

Characterization of Ca aggregates on CaF₂ (111)-surfaces by atomic force, XPS, and fluorescence microscopy

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In this contribution we report on the metallization of (111)-surfaces of CaF₂ single crystals as a result of low energy electron irradiation. An in-situ control of the spatial distribution of the metal coverage was obtained by rapidly scanning a low intensity electron beam across the irradiated area and monitoring the STE luminescence radiation. Metallized spots are identified by a reduced luminescence intensity. Surface stoichiometry was tested by XPS-microscopy. The spatially resolved observation of line intensities as well as line shifts revealed an effective metallization and oxidation of the surface. Using atomic force microscopy we found evidence for a 3-dimensional island-like formation of Ca aggregates with a size up to 12 μm diameter. Results for cluster formation in the center of the irradiating beam are compared to those from outer regions. The size distribution of the aggregates reproduces the different levels of electron dosage across the beam profile.

1. Introduction

The metallization of a CaF₂ (111)-surface by low energy electron irradiation has been studied by several techniques. In early work, Strecker et al. [1] presented results on the metallization process by Auger electron spectroscopy and photoemission studies. Metal cluster formation in the bulk of CaF₂ has been studied extensively by Alcalá et al. [2] with optical spectroscopy.

In previous papers [3–5] we have investigated the development of metallization as a function of electron dosage and crystal temperature by probe beam techniques. It has been shown that the overall rate of metallization is determined by a thermally stimulated process with an activation energy of about 0.3 eV.

The purpose of the present paper is to investigate some steps of the metallization process in more detail. We first introduce fluorescence detection as a simple tool for the identification of metallized spots on an irradiated surface. Second some features of surface oxidation are investigated by X-ray photoelectron spectroscopy (XPS). Third, AFM images from surface regions exposed to different doses of electron irradiation are presented.

One striking observation found by visually inspect-

ing metallized spots is the appearance of a higher density of smaller scattering centers at the periphery of the metallized spot for higher electron dosages as shown in Fig. 1. The size and shape distribution of aggregates across the electron beam diameter is determined by two factors, (1) the electron beam intensity profile providing different metal production rates, and (2) surface diffusion of metal during irradiation. To investigate these phenomena in detail, AFM images of metallized surface regions have been taken at several locations across the irradiated spot and are compared with each other.

2. Experimental

The CaF₂ crystals were irradiated under UHV conditions utilizing an electron gun operated at 900 eV beam energy and 1.5 μA beam current focused into a spot of approximately 1 mm diameter. For metallization experiments typical irradiation times at one spot ranged from 10 s to 1000 s (see Fig. 2). Fluorescence detection was done in-situ by scanning the electron beam at lower beam current over the entire surface within 150 s, thus maintaining a much lower electron dose than for the primary irradiation. The fluorescence light was collected by a solar-blind photomultiplier mounted at a sapphire window facing the sample surface. To enhance sensitivity and reduce dosage the electron beam was chopped during the fluorescence

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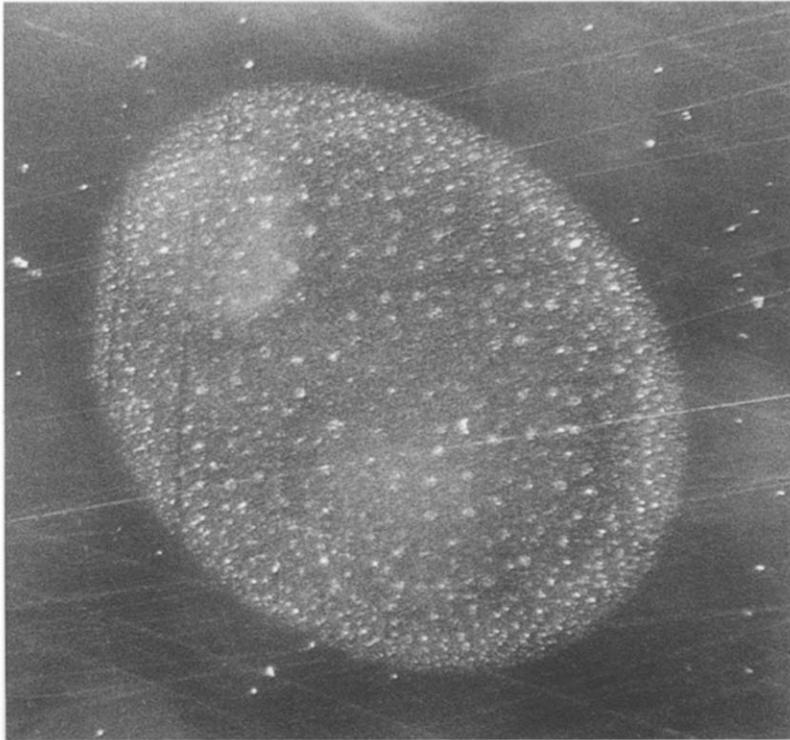


Fig. 1. Optical microscopy image of a spot irradiated for 1000 s. Surface area shown is approximately 4 mm².

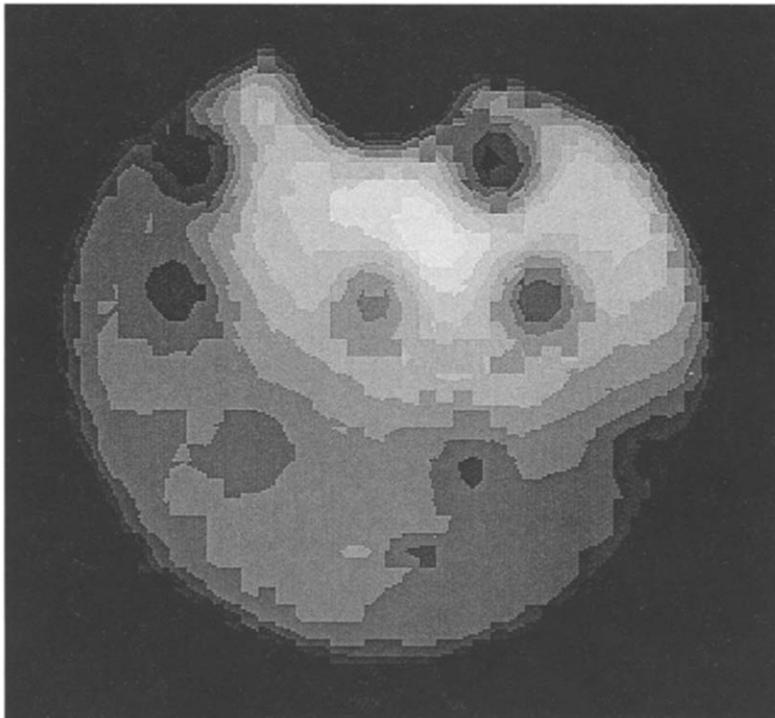


Fig. 2. Fluorescence image of the entire crystal (7 mm \varnothing). Areas with reduced luminescence intensity indicate spots that have been irradiated for 10, 20, 50, 100, 200, 500 and 1000 s.

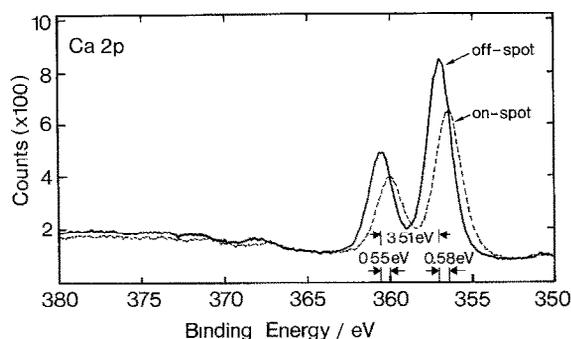


Fig. 3. Ca $2p_{3/2}$ line doublet. Details from XPS spectra taken at a spot irradiated for 200 s (on-spot) and in an unirradiated surface region (off-spot).

measurements and the photomultiplier signals were processed by a lock-in amplifier. More details about the experimental apparatus as well as sample preparation can be found elsewhere [4,5]. In contrast to previously presented measurements, results shown here were obtained from crystals cleaved in air and immediately transferred into the vacuum without polishing or any other surface treatment. The crystal temperature was kept constant at 180°C.

Both XPS and AFM investigations were performed ex-situ: the former in another UHV chamber equipped with an Al- K_{α} X-ray source and an electron energy dispersive imaging system with a lateral resolution of approximately 10 μm while AFM imaging was done in air with a Nanoscope II from Digital Instruments.

Since samples were exposed to the ambient atmosphere surface oxidation probably plays an important role for such ex-situ investigations.

3. Fluorescence measurements

A fast qualitative in-situ identification of metallized areas can be obtained by observing the STE luminescence radiation while rapidly scanning a low intensity electron beam across the crystal surface. A typical result of such a measurement is shown in Fig. 2. On unirradiated regions the electron impact produces a homogeneous background of UV radiation exhibiting only smooth variations in intensity due to shadowing effects from the sample holder. A clear contrast, however, is obtained at metallized spots. The sample shown here has been irradiated with seven different dosages ranging from 10 s to 1000 s that can be discriminated qualitatively by the on/off spot contrast in luminescence intensity. A quantitative prediction of the change in intensity for a specific degree of metallization is difficult since the fluorescence intensity is determined by several processes. First, metallization changes the backscattering coefficient for the incoming electrons and metallic islands screen the CaF_2 surface, thus affecting the effective electron dose in two different ways. Second, UV radiation may be absorbed by the metallic layer, a process resulting in a reduction of fluorescence intensity. Therefore, for a quantitative analysis it would be necessary to calibrate the intensity

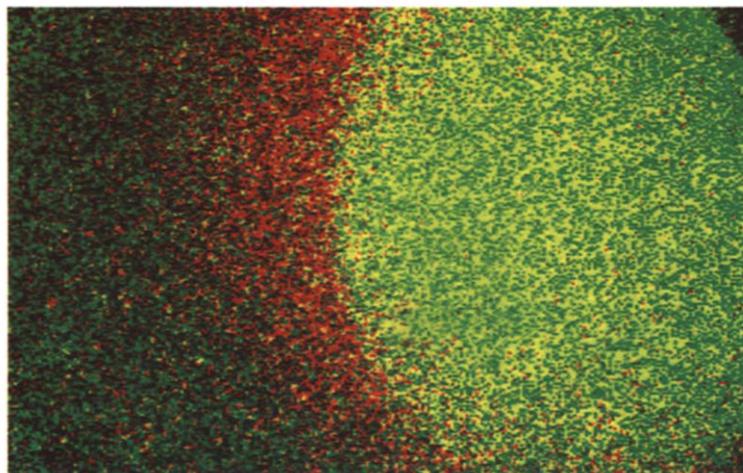
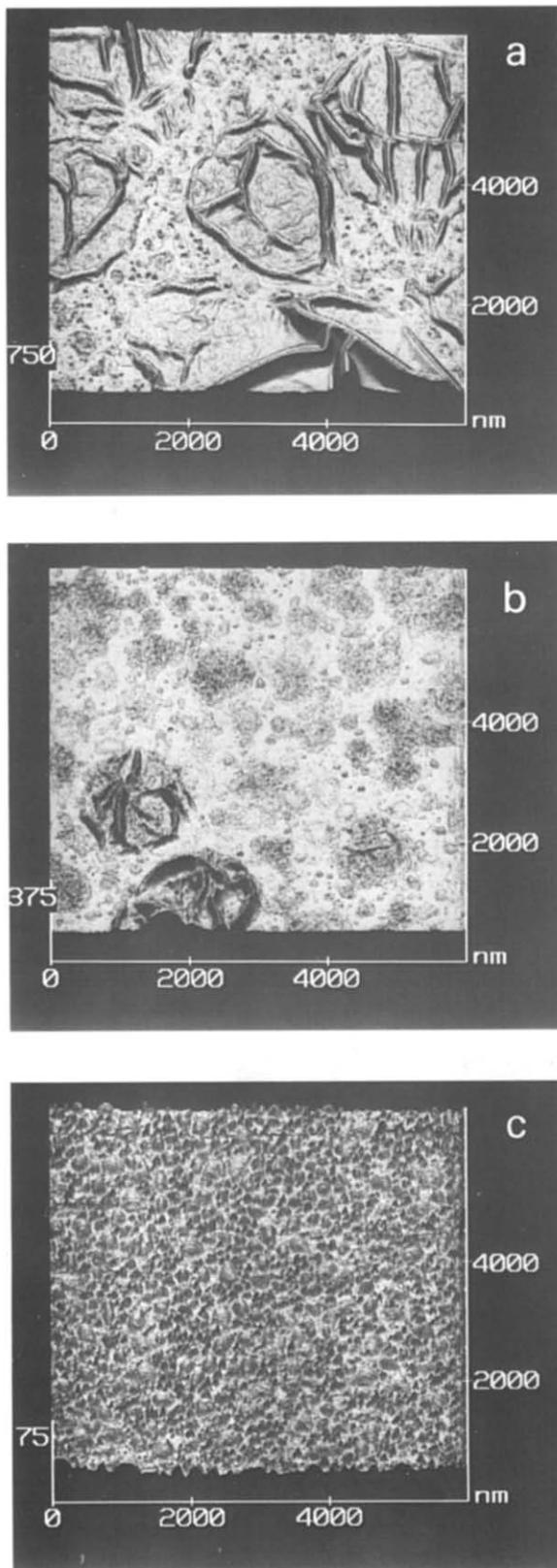


Fig. 4. XPS-overlay image for O 1s line (540 eV) and Ca line shift (356 eV). Green indicates the oxygen signal, red represents the Ca line shift signal and in the yellow shaded regions both signals are present.



curve for a reference sample under realistic measurement conditions and then apply the technique for in-situ measurements.

4. XPS-microscopy

Changes in surface stoichiometry have been monitored by spatially resolved XPS measurements. For a spot irradiated for 200 s it was found that the F 1s line intensity decreased by 55% for an on-spot measurement compared to the unirradiated crystal while the Ca $2p_{3/2}$ doublet intensity was reduced by only 20%, a result yielding clear evidence for an enrichment of Ca on the surface at irradiated spots.

Since XPS measurements were performed ex-situ we expected that metallized areas would also experience considerable oxidation. In fact, a strong rise in the O 1s line intensity was observed at irradiated spots. Furthermore, in these regions the Ca lines shifted by approximately -0.6 eV which is typical for the presence of CaO or CaOH (see Fig. 3) [6]. The oxidation effects, however, exhibited a non-uniform distribution when examined by XPS imaging. Fig. 4 shows an overlay image of the O 1s signal (green) and the signal of maximum Ca line shift at 356 eV (red). The circular pattern represents the shape of the metallized spot. The yellow colour in the center region indicates the presence of both signals at the same location as expected since both signals are caused by oxidation. The striking result of this measurement, however, is the appearance of a red ring surrounding the central region of oxidation. While the origin of this structure is not yet completely understood it can be anticipated that it is related to the peripheral ring of higher density, smaller clusters observed by visual inspection of the irradiated spots and confirmed by AFM. The cluster size distribution in the ring probably results in a different chemical reactivity at work in this region. Although the irradiation of the crystals was done under UHV conditions oxidation during the formation of metal aggregates cannot be excluded. Strecker et al. [1] and recently Richter et al. [7] have pointed out that due to the high reactivity of Ca metal, oxidation effects have to be considered even at very low O_2 or H_2O partial pressure. For a more detailed understanding of the physico-chemical processes occurring during metal layer formation, systematic measurements at various partial pressures of the oxidizing species have to be performed.

Fig. 5. Series of AFM images taken at a spot irradiated for 440 s. Images represent results from (a) the center region, (b) the surroundings and (c) the outer ring of the metallized area. Scales are in nanometers.

5. Atomic force microscopy

A large series of AFM images at spots of various dosages have been recorded and special care was taken to scan different regions across the irradiation beam profile. The general observation was the appearance of a great variety of metallization topographies and cluster size and shape distributions that crucially depend on the irradiation conditions.

Figs. 5a, 5b and 5c show a series of $6\ \mu\text{m} \times 6\ \mu\text{m}$ scans taken at a spot that has been irradiated for 440 s. Images were taken in the center, the intermediate region and the outermost ring, respectively. The center region that was subject to the largest dosage exhibits flat aggregates surrounded and intersected by ridges with an elevation of a few hundred nanometers. While the lateral extension of aggregates is restricted to approximately $2\ \mu\text{m}$ in this image we found metallic islands with a size up to $12\ \mu\text{m}$ at other spots. A general observation is that the elevation of the islands never exceeds about one fifth of their lateral dimension. The image taken in the outer ring is characterized by a densely packed structure of small, regularly shaped clusters. This corresponds well with the observation of strong light scattering in the ring since the cluster size distribution with a mean value of several hundred nanometers matches the range of optical wavelengths in the visible spectral region. In the image of the intermediate region both phenomena are present: large aggregates as well as small clusters and smooth surface regions without metal coverage are found for areas between metal particles. Although size and shape of metal islands vary with dosage and other experimental conditions, such a gradual change of metal island size across the metallized spot is a typical feature found for most investigated spots.

It was expected that due to the relatively high crystal temperature of 180°C during irradiation thermally stimulated surface diffusion would play a more significant role than in previous experiments done at 105°C . In fact, we found evidence for surface diffusion in several images taken at different spots within the irradiation profile. A discussion of surface diffusion phenomena will be presented in a forthcoming publication.

6. Discussion and conclusions

From the results obtained so far several conclusions about the formation of metallic layers on the electron irradiated CaF_2 surface at elevated temperature can be drawn. First, small regularly shaped metallic colloids are formed covering the surface uniformly. The details of formation of these colloids however are not yet clear

and are currently being investigated. Second, surface diffusion results in a redistribution of metal on the surface and the formation of larger aggregates at the expense of smaller clusters. As a result of this process regions between the aggregates are cleaned from metal. Third, step edges, scratches or other surface defects can act as nucleation centers for the formation of aggregates.

Presently most unclear is the development of the larger-shaped metallic islands. Depending on irradiation conditions a great variety of mostly irregular shapes has been found (also from measurements not shown here). Several mechanisms may play a significant role during aggregate formation. First, adhesion and surface tension phenomena will certainly determine the smooth surface structure and sharp boundaries of the aggregates. Second, surface defects can introduce random distortions determining specific unexpected configurations. Third, surface oxidation of the metal during aggregate formation may be a limiting factor for the amalgamation of clusters. Fourth, we recently found indication for a strong interaction of the electron beam with existing colloids leading to changes in the optical absorption spectrum [8]. Such an interaction may influence the apparent shape and distribution of aggregates and interfere with the amalgamation process.

Acknowledgements

Stimulating discussions with B. Schröter and W. Richter about the problem of in-situ oxidation are gratefully acknowledged. This work was supported by the Sonderforschungsbereich 337 of the Deutsche Forschungsgemeinschaft. R.M.W. and R.T.W. acknowledge support of NSF grant No. 9206745.

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