Photoemission from pure and electron irradiated CaF$_2$

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Abstract

We describe changes of the electronic structure of CaF$_2$ (1 1 1) surfaces caused by electron irradiation, with an emphasis on radiation stimulated oxidation. CaF$_2$ crystals cleaved in air and in ultra high vacuum (UHV) were investigated with ultraviolet photoelectron spectroscopy using HeI light (21.2 eV). Surfaces produced by cleavage in air show a large density of states in the band gap region, in contrast to those cleaved in UHV. When irradiating the air cleaved crystals with low energy electrons, we observed the formation of a new peak in the band gap region that is attributed to oxygen. From the electron dosage dependence of this new peak, we conclude that it is mainly formed during irradiation by oxygen already present at the crystal surface. For crystals cleaved in UHV, no new features are observed following irradiation, although a metallic film on the crystal surface is visible with the bare eye. However, dosage with oxygen also yields the band gap peak. The oxidized surface is modeled by ab-initio calculations, based on the Hartree–Fock method. Results are compatible with experimental observations. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Radiation damage and surface metallization of CaF$_2$ due to low energy electrons has been the subject of several studies. Stoichiometry and topography of the (1 1 1) surface have been investigated by X-ray photoelectron spectroscopy [1], electron energy loss spectroscopy [2] and scanning force microscopy [3,4]. The oxidation of surface metal by oxygen dosage following irradiation has been studied by Auger spectroscopy on thin films [5].

In this paper we report on experiments with air and ultra high vacuum (UHV) cleaved CaF$_2$ crystals. Ultraviolet photoelectron spectroscopy (UPS) performed after irradiating the samples with 1.5 to 2.5 keV electrons showed the formation of a peak about 3 eV above the F2p valence band maximum (VBM) for air cleaved crystals. A similar feature on UHV cleaved crystals could be obtained by oxygen dosage following irradiation. For comparison with experimental results, ab-initio calcul-

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ations of different types of oxidized CaF_2 surfaces have been performed.

2. Experimental

Experiments were performed in an UHV chamber with a base pressure in the low 10^{-10} mbar range. Air cleaved crystals were heated in UHV to 800 K for approximately 1 h to clean them as much as possible. For UPS measurements the sample was irradiated with 21.2 eV photons from a commercial HeI source. The angle of incidence of the ultraviolet photons on the surface was 55°. Photoelectrons were recorded in normal emission. Charge-up of the bulk crystals during UPS measurements was reduced by heating the sample to typically 500 K [6]. Since spectra might nevertheless be shifted by charging in the order of 1–2 eV, we displayed the photoelectron yield as a function of electron kinetic energy rather than binding energy. This 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. Electrons from the Fermi energy of an uncharged metallic sample are expected at 16.4 eV kinetic energy, as has been verified with a silver crystal. Exposure of the surfaces to electrons of 1.5 or 2.5 keV primary energy was done with a commercial Auger source at a sample temperature of 400 K. Dosage of the surfaces with oxygen, nitrogen, carbon dioxide and water was accomplished by an evacuated gas inlet system connected to the UHV chamber by a leak valve.

3. Experimental results

In Fig. 1 we show the effect of electron irradiation of CaF_2 (1 1 1) as measured by UPS for an air cleaved crystal. The spectrum taken from the unirradiated surface already exhibits a large density of states in the band gap region. Note also the asymmetric shape of the valence band peak. Changing the emission angle by turning the sample holder did not change the shape of the peak. Upon electron irradiation, the fluorine 2p valence band emis-
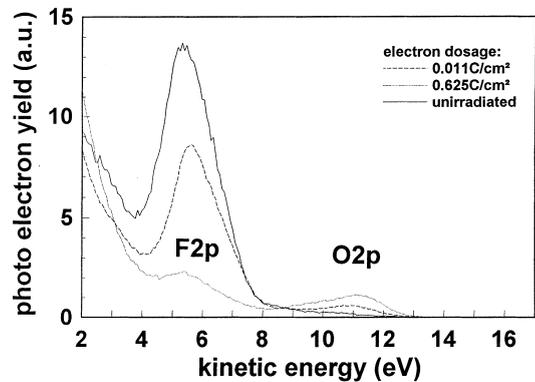
Fig. 1. Ultraviolet photoelectron spectra of CaF_2 (1 1 1) as cleaved in air and after irradiation with two dosages of 2.5 keV electrons at a current density of 180 µA/cm². Sample temperature was 400 K during irradiation and 490 K during UPS measurements. For increasing dosage the F2p intensity decreases while the O2p peak emerges.

sion intensity decreases while a smaller new feature 3 eV above the VBM emerges. The integral intensity of this new feature saturates at an electron dosage of roughly 0.2 C/cm². Annealing the crystal at a temperature of 700 K for 4 h reduces the intensity of the feature to one half. After irradiation, a gray film can be seen with the bare eye, an ex-situ measurement confirmed that the film is conductive and therefore metallic. The striking result is that 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.

Fig. 2 displays a result for a corresponding measurement on a surface cleaved in UHV where we observed a distinctly different behavior. The lower curve shows the photoelectron spectrum for the as-cleaved surface with a negligible density of states in the band gap. In this case, the valence band peak appears to be symmetric. In contrast to the findings for air cleaved crystals, photoelectron spectra drastically changed when probing at different emission angles. The middle curve represents a spectrum measured after electron irradiation with a dosage of 0.15 C/cm². Similar to the air cleaved crystal, a decrease in fluorine 2p emission is observed, and no emission from the Fermi level is seen. Here we found only very small radiation induced changes in the band gap. Similar to the air
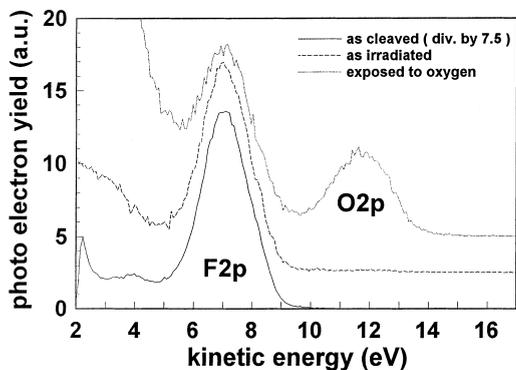
Fig. 2. Ultraviolet photoelectron spectra of CaF_2 (1 1 1) cleaved in UHV, irradiated at 400 K with 150 mC/cm^2 of 1.5 keV electrons and subsequently dosed with 15 L oxygen at a pressure of 5×10^{-8} mbar. For a better representation, the photoelectron yield for the unirradiated surface was divided by a factor of 7.5, and the other two spectra were shifted upwards.

cleaved samples, a gray film can be seen on the surface, which in an ex-situ measurement was found to be conductive. However, when exposing the metallized surface to 15 L of oxygen, the band gap feature known from the air cleaved crystal emerges, as shown in the upper trace. A similar feature has been observed when dosing with water, while exposure to N_2 and CO_2 had no effect on photoemission spectra.

4. Calculations

The electronic structure of the CaF_2 surface was calculated using the Hartree–Fock method and a slab model as implemented in the CRYSTAL95 computer code [7]. From Ref. [8] we took the Gaussian basis set for the Ca^{2+}, F^- and O^{2-} ions optimized for bulk CaF_2 and CaO crystals. The CaO crystal has the rock salt structure with a lattice constant only 10% smaller than that of CaF_2, and Ca ions form a cubic face centered sublattice in both crystals. This allows the epitaxial growth of thin CaO film of (1 1 1) orientation on top of CaF_2 (1 1 1). The structure of the interface has been proposed in Ref. [9] where also results from X-ray photoelectron diffraction experiments indicating the existence of such an oxide film are shown. The CaO (1 1 1) surface has a dipole mo-

ment and is, therefore, unstable unless it is reconstructed or covered by some adsorbate layer. So far the structure of oxide films created on the CaF_2 surface by electron bombardment and subsequent oxygen exposure is unknown. Therefore, we have studied the following stable surface geometries. (1) A sandwich structure, where the CaO layer is enclosed between two CaF_2 layers. In this configuration, there are two equivalent CaO (1 1 1)/CaF_2 (1 1 1) interfaces in the slab, and the open CaO (1 1 1) surface is avoided. (2) A CaO (1 1 1) 2×2 reconstructed film on CaF_2 (1 1 1). The surface has a threefold symmetry and small facets of (1 0 0) orientation. (3) A CaOH film on CaF_2 (1 1 1). In this case, the top layer of F ions is replaced by OH^- ions oriented normal to the surface.

While optimizing the geometry for all slabs we kept the lattice constant of CaF_2 unchanged. Therefore, the CaO layers were stretched in lateral direction and consequently compressed in the direction perpendicular to the interface. The total density of states for all considered structures is shown in Fig. 3. Spectral position and shape of the O2p band depend on the atomic structure of the surface. In the case of the 2×2 reconstructed surface, there are three inequivalent O^{2-} ions with
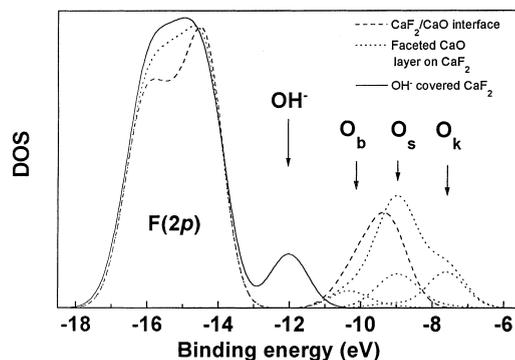
Fig. 3. Calculated density of states (DOS) for the CaO/CaF_2 structures described in detail in the text. The sandwich structure gave a single peak at 4.0 eV above the VBM (dashed line). The DOS of the reconstructed CaF_2/CaO surface is represented by the dotted lines. It consists of three contributions: states related to bulk (O_b), steps (O_s) and kinks (O_k) at 3.0, 4.4 and 5.8 eV above the VBM, respectively. States from OH^- are found 1.6 eV above the VBM (solid line).

different numbers of nearest Ca neighbors. Therefore, the total density of states in the O2p band is a superposition of three bands corresponding to bulk (6-coordinated), surface (5-coordinated), and kink (3-coordinated) O^{2-} ions with energies 3.0, 4.4, and 5.8 eV above the top of the F2p band, respectively. A broad oxygen feature with a maximum at 4.0 eV was found for the sandwich structure. The OH^- peak in the density of states is at 1.6 eV above the F2p band.

5. Discussion

In this chapter, we will first present reasons for the lack of metallic emission at the Fermi level. Furthermore, we discuss oxygen storage observed for air cleaved crystals and irradiation induced reactions.

In the UPS spectra of both, the air and UHV cleaved crystals, not even the slightest 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 in the form of a gray conducting film is evident from an ex-situ inspection of the sample. To explain this, we assume that the metal grows epitaxially on the (1 1 1) surface of CaF_2, what can be expected at least for the beginning of metallization [4]. In our experiment we sample photoelectrons emitted normal to the (1 1 1)-surface, i.e. a line from the Γ to the L point in the face centered cubic Brillouin zone of Ca. Band structure calculations of bulk calcium [10,11] show that the Fermi surface crosses the Brillouin zone at the U and K points and close to the W point, thus the emission of electrons with energies close to the Fermi energy cannot be expected normal to the surface. Additionally, these calculations have shown that the relevant states are to a large extent s-like. It is known that photoemission from s-like initial states is specifically weak for photon energies between 10 eV and the soft X-ray regime [12]. In conclusion we realize that for our experimental conditions it cannot be expected to measure significant photoemission from calcium metal at the CaF_2 surface.

We assign the radiation induced peak found 3 eV above VBM in the UPS spectra of air cleaved

samples to the oxygen 2p level. This assignment is supported by the comparison of the measurement on UHV cleaved crystals involving oxygen dosage of the metallized CaF_2 surface (Fig. 2) as well as by our theoretical calculation predicting photoemission peaks from bulk oxygen at approximately the experimentally observed position (Fig. 3, peak labeled O_b). It is thus found that an air cleaved CaF_2 surface is loaded with a considerable amount of oxygen in whatever chemical state. As there is no oxygen peak visible in the spectra taken prior to electron irradiation, it cannot be simply present as bound O^{2-}. As the most likely species we assume OH^- to be existing on the surface, which probably substitutes F^- ions during cleavage. According to our calculations, photoemission from OH^- states is expected to be close to the VBM (Fig. 3), which could account for the asymmetric shape of the valence band emission from the air cleaved crystal. Under electron irradiation, a surface reaction takes place:

$$F^- - Ca^{2+} - OH^- \rightarrow Ca^{2+} O^{2-} + HF \uparrow$$
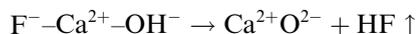
In conclusion, we investigated differences in the damage behavior of air and UHV cleaved crystals. We were able to explain the lack of a metallic feature at the Fermi level as well as the origin of the oxygen peak found in the spectra from air cleaved crystals subject to electron irradiation.

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