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Direct detection of neutral metal atoms in electron-stimulated desorption: Al from CH₃O/Al(111) - velocity distribution and absolute yield*

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Direct detection of neutral metal atoms in electron-stimulated desorption: Al from CH₃O/Al(111) - velocity distribution and absolute yield*

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Electron-stimulated desorption of neutral aluminum from the system CH₃O/Al(111) has been *directly* monitored via quasiresonant photoionization with 193 nm excimer laser light and confirmed by two-step resonant ionization, utilizing the Al 3d ²D manifold. Velocity distribution measurements for the neutral Al peak at ~800 m/s for 1 keV incident electron energy. An absolute yield of 3.2×10^{-6} Al atoms/electron was determined by comparison with sputtering measurements in the same apparatus. This is the first observation of electron-stimulated metal desorption from adsorbate-covered metallic surfaces.

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It is well known that desorption of atomic and molecular fragments from an adsorbate-covered surface can occur following a localized electronic excitation in the surface region, induced by electron or photon collisions. In the traditional view,^{1,2} release of initially strongly bound species requires the dissociating bond to be raised to a repulsive electronic state and remain there with a lifetime adequate for the accumulation of sufficient nuclear kinetic energy to permit escape from the surface region. Consequently, it has been commonly believed that electronically stimulated desorption of *metal* atoms from clean metal surfaces is rendered impossible by the existence of pathways that provide rapid de-excitation of the surface metallic bond. In this context, Menzel³ notes that "desorption of metal atoms from metal surfaces is immeasurably small."

The presence of adsorbates on metal surfaces can modify the situation significantly. In the case of aluminum, removal of an oxidized layer by electron impact in Auger electron spectroscopy (AES) has been documented⁴⁻⁶ under

conditions where electron-stimulated desorption (ESD) rather than local heating may be identified as the operative removal mechanism. Since AES detects only the disappearance of the adsorbate O atoms, no conclusions were possible regarding the possible simultaneous loss of surface Al atoms. The present study on the $\text{CH}_3\text{O}/\text{Al}(111)$ system exploits laser ionization mass spectrometry to detect neutral desorbates *directly*. The atomic Al species was identified unambiguously via 2-step resonance ionization spectroscopy (RIS). The Al velocity distribution, obtained by time-of-flight measurements, showed the low kinetic energies typical of neutral desorption.⁷⁻⁹ The absolute yield for Al atoms produced by ESD has been obtained through the use of a comparison measurement on atoms *sputtered* with known yield from aluminum, with adjustments for the differing velocity distributions in the two cases.

Previously, we have reported detailed studies of neutral desorption from methanol-dosed aluminum surfaces, detected by laser mass spectrometry at 193 nm.^{9,10} Those papers contain descriptions of the general laser techniques and the ultrahigh vacuum methods for the cleaning of the aluminum sample and the preparation of the saturation coverage $\text{CH}_3\text{O}/\text{Al}(111)$ surface employed here. The present observations were made during investigations at 1.0 keV in an apparatus of higher mass resolution and sensitivity.^{11,12} Desorption was induced by electron pulses of approximately 1 μs duration, repeated at a typical rate of ~ 25 Hz, limited by the need for stable operation of the 193 nm excimer photoionization laser. Under the conditions employed (equivalent steady electron current ~ 1 μA , beam diameter ~ 1 mm), sample heating can be shown to be completely negligible,¹³⁻¹⁵ eliminating consideration of thermal desorption mechanisms.

The principal result reported in this letter is the direct observation of desorbed aluminum metal, detected as the photoion Al^+ . At 193 nm and intensities of ~ 5 MW/cm^2 , the neutral desorption spectrum is dominated by a peak at mass 27. In the regime ≥ 100 MW/cm^2 , photoions containing C, H, and O atoms are efficiently detected, accompanied by some background from photoionization of static gas-phase species which is detected and subtracted to arrive at the net ESD signals reported in these studies. The great utility of 193 nm excimer laser light for the sensitive detection of neutral aluminum atoms results from the very close energy-resonance between a known auto-ionizing state¹⁶ of Al at 51753 cm^{-1} , and the ability to reach the ionization level in a 1-photon process. Since a substantial part of the ArF laser

bandwidth overlaps the autoionizing line, resonance ionization detection is effectively being performed.

Two strong tests demonstrated the identity of the mass 27 desorbate. Dosing with $^{13}\text{CH}_3\text{OH}$ to produce a $^{13}\text{CH}_3\text{O}/\text{Al}(111)$ surface caused the expected unit shifts in the positions of the C^+ , CH^+ , and CO^+ signals (fig. 1), while maintaining a dominant peak at the 27 position. Residual mass 28 signal in fig. 1 may possibly be attributable to AlH , which has recently been observed in thermal desorption from an $\text{Al}(111)$ surface dosed with hydrogen atoms.^{17,18} Confirmation of the neutral atomic Al desorbate was obtained in a RIS experiment in which the first excitation step involved tuning a frequency-doubled dye laser through a component of the Al $3p\text{-}3d\ ^2\text{D}_J$ multiplet in the 309 nm region, as indicated in fig. 2, followed by ionization via KrF excimer laser radiation at 248 nm. As seen in fig. 3, resonantly enhanced signal appears at the expected positions within experimental error. Some residual nontunable signal results from the relatively intense KrF radiation ($\sim 14\text{ MW/cm}^2$).

Additional experiments established the following facts. (1) No mass 27 signal was observable when the ESD experiment was performed on clean $\text{Al}(111)$. (2) The Al signal appeared clearly upon deposition of a saturation methoxy coverage. (3) Pyrolysis at 600K, a process known to leave only surface oxide and carbide species,¹⁹ caused a drastic reduction in the mass 27 ESD. (4) In the case where an oxide was prepared by exposure of the cleaned surface to O_2 , the mass 27 ESD signal was present but at least an order of magnitude below that for $\text{CH}_3\text{O}/\text{Al}(111)$.

Velocity distribution data for the Al species, shown in fig. 4, was obtained by standard time-of-flight techniques with a path length from sample surface to laser photoionization region of 2.2 mm and confirmed at the longer distance of 4.4 mm. The two experimental distances sample somewhat different ranges of desorbate ejection directions, but no strong angular effect can be seen in the data. The Al velocity distribution was observed to peak at $\sim 800\text{ m/s}$, corresponding to a peak kinetic energy of 0.09 eV, for mass 27. The parametric curves in fig. 4 are a function containing a significant high-energy component (the "planar barrier/power-law" model^{9,10}) and a Boltzmann distribution, which gives a somewhat better fit to the data. In the case where desorption of methoxy was monitored, a substantial high-energy tail was more evident.⁹

Measurement of the absolute ESD yield for Al involved a companion sputtering experiment to calibrate the overall instrumental detection sensitivity. Operation in the sputtering mode^{11,12} involved the use of 1 μ s pulses of 3.6 keV Ar⁺ ions to achieve steady-state concentration of Al atoms in the mass spectrometer photoionization region, where the excimer laser pulses and ion extraction conditions were kept identical to those employed in the ESD portion of the experiment. In the latter case, long-pulse conditions (15 μ s) were employed for the electron beam so that again steady-state analysis of the desorbate density at the position of the laser beam is appropriate. Since sputtering or desorption yields are *fluxes* of species from the surface while detected signals are proportional to *densities* of species in the photoionization volume, velocity data is needed in the normalization of the Al ESD yield, Y_e , to Y_s , the sputtering yield of aluminum atoms. We employ $Y_s = 2.2$, based on the normal incidence data of Robinson and Southern²⁰ for the Al(111) surface. No measurement of the velocity distribution of sputtered Al atoms was performed, but a reliable model is available.^{21,22} Let $f(u, \theta) du d\Omega$ represent the flux of atoms into solid angle $d\Omega$ and reduced velocity interval du , with u related to the actual lab velocity v by $u = v/v_b$. The latter quantity is defined by $v_b = (2E_b/m)^{1/2}$ for surface binding energy E_b and atomic mass m . Normalized to unit flux,

$$f(u, \theta) = [(\cos\theta/\pi) d\Omega] [4u^3/(1 + u^2)^3 du]. \quad (1)$$

Using the thermochemical heat of sublimation²³, $E_b = 3.36$ eV, we obtain $v_b = 4.90$ km/s. Straightforward calculation then yields the value for the steady-state atomic density n_s at a distance R from the sputtered surface in a direction at angle θ to the surface normal:

$$n_s = \frac{I_s Y_s}{4v_b} \left\langle \frac{\cos\theta}{R^2} \right\rangle \quad (2)$$

for sputtering current I_s (ions/s), the geometric factor $\cos\theta/R^2$ being averaged over the contributing solid angle.

A corresponding analysis of the ESD measurement was made in terms of the Boltzmann distribution, with flux

$$f(u, \theta) = [(\cos\theta/\pi) d\Omega] [2u^3 e^{-u^2} du] \quad (3)$$

for the standard parameters $u = v/v_m$ and $v_m = (2kT/m)^{1/2}$. Our measured experimental peak velocity v_p from fig. 4 is used to determine $v_m = v_p/\sqrt{2} \approx 0.8$ km/s. Designating quantities in the ESD experiment by the subscript e , the desorbate density n_e is given by the formula analogous to eq. 2:

$$n_e = \frac{I_e Y_e}{\sqrt{2} \pi v_m} \left(\frac{\cos \theta}{R^2} \right) \quad (4)$$

With the detection efficiency and geometric factors maintained constant between sputtering and ESD measurements, the signal ratios can be taken as equal to n_e/n_s , with the resulting yield for Al atoms $Y_e = 3.2 \times 10^{-6}$ atoms/electron at 1.0 keV primary beam energy.

Uncertainty in the velocities employed in eqs. 2 and 4 are expected to influence the yield value only at the level of a few percent.²⁴ A similar error may be expected from the fact that the form of the ESD neutral velocity distribution is not precisely determined (cf. the slightly different numerical factors in eqs. 2 and 4), though the Boltzmann form appears to fit somewhat better. Energy distribution effects can influence the apparatus transmission factor, but ion optics calculations¹² show that the voltage drop across the photoionization region causes a much larger energy spread, justifying the assumption of constant detection efficiency. Somewhat greater uncertainty is involved in converting Y_e to the equivalent cross section σ_e via $\sigma_e = Y_e/n'$ with n' signifying the surface density of the adsorbate species, giving rise to the desorption of the detected Al atoms. Although the surface morphology of the $\text{CH}_3\text{O}/\text{Al}(111)$ system has not been established, a zero-order procedure is to assume the 1×1 coverage pattern appropriate to the atomic oxygen overlayer,²⁵ though steric effects in the methoxy/aluminum system are expected to reduce this estimate. For $\text{Al}(111)$, a value $n' = 1.41 \times 10^{15}$ atoms/cm² is appropriate,²⁶ giving $\sigma_e = 2.3 \times 10^{-21}$ cm².

No data are available for direct comparison with these measurements, but the related work on electron-induced oxide removal from aluminum surfaces can be mentioned. Auger measurements on polycrystalline aluminum have been analyzed⁶ to yield a value of $\sigma = 1 \times 10^{-19}$ cm² for the loss of the 54 eV AES line characteristic of Al^{+3} in a layer of surface oxide. Analysis of published results on surface oxide deposited on $\text{Al}(111)$ through heavy O_2

dosing and heating cycles²⁷ leads to virtually the same value for the cross section for O atom loss under 3 keV electron impact. However, under conditions of lower oxygen coverage, sufficient to produce vibrations characteristic of an oxygen underlayer, no ESD effects could be observed. Relevance to the present measurements arises from the likelihood that desorption leading to gas-phase O atoms probably involves breaking Al-O rather than Al-Al bonds, on the basis of de-excitation rate arguments.

A question remains as to the identity of the neutral desorbate giving rise to our observation of Al⁺ photoions. The desorbate species may be atomic or molecular, e.g., AlOCH₃, a species which has been observed as the cation in SIMS studies.²⁸ Recent calculations²⁹ show the Al-O bond in neutral AlOCH₃ to be strong (~ 5 eV), supporting the view that such a species could survive the desorption process intact. Both the sputtering and ESD experiments were carried out with a high degree of optical saturation at 193 nm, but a search over several orders of magnitude failed to show any signal from a possible molecular, aluminum-containing species. There remains the possibility that complete dissociation of a molecular precursor, AIX say, occurs at any laser intensity giving adequate photoionization efficiency. If, rather than being desorbed directly, aluminum atoms were produced through a sequence such as $AIX + h\nu \rightarrow AIX^* \rightarrow Al + X$, followed by subsequent, very efficient, photoionization of the metal atoms, two observable effects would be expected. Under the assumption that the cross section for quasis resonant photoionization of Al atoms is much greater than that for the nonresonant excitation to AIX*, optical saturation of the Al⁺ signal in the sputtering experiment (where neutral atom release is strongly dominant) should occur at lower intensities than in the corresponding ESD measurements. Secondly, at low laser intensities, I, the molecular pathway should approach Al⁺ ~ I² behavior because of the sequential steps of photolysis and ionization in contrast to the atomic precursor case where Al⁺ ~ I is expected. Preliminary experimental data show both predicted effects, implying a molecular precursor. The failure to observe any such species could be explained provided the dissociation of the intermediate AIX* species were sufficiently rapid relative to the competing rate of photoionization to produce AIX⁺. Detailed rate-equation models indicate plausibility for such a situation.

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Figure Captions

Fig. 1 Mass spectra obtained by excimer laser photoionization, at 193 nm and $\sim 20 \text{ MW/cm}^2$, of neutral species desorbed by 1 keV electrons.

Fig. 2 Energy level diagram for aluminum atoms showing the ionization path for fixed frequency, 193 nm laser ionization, and for resonance ionization through the 2D_J system.

Fig. 3 Resonance ionization spectrum of neutral Al atoms desorbed by 1 keV electrons from the $\text{CH}_3\text{O}/\text{Al}(111)$ system and detected by the photoionization scheme given on the righthand side of fig. 2. Note the split (linear) scale. Scan is given in terms of the visible dye laser wavelength scale on which are indicated the expected positions of the $^2P_J^0 \rightarrow ^2D_J$ lines, excited by crystal second harmonic generation.

Fig. 4 Velocity distributions from neutral ESD at 1 keV on the $\text{CH}_3\text{O}/\text{Al}(111)$ system, obtained by time-of-flight over paths of 2.2 mm (open squares), and 4.4 mm (solid circles) from sample surface to photoionization volume.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

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