Electron- and photon-stimulated metallization and oxidation of the CaF_2(111) surface

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Abstract

Calcium difluoride bulk crystals cleaved along (111) planes in air and in ultra-high vacuum have been irradiated with 2.5 keV electrons and 1486 eV photons. Radiation induced changes in the surface electronic structure were monitored as a function of irradiation dosage with ultraviolet photoelectron spectroscopy (UPS) and metastable impact electron spectroscopy (MIES). The radiation induced decomposition of the surface is directly evidenced in MIES spectra where upon increased dosage a continuous band appears at the Fermi energy while UPS performed with 21.2 eV photons is found not to be sensitive for the detection of metallized areas at the surface. For crystals cleaved in air after irradiation an additional structure 3 eV above the fluorine 2p valence band edge is found in UPS and MIES spectra that is attributed to oxidized metal patches at the surface. This assignment is confirmed by spectroscopy on Ca films on silicon surfaces dosed with oxygen. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Calcium difluoride crystals are known to be sensitive to radiation damage and the effects of low energy electron irradiation on the stoichiometry and topography of the (111) surface have been demonstrated by X-ray photoelectron spectroscopy [1], electron energy loss spectroscopy [2] and atomic force microscopy [3,4]. Also the oxidation of surface metal has already been subject of a systematic study [5].

The present paper reports experiments where the (111) surface of CaF_2 crystals was irradiated with 2.5 keV electrons and 1486 eV photons. The formation of band gap states was observed by ultraviolet photoelectron spectroscopy (UPS) and metastable impact electron spectroscopy (MIES). It is demonstrated that the formation of a radiation induced metallic band at the Fermi energy (E_F) can directly be observed with MIES, but not by UPS, while both techniques reveal the in situ formation of oxide even in the ultra-high vacuum (UHV) provided crystals have been cleaved in air. The assignment of a band gap feature formed during irradiation to oxide formation is supported by experiments involving oxygen dosage of an

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electron irradiated CaF_2 surface that had been produced by cleavage in UHV and dosage of an evaporated calcium film.

2. Experimental procedures

Experiments were performed in two similar UHV set-ups (base pressure typically 10^{-10} mbar) where one was designed for electron irradiation and UPS measurements while the other allowed irradiation of the sample with photons and simultaneous analysis with UPS and MIES. The latter apparatus has been described in detail previously [6]. Briefly, it is equipped with a cold-cathode gas discharge source for the production of metastable He*(2^3S) ($E^* = 19.8$ eV) atoms with thermal kinetic energies and HeI photons ($E = 21.2$ eV) for UPS. Metastable and photon contributions within the beam are separated by means of a time-of-flight technique combined with a double counter system allowing to measure MIES and UPS spectra simultaneously. The angle of incidence of the ultraviolet photons on the surface was $55°$ and electrons emitted normal to the surface were recorded. The photoelectron emission yield is displayed as a function of binding energy relative to the Fermi level that in some cases was shifted on the electron kinetic energy scale due to charging. Charge-up of the bulk crystals during MIES and UPS measurements was minimized by heating the sample to typically 500 K, which does not affect data interpretation since the energetic position of all observed features can be related to the position of the fluorine 2p valence band emission peak. Exposure of surfaces to electrons of 2.5 keV and photons of 1486 eV energy was done with commercial electron and X-ray sources, respectively. A calcium film on Si(111) was prepared by evaporating Ca in a commercial Knudsen-cell on a Si(111) surface cleaned by several short flashes to ca 1300 K. Results obtained with the two different apparatus are linked to each other via UPS, the technique common to both apparatus.

3. Results

Fig. 1 shows the effect of electron irradiation of CaF_2(111) as measured by UPS for an air cleaved
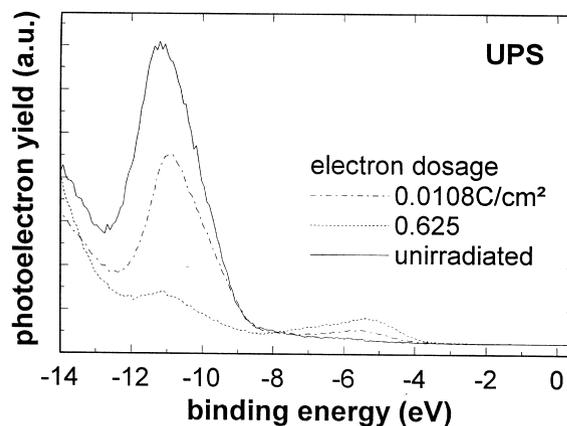

Fig. 1. UV photoelectron spectra of CaF_2(111) as cleaved in air and after irradiation with different dosages of 2.5 keV electrons at a current density of 180 µA cm^{-2}. Sample temperature was 400 K during irradiation and 490 K during UPS measurements. For increasing dosage the F 2p intensity decreases while the O 2p peak is formed. The Fermi level is that of the analyser corrected by 1 eV sample charging.

crystal. With increasing electron dosage the fluorine 2p valence emission intensity decreases monotonically while a smaller new feature 3 eV above the valence band edge emerges. Surprisingly, not even smallest radiation-induced changes could be observed in the vicinity of the Fermi level where the formation of a metallic band would be expected. However, a strong decrease in fluorine 2p emission is observed with increasing dosage.

Fig. 2 displays a corresponding result for a surface cleaved in the UHV where a distinctly different behaviour was observed. The lower trace shows the photoelectron spectrum for the as-cleaved surface with an almost negligible density of occupied states in the band gap. The striking result observed here is that, although, the surface is strongly metallized at this dosage, the feature 3 eV above the valence band is extremely small compared to the feature found in the spectrum of the air-cleaved sample. However, as shown in the upper trace, its intensity increases dramatically when exposing the metallized surface to 15 L (1 L = 10^{-6} Torr s) of oxygen.

The MIES spectra of CaF(111) are identical to the UPS spectra as far as the fluorine 2p valence band emission is concerned except for a shift by ca 1.4 eV to lower kinetic energies caused by the
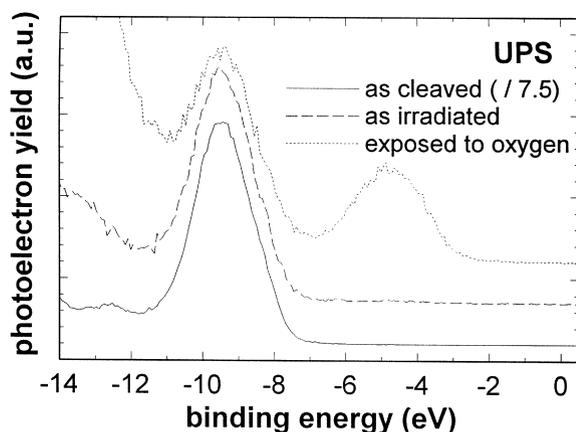
Fig. 2. UV photoelectron spectra of $CaF_2(111)$ cleaved in UHV, irradiated with $150\ mC\ cm^{-2}$ of 1.5 keV electrons and subsequently dosed with 15 L oxygen at a pressure of 5×10^{-6} Pa. The photoelectron yield for the unirradiated surface was divided by a factor of 7.5 while the other two spectra are shifted upwards in this representation. E_F refers to the Fermi energy of the spectrometer.

excitation energy of 19.8 eV [He*(2^3S)] as compared to 21.2 eV (HeI photons). The air-cleaved sample displays also the oxygen induced features.

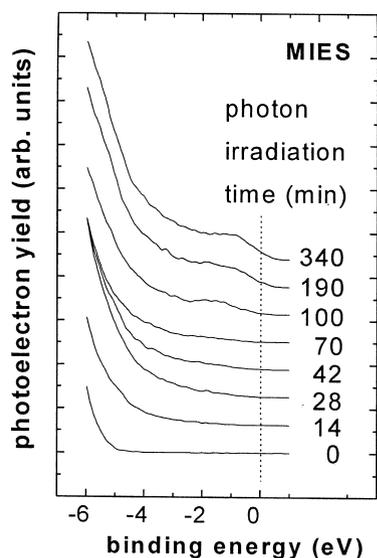Fig. 3 displays MIES spectra of an air cleaved

Fig. 3. MIES spectra of the time development of the emission from air cleaved $CaF_2(111)$ during irradiation by 1486 eV photons. Only the region between the oxygen emission and the Fermi energy is shown.

crystal taken during irradiation with X-ray photons in the region of the Fermi energy. It shows details of the development of the photoelectron emission with irradiation time where the main feature is the development of a band at the Fermi energy. The small contribution at and beyond E_F is due to the Auger de-excitation involving He(2^1S) atoms (contributing ca 11% to the total beam intensity). However, as in the case of electron irradiation (Fig. 1) a peak ca 3 eV above the valence band edge is found. MIES/UPS data for $CaF_2/Si(111)$ (not shown) show exactly the same fluorine 2p valence band emission as the $CaF_2(111)$ results.

MIES data for a Ca/Si(111) film shown in Fig. 4 are useful for the interpretation of the data in Figs. 1 and 3. Shown is the MIES spectrum of a thick (>20 nm) Ca layer on Si(111) and the same layer exposed to ca 300 L O_2. The Ca/Si(111) spectrum is essentially flat except for a peak close to the Fermi energy. The emission at low kinetic energy may be caused by secondary electrons. The oxygen exposed Ca-layer (2) shows a strong peak 5.5 eV below E_F which is caused by the ionization of the oxygen 2p orbital.

4. Discussion

The most striking observation in the series of photoelectron spectra of air cleaved surfaces irradiated with various doses of electrons (Fig. 1) is that with increasing electron dosage the valence band emission intensity decreases drastically while a smaller new feature 3 eV above the valence band edge emerges. Surprisingly, not even smallest radiation-induced changes could be observed in the vicinity of the Fermi level where the formation of a metallic band would be expected. A surface metallization, however, is evident from the strong decrease in fluorine 2p emission observed with increasing dosage and a severe surface modification in the form of a grey film is also evident from a visible inspection of the sample. The situation is markedly different for the MIES measurements of a photon irradiated crystal (Fig. 3) where the formation of a metallic band at the Fermi edge can clearly be observed.

The difference between UPS and MIES measurements can be explained by the different processes involved in both techniques. In the present experiments photoelectrons emitted normal to the (111)-surface were mainly sampled, that is, from a line from the Γ to the L point in the face centred cubic Brillouin zone of Ca assuming that the metal epitaxially grows on the (111) surface of CaF_2 what can be expected at least for the beginning of metallization [4]. An analysis of the Ca band structure, however, reveals that the Fermi surface crosses the Brillouin zone at the U and K points and close to the W point [7,8] and the emission of electrons with energies close to the Fermi energy has to be expected in other directions than those covered by the detector. Additionally the emission along the Λ direction is strongly suppressed in the present case because of selection rules [9]. Here the photon energy plays an important role since it selects the final state and, therefore, determines the photoemission matrix element, that is, photoemission intensity. It is known that in the solid state the cross-section for emission from s-like initial states is specifically weak for photon energies >10 eV up to the soft X-ray energy regime [10]. However, states between the Γ and L points in the Brillouin zone that are probed with UPS are to a large extent s-like [7,8]. In conclusion it is realised that these experimental conditions cannot be expected to measure significant photoemission from calcium metal at the CaF_2 surface in perfect agreement with the measurement. All these arguments do not apply to electron emission from a MIES process where the final state in the ionization process is essentially a free-electron state, namely the 2s electron state. The electrons emitted in the Auger de-excitation process originate from the He probe atom interacting with the Ca ad-atom and are not influenced by optical selection rules.

The formation of the radiation induced peak 3 eV above the fluorine 2p valence band edge is found in UPS as well as MIES spectra of air cleaved samples and this feature is attributed to the formation of oxide on the metallized surface. As soon as metallic areas are formed on irradiated CaF_2, the surface becomes very reactive against adsorbates, such as CO_2, H_2O and O_2 or oxygen already incorporated in the surface. This assign-

ment of the band gap peak to the oxygen 2p level is supported by the comparison of measurements involving oxygen dosage of the metallized CaF_2 surface (Fig. 2) and the evaporated calcium film (Fig. 4). Further support is provided by a recent theoretical calculation predicting the oxygen peak at the observed position [11].

A comparison of Figs. 1 and 2 representing measurements on air and vacuum cleaved crystals, respectively, yields some insight into the nature of the oxidation process. Although, the vacuum cleaved surface has been subject to an electron dosage density of 0.15 C cm^{-2}, that is, a dosage 14 times higher than that of the weakest irradiation displayed for the air cleaved surface where a pronounced oxide peak is found, the oxidation prior to oxygen dosage is barely to be recognized in the UPS spectrum. The residual gas pressure was similar in both experiments and a simple order-of-magnitude-estimate for the possible uptake of oxygen from the residual gas yields that such a process provides a plausible explanation of the weak oxidation for the vacuum cleaved surface but not for the air cleaved surface. To explain the strong oxidation of the air cleaved surface it is
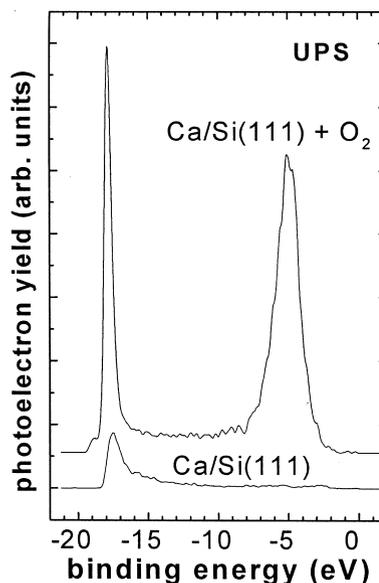
Fig. 4. MIES spectrum of a Ca on Si(111) film (thickness >20 nm) prepared in the UHV and Ca/Si(111) exposed to ca 300 L oxygen.

proposed that an air cleaved surface is loaded with a considerable amount of oxygen invoking an instantaneous oxidation of metal during electron dosage. As a consequence of this idea it is assumed that the clusters formed on the air cleaved surface during irradiation are conglomerates of small oxidized particles rather than homogeneous metallic colloids covered with an oxide skin. This interpretation is supported by the observation that it is possible to "ex situ" measure currents through a metallic film produced by electron irradiation in the UHV while films produced on air cleaved surfaces exhibit an unmeasurably small conductivity. Within this picture the strong instantaneous oxidation of metal on the air cleaved surface could also serve as an explanation for the peculiar forms of metallic precipitates produced on such surfaces by electron irradiation [3]. MIES results obtained for the photon irradiated air cleaved surface (Fig. 3) may imply that some purely metallic precipitates formed in this experiment are at least large enough to form a metallic band structure since electron emission up to the Fermi level is observed. The continuous emission up to E_F may, however, also be due to an agglomeration of defects with overlapping energy levels without the formation of a metallic band.

In summary band gap states appearing on the $CaF_2(111)$ surface upon irradiation with low energy electrons and photons have been studied. The main features are a continuous band at the Fermi level formed when enough defects or metal are collected at the surface and a peak from the ionization of the oxygen 2p level appearing 3 eV above the fluorine 2p band edge when surface metal is oxidized. The amount of oxidation strongly depends on the pre-treatment of the irradiated surface. For a vacuum cleaved surface the oxidation is weak and is due to oxygen from the residual gas. Oxidation of an air cleaved crystal is much stronger and controlled by oxygen already present at the surface.

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