

The role of defect diffusion and metallization for electron-stimulated desorption from CaF_2

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Abstract

The desorption of neutral and ionized anion and cation species from CaF_2 and LiF was studied for 1 keV electron irradiation. Experiments were performed for temperatures ranging from room temperature to 400°C at dosage levels resulting in a notable metallization of bulk and surface at elevated temperatures. There we found desorption of neutrals as well as ions from both crystals except calcium ions from the CaF_2 surface in contrast to LiF where Li^+ was the predominant ionic desorbant. For CaF_2 the F^+ desorption yield was investigated in more detail. It was found that this yield increases as a function of temperature and is strongly dependent on dosage and irradiation intensity. Furthermore F^+ desorption is most efficient at the lowest beam intensity and a peaked structure in the dosage-dependent yield indicates a limiting process and/or depletion of a surface layer from fluorine. Results for emission of F^+ are explained by a model including the precipitation and growth of Ca colloids from F-centers as well as halogen formation from H-centers and halogen transport to the surface.

1. Introduction

It is well established in literature that stimulated emission of F^+ from the CaF_2 (1 1 1)-surface results from an inter-atomic Auger-initiated process following the ionization of the Ca 3p core level. This follows from threshold measurements for electron- and photon-stimulated desorption from CaF_2 films epitaxially grown on semiconductor substrates [1–3]. Earlier work had already shown that the desorbing ions leave behind a modified Ca rich surface with a half-filled energy band formed by the Ca^+ ions of the topmost surface layer that was interpreted as an ordered array of F-centers [4]. Furthermore, EELS-investigations revealed that immediately after completion of this monolayer array a precipitation of metal colloids starts that was identified by plasmon excitations in the energy loss spectrum [5]. The development of bulk [6,7] and surface [8] metallization during continued electron irradiation is also a well established process for the CaF_2 crystal. The question of color center formation and its influence on desorption has been widely studied for the case of LiF where F-, M- and R-center coloration at room temperature and the formation of Li colloids on the surface at higher temperatures have been found [9]. Later studies revealed a delayed emission of Li atoms after irradiation at temperatures above 400°C that was attributed to evaporation from Li clusters on the surface

[10] and the influence of this surface metallization on the desorption process was studied [11]. LiF strongly contrasts CaF_2 with respect to F-center production efficiency and metallization. While LiF exhibits the highest F-center production efficiency among the alkali halides [12] the coloration of CaF_2 is extremely hard [13].

Based on these observations the main issue of the present paper is a study of the influence of the metallization on the fluorine desorption process from CaF_2 . We not only discuss F^+ emission in the context of the metallization problem but also the emission of F^0 and the role of diffusion processes required for a transport of fluorine to the crystal surface. An experiment where the desorption from LiF and CaF_2 is investigated under the same experimental conditions allows a direct comparison between both materials and a discussion of CaF_2 results in view of the LiF results.

2. Experimental

Experiments were carried out on high purity CaF_2 single crystals cleaved in air along their (1 1 1)-plane and polished to obtain good optical quality. After insertion into the UHV (base pressure 2×10^{-10} mbar) the sample surface was cleaned by a bakeout at a temperature of approximately 300°C . In one case we additionally

introduced a LiF crystal with a polished (100)-surface mounted in the same copper sample holder as the CaF₂ crystal. During bakeout and experiments the sample temperature was kept constant at temperatures ranging from room temperature up to 400°C by a resistive heater element attached to the sample holder. Crystal temperature was measured by a thermocouple attached to the side of the crystal where the temperature might be slightly different from that at the surface.

The arrangement of the electron source used for excitation and the components for desorption and reflectivity analysis is schematically depicted in Fig. 1. The electron source provided 1.5 μA of 900 eV electrons. Under high focussing conditions the beam was focussed into a spot of 0.3 mm² at the sample surface. In this case the average current density at the surface was 500 μA/cm², however, the beam had a bell-shaped profile and contained a small spot with higher intensity leading to an inhomogeneous distribution of excitation density. Therefore, all results are given as a function of total dosage (mC) rather than dosage density (mC/cm²). For low focussing measurements the beam had a cross-section of 30 mm² and a fairly homogeneous intensity distribution providing a well defined current density of 5 μA/cm².

For the analysis of desorbed neutrals and ions we used a quadrupole mass filter equipped with an ionizer and an electrostatic sector field analyzer. The first electrode of the ion optics collecting charged particles from the surface was set to the same ground potential as the sample holder to create a nominally field free region between

sample and analyzer. However, during electron irradiation, surface charging unavoidably created an electric field leading to a strong dependence of the measured ion kinetic energy on surface charging. Therefore, the kinetic energy as determined by the analyzer does not have a physical significance with respect to the desorption process but is mostly determined by charging while dosage-dependent changes in this energy indicates a variation in the charging behavior [14]. Ion kinetic energies found in the literature [1,3] for desorption from thin films where charging is not relevant are not consistent with each other. Therefore, presently we are not able to quantify the contribution of charging to the measured energy.

Metallization was monitored by a measurement of reflectivity at 633 nm utilizing a HeNe-laser beam reflected from the CaF₂ surface about at the center of the electron spot where the electron density was most homogeneous. For measurements under high focussing conditions care has been taken to position the HeNe-focus in the low intensity area of the electron beam profile. The reflected light was collected by the sensor-head of an optical power meter and its intensity monitored as a function of dosage.

3. Neutral and ion desorption

Generally we observed the desorption of various neutral and ionic species during and after electron irradiation. For reasons given below we mostly investigated the emission of F⁺ ions. The main features of the F⁺ desorption signal from CaF₂ under high focussing conditions are illustrated in Fig. 2. The energy spectra (Fig. 2(a)) consisted of two distinct peaks that we attribute to the low-intensity region (peak 2) of the beam profile and the high-intensity spot (peak 1), respectively. The special choice of the intensity profile offered the possibility to investigate the effects of different excitation densities under exactly the same experimental conditions. Common to both desorption peaks is an initial rise and a slow decay of the count rate as a function of dosage (Fig. 2(b)); however, the maximum yield is much higher for the hot spot while the low-intensity peak exhibits much longer rise and decay times. Fig. 2 also reveals the local nature of sample charging. Since both peaks had distinctly different energies during the total time of the experiment it can be concluded that the irradiation established a stable potential difference of about 2 V over a distance of some 10 μm on the surface. The details of charging are described elsewhere [14] while in the present contribution we focus our attention on the desorption yield as a function of dosage.

In a first set of experiments performed with a low-intensity electron beam the desorption of neutral and ionic species from LiF and CaF₂ irradiated with identical

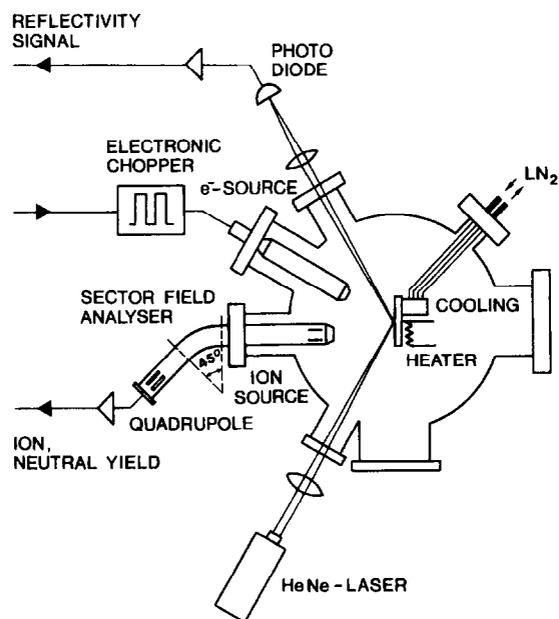


Fig. 1. Experimental setup for electron-stimulated desorption and reflectivity studies.

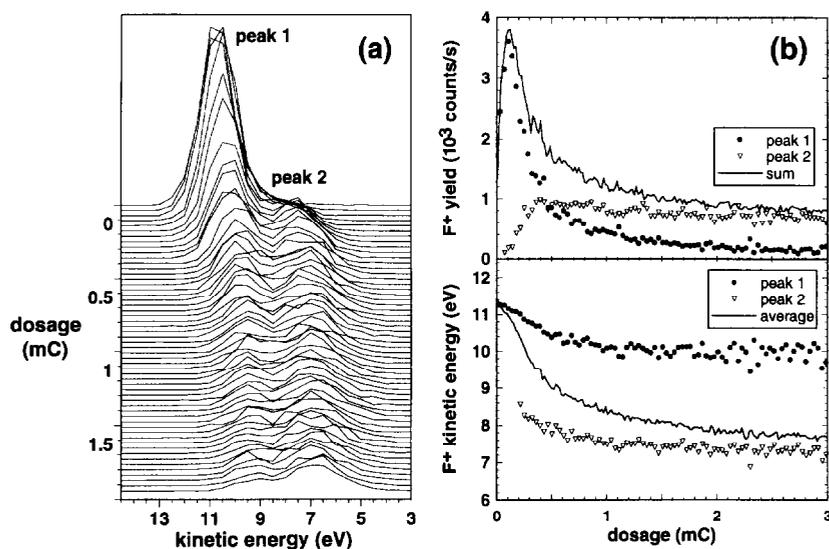


Fig. 2. (a). Energy spectra for F^+ -desorption from CaF_2 after application of various electron doses. Peaks 1 and 2 correspond to emission from the hot spot and the low intensity region of the electron beam profile, respectively, (b) dosage-dependent yield and mean energy curves extracted from the spectra by fitting Gaussians to both peaks.

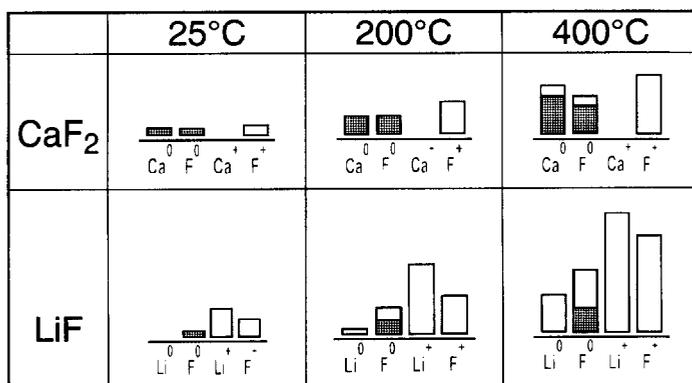


Fig. 3. Comparative study of electron-induced neutral and ion emission from LiF and CaF_2 under identical experimental conditions. Shaded areas indicate background emission that is independent of electron irradiation.

dosages and under the same experimental conditions were compared to each other. In Fig. 3 a compilation of the neutral and ion yield data at room temperature, 200°C and 400°C is presented (the heights of the bars roughly represent the maximum yield of the dosage-dependent emission). Shaded areas indicate the presence of an electron beam independent background either from the residual gas or thermal desorption of atoms from the sample. It should be pointed out that the purpose of this figure is to demonstrate some general trends in the desorption behavior of LiF and CaF_2 and does not allow any kind of quantitative interpretation. While the yields for different masses are dependent on sensitivity factors determined by the quadrupole filter, a comparison of

neutral and ion yield for one species is not possible since the efficiency of the ionizer is not known. Therefore Fig. 3 only allows an interpretation of the changes in yield as a function of temperature and a rough comparison of yields for the same species desorbing from LiF and CaF_2 .

In both sets of data the yield of both, neutrals and ions, shows a significant increase with temperature. It is notable that the Ca^0 desorption is dominated by thermal evaporation while the electron stimulated Li^0 signal is certainly affected by temperature but does not exhibit any background at these temperatures. For Li^0 as well as Ca^0 we found a delayed emission for the 400°C measurement. Both observations, the virtually missing background as well as the delayed emission, are well in

accordance with previously published data [10]. Since the vapor pressure for thermal desorption from these bulk metals is roughly the same in the temperature region covered by these experiments the missing background may be an indication that in the case of Li^0 with a weaker tendency for colloid formation, during irradiation metal atoms directly desorb from the LiF surface while the metal desorption observed from CaF_2 predominantly results from small surface colloids where the vapor pressure may easily exceed that of the bulk metal by one order of magnitude or more [15]. For F^0 there is strong thermal evaporation in both cases clearly dominating in the case of CaF_2 . The mechanism for thermal evaporation of fluorine is not clear at present. Direct emission from the lattice can be excluded due to the high binding energy. A possible origin might be the annealing of stable defect centers at the surface or a detachment from surface steps that has been observed for molecular desorption from NaCl [16]. A clearly nonthermal contribution to the desorption, however, comes from the ions where both species are present for desorption from LiF while from CaF_2 only F^+ is emitted. Since we observe Ca^0 but no Ca^+ emission we take the lack of this species as strong evidence that gas-phase ionization does not play any significant role for the observed positive ion yield in our experiments [17].

4. F^+ desorption from CaF_2

The emission of F^+ ions was the main topic of investigation in most previous ESD measurements on CaF_2 thin films. In the context of this work we studied certain aspects of F^+ desorption from bulk CaF_2 with a special emphasis on the role of defect diffusion and metallization. This implied a series of measurements with sample temperature and irradiation dose as the main parameters since diffusion and metallization are controlled by these quantities.

Results from a series of desorption measurements with the focussed electron beam taken at various temperatures are shown in Fig. 4. The energy spectra (see Fig. 2(a)) for each data point were fitted by two Gaussians for the low and high energy peak and the integrated yields derived from these Gaussians were plotted as a function of dosage (similar to Fig. 2(b)). The most striking feature of both plots is the increase of the maximum ion yield as a function of temperature. Integration of the curve yields that the total ion emission also increases. For the high-intensity peak we also observed a strong dependence of the times for the initial rise and decay of the desorption signal. Two important conclusions can be drawn from the graphs in Fig. 4. First, the peaked structure of the ion desorption curves implies that during irradiation the crystal undergoes a certain modification that initially leads to an enhanced desorption and later a limiting

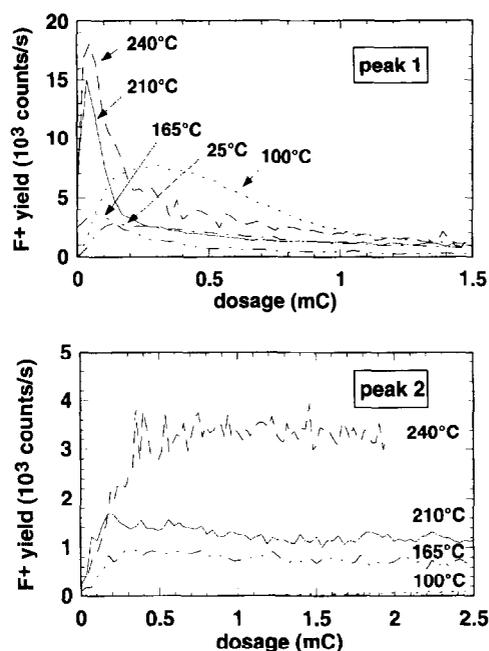


Fig. 4. Dosage dependence of electron-stimulated F^+ -emission yield from CaF_2 at various temperature levels for high intensity (peak 1) and low intensity (peak 2).

process suppresses further desorption down to less than 10% of the maximum yield. Second, the desorption yield as well as the time constants for its temporal evolution are controlled by temperature. Although fluctuations in the absolute F^+ yield presently prohibit a precise quantitative analysis of its temperature dependence a super-linear increase with temperature is anticipated.

In another set of experiments under high focussing conditions we addressed the question of the desorption efficiency as a function of the excitation density. To accomplish this the sample was irradiated with different electron currents ranging from 2 to 16 μA and the F^+ yield was monitored as a function of dosage. As a measure for the desorption efficiency we take the count rate from the quadrupole divided by the applied electron dose. The efficiency as a function of dosage is plotted in the upper graph of Fig. 5 for different current levels. In this plot each ordinate value is proportional to the number of ions desorbed per incident electron and the integral over the efficiency up to a certain dosage yields the total amount of F^+ desorbed by the application of this dosage. The striking feature evidently appearing in Fig. 5 is the strong dependence of the efficiency on electron current revealing that both, the maximum efficiency as well as the total amount of desorbed fluorine ions, strongly decrease for higher irradiation currents. Furthermore, it is noted that at a dosage of about 2 mC all curves have decayed to a saturation value that is roughly

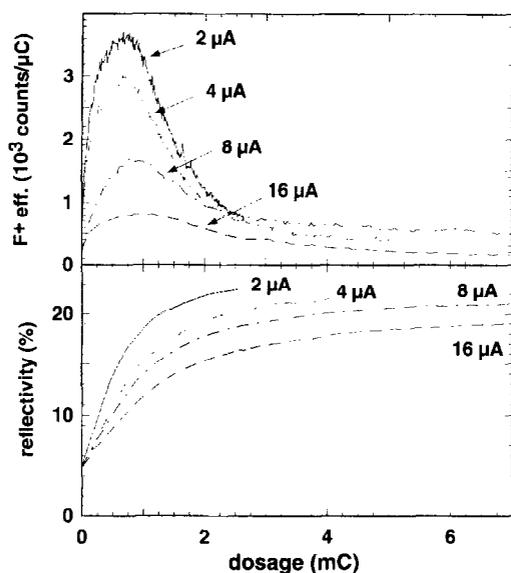


Fig. 5. Dosage dependent F^+ -desorption efficiency (upper curves) and degree of metallization (lower curves) for electron irradiation of CaF_2 at various current levels.

independent of electron current. Parallel to the desorption we monitored surface reflectivity and results are displayed in the lower part of Fig. 5. As observed previously [18] we found a monotonous increase with dosage where saturation starts at about 2 mC. In correspondence to the upper figure also in the reflectivity data the curves representing different irradiation currents are distinctly different from each other and well ordered in the sense that the lowest current yields the steepest rise in reflectivity (i.e. highest metallization efficiency) and reaches the highest absolute reflectivity in the saturation limit while the curves for the higher currents consecutively follow at lower reflectivity levels. Many of the observations described above appeared to be rather surprising at first, however, in the next section we present some ideas forming a consistent picture for their interpretation.

5. Discussion and conclusions

As discussed in the introduction, presently it is well established in literature that the desorption of F^+ from CaF_2 at least predominantly if not exclusively results from a Knotek–Feibelman process following ionization of the Ca 3p core level and we have no reason to doubt that this also applies to the measurements presented here. Our second basic assumption is that the measured F^+ desorption yield exclusively results from surface emission by the Auger-induced process and not from any kind of diffusive motion towards the surface. In fact, F^+ is an extremely unstable species in the bulk of CaF_2 due to its

high electronegativity [19] and will rapidly capture an electron or an I-center after its creation in the bulk. Also direct ionization of neutral fluorine is highly improbable considering the high ionization energy and low cross-section [19]. From this point of view there seems to be a contradiction between our experimental results concerning the temperature dependence and dosage behavior and the Auger excitation model since the latter is not expected to show any strong temperature dependence nor a decrease in yield for increased excitation density.

The key hypothesis we propose here to solve the peculiarity is that F^+ desorption is indeed a surface process, however, after the first few monolayers of fluorine have been removed, the surface is already fairly metallized and the initial Auger process tends to vanish, further F^+ emission is completely controlled by a diffusive supply of fluorine from subsurface layers substituting the desorbed atoms.

This hypothesis allows a consistent interpretation of the main experimental observations described in the previous section. The strong increase of the F^+ desorption yield with temperature (Fig. 4) results from thermal activation of H-centers as the source of fluorine while the temperature-dependent time constants may be attributed to both an enhanced diffusion of fluorine at higher temperatures as well as to the temperature-dependent evolution of the metallization that is closely related to fluorine creation since both originate from F–H pair separation. The initial rise in the desorption yield means that the transport of fluorine is enhanced by the developing metallization, a phenomenon discussed in detail later. On the other hand metallization is also the limiting factor for desorption since during continued irradiation a rapidly increasing fraction of the surface is masked by large metal colloids that cannot be penetrated by the impinging electrons. Consequently the desorption efficiency decreases rapidly approaching a slowly decaying limit at a dosage of 2 mC where the reflectivity curve indicates a saturation for the surface metallization. The decrease of desorption efficiency as a function of current density is ascribed to a quenching of fluorine production due to recombination of F–H center pairs. Recently a saturation for F-center formation in NaCl due to recombination has been described where a saturation value of one defect per 30 lattice sites was given [20]. Since we are well above this value even for the smallest beam currents used for our experiments and know that the creation of stable F-centers is much harder in CaF_2 than in alkali-halides, it is straightforward to conclude that recombination quenching is the reason for the low desorption efficiency at high excitation density. This interpretation is strongly supported by the complementary reflectivity data revealing that the metallization efficiency also is the smallest for the highest electron density and vice versa. In conclusion we can say that we found that F^+ desorption from CaF_2

may be used as a sensitive probe for diffusion phenomena in near-surface regions of the irradiated crystal.

The last question to be answered is that about the nature of the fluorine transport from the bulk to the surface. Presently our experiments do not allow to determine which of the possible species will predominantly account for the substitution of fluorine at the surface. However, from literature we know that in CaF_2 fluorine can be stored in (and consequently also released from) H-center clusters that may grow to a mesoscopic size in the form of dislocation loops [6]. Furthermore, I-centers have been shown to be very effective for fluorine transport in CaF_2 [21,22]. Especially in a situation where charging induces strong electric fields in the crystal it is very likely that I-centers (carrying negative charge) are driven towards the positively charged region very close to the surface [14]. Also, it cannot be excluded that F^0 or even F_2 gas is created in the bulk and migrates to the surface. Possible processes for the creation of these species might be an ionization of I-centers or their neutralization by V_k -centers or F^+ . Although, direct evidence for cavitation in fluorides and a subsequent release of neutral fluorine could not be presented, several authors proposed such a process [23,24].

Also for the discussion of fluorine transport we believe that the electron-induced metallization plays an important role. As can be seen on AFM images, metallization leads to a highly eroded CaF_2 surface layer opening many channels for pipe-diffusion to the surface [25]. We also recognize that in CaF_2 with its high efficiency for the formation of both, anionic as well as cationic clusters, electron irradiation eventually leads to the formation of two stable phases namely metal colloids and H-center clusters that are chemically relatively inert due to their band-like electronic structure and, hence, fluorine is not easily captured by metal colloids on its way to the surface. We believe that this is the main reason for the initial rise in fluorine desorption efficiency observed for low dosages.

Our present understanding of electron-stimulated desorption from CaF_2 with high excitation density at elevated temperatures can briefly be summarized as follows: The emission of neutrals predominantly results from thermal or thermally stimulated processes; i.e. fluorine is released after diffusion to the surface while calcium is thermally evaporated from the surface or even more likely from surface colloids. The latter process accounts for the delayed emission of metal. F^+ desorption originates from an Auger-initiated desorption solely at the surface, however, after removal of the first fluorine layers this process is controlled by diffusive fluorine substitution from the bulk.

However, we expect that there are additional mechanisms contributing to the desorption of neutrals namely desorption resulting from excitonic processes [20] at the surface that may either be hidden in the background of

thermal emission or appear as a hyper-thermal component as predicted by first theoretical studies [26,27]. Recently, it has been shown by inverse photoemission that the irradiation of CaF_2 by electrons with energies as low as 10 eV results in metallization phenomena similar to those observed for higher energies [28]. This observation strongly supports the assumption that also in CaF_2 there are desorption mechanisms beyond the dominant Knotek–Feibelman process. More low-temperature experiments with low excitation energy and density and well prepared surfaces are needed for the investigation of these interesting new features.

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