Photon- and electron-stimulated desorption from a metal surface

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Parallel measurements have been made on photon-stimulated and electron-stimulated desorption of F^+, Cl^+, and O^+ ions from W(100). Ion energy distributions, angular distributions, and threshold yield behavior all indicate that the mechanisms for desorption by photons and electrons are essentially identical. The extent to which the results are consistent with the core-level Auger model of Knotek and Feibelman is discussed.

The electron-stimulated desorption (ESD) of ions from surfaces is already established as a valuable technique for studying surface-adsorbate systems.[1] The emission directions and kinetic energies of the ions, along with their desorption-threshold electron energies, appear to characterize the original adsorption states and sites.[2] Theoretical models for the ESD process indicate that the initial step of electronic excitation or ionization could be achieved by incident photons as well as by electrons.[3,4] Knotek *et al.*[5] recently confirmed this idea for ionic surfaces. They observed photon-stimulated desorption (PSD) of H^+, OH^+, and F^+ ions from TiO_2 and showed that PSD is initiated by the same core-hole Auger-decay mechanism[4] responsible for ESD in this material. For metal surfaces, however, the occurrence of PSD as a primary process on the same footing as ESD has not been well established.[6,7] We have therefore studied the (100) surface of W, and we report in this paper the observation of F^+, Cl^+, and O^+ ions desorbed directly by photon stimulation. We also present here the first angle-resolved and angle-integrated measurements of PSD ion energy distributions and compare them with ESD measurements taken in the same experiment. The data are discussed in terms of the Knotek-Feibelman (KF) desorption model.[4]

The apparatus used was a straightforward adaptation of a conventional photoemission-spectroscopy system. A cylindrical mirror analyzer (CMA) was operated in reverse polarity in order to detect positive ions rather than photoelectrons. Light was obtained from the Tantalus storage ring using a normal-incidence monochromator giving good intensity in the range $\hbar\omega \sim 10-30$ eV and acceptable intensity up to $\hbar\omega \sim 60$ eV. The W(100) crystal was prepared by alternately heating to $\sim 1000-1200\,^{\circ}C$ in 10^{-6} Torr of oxygen and flashing to $\sim 2500\,^{\circ}C$. Cleaning was accomplished by further flashes in ultrahigh vacuum to this latter temperature. PSD measurements were made on the desorption of O^+ and Cl^+ from adsorbed oxygen and chlorine, but our most systematic studies were made on the desorption of F^+ which was found to segregate to the surface of the tungsten crystal. The cleaning procedure described above produced a surface which showed the surface state near the Fermi level in photoemission spectra[8] and no ESD signal. Within 5–10 min of cleaning, as the sample cooled, the surface-state photoemission diminished and ESD for an impurity species identified as F grew to an equilibrium coverage even with background pressures below 5×10^{-10} Torr.[9] The oxygen- and chlorine-covered surfaces were obtained by saturation (10–100 L) exposure.

In performing the parallel ESD experiments, the CMA system was further adapted so as to function as a simple time-of-flight mass spectrometer[10] giving approximately unity mass resolution up to atomic mass 20. This was done by pulsing the incident electron beam and gating the detection system to a fixed-delay time after the electron pulse. Mass analysis permitted identification of the segregating species as F. This ability to switch rapidly back and forth between photoemission spectroscopy, PSD and time-of-flight ESD, is an attractive feature of this experimental approach, and proved valuable in the characterization experiments described below.

Ion-energy distributions obtained by ESD and PSD for F^+ desorption are compared in Fig. 1. The curves

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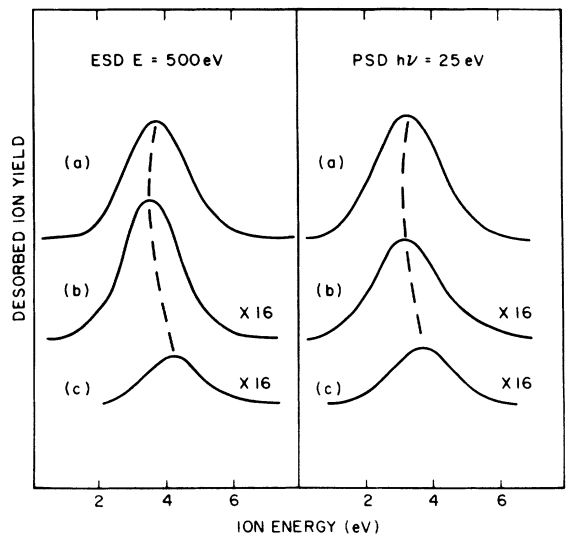

FIG. 1. Desorbed ion-energy distributions in ESD and PSD for F^+ desorption from W(100): (a) angle-integrated distributions (normalized to have the same amplitude) using the full CMA acceptance angle; (b) angle-resolved spectrum at normal emergence; and (c) angle-resolved spectrum for an angle $\sim 30°$ away from the normal.

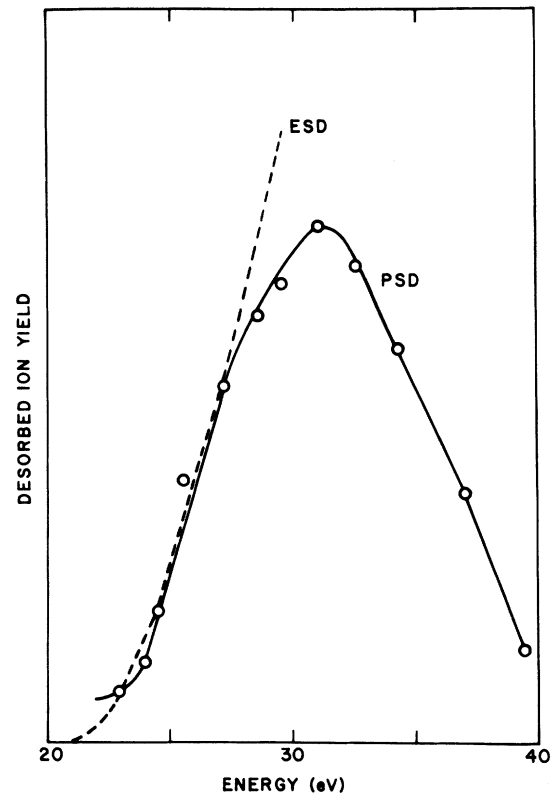

FIG. 2. Ion yield vs exciting beam energy for PSD and ESD at the ion peak seen in Fig. 1(a). Desorbed-ion yields are normalized approximately to the same incident photon or electron flux.

labeled (a) are the angle-integrated spectra and are seen occurring at the same energy for ESD and PSD. A further test of the similarity of ESD and PSD is provided by measurements of the anisotropy of the ion emission. In ESD the angular distributions have been shown to be characteristic of the adsorption state and the desorption mechanism.[1,2] Using a movable aperture inside the inner cylinder of the CMA we were able to investigate the angular distributions. First, using ESD, the emission was found to peak sharply in one direction (at or near to the surface normal) while displaying a weak maximum at a polar emission angle of approximately 30° from the main maximum. PSD was found to peak in a similar fashion but with some angular smoothing which could result from the larger photon-beam size. The ion-energy distributions at these peak angles are shown in Fig. 1. It is seen that there is a clear shift of the maximum in the ion-energy distribution to high energy at the higher take-off angle, and that the shift is the same for both ESD and PSD. A similar effect has been noted in the ESD of O^+ from W(100) at elevated temperatures, and has been interpreted in terms of differences in adsorbate-substrate distances.[11]

The dependence of the ion yield on incident photon or electron energy is shown in Fig. 2 for F^+ desorption. The measurements were taken at the peak in the angle-integrated ion-energy distribution. The ESD-yield curve has been shifted to higher energies by ~ 5 eV to take account of the work-function correction required to equate the effective incident energies for the two alternative excitation probes. The result of this correction is to show a clear alignment of the threshold behavior in each process. This finding agrees with the earlier work on TiO_2 by Knotek *et al.*[5] We have also found similar correspondences in threshold behavior and ion-energy distributions for the adsorption of oxygen and chlorine on the W(100) surface.

The similarity of threshold and ion-energy distribution behaviors for ESD and PSD might readily be explained if the observations using photon stimulation resulted from ESD by the emitted photoelectrons. However, two observations clearly rule this out. First, the observed fall of PSD yield with increasing energy above the immediate threshold region is characteristic of photoionization but not electron ionization.[5,12] Second, the absolute cross sections in the threshold region are very close (10^{-7}–10^{-8} ions per incident particle) for the two effects. Difficulties of relating total photoyield to the number of photons, and correcting for the difference in photon- and electron-beam sizes on the sample relative to the area seen by the detector could mean that absolute yields

are in error by as much as a factor of 3 or 4. However, the number of photoelectrons having sufficient energy to produce ESD is several orders of magnitude less than the number of incident photons. The observed PSD yield is therefore far too high to be accounted for by an ESD-mediated mechanism, thus establishing that PSD is a primary excitation mechanism.

Let us turn to the species dependence of the desorption. Results for the energy dependence of the ion yield for Cl^+ and O^+ desorbing from W(100) are shown in Fig. 3, and are to be compared with the F^+ data of Fig. 2. The threshold of ~ 17 eV measured for Cl^+ corresponds well with the binding energy of the Cl 3*s* level[13] in agreement with the KF *intra*-atomic Auger mechanism for desorption.[4] For the case of O^+ PSD, a sequence of thresholds appear at photon energies of about 30, 33, 40, and 49 eV. The ion yield of O^+ may be compared, in Fig. 3(b), with the photoelectron yield (PEY) spectrum measured on a W film by Olson.[14] Structure in the PEY is associated with photoemission from the W 4*f* and 5*p* core levels. The remarkable similarity in line shape and position for the PSD and PEY is strong evidence for an *inter*atomic Auger mechanism, once more in agreement with the ideas of KF.

On the other hand, there are features of the data which are not readily accommodated within the KF picture. In particular, the threshold for F^+ emission, shown in Fig. 2, is ~ 24 eV, a value which is well below the F 2*s* binding energy[13] of ~ 31 eV, and which is well removed from any of the W core levels. The discrepancy is too large to be accounted for by a chemical shift, especially since the Cl 3*s* level would appear to have undergone no such shift at all. Furthermore, neither the F^+ nor the Cl^+ emission data show any indication of a W core-level threshold as seen for O^+. This suggests that F^+ and Cl^+ desorption proceeds via a mechanism akin to the more traditional Menzel-Gomer-Redhead model[3] which involves electronic and vibrational structure rather than core excitations. Even in the case of O^+ emission where the KF model works well, we cannot be very conclusive about its applicability to pure metal substrates since it is possible that the desorption occurs not from the free metal surface, but from a maximal valency oxide WO_3 concentrated at defect sites.

In conclusion, we have observed photostimulated desorption of various ions from a tungsten surface. Some of the data appear consistent with the Knotek-Feibelman mechanism, and some not. Whatever the excitation mechanism, however, our detailed experimental comparisons of the ion-energy distributions as a function of the energy and nature of the incident radiation show that the desorption process is essentially the same in ESD and PSD, and that PSD from a metal does exist as a primary low-energy effect. These findings lead us to suggest that the bulk of further ion desorption studies might well be done with ESD, and that the more difficult and elaborate synchrotron-radiation-based technique of PSD could be reserved for those tasks where, through polarization effects or core-level selectivity, for example, it offers information not obtainable with ESD.

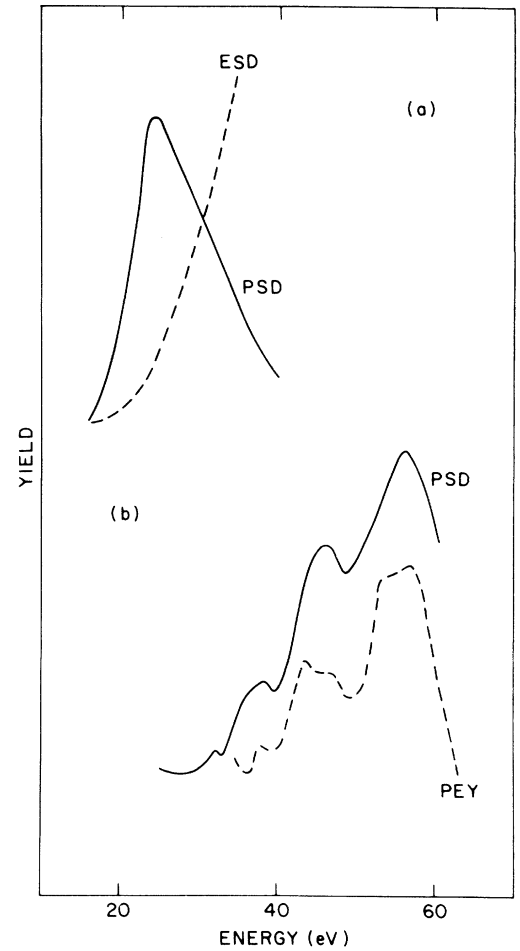

FIG. 3. (a) ESD and PSD yields for Cl^+ desorption from W(100) taken at an ion kinetic energy of ~ 2 eV; (b) PSD yield for O^+ desorption at a kinetic energy of ~ 8 eV from W(100) and total photoelectron yield (PEY) from an evaporated W film (Ref. 14). PSD and ESD curves are only roughly normalized to the incident flux; scaling for the PEY curve is arbitrary.

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