Combined electron-microscope surface-decoration and helium-atom-scattering study of the layer-by-layer photon-stimulated desorption from NaCl cleavage faces

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The electron-microscope surface-decoration technique and He-atom scattering (HAS) have been used to characterize the topography of NaCl(001) cleavage faces during vacuum ultraviolet (VUV) photon-stimulated desorption (PSD). The experiments were carried out at crystal temperatures below 550 K for which pure thermal desorption can be neglected. In the temperature range from $T=550$ to 440 K the decoration experiments reveal that PSD progresses mainly by the creation and subsequent spreading of two-dimensional (2D) holes of monolayer depth in the surface plane. From $T=550$ K down to 240 K the HAS experiments reveal periodic oscillations of the specularly scattered He intensity with exposure. These oscillations are attributed to the same process of creation and subsequent spreading of 2D holes which leads to a layer-by-layer removal of the surface. The HAS results indicate that the rate of PSD decreases strongly with decreasing temperature whereas the density of photon-induced 2D holes increases. The evolution with time of the specular He intensity also indicates that isolated adparticles are created during VUV irradiation. Simultaneous mass-spectrometer studies of the desorbing species reveal in addition to Na and Cl atoms a considerable PSD flux of NaCl molecules not predicted by the currently accepted models of PSD. Moreover the photon-induced desorption fluxes of the different species are found to be independent of the actual step density. Thus, the observed temporal alterations of the surface topography (step density) have no effect on the PSD process but solely reflect its progress.

I. INTRODUCTION

Desorption induced by electronic transitions (DIET) following excitation by photons, electrons, and ions is a well-known phenomenon which has been extensively studied during the last two decades for a wide variety of materials (see, e.g., Ref. 1). As recently reviewed by Johnson and Sundqvist,[2] the ejection or desorption of atoms and molecules in response to electronic excitations of condensed matter has fundamental importance for fields as diverse as astrophysics and biomolecular mass spectrometry. Although the basic processes of electronic excitation and relaxation are not yet completely understood, they are frequently encountered in various venerable technical applications such as the photographic process,[3] as well as in recent applications, such as in material processing by ion and electron bombardment as well as by photon-induced reactions.[4]

The present study deals with surface morphological changes accompanying desorption resulting from valence-electron vacuum ultraviolet (VUV) excitation. Photon-stimulated desorption (PSD) and especially electron-stimulated desorption (ESD) have previously been observed solely for a few insulators such as the alkali halides, which distinguish themselves by a large band gap as well as by nonradiative decay channels of excitation. Several authors studied the energy transfer mechanisms and the nature of the ejected species, mainly by mass spectroscopy.[5-8] The excitation by photons[9] as well as by low-energy electrons[10] was observed to lead to the emission of neutral alkali-metal atoms and halogen atoms. The halogen atoms were found to be emitted with both thermal and hyperthermal velocity distributions whereas the alkali-metal atoms desorb only with thermal energies.[10] At low temperatures the electron-bombarded surfaces were observed to be enriched with alkali-metal atoms[11,12] and the same is expected for photon excitation.

The preceding studies have established that the excitation by low-energy electrons (100–600 eV) and by photons with wavelengths at the fundamental valence absorption edge can be explained by related mechanisms.[6] Bombardment with low-energy electrons, however, not only creates excitons as with photon excitation but is also accompanied by core-level excitations and significant surface charging. Since these complications are avoided in PSD it is of particular interest in investigating excitonic mechanisms of desorption.

Before describing the present experiments on PSD-induced changes of surface topography and composition we briefly review some models presently under discussion. Pooley and Hersh[13,14] developed a model of ESD and PSD from alkali halide crystals. Their model has

been subsequently refined by several groups.[11,15-18] In the case of PSD, free excitons are created by the incident photons in a surface layer only a few tens of nanometers thick. Most of the excitons self-trap rapidly (the relaxation time is about 10^{-8} sec) and a subsequent nonradiative decay channel (about 10^{-9} sec) leads to the formation of 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). Thus, the excitation involves mainly the halogen sublattice. As the result of an "adiabatic instability"[16] the H centers can travel in the $\langle 110 \rangle$ directions by so-called replacement collision sequences. When these happen to reach the surface, a neutral halogen atom is ejected with significant excess energy in the direction of the replacement sequence. Otherwise, the H centers thermalize in the bulk and the excess halogen atoms finally become localized on interstitial lattice sites. These interstitial halogen atoms can diffuse within the bulk and if they arrive at the surface are also emitted but with thermal energy. Note that both of the above processes of desorption of halogen atoms do not change the surface stoichiometry. F centers diffusing to the surface are assumed to neutralize alkali-metal ions to form atoms that are able to desorb thermally, leaving behind molecular vacancies within the topmost lattice plane. With decreasing temperature the irradiated surfaces are expected to be enriched with alkali-metal atoms as soon as their creation rate exceeds their desorption rate.

Besides the above mechanisms of ESD and PSD of single alkali-metal and halogen atoms, another nonradiative relaxation channel has been proposed by Townsend in 1976.[19] In this mechanism, in addition to the H centers, free or excited self-trapped excitons diffuse to the surface and cause desorption. In contrast to the above model shorter collision sequences are assumed. Thus, the energy is transported to the surface by excitons instead of the H centers. It has also been postulated that the recombination energy is first released to local lattice vibrations before being dissipated into the surrounding bulk by emission of an appropriate number of phonons (see, e.g., Refs. 20 and 21). Exciton decay is expected to occur preferentially at inhomogeneities such as surfaces and especially at surface steps because of their strong local electric dipole fields.[22] In this mechanism it is conceivable that even single alkali halide molecules could be photon desorbed.

The Pooley-Hersh mechanism, which explains the photon-induced desorption of thermal alkali-metal atoms and both thermal and hyperthermal halogen atoms, is widely accepted, whereas the mechanisms leading to a vibrational excitation of crystal units at the surfaces are regarded as being more speculative. In both models, however, many of the details of the excitation and the nonradiative relaxation processes involved are not yet fully understood. Indeed, a recent paper by Szymonsky et al.[23] presents experimental results of KBr crystals bombarded with 700-eV electrons which seem to be in contradiction with even the Pooley-Hersh model. The authors found an unexpected directional ejection of hyperthermal halo-

gen atoms along the $\langle 100 \rangle$ direction instead of the $\langle 110 \rangle$ directions of the collision sequences as predicted by the Pooley-Hersh mechanism. Therefore the authors proposed a model involving the fast diffusion of excited holes ("hot holes") to the surface and their sudden localization at the surface.

Up to now little attention has been paid to the influence of PSD on the surface topography. The only previous work on NaCl(001) and KI(001) (Refs. 24,25) had a limited resolution since it was based on electron-microscopy studies in which the surface-decoration technique[26,27] was used to reveal steps on irradiated cleavage faces. The most important results of these investigations are (i) monatomic spiral steps (developing around the emergence points of $\frac{1}{2}a_0$ screw dislocations under conditions of advanced thermal sublimation) show on irradiation a distinct increase of both their turn density and their shape anisotropy, and (ii) in step-free surface regions photon-induced two-dimensional (2D) holes are created in the uppermost lattice plane.

In the present investigation NaCl(001) cleavage faces have been used as starting surfaces for the study of photon-induced effects. From decoration experiments, the fresh NaCl cleavage faces are known to consist of atomically smooth surface regions separated mainly by steps of only one lattice-plane distance in height, i.e., half a lattice parameter ($\frac{1}{2}a_0 = 2.81$ Å). The topography of these surfaces has been found to remain almost unchanged by pure thermal excitation up to $T = 550$ K. In this temperature range only small alterations in the geometrical course of strongly curved steps occur. These changes are well understood and are caused by the diffusion of crystal units along step edges.[25,28,29] Detectable sublimation sets in only at temperatures higher than 550 K, as indicated by both the propagation of monatomic cleavage steps and the thermal nucleation of spreading 2D holes.[28,30,31] Moreover, steps emanating from the points of emergence of dislocations develop.[32] Extensive decoration studies of thermally induced step propagation showed that the advance of steps is controlled by mobile admolecules which, once they have been detached from steps, diffuse across the surface before they are either thermally desorbed into the vacuum or captured again at surface steps.[25,28] For this reason the present experiments have been restricted to temperatures below 550 K to avoid complications from pure thermal desorption. Hence, the observed surface changes studied here can be attributed entirely to photon-induced processes.

Unfortunately, the decoration technique cannot be used to study surfaces covered by steps of high density, because the lateral resolution is limited to about 10 nm, nor can it be used to follow the step kinetics in time. To overcome these limitations, in the present study He-atom scattering (HAS) has been applied as a complementary method. HAS can be applied not only to metal and semiconductor crystals but also to insulators, since the probing He atoms do not charge up the surface. HAS has the further advantage that it is extremely sensitive to both atomic surface defects (vacancies, adsorbates) and surface steps.[33,34] Moreover, in contrast to the more frequently

applied scattering methods using electrons [reflection high-energy electron diffraction (RHEED) and low-energy electron diffraction (LEED)] or ions, HAS is a completely nondestructive method. Thus the probing He atoms do not interact with the exciting photons nor because of their low energy and mass are they expected to affect the photon-desorbed species. Therefore HAS seems to be an ideal technique for the present study of photon-induced alterations on sodium chloride cleavage faces.

Some years ago Gómes *et al.* showed that HAS can be used effectively to monitor layer-by-layer epitaxial growth of metals on single-crystal metal substrates.[35] The intensity of the specularly scattered He beam as a function of coverage revealed maxima at the completion of successive monolayers. Recently the same method has been successfully used to study the epitaxial growth of alkali halides on alkali halide cleavage faces.[36] We found a similar behavior for PSD from NaCl(001) cleavage faces, indicating that it proceeds by the reverse process of a layer-by-layer removal.[37,38]

The article starts with a brief description of the experimental techniques. Selected surface-decoration results are then presented and briefly analyzed. In the following sections the HAS studies on the temporal course of the specular He beam intensity during and after PSD are described. Experiments combining a mass spectrometer for detection and analysis of the desorbing species and HAS are described next. Moreover, evidence for PSD-induced structure in the angular distribution of elastically scattered He atoms between the diffraction peaks is presented and discussed. The paper closes with a summary of the present understanding of structural changes accompanying PSD. Preliminary results of these investigations were briefly reported previously.[37,38]

II. EXPERIMENTAL

In the surface-decoration technique experiments, which were carried out in Halle, a small amount of gold (about 10 Å mean thickness) is evaporated onto the surface after it had been irradiated to make the step edges visible to the electron microscope.[26,27] The evaporated Au atoms, which easily diffuse across the surface, nucleate preferentially at surface steps where they form small clusters. Thus, even steps of monatomic height are revealed in the electron microscope. However, the surface-decoration technique has two important disadvantages. (i) Only those steps present when the surface is decorated can be imaged, so that kinetic processes cannot be followed directly on the same surface region. Thus, in order to study step kinetics, a series of consecutive decoration experiments has to be carried out. (ii) The lateral resolution of neighboring steps is limited to spacings larger than about 100 Å, because the steps need a certain area to capture a sufficient number of Au atoms to produce Au clusters which can be observed.

The He-atom-scattering experiments were therefore carried out to elucidate the structure of irradiated surfaces at lower temperatures for which the decoration technique fails because of its limited lateral resolution.

Moreover, with HAS it was possible to follow photon-induced structural changes *in situ* during irradiation. The HAS experiments were performed in Göttingen in the scattering apparatus described in detail in Refs. 39 and 40. Briefly, a nearly monoenergetic He-atom beam is generated by supersonic expansion through a 10-μm nozzle into vacuum. By changing the temperature of the nozzle, the kinetic energy of the He atoms can be varied between 8 and 80 meV with a relative velocity spread of about 0.5% over this range of energies. The He beam incident on the crystal is collimated to 0.25° [full width at half maximum (FWHM)] and probes the surface over an area given by the beam diameter of about 3 mm. The scattered He atoms are detected by a sensitive magnetic mass spectrometer within an aperture of 0.12° (FWHM) after a flight distance of 1.428 m. The angle between the incident and the scattered He beams is fixed at 90°. High-resolution time-of-flight measurements could also be carried out by chopping the incident beam prior to scattering from the crystal surface. The time-of-flight measurements were used to discriminate against the inelastic scattering by separating off the elastically scattered He atoms, which alone provide the desired structural information. For more details on the time-of-flight technique and resolution see Ref. 41.

The high-purity NaCl specimens used in both the surface-decoration and HAS experiments were prepared from the same boule of NaCl which was grown in Halle and had a concentration of less than 10 ppm of divalent cations, as determined from the temperature dependence of the ion conductivity.[42] Samples of about $8 \times 8 \times 4$ mm^3 in size were used in both experiments. The crystal mounting and cleavage procedures are described in detail in Ref. 39. In both experiments the crystals were cleaved *in situ* at a pressure of less than 1×10^{-10} mbar after bakeout of the vacuum system to avoid the influence of contamination from the residual gas. After cleavage, the specimens were heated to the desired temperature and subsequently irradiated from a direction normal to the cleavage face. In contrast to the decoration experiments where only freshly cleaved faces were irradiated, in the HAS experiments a cleavage face was repeatedly used for several experiments. For this purpose the irradiated surface was smoothed between successive experiments by annealing the crystal to 610–630 K for about one hour. The crystal was heated from the back by radiation. Temperatures down to 130 K were achieved by liquid-nitrogen cooling. In both the HAS and the decoration experiments the crystal temperature was measured and controlled by a NiCr-Ni thermocouple mounted about 1 mm below the cleavage face in a drilled hole on the side of the crystal.

A D$_2$ lamp with a MgF$_2$ window[43] was used as the source of light. The MgF$_2$ window limits the short-wavelength side of the emitted spectrum to about 155 nm. Preliminary PSD experiments using appropriate filters indicated that only photons near the fundamental absorption edge of NaCl crystals at about 160 nm (7.75 eV) contribute to PSD.[44] The specified spectral emission of the D$_2$ lamp at this wavelength is of the order of 1 mW nm^{-1} sr^{-1}.[43] The 250 times lower VUV intensity in

the decoration experiments as compared to the HAS experiments was compensated for by longer exposure times. A few decoration studies, not described here, have also been done at higher photon intensities.[44] With increasing photon intensity the PSD process was found to proceed faster, but no qualitative differences in the structure of the irradiated cleavage faces were observed except for a slightly enhanced density of the photon-induced 2D holes created in the uppermost lattice plane.

In most of the HAS experiments the discharge cell of the D_2 lamp was mounted at a distance of 17 cm from the NaCl crystal and directed normal to the cleavage face. For this geometry the photon flux onto the crystal surface in the wavelength range from 150 to 170 nm has been estimated to be of the order of $10^{13}-10^{14}$ photons sec^{-1}cm^{-2}. The experimental setup had to be modified to measure simultaneously the yield of desorbing species with a quadrupole mass spectrometer (Balzers QMS420). In this configuration the D_2 lamp had to be relocated to a distance of about 32 cm and irradiated the surface at an angle of about 17° from the surface normal. This made it possible to position the ionizer of the mass spectrometer at an angle of about 13° from the crystal normal at a distance of about 10 cm from the sample.

III. RESULTS AND DISCUSSION

A. Photon-induced 2D holes observed by surface decoration

Figure 1 compares electron-microscope images of a nonirradiated surface region [Fig. 1(a)] with two other similarly structured surface regions of the same crystal which had been irradiated for different periods [Figs. 1(b)
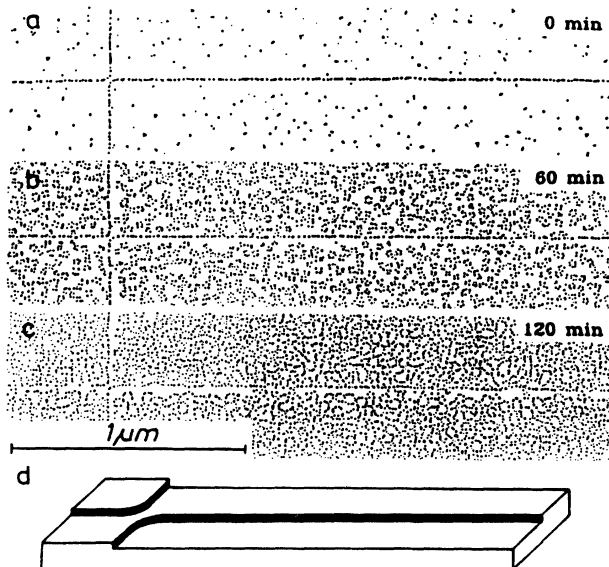

FIG. 1. Similar but different regions of NaCl(001) cleavage faces observed by surface decoration at a crystal temperature of $T = 453$ K: (a) before irradiation and after photon excitation for (b) 60 min and (c) 120 min. The interpretation in terms of monatomic steps is shown schematically in (d).

and 1(c)]. The pristine surface shown in Fig. 1(a) is characterized by extended atomically smooth terraces. The terrace regions are separated by two monatomic straight steps which intersect each other at the left, one "vertical" slip line of a single $\frac{1}{2}a_0\langle 110\rangle$ dislocation and one "horizontal" monatomic cleavage step. The two types of steps, which cannot be distinguished in the part of the surface shown, were identified by considering their geometrical course over a more extended surface region. The rounding offs to be seen at the point of step intersection are caused by crystal units diffusing along the step edges. A certain amount of edge diffusion which leads to a decrease of the total step length is known to proceed without desorption of crystal units even at temperatures lower than 550 K.[25,28]

Figure 1(b) shows a similar surface region which was irradiated for 60 min. The nonuniform distribution of gold clusters indicates that the terraces are now covered with closed step lines surrounding extended monolayer depressions (2D holes) in the topmost lattice plane. The occurrence of 2D holes of finite density indicates that there must be some long-range interaction preventing the nucleation of further holes in the neighborhood of steps already present. Such interactions could be mediated by diffusing F centers if they are preferentially captured at steps before they give rise to the formation of Na atoms. If the direct deexcitation of excitons also contributes to PSD and if these are assumed to detach mobile NaCl admolecules preferentially from steps, this could inhibit the formation of 2D holes near existing steps. Figure 1(c) shows that upon irradiation the 2D holes spread across the surface until they finally begin to coalesce. The beginning of coalescence of adjacent holes can be seen more clearly in Fig. 2, especially at $T = 543$ K. Near monatomic straight steps the distribution of holes on both sides of the step becomes increasingly asymmetrical with continued irradiation, since the steps themselves also propagate [Figs. 1(b) and 1(c)]. This asymmetry has been used to determine both the advance directions of the crossing straight steps and the topographic arrangement of the terraces, as shown schematically in Fig. 1(d). At somewhat more advanced stages of PSD, 2D holes have been observed to occur in the second layer before the topmost layer is completely removed.[44] This behavior is caused not only by statistical variations in the local nucleation rate on flat surface regions but also by the pres-
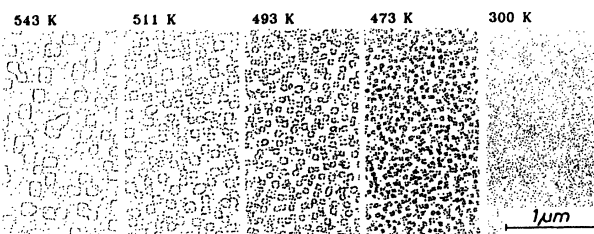

FIG. 2. Photon-induced 2D holes on NaCl(001) cleavage faces observed at various crystal temperatures after 120 min of photon excitation. The intensity of VUV irradiation was somewhat lower than that applied to the surfaces shown in Figs. 1(b) and 1(c).

ence of steps (cleavage steps, slip lines of single disloca-
tions, and steps surrounding 2D holes already created)
which appear to be effective in preventing the formation
of further holes in their neighborhood.

Figure 2 shows the influence of the crystal temperature
on the density of photon-induced holes on step-free sur-
face regions. The cleavage faces were photon excited for
120 min at different temperatures between 300 and 543
K. This sequence of pictures indicates that the maximum
density of photon-induced 2D holes created in the surface
plane increases as the crystal temperature decreases. At
temperatures below 450 K, individual 2D holes can no
longer be clearly distinguished. Finally, at $T < 400$ K,
the decoration technique fails completely and no
structural details are resolved. This is especially ap-
parent at $T = 300$ K in Fig. 2, where only a nearly sta-
tistical distribution of small Au particles of high density
is observed. In the decoration experiments the maximum
density of photon-induced holes $\rho_m(T)$, observed in the
outermost surface plane before adjacent holes have
coalesced, was found to depend on the temperature in the
range from $T = 543$ to 473 K as

$$\rho_m(T) = 2.56 \times 10^{-5} \times \exp(0.65 \text{ eV}/k_B T) , \qquad (1)$$

where k_B is the Boltzmann constant. The apparent "ac-
tivation energy" of 0.65 eV in the exponential can, unfor-
tunately not be uniquely assigned to a single elementary
process because this energy has been observed to also de-
pend weakly on the irradiation intensity. For a given
temperature the maximum 2D hole density was found to
increase slightly with increasing photon intensity.[44] Ex-
trapolation of Eq. (1) to lower temperatures predicts that
the density of photon-induced holes becomes equal to the
density of molecular surface lattice sites ($6 \times 10^6 \ \mu m^{-2}$)
at about 300 K. Thus, the surface might be expected to
be entirely rough on an atomic scale at $T < 300$ K.
Surprisingly, however, the HAS measurements reported
below, where even a 250 times higher photon intensity
was used, indicate a similar photon-induced creation and
spreading of 2D holes down to $T = 240$ K as observed in
the decoration experiments at considerably higher tem-
peratures.

B. Rate of layer-by-layer PSD observed by HAS

The measurements of the specular intensity of scat-
tered He atoms were used not only to extend the surface
structural studies of PSD down to lower temperatures
but also to make it possible to follow the kinetics in real
time. Figure 3 shows the specularly scattered He intensi-
ty before and during photon excitation for different crys-
tal temperatures as a function of time. A beam kinetic
energy of 16.3 meV corresponding to an incident wave
vector $k_i = 5.58$ Å^{-1} was chosen, and the scattered He
intensity was measured in time intervals of 5 or 10 sec,
respectively.

It is also seen in Fig. 3 that the specular He intensity
does not change before the irradiation is turned on, in
agreement with the surface-decoration experiments
which indicated no noticeable thermal alterations of the
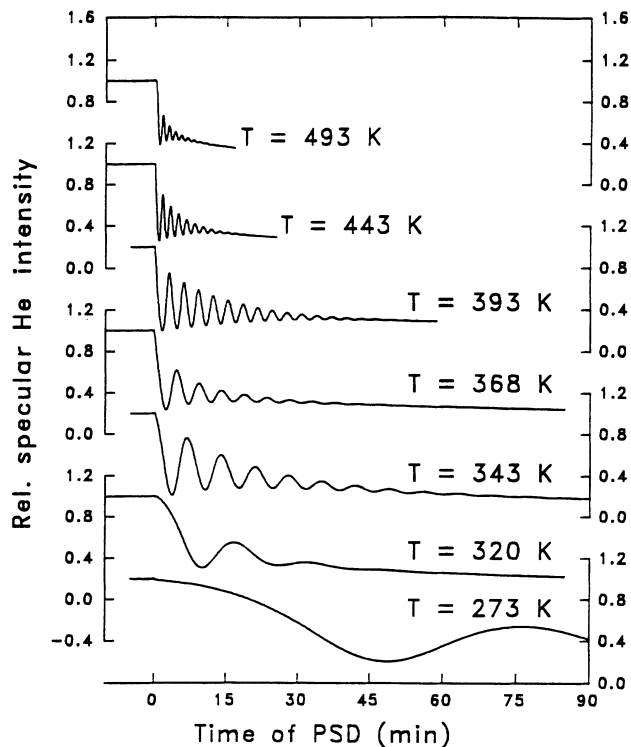surface topography (step density) at $T < 550$ K. As soon

FIG. 3. Normalized specular intensity of He atoms scattered
along the $\langle 110 \rangle$ azimuth from NaCl(001) cleavage faces shown
for various temperatures as a function of the time of photon-
stimulated desorption by VUV irradiation. The incident He
wave vector was $k_i = 5.58$ Å^{-1}.

as the photon excitation is turned on, however, the specu-
lar intensity first decreases sharply and this is followed by
damped periodical oscillations. These oscillations have
been detected down to the lowest temperature studied,
$T = 240$ K, for which an extrapolation of the surface-
decoration experiments to lower temperatures would
have predicted a completely rough surface. The observed
oscillations of the specular peak show a remarkable simi-
larity to those observed during layer-by-layer epitaxial
growth in RHEED (Refs. 45–47) and HAS experi-
ments.[35,36,48,49] A quite similar behavior has also been
observed for ion sputtering of metal surfaces in related
HAS experiments.[50] Most interesting for the present
study are the HAS investigations of the homoepitaxial
growth on NaCl cleavage faces recently reported by
Duan and co-workers.[36] This epitaxial growth which
takes place far from equilibrium is known to proceed by
the repetitive nucleation and spreading of successive gen-
erations of 2D islands.[51,52] This layer-by-layer growth
mode was impressively verified by oscillations of the scat-
tered He intensity. Figure 4 demonstrates that there is a
close similarity between the HAS results obtained during
homoepitaxial growth and during PSD. The correspon-
dence suggests that in the present situation of PSD the
reverse process, the layer-by-layer removal of the surface,
is taking place. This interpretation is entirely consistent
with the surface-decoration results at higher tempera-
tures between 400 and 550 K, which revealed the forma-
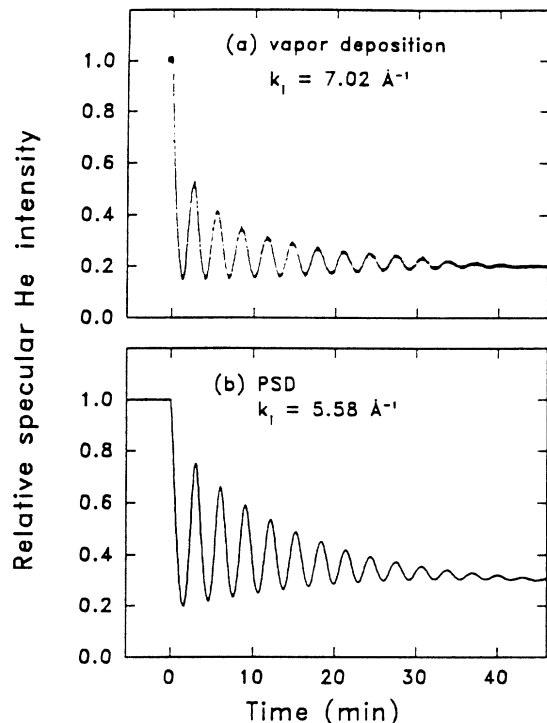tion and spreading of 2D holes.

FIG. 4. Comparison of typical oscillations of the He intensity specularly scattered from NaCl(001) cleavage faces during (a) homoepitaxial growth at 210 K, $k_i = 7.76$ Å^{-1}, [by courtesy of J. Duan (Ref. 36)] and (b) photon-stimulated desorption at $T = 393$ K, $k_i = 5.58$ Å^{-1}. Both He wave vectors $k_i = 7.76$ and 5.58 Å^{-1} are very close to the out-of-phase scattering condition.

The results of Fig. 3 were recorded for the $\langle 110 \rangle$ azimuth before and during photon excitation. Similar results were also obtained for the $\langle 100 \rangle$ azimuth. The wave vector used in the present study, $k_i = 5.58$ Å^{-1}, is close to the out-of-phase condition

$$k_i = 2\pi(n + \tfrac{1}{2})[a_0\cos(45°)]^{-1}, \quad n = 0,1,2,\ldots ,$$

($k_i = 5.53$ Å^{-1} for $n = 3$), in which waves scattered from two different terraces separated by one or an odd number of lattice planes (monatomic step height $\tfrac{1}{2}a_0 = 2.81$ Å) interfere destructively. By varying the incident wave vector to the in-phase scattering condition

$$k_i = 2\pi n[a_0\cos(45°)]^{-1}, \quad n = 1,2,3,\ldots ,$$

($k_i = 6.32$ Å^{-1} for $n = 4$), oscillations with nearly the same amplitudes were found. This behavior indicates that the observed loss of the specularly scattered He intensity is mainly controlled by the incoherent diffuse scattering from surface defects like steps, adatoms, or admolecules and less influenced by the interference of He atoms scattered from different layers.

Recalling the mechanisms of PSD briefly sketched above, the sharp decrease in the specular He intensity at the onset of irradiation could be due not only to scattering from the increasing number of steps accompanying the creation and spreading of 2D holes, but also to scattering from an increasing number of free adatoms

and/or NaCl admolecules created on terraces during irradiation. Neglecting for the moment the influence of adsorbed particles, we discuss next those effects which can be explained in terms of the temporal development of 2D holes. Once created, the 2D holes spread across the surface, thus increasing the total step length per unit area from which the incident He atoms are scattered. The first minimum of the specular He intensity is reached as soon as the total diffuse scattering from step edges reaches a maximum. Thereafter, the specularly scattered He intensity increases again as the effective step length decreases with the progressive coalescence of adjacent 2D holes. The first maximum of the scattered He intensity is then reached when the total diffuse scattering from the step edges is at a minimum. In an ideal layer-by-layer removal, in which the topmost layer is first entirely removed before the next layer is affected, the scattered He intensity would return to the initial value of the virgin surface each time a complete monolayer had been removed. In reality, however, holes are also created in the second layer before the previous layer has been entirely removed. Thus additional layers will be involved as PSD progresses, until finally a certain steady state will be reached in which the holes are distributed among several successive layers. This is the main reason why the amplitude of the oscillations observed in Fig. 3 is nearly exponentially damped. We note that the damping of the He intensity oscillations might also be caused by small temperature gradients along the probed surface as well as by inhomogeneities of the photon excitation and finally by the presence of surface steps. Although NaCl cleavage faces are known to be very smooth, the few surface steps will influence the photon-induced nucleation of 2D holes in their neighborhood and thus contribute to a damping of the He oscillations. To diminish these undesired influences, only a small central part, 3 mm in diameter, of the cleavage faces was probed by the helium beam. Moreover, to guarantee a homogeneous photon excitation the crystals were irradiated perpendicular to their cleavage faces with an unfocused VUV beam.

All experiments shown in Fig. 3 were performed on the same cleavage face, which was annealed at 610 K for 40 min between subsequent measurements. This treatment smooths the surface to such an extent that the initial specularly scattered He intensity is fully recovered. Nevertheless, there was some evidence that minor systematic changes of a repeatedly annealed surface had an effect on the damping in subsequent PSD experiments. The measurements shown in Fig. 3 were taken in the following "random" order of temperatures: 443, 393, 493, and 343 K. The measurement at 493 K (not shown in Fig. 3) was then repeated and exhibited a larger damping than before. Thereafter the series of experiments shown in Fig. 3 was continued at 368, 320, and 273 K. Even when freshly cleaved surfaces were used, the damping was still found to be not entirely reproducible. These observations are consistent with the presence of surface defects, as discussed in the previous paragraph. Note, however, that the oscillation periods were found to be fully reproducible in different experiments at a given temperature.

At temperatures lower than about 360 K, the initial

photon-induced attenuation of the specular He intensity in Fig. 3 exhibits a slight convex curvature, which becomes more distinct with reduced crystal temperature. This behavior was observed not only on thermally smoothed surfaces but also on freshly cleaved faces. Presently we have no consistent explanation for this phenomenon. An incubation delay of the desorption processes cannot be involved because, as shown below, the observed yields of all desorbing species jump immediately to constant values at the onset of irradiation.

It is interesting to observe in Fig. 3 that the period of oscillations, which is constant for a given run, decreases significantly with increasing temperature. Using the inverse oscillation period as a measure of the rate of PSD, then Fig. 3 indicates that this rate increases with increasing crystal temperatures. In Fig. 5 the strong temperature dependence of the inverse HAS oscillation period is compared with the desorption flux of particles measured in another apparatus with a surface ionization (Langmuir-Taylor) detector in a similar way as done in Ref. 24 for irradiated KI(001) cleavage faces. The open circles represent the results derived from the HAS measurements and correspond to the scale on the right while the solid symbols show the desorption flux measurements corresponding to the scale on the left. The filled squares indicate the photon-stimulated desorption while the dotted line and the filled triangles are for pure thermal sublimation. For temperatures lower than about 360 K the
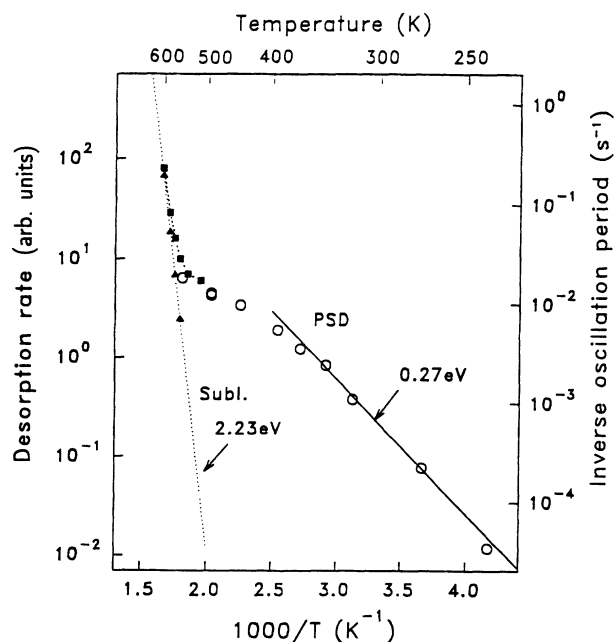

FIG. 5. Comparison of the inverse He intensity oscillation period as a function of the crystal temperature with desorption rate measurements. The open circles are the HAS measurements and correspond to the right scale. The Langmuir-Taylor sublimation rate measurements of the pure thermal (triangles and dotted line) and the photon-induced desorption (squares and dashed line) correspond to the left scale. The solid line is a fit through the HAS data at low temperatures and yields an activation energy of 0.27 ± 0.02 eV.

HAS measurements follow nearly a straight line. It is not clear if this is related to the observation that the initial photon-induced decrease of the scattered He intensity shows a slight convex curvature. The slope reveals an activation energy for the VUV induced desorption of $E_{d,\text{VUV}}=0.27\pm0.02$ eV. The much greater slope in the flux measurements under VUV irradiation at higher temperatures, $T>550$ K, is apparently due to a dominant contribution from pure thermal desorption which increases strongly with rising temperature. The observed slope yields a sublimation enthalpy, $H_{d,\text{therm}}=2.23$ eV in good agreement with the value of 2.39 eV given in Ref. 53, where several reported values are summarized.

In the following, a possible explanation for the activation barrier of 0.27 ± 0.02 eV observed at $T<360$ K is proposed. We first consider the possibility that vibrational excitation of crystal units resulting from the direct decay of excitons contributes to PSD. Previous studies indicated that the most important barrier for pure thermal desorption of single NaCl molecules is their initial detachment from a step site onto the adjacent terrace. The barrier for this process was found to be higher than 1 eV.[24,28] This high barrier inhibits detectable pure thermal desorption of NaCl admolecules into vacuum at crystal temperatures lower than about 550 K. In PSD, we assume that the deexcitation of excitons occurs preferentially at step edges and that the energy released may be sufficient to detach single molecules from the step onto the adjacent terrace. After detachment the NaCl admolecules diffuse freely over the terraces, from which they either can desorb by pure thermal activation or are recaptured at step edges. The desorption energy of isolated admolecules from terraces into vacuum was estimated by Madelung-like calculations to be only about 0.31 eV.[54] Thus, the thermal desorption from terraces of single photon-detached admolecules becomes easily possible even at low temperatures. Since the measured activation energy of photon-induced desorption, 0.27 eV at $T<360$ K, coincides remarkably well with the energy for desorption of a single NaCl admolecule from a flat surface, the latter process appears to be the rate-determining step in the case of PSD at lower temperatures. As seen in Fig. 5, at intermediate temperatures between 400 and 550 K the slope of the inverse oscillation period flattens out. This behavior can be explained by assuming that the creation of admolecules is no longer rapid enough to provide a sufficient surface concentration of photon-induced admolecules.

In related measurements of the rate of desorbing species due to pulsed photon excitation of RbBr(001) faces by Kanzaki and Mori,[9] a different explanation was given for the corresponding activation energy observed in the low-temperature range. The measured activation energy of PSD (0.22 eV for both Rb and Br atoms) was assigned to the diffusion energy of self-trapped holes. However, the mean lifetimes of self-trapped holes derived from their measurements are much too long. As an explanation the authors assumed, without providing any quantitative estimates, that interactions with point defects lead to a prolongation of the decay time. The reduction in slope of the desorption yield at higher tem-

peratures also observed for irradiated RbBr crystals was attributed to an increase of the rate of electron-hole recombination within the bulk, leading to a change in the dominant relaxation process.

The temperature dependence of the rate of PSD could conceivably also be caused by changes of the mobility and the relaxation probabilities of photon-induced electronic excitations. At present, however, the overall influence of these processes is quite difficult to estimate quantitatively.[6,55] Another possible temperature effect could arise from the broadening and shift of the fundamental absorption edge of alkali halides to longer wavelengths with increasing temperature.[56] The influence of this effect on the observed rate of PSD should, however, be small, since in the present study the incident VUV photons have a broad spectral distribution.

Finally we point out that the desorption of single NaCl molecules contradicts the widely accepted Pooley-Hersh theory of PSD,[13,14] according to which only single Cl and Na atoms are expected to desorb. Direct evidence that NaCl molecules do desorb under photon excitation has been confirmed by the mass-spectrometric observations to be described below. These observations support those models in which NaCl molecules at step sites are vibrationally excited by the decay of mobile excitons.

C. Postirradiation recovery studied by HAS

Several HAS experiments were carried out to detect the adsorbed particles on the terraces. From the above discussion we expect that the surface will be enriched with atomic Na up to some equilibrium concentration, provided that the rate of creation of Na adatoms by diffusion of F centers to surface steps exceeds the thermal desorption rate of Na adatoms. Even the formation of 3D clusters of Na seems to be possible, as already observed in the case of ESD.[11,12] In these ESD experiments the yield of desorbing Na atoms decays to zero at temperatures lower than about 300 K. The concentration of single NaCl molecules detached from steps by vibrational excitation will also depend on the balance between their creation rate and their removal rate, either by capture at step sites via surface diffusion or by thermal desorption.

As shown in Fig. 6, immediately after irradiation the specular He intensity increases and approaches finally a certain constant value. This behavior is less pronounced at lower crystal temperatures and finally disappears at about $T = 360$ K. The observed increase of the specular He intensity is due either to the decrease of the surface concentration of both photon-induced Na and Cl adatoms as well as NaCl admolecules by both their thermal desorption and/or their capture at steps via surface diffusion, or to step removal or smoothening. In the case of Na adatoms the formation of 3D clusters[11,12] would also decrease the concentration of single Na adatoms, thus reducing their influence on the diffuse scattering of the incident He beam.

The observed recovery times of several minutes are, however, much too long to be attributed to the desorption of adsorbed particles alone. For the same reason, the relaxation of electronic processes can also be ruled out.
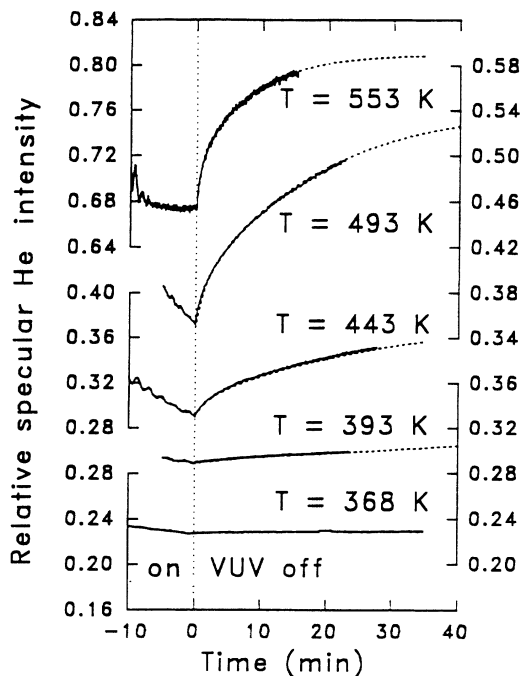

FIG. 6. Temperature dependence of the recovery of the specular intensity ($\langle 110 \rangle$ azimuth, $k_i = 5.58 \text{ Å}^{-1}$) in the postirradiation period. The dashed lines represent the double-exponential fit curves described in the text.

The decay times of the PSD rates from KI and RbBr(001) faces were measured by Kanzaki and Mori,[9] by lock-in detection of the mass-spectrometer signals under chopped excitation, to be less than 3×10^{-3} sec at 300 K for alkali-metal atoms and still shorter for halogen atoms. Similar values may be expected for NaCl(001) faces. Thus the most plausible explanation of the observed postirradiation recovery in the HAS intensity is step smoothing due to diffusion of adsorbed particles near and along steps. In strong nonequilibrium conditions, as in the desorption experiments discussed here, the geometrical course of steps may be very rough due to a high concentration of low-coordinated crystal units similar to those observed in Monte Carlo simulations of molecular-beam growth.[57] Therefore, step smoothing due to the interchange of sites of single crystal units can explain the observed postirradiation increase in the HAS intensity by lowering the effective scattering cross section of steps. Thus the intensity increase proceeds similarly to the recovery observed by RHEED from low-index surfaces after interrupted epitaxial growth of GaAs.[46,47] As shown by Neave et al.[58] in GaAs growth experiments, the recovery of the RHEED intensities following the cessation of growth can be well fitted by the functional form

$$I(t) = I_0 - I_1 \exp[(t - t_0)/\tau_1] - I_2 \exp[(t - t_0)/\tau_2] , \quad (2)$$

where I_0, I_1, I_2, τ_1, and τ_2 are fit parameters and t_0 the time of interruption. For GaAs this expression has been justified by the solid-on-solid Monte Carlo simulations of Vvedensky and Clarke.[59] They found that the recovery of the surface occurs in two stages. One involves a fast process in which the surface looses its "dendritic structure."

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In this stage, mainly adsorbed units without or with only one nearest lateral neighbor in the surface plane move to higher-coordinated sites. This process is followed by a second stage of slow equilibration of large surface structures such as steps or islands, involving mainly adsorbed units with one or more nearest lateral neighbors.

Equation (2) was also used to describe the recovery of the NaCl(001) surface after irradiation. As shown in the Arrhenius plot in Fig. 7, the two relaxation times τ_1 and τ_2 follow straight lines reasonably well,

$$\tau_i = \tau_{i0}\exp(E_i/k_B T) , \quad i=1,2 . \tag{3}$$

Although the preexponentials $\tau_{10}=0.13$ sec and $\tau_{20}=2$ sec differ by more than one order of magnitude, the two activation energies nearly coincide, $E_1=E_2\approx0.3$ eV.

We note that the agreement with the activation energy for the desorption of single admolecules from terraces according to this explanation is probably only a coincidence. Moreover, the above result disagrees with the model of Vvedensky and Clarke[59] which because of the fewer number of nearest neighbors predicts a smaller effective activation energy for the fast process than for the second one. The activation barrier for surface diffusion of free NaCl admolecules is expected to lie somewhere in the range between 50 meV [as estimated from condensation and evaporation kinetics of LiF(001) crystal faces[52]] and less than 0.2 eV (as estimated from homoepitaxial growth at low temperatures[60]). The mea-

sured "effective activation energy" of 0.3 eV for the postirradiation smoothing process thus lies well above the diffusion energy of single NaCl admolecules but far below the known activation energy of 0.975 eV for the diffusion of NaCl molecules along monatomic steps close to equilibrium.[11,28,29] This comparison may indicate that due to irradiation the structure of the step edges becomes indeed irregular, and the average number of nearest lateral neighbors of the diffusing adsorbed particles decreases significantly. Because of the observed low effective activation barrier of 0.3 eV, however, the irregular step lines will give way to more regular shapes with smoother step edges during the recovery in the post-irradiation period.

D. Results of a simultaneous HAS and mass-spectrometer study

Since there is evidence for a sizable concentration of free adsorbed particles on the surface, we must also consider the possibility that a delayed desorption of Na and Cl adatoms as well as of NaCl admolecules contributes to the slowly proceeding recovery process. To test this assumption, we have used the HAS apparatus in the second configuration with a mass spectrometer in front of the crystal as described in Sec. II A. Figure 8 compares
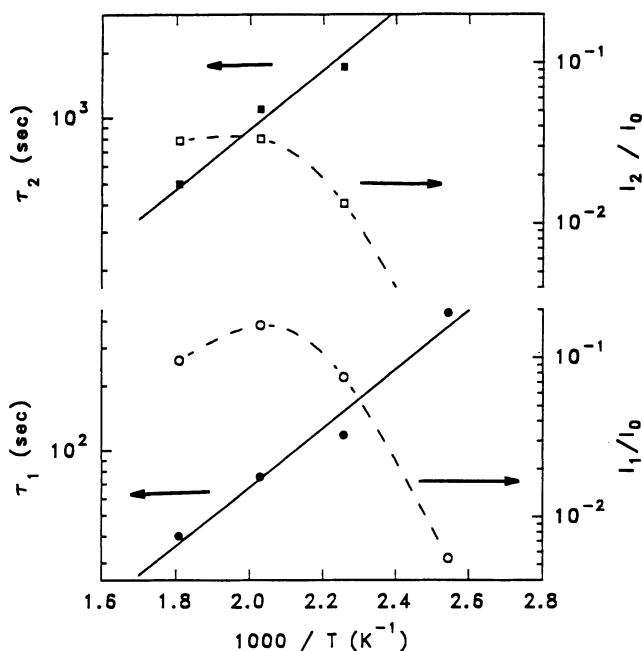
FIG. 7. Arrhenius plot of the fit parameters derived from the fits to the recovery of the HAS signal in the postirradiation period as shown in Fig. 6. Left scales and solid symbols denote the relaxation times τ_1 and τ_2, respectively. The solid lines are linear regressions through the data. Right scales and open symbols denote the preexponential factors I_1/I_0 and I_2/I_0, where I_0 is the initial specularly scattered He intensity from the nonirradiated surface. The dashed lines are guidelines to the eye.
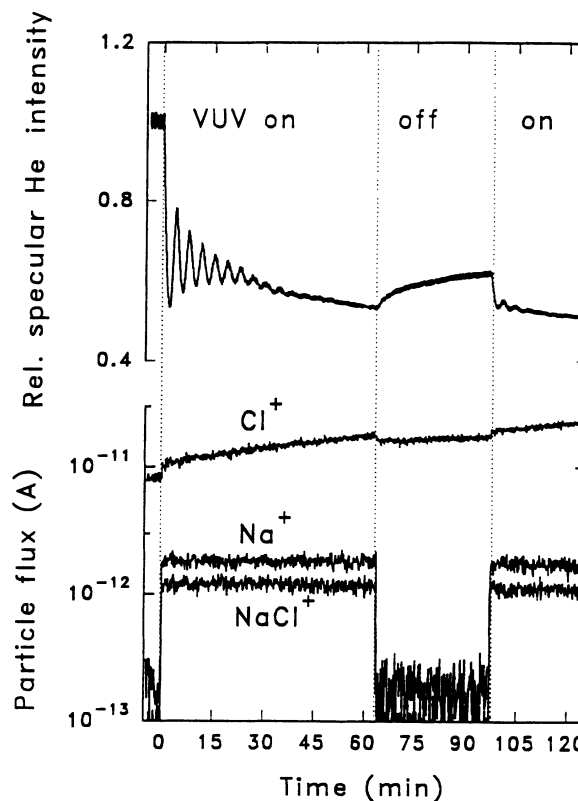
FIG. 8. Specular He intensity ($\langle 110\rangle$ azimuth, $k_i=5.58$ Å^{-1}) and corresponding mass-spectrometer yields for Cl^+, Na^+, and $NaCl^+$. The crystal was at 493 K. Due to the different experimental setup used in these experiments the VUV intensity was about three times lower than in the measurements shown in Fig. 3.

the time dependence of the specular He intensity with the mass-spectrometer signals taken at a crystal temperature of 493 K. At the top the specular intensity exhibits a similar behavior as already shown in Fig. 3. The differences in the periods of oscillations and time constants from the results in Fig. 3 and Fig. 6 are due to a lower photon intensity. We recall that in these experiments the VUV source had to be mounted further away from the sample to accommodate the quadrupole mass spectrometer. The spectrometer traces show the expected sharp rise in the Cl^+ and Na^+ signals on irradiation, but there is also a strong increase in the $NaCl^+$ signal, which indicates that there is also a considerable photon-induced desorption of single NaCl molecules. The slight linear increase of the Cl^+ intensity over the entire period of irradiation is attributed to an increase of the Cl background due to a progressive contamination of the mass spectrometer. Thus all signals were found to be essentially constant during the irradiation time. The increase in the mass-spectrometer signals shown in Fig. 8 was about the same for all three species: 1.6×10^{-12} A for Na^+, 2.3×10^{-12} A for Cl^+, and 1.2×10^{-12} A for $NaCl^+$. At the electron impact energy used in this experiment of 70 eV, NaCl molecules fragment partially into Na^+ ions[61] and to a lesser extent to Cl^+ ions, thereby contributing to the signals of desorbed Na and Cl atoms. For a more quantitative determination of the desorption yields, a complicated calibration of the mass-spectrometer signals would have been necessary.

It is surprising to see in Fig. 8 that the rate of PSD does not appear to depend on the actual density of steps (2D holes). Thus we must conclude that the observed photon-induced incomplete layer-by-layer removal reflects only the progress of the PSD process but does not directly control it. This result is quite interesting, because in the case of growth or pure thermal sublimation the desorption flux from low-index crystal faces is expected to be substantially controlled by the density of surface steps acting as sinks or sources, respectively, for isolated adsorbed units on terraces. Indeed, Meyer and Dabringhaus found in vapor-growth experiments on KCl cleavage faces distinct oscillations in the simultaneously recorded desorption rate of KCl molecules.[62] These oscillations were found to be strongly correlated with the completion of subsequent layers by spreading islands of monatomic height.

We now proceed to discuss further the mass-spectrometer results shown in Fig. 8. As soon as the VUV irradiation is turned off all three mass-spectrometer signals return instantaneously to the values already measured before irradiation. This is compatible with the 10^{-3}-sec decay times observed by Kanzaki and Mori.[9] Because of the fast dropoff to the initial value, we can rule out any appreciable desorption of adsorbed particles during the recovery of the He intensity in the dark period.

As seen in Fig. 8 there is a renewed onset of weak oscillations of the specularly scattered He intensity during the second irradiation period, although the oscillations were damped out completely in the first irradiation period. This behavior clearly indicates that there must have been

some surface smoothing during the preceding dark period. This is entirely consistent with the explanation of the previous subsection that the postirradiation increase of the specularly scattered He intensity is caused by thermally activated diffusion processes of adsorbed particles near and along steps. These processes lead to a lowering of the effective step length and thus to an enlargement of the terraces. As these terraces become sufficiently large, repetitive photon-induced nucleation and spreading of 2D holes become possible again.

E. Indications for surface defects from HAS

In the previous sections we analyzed the period of the oscillations seen in Fig. 3 in terms of possible desorption mechanisms. In addition to the rate of desorption, the decay of the amplitudes and the specular He intensity at the minima provide independent information on the increase in the concentration of surface defects and their evolution during PSD.

Besides the results discussed above, there are also further indications for the occurrence of diffusion processes below $T = 550$ K. The evidence comes from the temperature dependence of the intensity of the specular He beam in the first minimum. We recall that the temporal course of the He intensity is mainly determined by the diffuse scattering from steps and surface defects such as adatoms and admolecules. In Fig. 9 the intensity in the first minimum relative to the initial intensity I_0 is plotted as a function of the crystal temperature. At low temperatures this ratio is nearly constant but at about $T = 440$ K it increases from a value of about 0.25 up to about 0.7 at 553 K, the highest temperature used in the HAS experiments. Extrapolating the intensity ratio to zero, one gets an onset temperature of thermally activated diffusion processes of about 400 K. This onset temperature agrees with the lowest temperature of about 390 K for which an increase of the specularly scattered He intensity has been observed
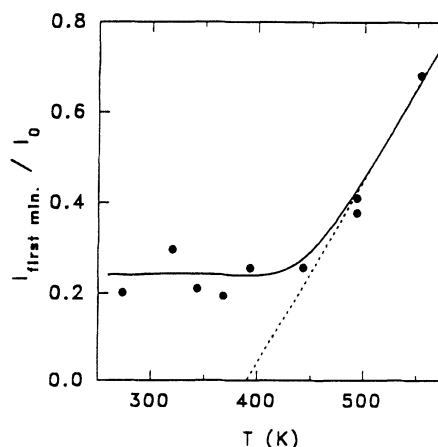
FIG. 9. Specular He intensity in the first minimum relative to the initial intensity versus the crystal temperature. To get the onset temperature of 390 K of the thermally activated process or processes, the dashed line is extrapolated to zero intensity as discussed in the text.

in the postirradiation period (see Fig. 6). The correspondence of both phenomena suggests that at $T > 390$ K the concentration of photon-induced adsorbed particles decreases with increasing temperature, either by their recapture at step sites, or by their desorption into vacuum, or possibly by the formation of 3D structures on the surface.

In principle, more direct information on single randomly distributed defects can be obtained from the angular distribution of scattered He atoms. As demonstrated in several instances,[33,63] these incoherent (diffuse) elastic components of the time-of-flight spectra between diffraction peaks provide information on the structure and density of single defects. In the temperature range
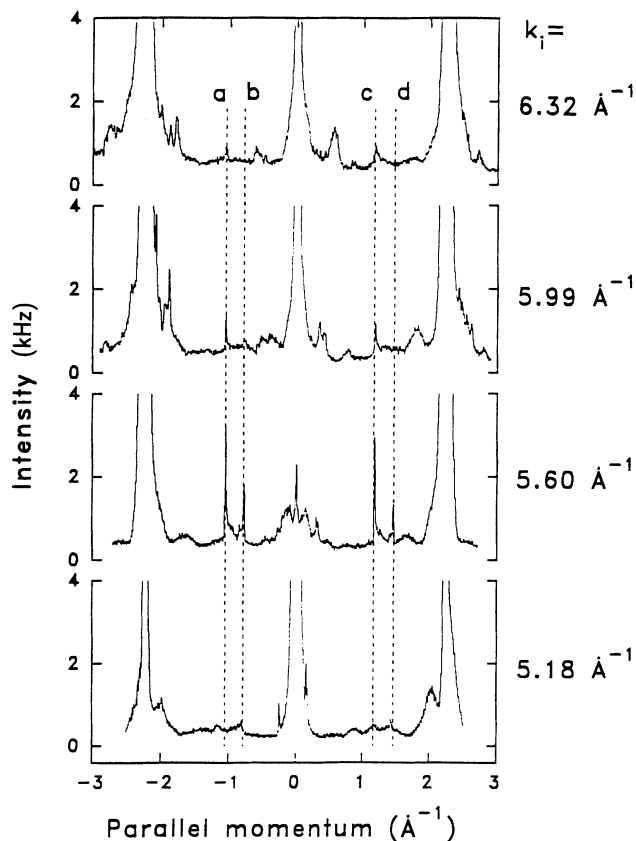

FIG. 10. Angular distribution along the $\langle 100 \rangle$ azimuth of the elastically scattered He intensity for an irradiated NaCl(001) surface at 300 K for various incident wave vectors k_i. Ten monolayers were first removed by PSD before these measurements were recorded. The structures between the Bragg peaks are all produced by the PSD process. The sharp structures $a,b,c,$ and d marked by dashed vertical straight lines, which do not change in position with the incident wave vector k_i, refer to diffraction from structures exhibiting a broken symmetry and a large superstructure with respect to the NaCl(001) face. The additional peaks, which shift with the incident wave vector, are probably caused by diffraction from facets of 3D Na clusters. Note that the distinct attenuation of the specularly scattered intensity at $k_i = 5.60$ Å is due to destructive out-of-phase interference, which is predicted to occur at $k_i = 5.53$ Å. In-phase scattering of the specular intensity occurs at $k_i = 6.32$ Å, as shown in the top curve.

$T > 350$ K, the angular distribution of He atoms elastically scattered from irradiated NaCl(001) surfaces gave no evidence for any significant structure. However, at lower temperatures, $T < 320$ K, as shown in Fig. 10, weak but partially very sharp peaks could be observed in addition to the Bragg peaks in the elastic HAS angular distribution. After the photon-induced removal of ten monolayers at 300 K, several elastic angular distributions were recorded at various wave vectors ranging from 6.32 to 5.18 Å^{-1}. The elastic part of the scattered He atoms was separated by carrying out time-of-flight measurements at each angle and ascertaining the elastic intensity in an energy window of about 0.4 meV. All the structure between the diffraction peaks shown in Fig. 10 was absent before irradiation. Some of the very sharp features have the same surface wave vector $\Delta K_{\parallel}$ independent of the incident wave vector k_i. Especially in the $k_i = 5.6$ Å^{-1} angular distribution in Fig. 10, two intense pairs at $\Delta K_{\parallel} = -1.05$ and -0.78 Å^{-1} (denoted as a and b) and at $\Delta K_{\parallel} = 1.7$ and 1.47 Å^{-1} (c and d) are visible. The positions of these peaks are not symmetrically located with respect to the specular direction of the NaCl crystal, indicating that the mirror symmetry of the surface is broken. The small separation distances between the peaks a and b and the peaks c and d, respectively, indicate a rather large superstructure of at least 22.5 Å in the $\langle 100 \rangle$ direction. Similar structures were found in the elastic angular distribution in experiments on NaCl cleavage faces evaporated with sodium. Therefore the sharp peaks might refer to diffraction from photon-induced Na islands exhibiting a broken symmetry and a large superstructure with respect to the NaCl(001) face. The other peaks seen in Fig. 10 which change with the incident wave vector cannot be explained by diffraction processes either from single defects or from a periodic structure parallel to the NaCl(001) face. Phonon-assisted selective adsorption[64] can also be ruled out, because it affects the inelastically scattered part of the time-of-flight spectrum only. We assume that the wavelength-dependent peaks are caused by diffraction from facets of 3D Na clusters created during the preceding PSD process.

IV. CONCLUSION

The present results obtained by surface decoration and especially by He-atom scattering provide a consistent picture of the structural changes accompanying photon-stimulated desorption by valence-electron excitation from NaCl cleavage faces in vacuum. At temperatures too low for pure thermal sublimation to occur, an incomplete layer-by-layer removal, which proceeds mainly by the photon-induced creation and growth of 2D holes, is found.

The yield of PSD is temperature dependent but does not significantly depend on the actual step density during VUV irradiation. From the periods of the oscillations in the HAS specular intensity as a function of temperature below 360 K, an activation energy for the photon-induced desorption of 0.27 ± 0.02 eV was derived. This is close to the desorption energy of a single NaCl admolecule from a flat terrace. We therefore conjecture

that the desorption of NaCl admolecules, which have been photon detached from step edges, contributes substantially to PSD in this temperature range of $T < 360$ K.

In addition to the layer-by-layer mode by PSD there are clear indications of diffusion processes of photon-detached adsorbed particles. The activation energy of the dominant process in the postirradiation recovery of the HAS specular intensity observed in the temperature range from 360 to 550 K has been found to be about 0.3 eV. The nature of the particles involved in this process has not yet been uniquely determined. On the basis of the experimental findings, the observed recovery has been assigned to step smoothing due to the diffusion of low-coordinated adsorbed particles near and along step edges. Processes involving substantial desorption of particles during the dark period can definitely be ruled out.

Mass-spectrometer measurements during the excitation period reveal a substantial signal of NaCl molecules, which in addition to Cl and Na atoms desorb from the surface even at temperatures as low as 240 K, the lowest temperature studied. The desorption of molecular NaCl is not consistent with the Pooley-Hersh mechanism briefly described in the Introduction. This implies that excitons decay at surface sites, leading to vibrational exci-

tation and detachment of NaCl molecules at step edges onto the adjoining terraces.

At temperatures T lower than 320 K, additional structures were found in the angular distributions of the intensity of elastically scattered He atoms and attributed to the formation of sodium during the PSD process. At temperatures above 350 K, no additional defect structures could be observed.

Further work is needed to clarify the excitation and relaxation mechanisms involved in the photon-stimulated desorption from alkali halides. It would be of great interest to analyze photon-induced surface alterations on an atomic scale using the atomic-force microscope. Such experiments would complement the present work and further extend our understanding of photon-induced surface modifications on this important model system.

ACKNOWLEDGMENTS

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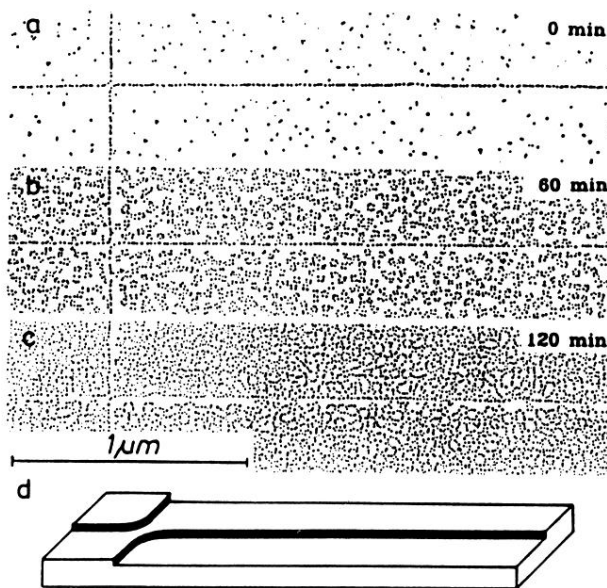
FIG. 1. Similar but different regions of NaCl(001) cleavage faces observed by surface decoration at a crystal temperature of $T = 453$ K: (a) before irradiation and after photon excitation for (b) 60 min and (c) 120 min. The interpretation in terms of monatomic steps is shown schematically in (d).

FIG. 2. Photon-induced 2D holes on NaCl(001) cleavage faces observed at various crystal temperatures after 120 min of photon excitation. The intensity of VUV irradiation was somewhat lower than that applied to the surfaces shown in Figs. 1(b) and 1(c).