

The electronic structure of NaCl adlayers on W(110) studied by ionizing radiation

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The electronic structure of thin NaCl adlayers deposited on W(110) at room temperature is studied with electron energy loss spectroscopy (EELS), ion impact electron spectroscopy (IIES) with He^+ and He^{2+} ions, metastable impact electron spectroscopy (MIES) with He^* atoms, ultraviolet photoelectron spectroscopy (UPS), and AES. It is concluded that NaCl adsorbs molecularly under the studied conditions. The transition from the electronic structure of single adsorbed NaCl molecules to the well-known bulk structure could be studied by following the emergence of bulk properties, such as interband transitions and excitonic excitations, as a function of the NaCl exposure. Our results are consistent with lateral growth of two-dimensional islands during the formation of the first adlayer.

The electronic transition processes at the surface induced by electrons as well as He projectiles in different excitation and charge states, in particular the vacancy production in the Cl^- 3p valence band, are studied. Their relevance for desorption induced by electronic transitions (DIET) is discussed.

1. Introduction

The bulk properties of alkali halides are known rather well [1–3]. Less is known about adlayers of these compounds on metals or semiconductors [4–7]. The surface properties of alkali halides are of interest in several respects, such as for electron stimulated desorption (ESD) [8], ion sputtering [9] and the formation of colour centers at surfaces or their migration to surfaces [29]. The charging of insulators is intimately related to the presence and the electronic structure of surface defect states; it finds its technical application in the electrostatic separation of minerals [5].

To our knowledge the emergence of the electronic band structure during the deposition of alkali halide layers on metallic or non-metallic substrates has not yet been studied at great detail; we are only aware of the studies concerned with the growth of NaCl adlayers on Ge(100) [6,27,31]. In the present study we have exposed W(110) surfaces to NaCl at room temperature.

The film growth is monitored by the combined application of several electron spectroscopic techniques which are sensitive to the valence and conduction band structure in the near-surface region: the transition from the electronic properties of single adsorbed NaCl molecules to the well-known NaCl bulk structure is studied with electron energy loss spectroscopy (EELS), UPS, ion and metastable impact electron spectroscopy (IIES and MIES) and AES.

It was also the intention of this work to supply information on primary processes of relevance for the desorption of heavy particles, primarily Cl atoms, from the NaCl adlayer under the influence of soft ionizing radiation, slow electrons and slow He projectiles in different excitation and charge states, namely He^* metastable atoms of thermal energy and singly and doubly charged He ions. This is achieved by analyzing the spectral features appearing in the electron spectra during the impact of the ionizing radiation on the NaCl adlayer grown on W(110) substrates.

2. Experimental

The apparatus for MIES and UPS has already been documented [10,11]. It is equipped with a cold cathode helium discharge source capable to produce both an intense metastable He beam of thermal energy and a He I photon flux sufficiently intense to perform UPS. The angle of incidence is 45° with respect to the surface normal. Electron energy spectra are recorded with a commercial angle-resolved electrostatic analyser operated at constant pass energy with 0.25 eV (FWHM) resolution. The detection angle is again 45° with respect to the surface normal. The system is furthermore equipped with AES and an additional electron gun to induce electron stimulated desorption (ESD).

The apparatus for EELS and IES has also been characterized previously [12,13]. The inert gas ions are generated in a low-voltage plasma discharge; the ion beam is mass/charge analyzed by a Wien filter, and hits the surface under grazing incidence (5° with respect to the surface plane). The electron energy spectra are recorded in normal emission with a commercial angle-resolved electrostatic analyzer operated at constant pass energy with 0.25 eV (FWHM) resolution. For EELS the electron energy was 250 eV, typically; the surface normal was adjusted for specular reflection. The energy resolution (0.5 eV FWHM) is due to the energy spread of the primary electron beam. In addition AES can be performed utilizing the EELS electron source.

NaCl molecules were deposited onto the W(110) surface by thermal evaporation of single crystal chips [7]. Measurements performed with the two different apparatus were linked to each other via AES and work-function (WF) measurements. The variation of WF upon the NaCl exposure was derived from the shift of the low-energy cut-off of the electron energy spectra obtained with MIES and IES.

All spectra (figs. 1 to 6) were recorded as a function of the NaCl exposure at room temperature. A $(1/E)$ correction is applied to all measured spectra in order to compensate for the energy dependence of the electron spectrometer's transmission [13].

The exposure is given in arbitrary units (A.U.): 1 a.u. corresponds to the exposure at which the MIES signal from $\text{Cl}^- 3p$ (see fig. 8) has essentially saturated. The exposure rate is chosen in such a manner that this stage is reached after ~ 25 min; as will be discussed later the W substrate is then completely covered by NaCl. This does however not necessarily imply layer-by-layer growth of the NaCl film.

3. Interpretation of the electron spectroscopic results

3.1. Electron energy loss spectroscopy (EELS)

A satisfactory identification of the features developing in fig. 1 during the NaCl exposure can be made by a comparison with previous EELS results on evaporated films and single crystals

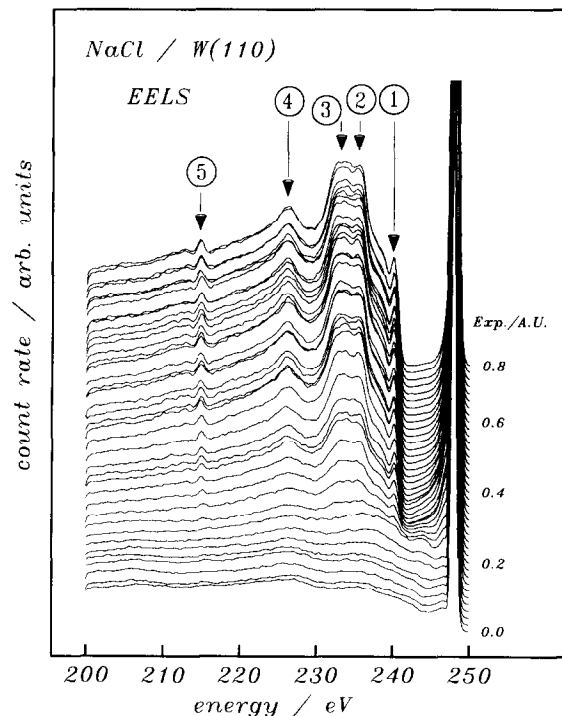


Fig. 1. EEL spectra obtained during the exposure of W(110) to NaCl. The bottom curve corresponds to zero coverage. The coverage is given in arbitrary units (A.U.), see text. Exposure rate: 0.02 A.U. per minute.

obtained in reflection [4,6,14] as well as in transmission [15,16], and recent calculations of excitonic excitations in NaCl [17].

Peak 1 (0.5 eV FWHM) at 7.8 eV energy loss corresponds to the formation of the Γ exciton [4,6,16]. Peaks 2 and 3 are mainly due to Δ_1 , $\Delta_5 \rightarrow \Delta_1$, Δ'_2 interband transitions around the X point [3,6]. The ($\Gamma 15-\Gamma 1$) transition manifests itself through the shoulder between the peaks 1 and 2 [6,14]. Peak 4 probably corresponds to transitions from the initial states Δ_1 and Δ_5 to the final state Δ_5 near X – the same transitions which are detected by UPS and MIES (see section 3.2).

Peak 5 at 33.1 eV is an excitonic excitation of the type $\text{Na}^+ (2p^6-2p^53s)$ [16,17]. We do not find peak 5 in EELS on clean Na layers (< 1 monolayer in units of the first complete adlayer at room temperature) deposited on W(110). We find that the structures attributed to exciton formation (peaks 1, 5) disappear when a metallic-like Na overlayer (about 1 monolayer thick) is generated by electron stimulated desorption (see also fig. 4). During this procedure an additional loss feature develops in the band gap at an energy loss of ~ 4.2 eV; we attribute this feature to surface plasmon excitation in the Na overlayer [14,15].

3.2. Ultraviolet photoelectron spectroscopy (UPS)

The bottom spectrum of fig. 2 is typical for clean W(110); the structure close to the Fermi level consisting of the two peaks with the binding energies E_B below 2 eV with respect to the Fermi level is due to W 5d-band emission. Upon exposure to NaCl the work function of the surface decreases by ~ 1.2 eV as is reflected by the change in the position of the low-energy cutoff of the spectra found between 8 and 6 eV [26,36]. Large exposures (not shown in fig. 2) lead to complete disappearance of the W substrate emission.

The exposure to NaCl produces an additional structure, labeled $\text{Cl}^- 3p$, between $E_B = 5$ and 9 eV which is composed from the contributions of two incompletely resolved peaks spaced by ~ 1 eV. At small exposures we attribute this structure

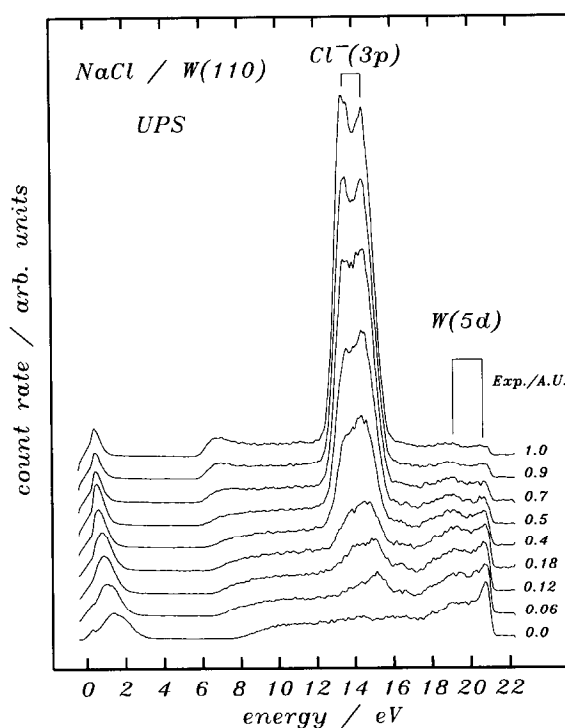


Fig. 2. UP spectra (He I 21.2 eV) obtained during the exposure of W(110) to NaCl. Otherwise as indicated with fig. 1.

to the ionization of Cl^- ions located in the combined field supplied by the Na^+ ion and the W substrate. With respect to the vacuum level the peak due to $\text{Cl}^- 3p$ ionization has an ionization energy of 10.2 eV (the work function plus the binding energy of $E_B = 6.1$ eV with respect to the Fermi level) which may be compared with the ionization potential IP (NaCl) = 8.9 eV [37] of gaseous NaCl. A Stark splitting caused by the axial molecular field is observed in the photoelectron spectra of gaseous NaCl [18,19]. The peak splitting observed in the present work on the other hand may reflect two different adsorption geometries which occur in the first adlayer, namely NaCl molecules pointing either towards or away from the surface with their Cl^- ion (see section 4). Further evidence for this interpretation comes from the MIES results of section 3.3.

For large exposures (> 0.7 A.U.) the NaCl induced emission agrees both in position and shape with UPS results on NaCl single crystals when using photon energies between 20 and 22

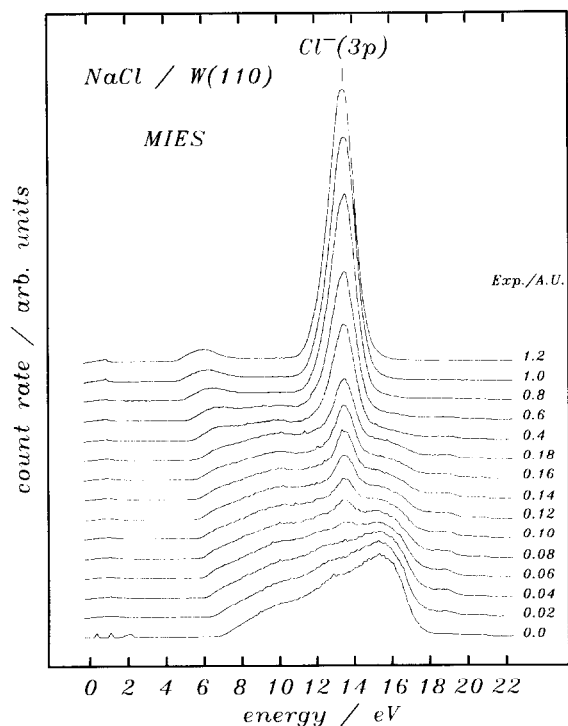


Fig. 3. MIE spectra obtained during the exposure of W(110) to NaCl. As in fig. 1.

eV [3,20]. In terms of the NaCl band structure we interpret the two maxima obtained for exposures beyond 0.7 A.U. as follows [3]: the final energy of the emitted electrons is well above the electron-electron scattering threshold. This guarantees that we detect direct transitions. Therefore the two detected maxima reflect maxima in the density of the 3p valence bands of Δ_5 and Δ_4 symmetry close to the points X'_5 and X_4 . This interpretation is consistent with the occurrence of peak 4 in the EEL spectra.

3.3. Metastable impact electron spectroscopy (MIES)

A preliminary discussion of MIE spectra obtained at a larger exposure rate was presented in ref. [22]. The bottom spectrum of fig. 3 is typical for Auger neutralisation (Auger capture (AC)) of He^+ ions formed by resonance ionization of He^* metastables in front of the W(110) surface [21,23].

Upon exposure to NaCl two new spectral contributions occur correlated with the weakening of the substrate emission:

(1) Emission appears beyond the high-energy end of the Auger capture spectrum (up to 19.8 eV). It is due to Auger deexcitation (AD) [21] of He^* involving W 5d electrons. The Auger deexcitation process becomes feasible because the work function of the surface decreases by 1.2 eV upon exposure to NaCl as indicated by the shift of the low-energy cutoff of the spectra. This decrease of the work function inhibits the resonance ionization of the He metastables. However, at least for > 0.5 A.U. the Auger deexcitation process involving W electrons cannot occur anymore because the adsorbed NaCl shields the W substrate from the interaction with He^* projectiles.

(2) Emission peaked at $E_B = 6.3$ eV with respect to the Fermi level (19.8 eV) appears. The peak position roughly agrees with the first maximum found in UPS. We attribute this emission to Auger deexcitation involving Cl^- 3p electrons. In contrast to UPS a second maximum at 1 eV larger binding energy is not observed. With increasing exposure to NaCl the emission due to the ionization of Cl^- 3p widens considerably; the width of the structure for > 0.6 A.U. finally coincides with the full width of the Cl^- 3p valence band [1,3]. For these exposures our results agree with previous MIES results obtained for NaCl films deposited on glass [24] and those obtained with NaCl single crystals [20].

Using some of the conclusions derived in section 4 the differences between UP and MIE spectra may be explained as follows:

(1) At small exposures the NaCl molecules are adsorbed perpendicular to the surface (see section 4); the Cl end of the molecule may either point towards or away from the surface. Auger deexcitation of the He^* in MIES will involve only the Cl^- ions which point away from the surface; those which are positioned underneath Na^+ ions will not interact sufficiently strong with the He^* projectile.

(2) At large exposures the excitation energy of He^* is insufficient to ionize valence band states in Δ_1 near X_4 (which would produce the maximum with the larger binding energy). Only one

maximum from the ionization of Δ_5 at X'_5 , is found; because Δ_5 is flat near X'_5 the corresponding maxima in the MIE and UP spectra are shifted by the difference in the excitation energies [3]. Nevertheless some emission from Δ_1 must also contribute to the MIE spectra in order to explain that the Cl^- 3p emission displays the full valence band width of 3.3 eV for large exposures [1,3].

MIES results obtained for the larger exposure rate of 0.4 A.U. per minute (not reproduced here, see refs. [22,28]) show in addition to the features discussed previously a shift of the Cl^- 3p emission towards larger binding energies [22]. The shift becomes recognizable around 8 A.U. and thereafter increases linearly with NaCl exposure. A similar shift is, however, not seen in the corresponding UP spectra [22]. We believe that the shift is caused by the positive charge-up of the surface by the formation of Cl^- 3p vacancies dur-

ing the Auger deexcitation process. The number of vacancies near the surface is ~ 50 times larger in MIES than in UPS as judged from a comparison of the total electron count rates. Obviously the annihilation of the Cl^- 3p vacancies proceeds slowly because of the small overlap of the wavefunctions of neighbouring Cl^- ions [5].

The MIE spectra shown in fig. 4 are obtained applying 300 eV electrons ($I_e = 1 \mu\text{A}$); strong emission develops at the Fermi level during the bombardment (for doses $> 4 \times 10^{-2} \text{ C/cm}^2$). Based on previous results obtained for partially alkaliated W(110) we identify it as Na 3s induced emission, namely autodetachment of He^{-*} [25,26] and Auger deexcitation of He^* [11,21]. We estimate that a metallic-like Na overlayer of a thickness between 0.65 and 1 monolayer (in terms of the first complete adlayer at room temperature) is formed during the electron bombardment. It shields the Cl^- ions efficiently from the interaction with the He^* projectiles: by gently heating to 700 K, the Na overlayer can be removed, and the original MIE spectrum present before the electron bombardment reappears. The presence of the Na adlayer has also been verified by EELS (see section 3.1).

3.4. Ion impact electron spectroscopy (IIES)

Figs. 5 and 6 present the electron spectra emitted during grazing incidence collisions of 50 eV He^+ and 100 eV He^{2+} , respectively, with W(110) as a function of the NaCl exposure.

We concentrate on the He^+ results first (fig. 5): as for He^* collisions the bottom spectrum is caused by Auger capture (AC) involving W5d electrons [21]. The decrease of the surface work function by 1.2 eV gives rise to a small contribution of Auger deexcitation (AD) of He^* atoms formed by resonance neutralization. This contribution can be seen very weakly beyond the high-energy cutoff of the Auger capture spectrum. It is confined to the small exposure range around 0.2 A.U. before the band gap of NaCl emerges and inhibits the electron transfer between the surface and the He^+ projectile.

For large exposures (> 0.45 A.U.) electrons are entirely due to Auger capture AC ($\text{Cl}3p$)

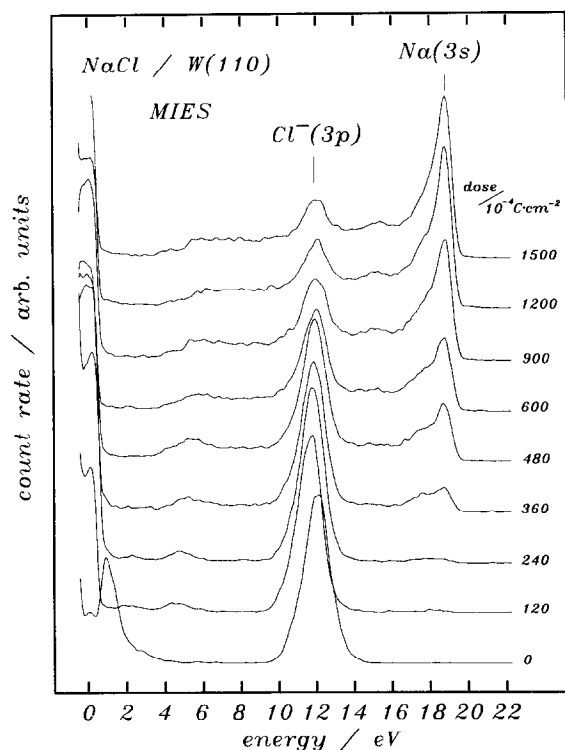


Fig. 4. MIE spectra of NaCl (3 A.U.)/W(110) obtained during electron induced desorption ($E_e = 300 \text{ eV}$; $I_e = 1 \mu\text{A}$). Numbers given with the spectra denote the applied electron doses.

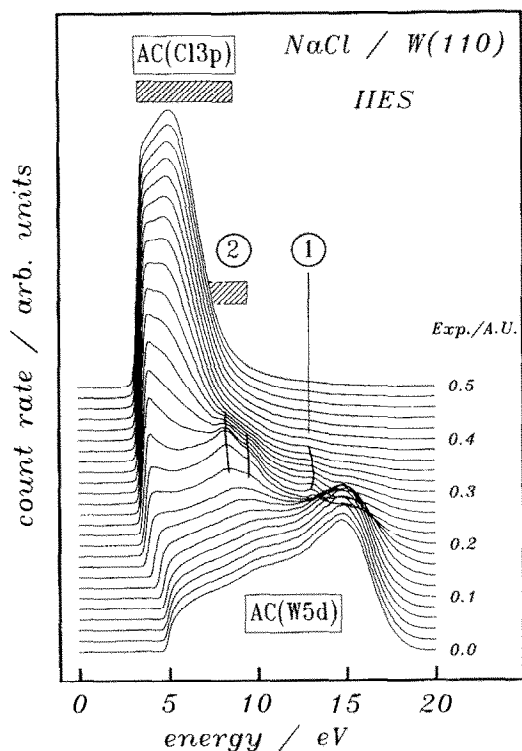


Fig. 5. IIE spectra induced by 50 eV He^+ during the exposure of W(110) to NaCl. As in fig. 1.

involving electrons from the valence band of the NaCl adsorbate. We have indicated in fig. 5 where the high-energy edge of this spectral contribution (involving two Cl^- 3p electrons from the top of the valence band of NaCl) is expected assuming a band gap of 9 eV [1,3] (see also the EELS and MIES results). Indeed a strong intensity rise occurs at this energy for the NaCl covered surface.

At sufficiently large exposures (> 0.45 A.U.) the MIE and IIE spectra are completely different although electrons from the same surface states, namely electrons from the Cl^- 3p valence band, are involved: metastable He^* atoms suffer an Auger deexcitation process because the projectile brings its 2s electron into the collision. On the other hand, He^+ ions are subject to Auger capture because the band gap in the NaCl layer inhibits the transfer of a surface electron into the 2s state; the projectile will then become neutralized in an Auger capture process involving two electrons from the Cl^- 3p valence band.

The additional features (1) and (2) observed at intermediate exposures are tentatively attributed to Auger deexcitation involving a Cl^- 3p electron (peak (1)) and to Auger capture involving one W 5d and one Cl^- 3p electron (feature (2)). The position of peak 1 agrees with that of the strong peak from Auger deexcitation involving Cl^- 3p observed by MIES.

The results of fig. 6 are obtained for the impact of 100 eV He^{2+} ions under grazing incidence upon W(110) as function of the exposure to NaCl. They can be discussed most conveniently on the basis of the reaction scheme of fig. 7 (introduced in refs. [23,32] and employed by us in refs. [26,36]). Spectra obtained from clean metals (see bottom spectrum in fig. 6) have been discussed at length in [32,33]. The structure located at the high energy end of the bottom spectrum is due to autoionization (AU) of He^{**} formed by the resonant capture of two surface electrons. The rest of the high energy part of the spectra

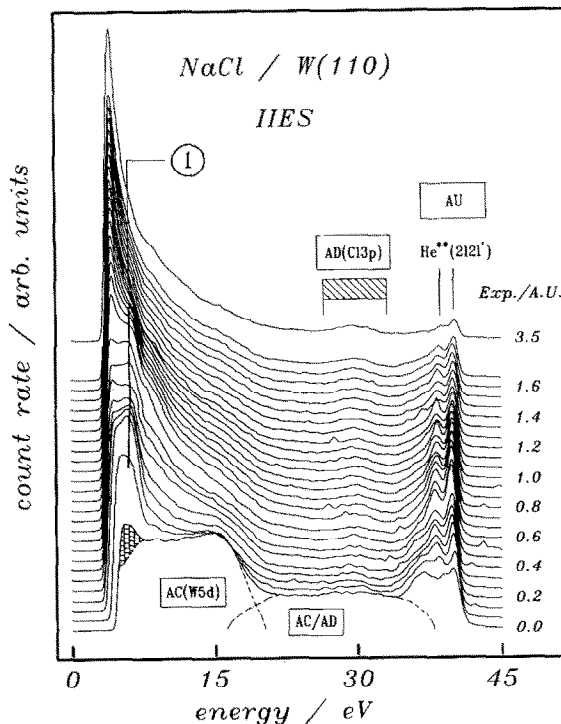


Fig. 6. IIE spectra induced by 100 eV He^{2+} during the exposure of W(110) to NaCl. As in fig. 1.

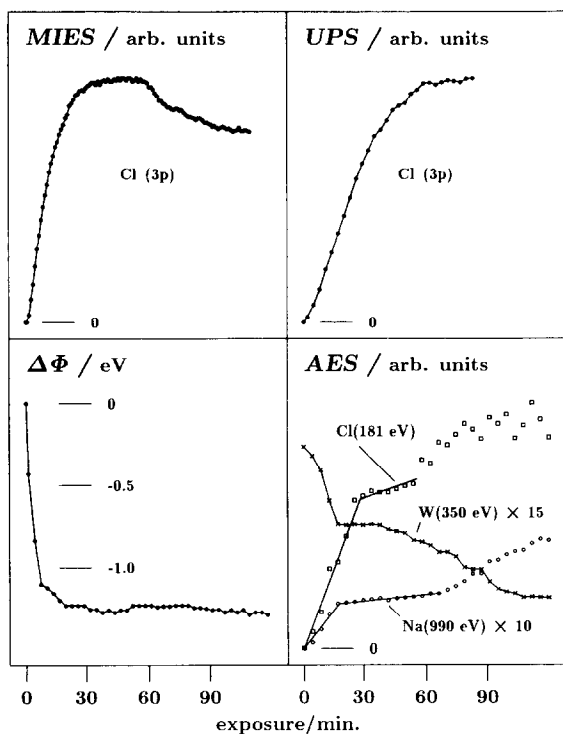


Fig. 8. The change of the intensities of various AES peaks, the Cl3p signals as detected by MIES and UPS, and the surface work function during the exposure of W(110) to NaCl. Exposure rate, 0.04 A.U. per minute.

the Na 2p level is involved in the Auger deexcitation of He^{+*} ($n=2$). The comparatively weak structure (labeled AD (Cl3p) in fig. 6) may be caused by Auger deexcitation of He^{+*} involving neighboring “undamaged” Cl^- ions (without 3p vacancies). The number of such events is, however, small because the slow He^{+*} ion will not travel very far from the site where it had captured its electron. An identification of the processes contributing to the slow structureless low-energy part of the spectrum is not possible.

4. Growth mode of the NaCl adlayer

Fig. 8 summarizes the exposure dependence of the MIES, UPS, and AES results; also shown is the variation of the work function of the surface with exposure as derived from the low-energy

cutoff of the MIE spectra. Together with the results of section 3 we can state:

(1) In the beginning there is the adsorption of single undissociated NaCl molecules because the UP spectrum closely resembles the photoelectron spectrum of gaseous NaCl molecules [18,19]. Signals attributable to neutral atomic Cl and/or Na can only be detected after electron bombardment of the NaCl adlayer (see fig. 4). Molecular adsorption of KCl on W(110) at room temperature was already invoked in ref. [7] on the basis of AES, TDS, and LEED results. NaCl adsorption on Ge(100) is found to be molecular as well up to room temperature [6,27,31].

(2) Bulk properties, in particular interband transitions and excitonic excitations, appear first at 0.2 A.U. indicating that the NaCl bulk electronic structure is present at least locally at this exposure. At about the same exposure the UP spectra already display the two-peak structure characteristic for the valence band ionization by 20 to 22 eV photons [3,38]. Above 0.28 A.U. the adlayer produces MIE spectra which are similar to those of NaCl single crystals [20].

(3) The emission involving electrons from the W substrate disappears around 0.7 A.U. in the MIE spectra and around 0.5 A.U. in the He^+ IIE spectra. In the He^{2+} IIE spectra the structure labeled (1) representing the Auger capture process $\text{He}^{2+} \rightarrow \text{He}^{+*}$ ($n=2$) remains visible up to 0.6 A.U. It was discussed in section 3.4 that this process can lead to electron emission only if there are filled surface states up to the Fermi level. This implies that the NaCl bulk structure cannot be present globally.

(4) The MIE signal due to the Cl^- 3p ionization saturates at ~ 1 A.U. (see fig. 8). Moreover the AES signals display kinks at this exposure. We conclude that at this exposure the adlayer becomes indistinguishable from NaCl bulk material, i.e., the W substrate is now covered by an adlayer which has essentially the electronic properties of a NaCl single crystal.

Summarizing, up to exposures > 0.5 A.U. the substrate is still accessible to the interaction with thermal metastable He^* atoms and slow singly and doubly charged He^+ ions under grazing incidence although features characteristic for the

NaCl bulk electronic structure appear much earlier (see (2)).

In order to explain our findings we adopt a model developed in ref. [31] to explain the growth of NaCl adlayers on Ge(100). We will show that it can also consistently explain our findings for the NaCl adsorption W(110):

In the beginning stage of the adlayer formation single undissociated NaCl molecules adsorb with their molecular axes perpendicular to the substrate. This explains why UPS (but not MIES) detects two peaks in this phase: they are due to the different binding energies of Cl^- 3p electrons in the two different adsorption geometries of the molecules, namely pointing toward and away from the surface.

The molecules serve now as nuclei for further adsorption of NaCl: the adlayer grows laterally in form of two-dimensional islands whereby neighboring molecules have opposite orientations with respect to the surface direction. This explains the early occurrence of excitonic features as well as the bulk like UP, MIE, and IIE spectra observed at this stage. Lateral two-dimensional growth of the islands is suggested by the linear rise of the MIES signal up to 0.6 A.U.

Further exposure leads to a compression of the intermolecular distance within the islands. This manifests itself in the increase of the width of the Cl^- 3p induced emission in the UP and MIE spectra between 0.4 and 1.0 A.U. Around 1 A.U. the intermolecular distance in the adlayer is essentially equal to that in the bulk; the electronic structure becomes indistinguishable from that of single crystals by those electron spectroscopical techniques which are sensitive to the near-surface region only. From our results it is not possible to decide whether the growth of a second layer has already started above an exposure of 0.6 A.U.

5. Electronic transitions induced by ionizing radiation

In this section the various ionization processes in the NaCl toplayer induced by the impact of electrons, He^* , He^+ , and He^{2+} will be discussed;

we will also comment on their possible relevance for desorption processes induced by electronic transitions (DIET) [8].

Electrons of < 300 eV create vacancies both in the Na^+ 2p and the Cl^- 3p valence bands of the adlayer. These events lead to the production of excitons and interband transitions. Moreover, the vacancy production as detected by EELS is thought to be responsible for the preferential desorption of Cl atoms and the accumulation of neutral Na atoms on top of the adlayer as detected in particular by MIES (see fig. 3). Metalization of the adlayer can be detected with MIES after doses of $> 10^{+15}$ electrons cm^{-2} of 200 eV.

Thermal He^* metastable atoms create one Cl^- 3p vacancy per collision event in the Cl^- ions located "on the outside" of the NaCl adlayer. These vacancies are distributed over the entire Cl3p valence band as judged from the width of the corresponding structure in the MIE spectra. Even after doses of 10^{+15} metastables cm^{-2} no accumulation of neutral Na could be detected with MIES although the extremely high sensitivity of MIES for surface adsorbed alkali atoms has been demonstrated by several groups [10,25,39]. Therefore stoichiometric changes at the surface induced by He^* seem not to occur solely as the consequence of the Cl^- 3p vacancy formation.

Slow He^+ collisions under grazing incidence create two vacancies per collision event in the Cl^- 3p valence band in an Auger capture process. These vacancies are located on the same Cl core. From shifts of the spectra observed after the emergence of the NaCl band structure we conclude that the vacancies stay localized for some time and lead to a positive charge-up of the surface. No accumulation of Na can be detected after doses of 10^{+15} He^+ ions cm^{-2} . This is consistent with the findings in refs. [9,30] that sufficiently slow rare gas ion collisions (Ne, Ar) do not lead to F desorption from LiF solely on the basis of the transfer of electrons from the LiF crystal to the projectiles. It was concluded [9,30] that a minimum kinetic energy of the impacting ions is required to remove the F species from the surface by momentum transfer in a second collision event. Classical trajectory calculations were performed on the behavior of a NaF lattice if the

negative F^- ion was suddenly changed into F^+ [34]. It could be shown that the initial large repulsive energy between F^+ and the NaF lattice became attractive due to lattice distortions; the F^+ ions became trapped in a stable state above the surface.

For soft He^{2+} collisions our interpretation of the spectra suggests that up to four Cl 3p vacancies may be created per collision through resonant transitions and Auger processes. However, only two such vacancies will be located at the same core. Again no Na accumulation could be detected after doses of the order of $10^{+15} He^{2+} cm^{-2}$. Therefore electronic transitions alone seem not to be sufficient to initiate Cl desorption. This is again consistent with ref. [30] that in slow Ne^{2+} collisions with LiF a neutralized projectile must sputter the F species which remains weakly bound to the surface after vacancy formation [34] in an electronic transition from the F valence band to the Ne^{2+} projectile.

6. Summary

The electron emission from W(110) exposed to NaCl at room temperature was studied with the electron spectroscopic techniques AES, EELS, UPS, MIES, and IIES. NaCl adsorbs molecularly. The transition from the electronic structure of single adsorbed molecules to that of the NaCl bulk could be studied in detail by monitoring the emergence of the insulator band gap and of the bulk properties, such as interband transitions and excitonic excitations as a function of exposure. It is concluded that the first NaCl adlayer grows laterally in form of two-dimensional islands. This model was proposed before for the NaCl adsorption on Ge(100) [31].

The electron transfer processes initiated by the impact of soft ionizing radiation, slow electrons, metastable, singly and doubly charged He projectiles, were studied as a function of the NaCl exposure. These processes are resonant electron transfer and interatomic Auger processes, Auger neutralization and deexcitation between the projectiles and the $Cl^- 3p$ states in the adlayer. It is concluded that slow He projectiles in different

charge and excitation states do not give rise to desorption of atoms from the adlayer solely on the basis of the creation of vacancies in the adlayer.

Acknowledgements

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