FIELD-ASSISTED PHOTODESORPTION OF IONS FROM METAL AND SEMICONDUCTOR SURFACES

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Abstract - The influence of strong electric fields on the photon-stimulated desorption of small molecules from metal and silicon surfaces has been studied. With hydrogen only field adsorbed H_2 as well as H_3 are desorbed as singly charged ions. Chemisorbed atomic hydrogen obviously has a photo-ionization cross-section at metal surfaces which is too small to be detected. From clean and oxidized Si surfaces H^+ as well as Si-containing hydrides and oxides are photodesorbed at field strengths as low as 6V/nm. Field adsorption of water leads to whisker-like layers, from which $H_3O^+ \cdot nH_2O$ -clusters are photo-desorbed with rather high quantum yields. The desorption spectrum exhibits a sharp onset at a wave length of 165 nm; the onset energy shifts with decreasing field strength towards higher energies.

I. INTRODUCTION

The simultaneous interaction of a high electric field and of photons of suitable energy on an adsorbed molecule can lead to desorption of ionic species. Two fundamentally different mechanisms can be considered, which we will refer to as:

- a. Photon-assisted field desorption. This mechanism has been brought forward by Tsong et al /1/; it assumes that the charge transfer from the adsorbate to the metal or semiconductor substrate proceeds via electron tunnelling from an excited state of the adsorbed molecule into an empty electron level of the solid.
- b. Field-assisted photodesorption. Here ionizing the adsorbate is done by electronic excitation as in the field free case. The mechanism is similar to those discussed for electron-stimulated desorption by Redhead /2/, Menzel and Gomer /3/,

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Antoniewicz /4/, Knotek and Feibelman /5/ and Gomer /6/. The electric field facilitates the removal of the ionized species from the surface and thus increases the escape probability. According to these mechanisms, the photon energy has always to be larger than the ionization potential of the adsorbate.

Previous experiments with tunable laser radiation in the visible and long-wavelength UV have shown that mechanism (a) could only be found, so far, for the case of ethylene on silver /7/. The aim of the present investigation is to elucidate which of the models, proposed under (a) or (b), describes the reaction in other systems.

II. EXPERIMENTAL

The apparatus used has been described elsewhere /8/. In short, it consists of a field ion microscope, where the tip to screen distance also serves as the mass analyzer in the time-of-flight (t-o-f) mode. Monochromatized synchrotron radiation (SR) was focussed onto the tip, and mass spectra of the desorbed ions were recorded, taking advantage of the pulsed structure of the SR light (5 MHz at BESSY, 1 MHz at DORIS). The substrates were shaped in the form of field emitter tips by chemical etching and electropolishing, following established procedures /9/. Most of the gases used were Messer Griesheim pressure cans with a nominal purity > 99.99 %. Deuterium was supplied by Linde in a break seal flask. Water was triply-distilled and thoroughly degassed by several freeze-pump-thaw cycles. In order to separate the surface signal from the background, due to field ionization and photoionization in the gas phase, it is mandatory to work at pressures less than 2×10^{-9} mbar. Therefore a good background pressure is essential for meaningful results. A pressure of $< 3 \times 10^{-10}$ mbar was routinely achieved 12 hours after a light bakeout using a 330 l/s turbomolecular pump and a liq. N₂ cooled Ti sublimation pump. The residual gas was analysed with a Balzers QMG 311 quadrupole mass spectrometer and found to consist mainly of H₂ and CO with traces of H₂O and CO₂. In order to avoid unwanted reactions on the hot filaments, gas composition and pressure measurements were only made after the photodesorption data had been taken.

III. RESULTS

Previous experiments with laser radiation /10/ had established in most of the studied systems that for photodesorption, light energies above the ionization energy are necessary. In this case, mechanisms involving electron tunneling can be excluded. If the photon energy, which leads to desorption is comparable to the ionization energy of the adsorbate, the Menzel-Gomer-Redhead (MGR) model describes the desorption process most accurately. On the basis of this model, one expects a very pronounced mass dependence of the desorption rate. Specifically on the system H₂/W(100) Jelend and Menzel /11/ found a H/D isotope effect as big as 150. We therefore investigated the desorption yield of H⁺ and D⁺ ions from W and Ni surfaces with wideband radiation from 30 - 120 eV. Pure H₂ and H₂/D₂ - mixtures (up to 60 % H₂ from the re-

sidual gas) were dosed onto the tip, and the desorbing ions recorded as a function of temperature and field strength. Within the uncertainty of our composition determination, no preferential adsorption or desorption could be found. This agrees well with another observation of Menzel, who found only a very small isotope effect for H_2^+ from W(100), contrasting the extreme isotope sensitivity for H^+ desorption. H_2^+ thus is the primary species in field-assisted photo-desorption. This becomes apparent also in the field strength dependence of the H^+ , H_2^+ and H_3^+ desorption yield [12]. No stimulated desorption is observed below approx. 15 V/nm. At higher field strength when field adsorption of hydrogen molecules sets in, H_2^+ is detected. If one

Fig. 1 - Ion yield for photostimulated desorption as a function of field strength

x x x H^+
o o o H_2^+
□ □ □ H_3^+

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Fig. 2 - Temperature dependence of the desorption signals: H_2/D_2 from Ni. Original traces; the peak on the right hand side is due to stray light from the desorption pulse.

increases the field strength further, the H^+ signal grows at the expense of the H_2^+ , presumably by field dissociation of the molecular ion. Neither on W nor on Ni did we find a detectable rate of isotope exchange at 80 K. Increasing the temperature to 120 K virtually suppresses the desorption signal (Fig.2); upon cooling back to 80 K, the composition of the desorbed species is almost identical to that at the beginning. On Ni, no mass 3 is detected, showing unambiguously that no HD has been formed. On Si and oxidized Si surfaces, larger signals were expected since reneutralization of the ions should be slower, due to the lower concentration of free electrons. Indeed, ca. 10 times more intense signals were recorded. Also, H^+ was found already at low field strength, and at room temperature. Obviously, a Si-H or SiO-H surface bond can be broken photolytically, leading to the desorption of H^+ . The H^+ -photodesorption threshold near 10 eV could be verified by inserting a LiF-filter in the SR beam. Unfortunately, the monochromator used at BESSY had too low a photon flux in this range to establish the desorption threshold more clearly.

In the search for a system with higher desorption yield we succeeded with H_2O -layers grown on a field emitter in the strong electric field. In the photodesorption mass spectra, we observed protonated water clusters similar to those seen by Tsong and Liou /13/ and earlier by Beckey /14,15/ and Schmidt /16/. At high field, H_3O^+ is the most abundant species. At low field, however, $H_3O^+ \cdot 2H_2O$ is most frequently observed though clusters up to $H_3O^+ \cdot 16H_2O$ are observed. All these clusters show a threshold at a wavelength near 165 nm, suggesting a common excitation step for all the clusters. This confirms the model of water whiskers (Fig. 3), which was derived by Anway /17/ on the basis of appearance energy measurements. Also, we want to point out that the observed desorption spectrum closely resembles the adsorption spectrum of liquid water /18/ measured by Painter et al. at the triple point.

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Fig. 3 - Field-assisted photodesorption from condensed water films

- a) ToF mass spectrum for the various species desorbing from H_2O on Ni
 $T = 80 \text{ K}$, $P_{\text{H}_2\text{O}} = 5.6 \times 10^{-9} \text{ mbar}$.
- b) desorption yield vs. wavelength of the excitation light at various applied fields (substrate iridium).
- c) proposed model of a "water whisker" growing in an electric field.

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