

The change of the electronic structure of alkali halide films on W(110) under electron bombardment

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NaCl and CsI films of up to four layers were deposited onto W(110) surfaces and investigated by metastable impact electron spectroscopy (MIES), UPS and AES. The electronic structure of the films under electron bombardment was then studied by MIES/UPS. The results are compared with the corresponding ones obtained by thermal desorption spectroscopy (TDS). An interpretation of the results is attempted on the basis of existing theories for desorption induced by electronic transitions (DIET) of alkali halides.

1. Introduction

Ion (ISD)-, electron (ESD)- and photon (PSD)-stimulated desorption from alkali halide surfaces has received considerable interest in recent years [1]. There still exist several unanswered questions and unresolved controversies as:

- the conversion of the electronic energy deposition by the stimulating particles into the kinetic energy of the desorbing particles,
- surface stoichiometry changes due to stimulated desorption,
- the role of surface excitons in desorption.

We have addressed the above mentioned questions by studying desorption from alkali halides layers on W(110). The electronic structure of the surface during the preparation of the alkali halide adlayers as well as during the desorption process is monitored by AES, work function (WF) changes, MIES, and UPS.

MIES is particularly suited for the study of the electronic structure of adlayers because of its extreme surface sensitivity [2]. Briefly, thermal metastable He atoms (2^3S , 2^1S) bombard the surface. The excitation energy of about 20 eV is utilized to eject electrons whose kinetic energy is characteristic for their binding energy in the adlayer atoms.

The combination with UPS is particularly appealing because of the utilization of the different information depth of the two techniques.

2. Experimental details

The apparatus has been characterized at several occasions [3,4]. Briefly, it consists of a facility to perform MIES and UPS by using the same source to produce either a metastable He(2^3S , 2^1S) (19.8; 20.6

eV) atomic or a HeI ($h\nu = 21.2$ eV) UV light beam. According to [5] the triplet/singlet ratio in our metastable beam is about 7:1. Due to the fact that most of the He(2^1S) atoms are converted into He(2^3S) prior to deexcitation in front of the surface [3,4], the excitation is almost purely induced by the triplet species. This facility enables us to start the collection of an UP spectrum within less than one minute after taking MIE spectra without any change of the surface position or state. The apparatus is also equipped with AES and the possibility for residual gas analysis. These tools are essentially employed to monitor the surface cleanliness and to perform WF measurements.

Alkali halide layers (NaCl, CsI) are produced by thermal evaporation of single crystal chips. The thickness of the alkali halide layers has been estimated by a combination of several methods:

- (1) by comparing our WF results with those of ref. [6] which were given as a function of the alkali halide exposure and thickness;
- (2) by inspection of the disappearance of the emission at the Fermi level (due to substrate emission) in the MIE spectra;
- (3) by establishing the saturation of the MIE signal from the halogen ionization as a function of the exposure.

More experimental details may be found in refs. [3,4] where the adsorption of alkali atoms [4] and the alkali/hydrogen coadsorption [3] were studied by MIES.

3. Results and discussion

Figs. 1a and 1b display MIE and UP spectra, respectively, obtained during the exposure of the W(110)

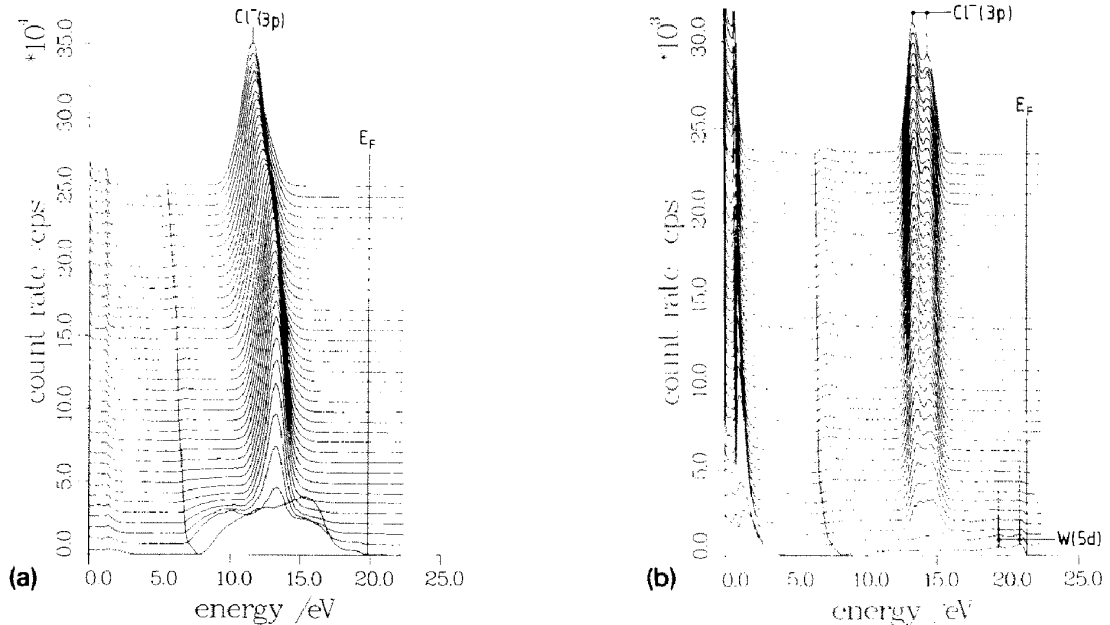


Fig. 1. MIE (a) and UP (b) spectra of the NaCl adsorption on W(110). The bottom spectrum corresponds to zero coverage. The coverage increases by 0.1 NaCl adlayers per spectrum.

surface to NaCl. The Fermi energy is at 19.6 (21.0) eV in the MIE (UP) spectra. The emission between $E_B = 6$ and 8 eV (with respect to the Fermi energy) is due to the ionization of $\text{Cl}^- 3p$ as is shown by a comparison with the UP and MIE spectra of refs. [7] and [8], respectively. UPS shows a two-peak structure which

must be due to the ionization of the $\text{Cl}^- 3p_z$ and $3p_{x,y}$ orbitals. The available excitation energy is however not sufficient to ionize Na 2p. The WF of the NaCl layer shows a decrease by about 1.2 eV in the initial stage of the exposure in agreement with [6]. From these measurements alone we cannot determine the growth mode

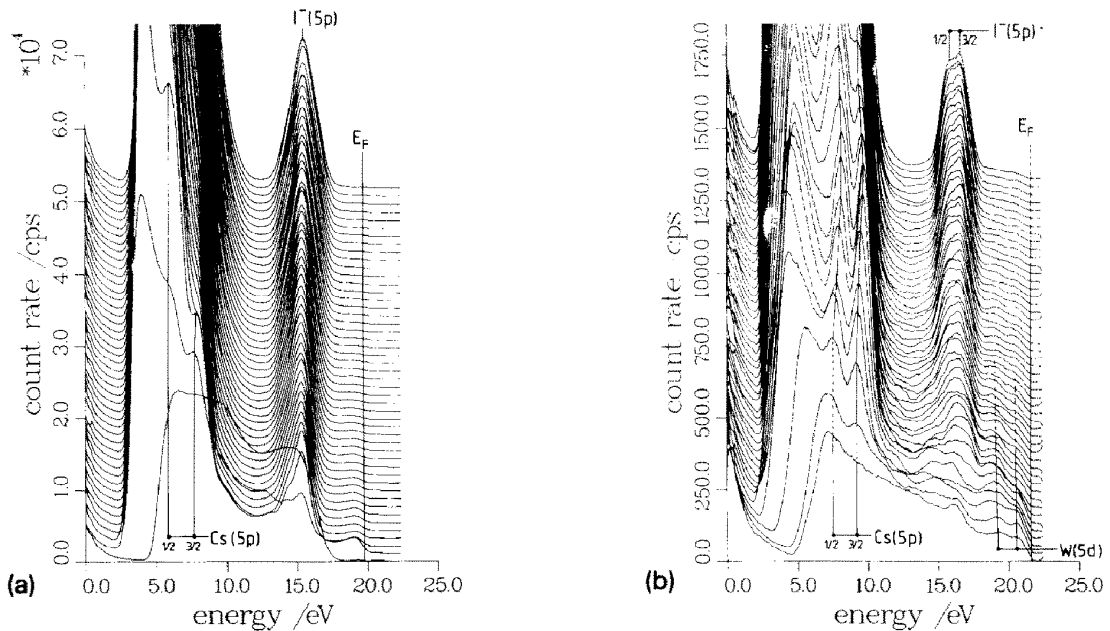


Fig. 2. MIE (a) and UP (b) spectra of the CsI adsorption on W(110). The bottom spectrum corresponds to zero coverage. The coverage increases by 0.1 adlayers CsI per spectrum.

of the adlayer. However, a preliminary analysis of AES results following the lines of ref. [9] suggests that NaCl adsorbs molecularly and that the thickness of the first layer is given by the full NaCl lattice constant ($d = 5.6 \text{ \AA}$), e.g. NaCl forms a layer of molecules which stand upright.

Figs. 2a and 2b show the corresponding results obtained when depositing CsI to the W(110) surface. In addition to the $I^- 5p_{1/2,3/2}$ emission we observe ionization of the $Cs^+ 5p_{1/2,3/2}$ subbands both in the MIE and UP spectra. This proves that both Cs^+ and I^- ions are found in the outermost layer.

A more careful analysis (see forthcoming paper ref. [10]) taking into account the exposure dependence of the peak areas of the MIE and UP signals as well as the WF changes and AES results of [6] indicates, that CsI also adsorbs molecularly and that the thickness of the first layer is given by half of the CsI lattice constant (3.87 \AA), e.g. the molecules are oriented along the surface direction.

The bottom spectra in figs. 1 and 2a are caused by Auger Neutralization of He^+ ions formed by resonant ionization of the He^* metastable atoms at large WF [2,3].

Fig. 3a documents changes in the surface electronic structure during the thermal desorption (TDS) of the adlayer. Emission at the Fermi level remains weak throughout the thermal treatment (up to 800 K). At binding energies larger than that of the $Cl^- 3p$ valence band continuum emission becomes of increasing importance with increasing temperature. Furthermore the

$Cl^- 3p$ emission splits into two peaks at high temperatures ($> 750 \text{ K}$). Our interpretation is that NaCl dissociates at least partly during the desorption process; the two peaks seen above 750 K are due to 3p ionization of Cl atoms bonded to the substrate.

Fig. 3b shows the changes induced by electron bombardment; MIE spectra are taken after the bombarding times indicated with the spectra. In addition to the $Cl^- 3p$ emission strong emission appears at the Fermi level with increasing bombarding time. The comparison with MIES results obtained from Na layers on W(110) reveals that this emission is due to ionization processes involving the Na 3s valence electrons [3,4], e.g. metallic-like Na appears at the surface.

We conclude that surface compositional changes occur upon electron bombardment: the adlayer is significantly enriched by Na while the Cl is desorbing preferentially. The appearance of the Na 3s emission near E_F furthermore indicates that a significant charge transfer to the Na atoms takes place in the electron bombardment process. These results are consistent with the desorption mechanism agreed upon for ESD from bulk alkali halides [11]: the interaction of electrons with the NaCl lattice is restricted to the halogen sublattice. Electron-hole pair formation leads to production of (F-H) center pairs. A F-center is an electron on a halogen (X^-) vacancy, and a H-center is comparable to a X_2^- -negative ion at the original X^- -site. H-centers are mobile at room temperature; if a H-center reaches the surface it will decay and emit a neutral halogen atom. F-center diffusion is limited to temperatures

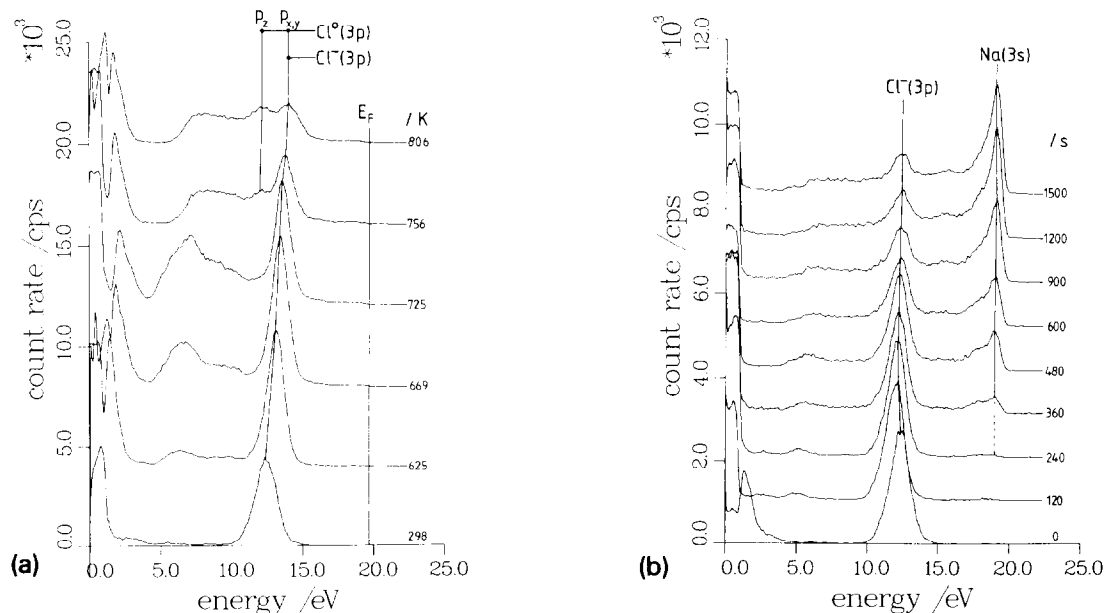


Fig. 3. MIE spectra of NaCl (3 ML)/W(110) obtained during thermal (a) and electron induced (b) ($E_c = 300 \text{ eV}$; $I_c = 1 \text{ \mu A}$) desorption. Numbers given with the spectra give the sample temperature and the bombarding time, respectively.

above a few hundred K. However, F-centers formed at the surface will decay in neutralizing a surface alkali ion and thus form an overlayer of neutral alkali atoms. At room temperature this Na overlayer will not desorb [3,4].

A quantitative analysis of the time dependence of the Cl^- and Na peak areas yields a cross section for ESD of $2 \times 10^{-17} \text{ cm}^2$ for Cl by 300 eV electrons. From the erosion yield given in [13] we estimate an ESD cross section of $5 \times 10^{-15} \text{ cm}^2$ of bulk NaCl held at 300°C by 500 eV electrons.

Fig. 4a and 4b show the changes observed for a CsI film (three layers thick) under thermal treatment and electron bombardment, respectively. Changes in stoichiometry occur during the heating process: the $\text{I}^- 5p$ emission disappears around 650 K; at this temperature only a metallic-like Cs adlayer remains. This layer is desorbed completely around 725 K.

We conclude that CsI decomposes before desorbing separately as atoms (ions). This is also reflected by the fine structure splitting of both Cs and $\text{I} 5p_{1/2,3/2}$ which becomes more pronounced during the heating process.

No stoichiometric changes can be observed during the electron bombardment: the $\text{I}^- 5p$ and Cs $5p$ emission decreases only during the first two seconds of the bombardment, and remain practically constant thereafter. No enrichment of Cs at the bombarded surface can be observed. The absence of Cs accumulation can probably not be explained by the difference in the evaporation temperatures for Na and Cs on the surface because an accumulation of Cs is indeed observed during the thermal treatment. As a consequence of this

argumentation we can conclude from the absence of any stoichiometric change during the studied bombarding time that the desorption cross section is $< 10^{-19} \text{ cm}^2$ for 300 eV electrons bombarding a three layers thick CsI film.

This comparatively small ESD cross section suggests that the H-center migration model (see above) which is effective for desorption from bulk alkali halides in general may not be applicable to explain ESD from CsI films ($\leq 3 \text{ ML}$ thickness). The results of [6] may give a hint as to what the eventual desorption mechanism may be: the threshold for desorption is found at an electron bombarding energy of about 40 eV; this threshold is compatible with the assumption that the electron induced ionization of $\text{I} 4d$ (and possibly Cs $4d$) leads to Auger stimulated desorption: the $4d$ -vacancy will be filled by an $\text{I}^- 5p$ electron while another $\text{I}^- 5p$ electron at the same site will be ejected. This Auger transition transforms the I^- ion into an I^+ ion which feels the strong Coulomb repulsion by the surrounding Cs^+ ions, and as a consequence is desorbed [12]. The emission of an Cs^+ ion may be initiated when a I^- ion located right underneath the Cs^+ is transformed into I^+ in an Auger process as described above [6].

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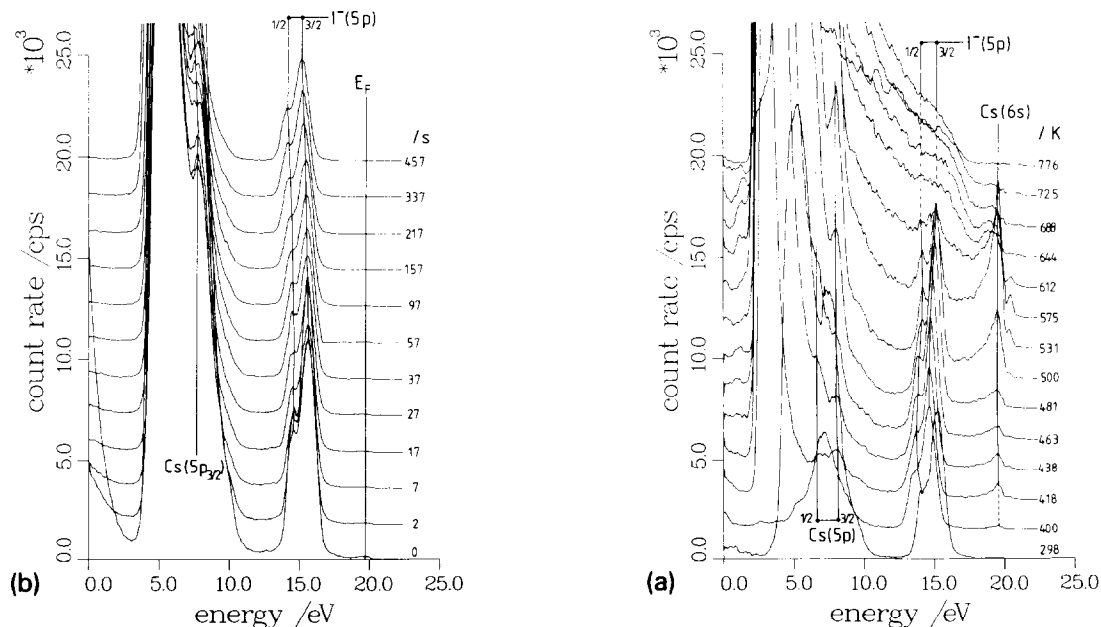


Fig. 4. MIE spectra of CsI (3 ML)/W(110) obtained during thermal (a) and electron induced (b) ($E_c = 300 \text{ eV}$; $I_c = 1 \mu\text{A}$) desorption. Numbers given with the spectra give the sample temperature and the bombarding time, respectively.

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