtered with a core hole,[8] and this model is strongly supported by the fact that the Si^{++} yield scales with primary ion energy in the same way as the yield of ion-excited Si *LVV* Auger electrons (also plotted in Fig. 3 using data from Wittmaack[9]). We conclude that the initiating event in F^+ ISD is core-hole creation in an energetic collision.

The identity of the atom in which a core hole is created can be determined in ESD by examining threshold behavior. That no clear thresholds exist in the present case is evident from Fig. 3. However, the ion energy distributions offer a less direct, but equally valid, way to identify, not only the type of

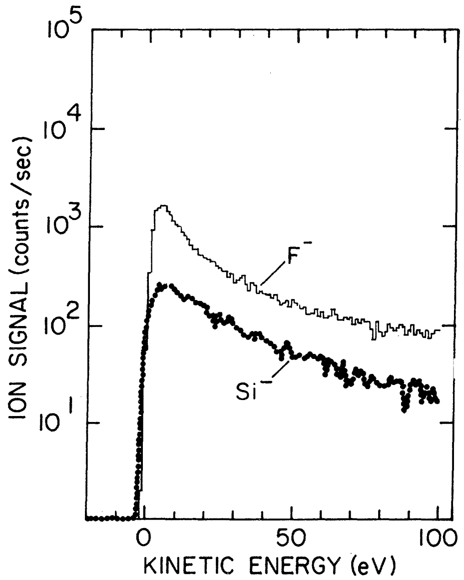

FIG. 2. Energy distributions of F^- and $^{30}Si^-$ ejected from fluorine-implanted silicon sample by 14.5-keV Ar^+ impact. Primary current approximately 500 nA.

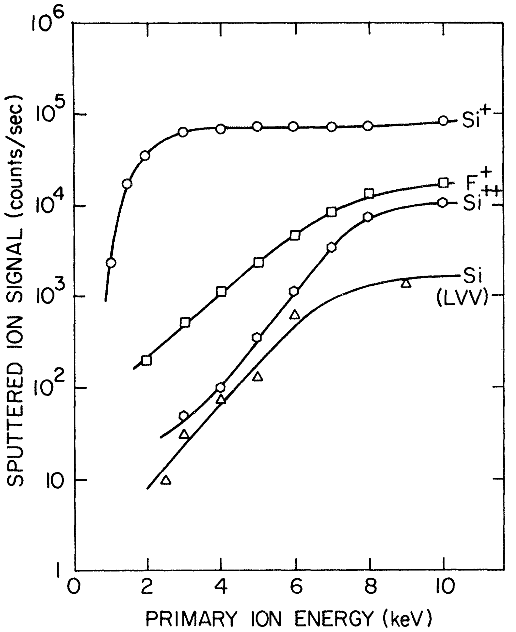

FIG. 3. Variation of ion yields with primary ion impact energy. Shown also is the variation of the silicon ion-excited *LVV* Auger signal, from Ref. 9.

atom in which a core hole is created, but also, to some extent, its location. Core ionization in heavy-particle collisions results from collisions of low impact parameter and high center-of-mass energy, and a significant fraction of this energy is therefore transferred to the target atom (a rough estimate is that the threshold collision energy in the center of mass is about 10 times the ionization potential of the core level[3]). Immediately, it can be seen that the ejected F^+ has not been involved in a core-ionizing collision, and, because the sample is dilute, no other fluorine atom is near enough to influence the ejected atom. The core hole must therefore have been created in a silicon atom. It is less obvious, but almost certain, that the core-ionized silicon atom cannot have been the nearest neighbor of the ejected F^+, because the energy distributions of Fig. 1 set an upper limit to the energy transferred to the F^+ (other than that available from Coulombic forces) at less than 1 eV. The center-of-mass energy required to ionize the silicon *L* shell is about 900 eV.[10] For the primary ion and a silicon atom, or two silicon atoms, to undergo so energetic a collision while transferring < 1 eV to a nearest-neighbor fluorine would seem to be extremely unlikely. In addition, the displacement of the silicon target atom during and after the collision would significantly reduce the probability of subsequent interatomic Auger decay involving electrons from the fluorine atom. We will assume in what follows that such collisions do *not* result in F^+ ejection, and examine the consequences of this assumption.

We must explain how the existence of a core-ionized silicon atom one or more atoms distant from a fluorine atom can lead to the ejection of that fluorine. Three possibilities exist: (a) The core hole might hop to a nearest neighbor of the fluorine; (b) the fluorine might participate in an interatomic Auger decay process involving the non-nearest-neighbor silicon; or (c) intra-atomic Auger decay results in a free electron (Si *LVV*) which initiates a true ESD event when it interacts with the fluorine. Possibilities (a) and (b) can probably be discounted because the orbitals involved have negligible overlap. If alternative (c) is correct, energy constraints lead to some specific conclusions about the ejection event. A Si (*LVV*) electron cannot recreate a Si *L*-shell hole because it lacks an amount of energy equal to that of the two valence electrons. (It might be argued that an argon *LVV* electron could ionize the silicon *L* shell. However, in Ar-Si collisions, the production of Ar-*L* emission is less probable than the production of Si-*L* emission by a factor of about 200.[9] Also, the ISD process for F^+ appears to proceed identically under oxygen ion bombardment.) Thus, for the KF mechanism to proceed, a core hole must be created on the fluorine atom. A level that is accessible is the F 2*s* level with an ionization potential of 31 eV. Ionization of this level has been shown by KF to result in efficient ejection of F^+, whereas ionization of an O 2*s* level gives only a very small yield of O^+.[1] If the mechanism discussed here is correct, it would predict ion-stimulated desorption of O^+ to be quite inefficient. The energy distribution of sputtered O^+ shown in Fig. 4(a) is entirely consistent with this prediction, showing no sign of a low-energy noncollisional peak. Similar arguments should apply in the case of an aluminum matrix. Figure 4(b) shows that Cl^+ from the chlorinated aluminum sample does have an energy distribution peaked at low energy, indicating ion-stimulated desorption, but the yield is low, as is the ESD yield from this sample, shown in Fig. 4(c), because the energy available from the decay of a Cl 3*s* hole is only marginally above the threshold energy required to convert Cl^- to Cl^+.[1] All these observations combine to confirm our postulate that the *direct* creation of a nearest-neighbor silicon core hole is of negligible importance. Such a hole would of course supply enough energy to desorb O^+ efficiently. We therefore conclude that F^+ (and Cl^+) ejection from silicon and aluminum surfaces by energetic ion bombardment results from *electron*-stimulated processes initiated by Auger electrons from relatively distant (non-nearest-neighbor) collisions.

Wittmaack has recently examined the ejection of H^+ from silicon by Ar^+ bombardment, and found behavior similar to that reported here—i.e., H^+ energy distributions were narrow, and the H^+ yield scaled with primary ion energy in the same way as the Si^{++} yield.[11] He proposed a mechanism which involved the H being sputtered together with the core-excited

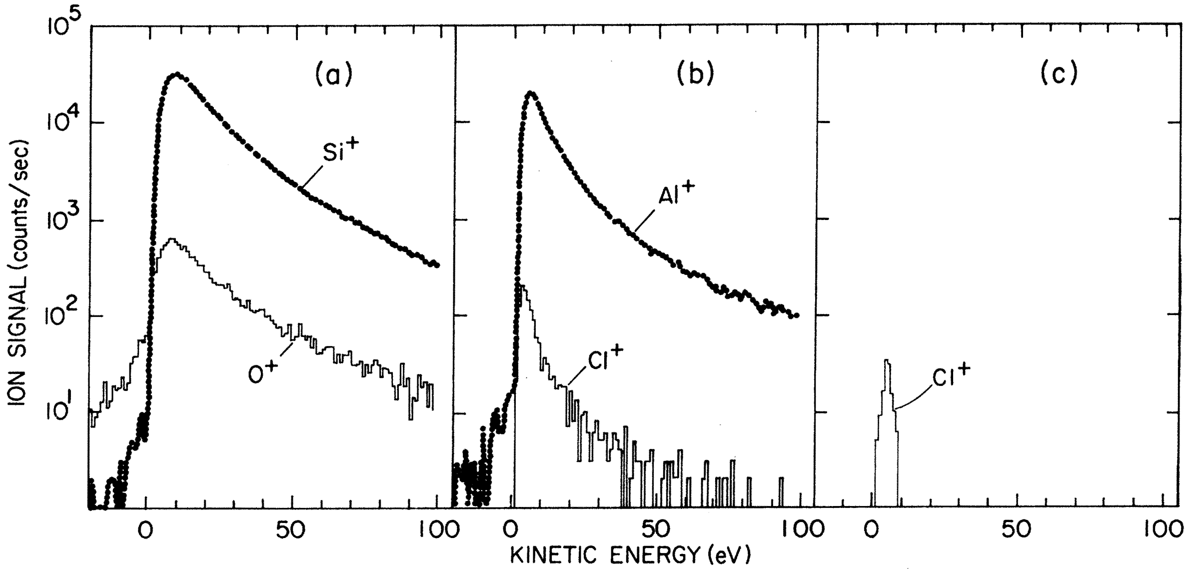

FIG. 4. (a) Energy distribution of O^+ and $^{30}Si^+$ ejected from oxygenated silicon by 8-keV $O_2{}^+$ impact. Primary current approximately 500 nA. (b) Energy distribution of $^{35}Cl^+$ and Al^+ ejected from chlorinated aluminum by 8-keV Ar^+ impact. Primary current approximately 500 nA. (c) Energy distribution of $^{35}Cl^+$ ejected from chlorinated aluminum by 14.5-keV electron impact. Primary current approximately 1000 nA.

Si as an SiH^+ molecule, which undergoes a *gas-phase* "Coulomb explosion" after the Auger decay of the silicon atom further ionizes the molecule. This mechanism cannot explain the F^+ results reported here because the F^+ energy distribution in this case should resemble the broad distribution of Si^+. The alternative possibility that H^+ may be directly ejected from the solid following core excitation of a nearest-neighbor Si cannot be ruled out, because kinetic energy transfer from a moving Si to H is inefficient, and the narrow H^+ energy distribution does not, in this case, rule out the possibility that the nearest-neighbor Si was involved in an energetic collision.

The significance of ISD for the general understanding of sputtered ion emission is that it is *not* a widespread effect. Auger processes may well play a role in the ionization of sputtered atoms (this is certainly the case for multiply charged ions), but the majority of singly charged ions appear to result from a distinguishably different process. Perhaps most significant is the fact that the species—F^+—which deviates most markedly from the ion yield *versus* ionization potential systematics of the majority of sputtered positive ions[12] is shown to be formed by a separate process. This fact leads to increased confidence that the ion yield systematics reflect an underlying physical reality, and that to make models which attempt consistency with these systematics[3,13] is a useful endeavor.

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