Photon-Stimulated Layer-by-Layer Desorption from NaCl(001) Surfaces Monitored by Helium-Atom Scattering

H. Höche
Max-Planck-Institut für Mikrostrukturphysik, Weinberg 2, Halle/Saale, Germany

J. P. Toennies and R. Vollmer*
Max-Planck-Institut für Stromungsforschung, Bunsenstrasse 10, Göttingen, Germany

(Received 14 October 1992; revised manuscript received 29 June 1993)

He-atom scattering and mass-spectrometer flux analysis have been used to study structural changes accompanying photon-stimulated desorption (PSD) by valence electron excitation of NaCl(001) cleavage faces *in situ*. Within the considered temperature range from 550 to 240 K an incomplete photon-induced layer-by-layer removal is observed. In contrast to previous experiments and models not only neutral Cl and Na atoms but also NaCl molecules have been observed to desorb upon excitation. The rate of PSD is found to be strongly dependent on the temperature but independent of the surface topography.

PACS numbers: 68.35.Fx, 61.80.Ba

The interaction of energetic particles such as atoms, ions, electrons, and photons with solids has been the subject of many investigations during recent decades and is still of special interest [1,2]. While energetic atoms and ions interact with matter by direct momentum transfer, the interaction of low-energy electrons and photons of a few eV is considerably more complicated. In the latter case the decay of direct electronic excitation causes desorption of particles from the surface, with both thermal as well as hyperthermal kinetic energies. These phenomena have been extensively studied for the alkali halides by irradiation with low-energy electrons or ultraviolet photons [3-7]. The generally accepted model for photon-stimulated desorption (PSD) and electron-stimulated desorption (ESD) due to valence electron excitation was initially proposed by Pooley [3] and Hersh [4] and subsequently refined by a number of authors [8-11].

In the case of photon excitation excitons are created in a surface layer only a few tens of nm thick. These excitons self-trap rapidly and decay in a time scale of nanoseconds to *H*-center–*F*-center pairs (an *H* center is a negative halogen molecule at an anion site, ordinarily occupied by a halogen ion, and an *F* center is an electron trapped at an empty lattice site of a halogen ion). The decay of a self-trapped exciton into an *F*-center–*H*-center pair may induce a collision sequence of the *H* center along one of the ⟨110⟩ directions. When a collision sequence reaches the surface the directional emission of a hyperthermal halogen atom takes place. Alternatively, the *H* centers can thermalize in the bulk and the diffusion of the resulting interstitial halogen atoms to the surface enables their thermal desorption. Mobile *F* centers can neutralize cations by charge transfer. At the surface the latter process leads to the formation of alkali adatoms which may desorb thermally. In a variation of this model Townsend [8] proposed that excitons created by ultraviolet irradiation first diffuse freely through the crystal before they decay into *F* and *H* centers either near defect sites or in the vicinity of the surface. In contrast to the above model the *H* centers release their energy during much shorter collision sequences.

Most investigations up to now have studied both the desorption rate and the properties of the desorbed species only and therefore little is known about the structural changes of the surface during the PSD process and the kinetics controlling the surface topography. Surface decoration electron microscope studies provided the first indication that PSD causes the creation of 2D holes within the uppermost lattice plane [12]. The subsequent spreading of these 2D holes enables the formation of a next generation of spreading holes before the topmost layer is completely removed by coalescing holes of the first generation. Finally, this repetitive process leads to an incomplete layer-by-layer removal in the course of which several subsequent layers are involved. Unfortunately, the decoration method is applicable only to low step densities of less than 10^{-2} Å^{-1}. Moreover, kinetic processes at the surface cannot be followed directly by this method.

Therefore, He-atom scattering (HAS) has been applied in the present study of structural changes due to PSD. HAS is uniquely sensitive to both atomic steps and surface defects like single adatoms and surface vacancies [13,14] and can be used to elucidate the surface structures and the kinetics during the PSD process. Since there are no space charge problems as with reflection high-energy electron diffraction (RHEED) and low-energy electron diffraction, HAS is well suited for insulators, too. Most important to the present investigation, HAS is a completely nondestructive method which does not influence the PSD process itself.

The HAS experiments have been performed in an apparatus described earlier [15,16]. The probing He-atom beam is prepared with a velocity spread $\Delta v/v$ of about 0.5% by supersonic expansion into vacuum. The incident beam is collimated to 0.28° and a sensitive magnetic mass spectrometer detects the scattered He atoms within an aperture of 0.12°. The angle between the incident and

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the outgoing beams is fixed at 90°. To measure the PSD particle yield simultaneously with the photon-induced surface alterations the target chamber was additionally equipped with a Balzers QMS420 quadrupole mass spectrometer, the ionizer of which was positioned about 100 mm in front of the sample. The NaCl crystals were cleaved *in situ* at a base pressure of 1×10^{-10} mbar. Each cleavage face was used for several experiments. Between subsequent PSD experiments the surfaces were smoothed by annealing at 610–630 K for about 1 h. This treatment leads to reproducible results. After heating the specimen to the desired temperature the crystal was irradiated with the total emission of a D_2 lamp through a MgF_2 window [17]. The MgF_2 window cuts off the small wavelength part of the incident spectrum so that mostly photons near the fundamental absorption edge of NaCl at about 160 nm contribute to PSD.

In the present study the PSD experiments were restricted to crystal temperatures $T<550$ K to avoid significant thermal sublimation which sets in at higher temperatures [18]. To monitor the structural changes occurring on the NaCl(001) surface during VUV irradiation the intensity of the specularly scattered He atoms was recorded as a function of time. Figure 1 shows the temporal course of the specular He intensity before and during photon excitation for selected crystal temperatures. The wave vector of the incident He beam ($k_i=5.58$ Å^{-1}) satisfies nearly an out-of-phase condition for which waves scattered from terraces separated by an odd number of monatomic steps (step height: 2.81 Å) interfere destructively. But, as expected [19], similar results were also observed for in-phase conditions, since the intensity of the specularly scattered He beam is mostly affected by the diffuse scattering from step edges.

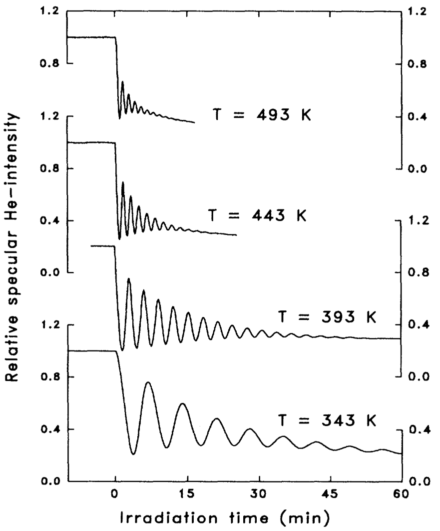

FIG. 1. Normalized specular intensity of He atoms scattered along the ⟨110⟩ azimuth from NaCl(001) cleavage faces shown for various temperatures at a constant VUV-irradiation intensity as a function of the irradiation time. The incident photon flux was of the order of 10^{13} to 10^{14} photons cm^{-2}s^{-1} and the incident wave vector was $k_i=5.58$ Å^{-1}.

As seen in Fig. 1, as soon as the photon excitation is switched on the He intensity decreases sharply and oscillates with a constant frequency afterwards. The observed damped oscillations clearly indicate an incomplete layer-by-layer removal of the crystal in which several subsequent layers are involved. Layer-by-layer removal has not been previously observed in PSD and ESD [20], but is well known from studies on ion sputtering of metal surfaces [21] and for the reverse process of epitaxial growth observed with RHEED [22] and HAS [19,23,24]. It is interesting to note the very close similarity between the oscillations in Fig. 1 and those observed in growth of NaCl on NaCl(100) [24]. In Fig. 1 the period of oscillations, which is inversely proportional to the total desorption yield, varies between 54 s at $T=553$ K and 3650 s at $T=273$ K. Oscillations were observed down to the lowest studied temperature of 240 K [25].

HAS measurements performed at various temperatures show that at temperatures below 360 K the inverse oscillation period follows an Arrhenius straight line with an activation energy for the VUV-induced desorption of $E_{d,\mathrm{VUV}}=0.27$ eV. This energy lies far below the sublimation enthalpy of NaCl crystals, $H_{\mathrm{sub}}=2.39$ eV [26], but close to the desorption energy of single NaCl molecules from a flat surface into vacuum, $E_d=0.31$ eV, as estimated by Madelung-like calculations [27]. This correspondence suggests that the thermal desorption of single NaCl molecules could be the rate-determining step in PSD at $T<360$ K [28]. Since the mechanisms proposed by Pooley and Hersh only predict the desorption of Na and Cl atoms we propose on the basis of mass-spectrometer experiments to be discussed below an additional relaxation channel which involves the desorption of single NaCl molecules. According to this model part of the mobile excitons decays preferentially at surface steps; the released energy can cause a local vibrational excitation of single NaCl molecules. The excited molecules leave the step sites for the adjacent terraces where they take part in facile surface diffusion until they are either recaptured at steps or thermally desorbed.

At temperatures above 360 K the temperature dependence of the rate of PSD decreases. Kanzaki and Mori [29] also observed a similar change in the temperature dependence in their flux studies of PSD from RbBr crystals. These authors assume that with increasing temperature the deexcitation of excitons within the bulk becomes increasingly important. An alternative interpretation could be that with increasing temperature the photon-induced desorption rate is no longer limited by the desorption of adparticles but by the rate of their creation.

The temporal course of the specular He intensity reveals another interesting phenomenon as soon as the photon excitation is switched off. This can be best studied after the photon-induced oscillations of the specular He intensity are damped out by continued photon excitation. As shown in Fig. 2 the intensity of the scattered He beam recovers a part of its initial intensity over a dark period of about 10 to 30 min with the greatest increase at the highest temperature.

We could rule out that the recovery of the He signal is due to the desorption of NaCl admolecules and/or Na and Cl adatoms created during the preceding irradiation period by mass-spectrometer measurements of the flux of neutral species leaving the surface. An example is shown in Fig. 3 for $T=493$ K. The top trace shows the specular He intensity versus time for alternating VUV irradiation and dark periods. Below, the corresponding mass-spectrometer signals for the Cl^+, Na^+, and $NaCl^+$ species are shown. Whenever the VUV excitation is switched on or off the mass-spectrometer signals of Na^+ and $NaCl^+$ change immediately by more than 1 order of magnitude, indicating that no significant desorption occurs in the dark period. The slight linear increase of the Cl^+ signal over the entire period of the experiment is due to a progressive contamination of the mass spectrometer. The absolute change, 2.3×10^{-12} Å, of the Cl^+ signal between dark and irradiation periods is of the same order of magnitude as the increase of the two other signals. Note the renewed onset of weak oscillations of the specular He intensity at the beginning of the second irradiation period. This effect also indicates that a certain surface smoothing took place in the preceding dark period.

The recovery is therefore attributed to a thermal annealing of surface defects such as adatoms, admolecules, and vacancies which have been accumulated during the preceding irradiation period. The observed time dependence can be well fitted by a sum of two exponentials plotted as dashed lines in Fig. 2. This functional form has been proposed by Neave *et al.* [30] to describe the recovery of the RHEED signal in GaAs growth after interruption of the gallium flux. Related Monte Carlo calculations of Vvedensky and Clarke [31] indicate a two-step smoothing of the surface by diffusion processes. The surface steps, having a rather "dendritic shape" during the growth, become more compact in the first stage of the recovery as single adunits enter higher coordinated lattice sites near steps via surface diffusion. This stage is followed by a second one in which diffusion of crystal units along the steps leads to a further smoothing of the step edges and thus to a lowering of the total edge free energy [18]. Similar mechanisms could be responsible for the recovery of NaCl(001) faces after their photon-induced alteration. The analysis of the fit parameters as a function of the crystal temperature indicates that the postirradiation increase of the He intensity originates from thermally activated processes which are characterized by an energy of about 0.3 eV [25]. This energy explains why recovery effects which could be observed down to 368 K disappear at lower temperatures. The agreement of this energy with the thermal desorption energy of single NaCl admolecules from terraces must be regarded as a coincidence since, as seen in Fig. 3, the flux of NaCl vanishes when the irradiation is turned off.

At low temperatures the creation rate of Na atoms at the surface is expected to exceed their desorption rate and consequently the surface will be enriched with Na [32,33]. These photon-induced Na atoms may be assumed either to cover the surface uniformly or to form 3D clusters. Since the oscillations of the specular He intensity were observed down to the lowest temperature studied, $T=240$ K, the formation of a uniform Na layer which would inhibit further PSD can be ruled out. To confirm the assumption of a 3D-Na-cluster formation the angular distribution of elastically scattered He atoms was measured between the diffraction peaks over a wide range of angles [14]. As expected, after VUV excitation at higher temperatures, $T > 350$ K, there are no additional

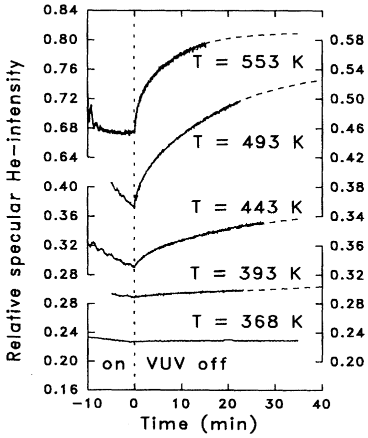

FIG. 2. Temperature dependence of the recovery of the specular intensity in the postirradiation period. The dashed lines represent the double exponential fit curves described in the text. The same scattering conditions of the He beam and the same VUV intensities were used as in Fig. 1.

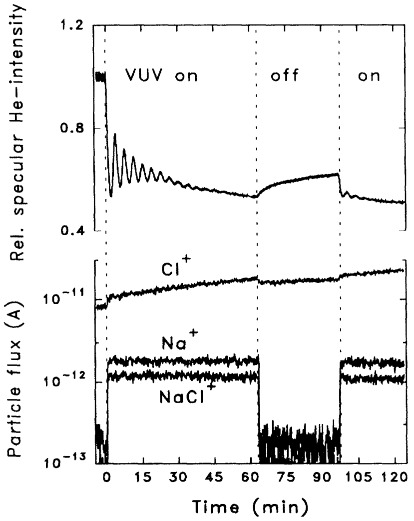

FIG. 3. Specular He intensity (⟨110⟩ azimuth, $k_i=5.58$ Å^{-1}) and corresponding mass-spectrometer signals for the Cl^+, Na^+, and $NaCl^+$ species for a crystal temperature of 493 K. The VUV intensity was about 3 times lower than in the measurements shown in Fig. 1.

scattering features caused by Na clusters. But at temperatures below 320 K weak but partially very sharp peaks were observed in addition to the Bragg peaks. There is considerable evidence that these additional structures are indeed caused by the scattering from clusters of Na atoms [14,25].

It is interesting to observe that the mass-spectrometer signals in Fig. 3 are not significantly affected by the temporal oscillation of the density of 2D holes. Thus we conclude that the observed incomplete layer-by-layer mode of desorption reflects only the result of PSD but it does not distinctly control the desorption yield itself.

In summary the present study provides the first evidence that photon-stimulated desorption from NaCl cleavage faces by valence electron excitation leads to a somewhat incomplete but distinct layer-by-layer removal. This behavior which was detected by intensity oscillations of the specularly scattered He atoms was observed down to the lowest temperature studied, $T=240$ K. Besides Na and Cl atoms, a considerable photon-induced desorption rate of NaCl molecules was detected by mass-spectrometer flux analysis. At crystal temperatures below 360 K the temperature dependence of the total rate of PSD seems to be dominated by photon-induced detachment from step edges of NaCl molecules which then desorb thermally from the terraces. The significant recovery of the helium specular intensity in the post-irradiation period indicates a thermally activated smoothening of the surface. This is due to the capture of low-coordinated adparticles at step sites as well as the annealing of step edges.

One of the authors (H.H.) gratefully acknowledges the support of the Deutsche Akademische Austauschdienst, Bonn, during a two-month working stay in Göttingen.

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*Present address: Materials Science Division, Lawrence Berkeley Laboratory, Berkeley, CA 94720.

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