

BULK AND SURFACE METALLIZATION OF CaF_2 UNDER LOW ENERGY ELECTRON IRRADIATION

R. BENNEWITZ, C. GÜNTHER, M. REICHLING, E. MATTHIAS, R. M. WILSON*
and R. T. WILLIAMS

Fachbereich Physik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany;

Dept. of Physics, Wake Forest University, Winston-Salem NC 27109, USA

Electron irradiation of CaF_2 with 2 keV electrons causes metallization of the surface and near surface layers by the formation of colloids. Colloids on the surface are significantly larger than those in the bulk indicating a higher mobility of defects on the surface. Optical spectroscopy on extinction bands of bulk colloids reveals Ostwald ripening as the driving force for aggregation, while scanning force microscopy results suggest that similar processes dominate the early stages of surface colloid formation.

Key words: electron irradiation, CaF_2 , defect diffusion, metallization.

The development of metal clusters in the bulk of metal halide crystals after irradiation with high energetic ionizing irradiation has been studied theoretically¹ as well as experimentally^{2,3}. Metallization has also been observed at the surface of these materials during electron stimulated desorption experiments.^{4,5} The study of these processes is not only of general scientific interest but may also be important for certain applications in semiconductor industry. CaF_2 is a promising candidate for insulating layers in three dimensional structures of silicon based microcircuits due to the small lattice constant mismatch between these materials. In order to explore the possibilities of creating structures in CaF_2 films, low energy electron beam processing of CaF_2 has been studied recently by a process including metallization patterns and subsequent removal of the metal by water.⁶ In our contribution, we compare metal aggregation at the surface and metal colloid formation in the bulk of CaF_2 resulting from 1.5–2.5 keV electron irradiation with regard to the size of aggregates and the aggregation processes.

Electron irradiation and optical absorption experiments have been performed in an UHV chamber with a pressure below 10^{-9} mbar. The specimens were CaF_2 single crystals of UV grade window material (Karl Korth company) and the (111) surfaces have been studied. For extinction experiments we used monochromatic light from a xenon high pressure lamp modulated with a mechanical chopper in combination with a grating monochromator. Photodiode signals from incident and transmitted intensity were processed by a lock in amplifier. The surfaces were studied *ex situ* with a commercial Scanning Force Microscope (SFM). Several series of measurements made sure that the surface topography did not change essentially as a function of time after irradiation and during scans with the SFM.

The penetration depth of primary electrons with energies used in these experiments is not well known. However, we assume a relation between the maximum penetration depth D and the electron energy E (E in keV) of the form D (nm) = $40 E^{1.3}$ i.e. 65 to 130 nm for energies ranging from 1.5 keV to 2.5 keV.⁷ The depth of maximum defect creation probability is about 1/5 of the maximum penetration depth.⁸ It can be anticipated that the ratio between bulk and surface metallization is determined by both, the depth profile for defect creation as well as diffusion of defects.

To study the influence of the sample temperature *during* irradiation on the metallization process we irradiated one crystal at 150 K and another at 450 K. Spectra of both taken at 450 K are presented in Figure 1. The pronounced extinction band for irradiation at 150 K

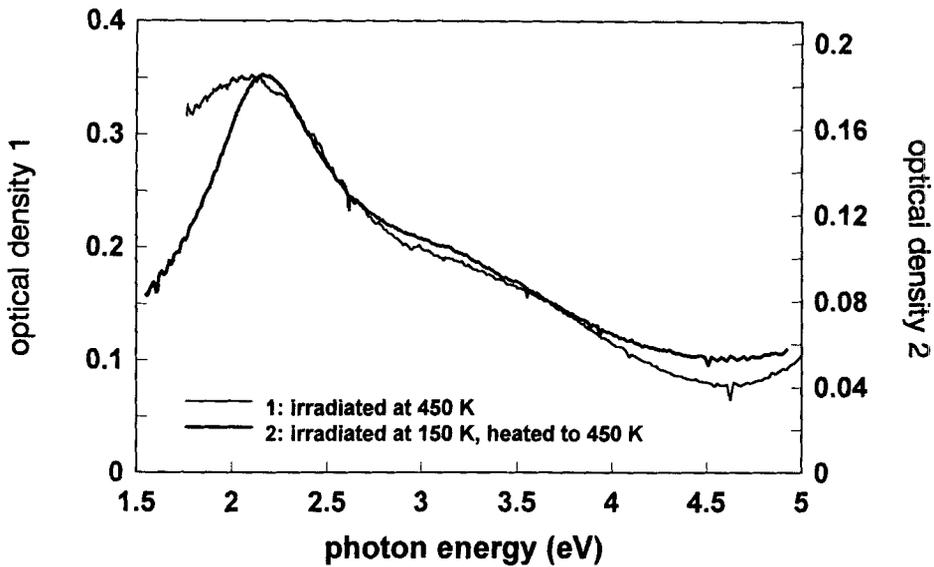


FIGURE 1 Extinction spectra of CaF_2 taken at 450 K after irradiation with 2.5 keV electrons. Different dosages have been chosen to obtain similar metallization for both irradiation temperatures.

with a maximum around 2.3 eV is in good agreement with calculations of light extinction by Ca colloids in the CaF_2 matrix based on a model of Orera *et al.*⁹ These calculations yield a monotonic relation between colloid size and peak position and a Lorentzian band shape of 0.9 eV width for colloids smaller than 40 nm. From Figure 1 we can extract a mean colloid radius of 23 ± 2 nm for the sample irradiated at 150 K and mean radius of 32 ± 3 nm for that irradiated at 450 K. The extinction band shape and width of the sample with low irradiation temperature represents a narrow size distribution while the one for high temperature exhibits a width much larger than predicted by the theory and, therefore, represents a colloid size distribution that is broadened toward larger colloid sizes. The weak shoulder at about 3.3 eV present in both spectra is due to absorption in F-centers.

Two samples have been irradiated at 150 K using 1.5 keV and 2.5 keV electrons. The development of the colloid extinction band has been studied during slow heating. At 150 K the samples exhibit a broad absorption between 1.5 eV and 4.5 eV photon energy after irradiation. We believe that this absorption is caused by a variety of F-center aggregates, like single F-centers (absorption peak at 3.3 eV), M-centers (2.38 eV), and R-centers (1.86 eV)¹⁰ up to small metallic clusters that are expected to absorb at about 2.5 eV. Heating the sample leads to the development of the Ca colloid absorption band starting at a temperature of about 230 K. The smallest colloid radius of 1 nm deduced from the spectrum is in agreement with the expectation for a F-center aggregate that develops a metallic band structure.¹¹ Further growth of the colloids during heating to 450 K is displayed in Figure 2. We find a sharp increase of the mean colloid radius from 1 nm to 25 nm in the narrow temperature range between 260 K and 300 K.

It should be noted that the integral amount of metallic calcium determined from the height and width of the absorption band does not change during the growth of the colloids below 350 K and that the number of F-centers, although it may change, is always very low

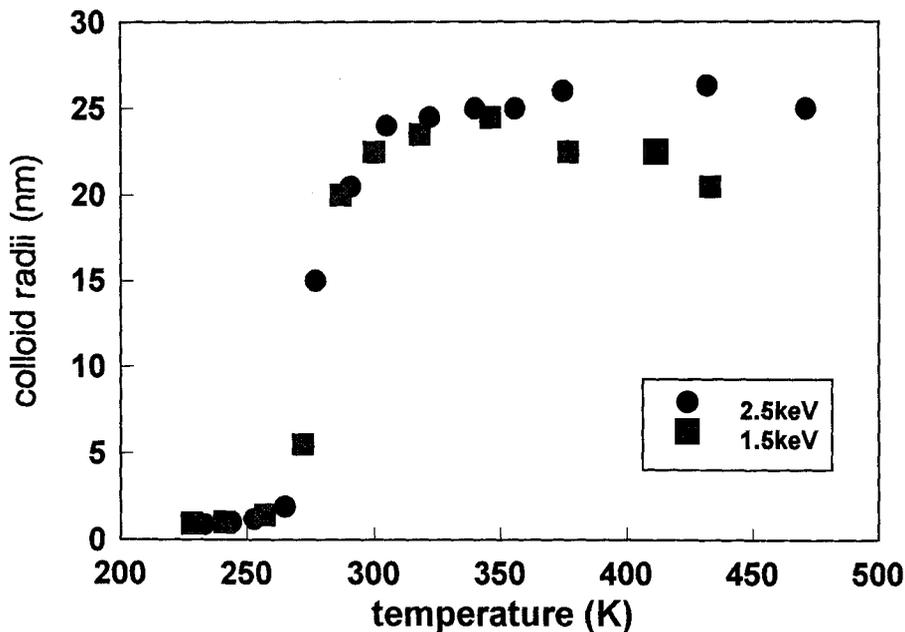


FIGURE 2 The development of Ca colloid size during heating after electron irradiation at 150 K.

compared to those aggregated in colloids. This indicates a colloid growth by a ripening process¹: the metal colloids and single F-centers are in an equilibrium that depends on the size of the colloids. The equilibrium concentration of F-centers exponentially approaches a minimum value for large colloids. In this way larger colloids will grow at the cost of smaller colloids when the concentration of F-centers is lower than the equilibrium for the small colloids but still higher than the equilibrium for larger colloids. Heating starts this process by increasing both the concentration and mobility of F-centers. The sharp increase of colloid size at 270 K may be due to the activation of F-centers from colloids or diffusion of F-centers.

For the irradiation at 150 K and subsequent heating, the assumption of a ripening process is supported by an analysis of the shape of the resulting absorption band which is similar to a Lorentzian curve with a band width of approximately 1.0 eV (Figure 1). This indicates a narrow distribution of colloid size in good agreement with predictions for the size distribution during a ripening process.¹

Above 350 K the amount of metal aggregated in bulk colloids decreases. This can be deduced from a lowering of the extinction observed in the original spectra. The enhanced mobility of F-centers causes diffusion of metal from the bulk to the surface, since the colloids are located in a layer close to the surface. The decrease of F-center concentration disturbs also the ripening process, i.e. the F-centers do not necessarily contribute to colloid growth but may alternatively be trapped by the surface. Consequently, colloid size decreases for temperatures above 350 K (Figure 2). This loss by diffusion is more

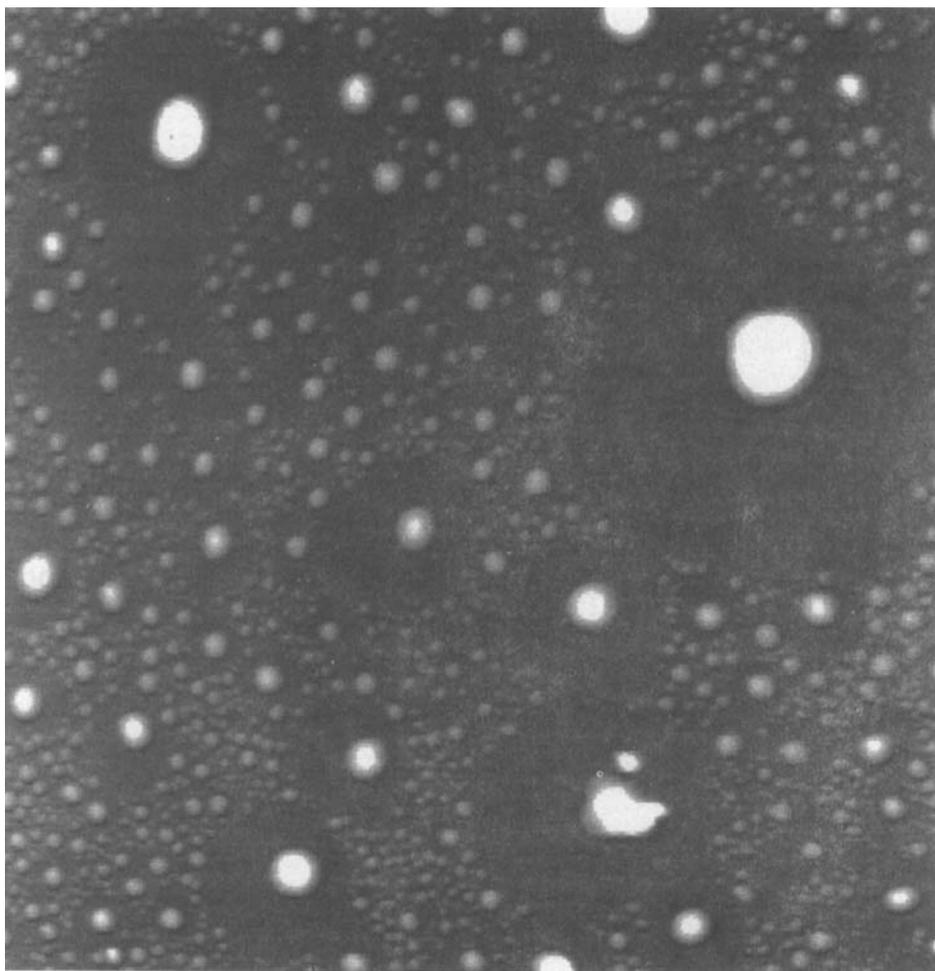


FIGURE 3 Scanning Force Microscopy image of the CaF_2 surface irradiated with 0.9 keV electrons (1 mm beam diameter), $12 \times 12 \mu\text{m}^2$, irradiated with less than $1 \mu\text{A}$ for 20 sec.

pronounced for the 1.5 keV irradiation because the effect depends on the mean distance of the colloids to the surface and, therefore, on the energy of the primary electrons.

The surface of CaF_2 is metallized by low energy irradiation not only by diffusion of F-centers, as mentioned above, but also by fluorine depletion. During the irradiation experiments we always find a strong fluorine desorption while calcium desorption is observed only for temperatures above 450 K. Scanning Force Microscopy was used to study the topography of surface metal aggregation. Figure 3 shows the SFM image of a cleaved surface irradiated with a low electron dose. The colloids on the surface are oblates with a typical relation of height to radius of 1 to 10. The smallest distinctable colloids on the surface are about the size of the largest ones in the bulk determined by optical spectroscopy, but many are significantly larger. This is a hint to a colloid mobility on the surface.

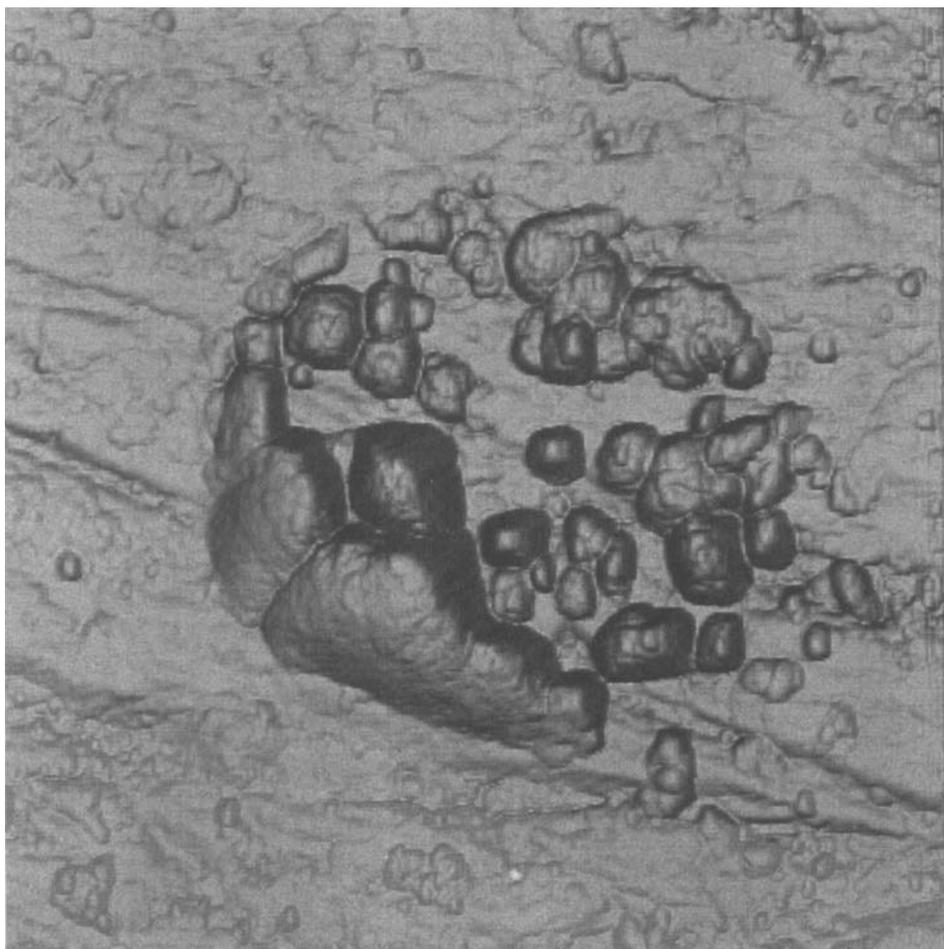


FIGURE 4 Scanning Force Microscopy image of the CaF₂ surface irradiated with 0.9 keV electrons, 3.3*3.3 μm^2 , irradiated with 1.5 μA for 200 sec.

The structure of the size distribution in Figure 3 suggests a model of diffusion of metal colloids on the surface, where smaller colloids which come into contact with large colloids will be swallowed by the latter. Bigger colloids grow at the costs of smaller similar to the process in the bulk what could be regarded as a ripening process at a larger scale. It is presently not clear whether the diffusion is driven by the higher temperature during the irradiation experiment or by the beam of primary electrons.

The result of longer irradiation is presented in Figure 4. The larger colloids tend to form torn up aggregates, which are circularly shaped but still show some reminiscent structure of their constituents. For a possible explanation of this feature we recall that even in UHV the developing metal on the surface can oxidize.¹² This might yield a passivation of the surface of the colloids that prevents the amalgamation of a crude aggregate into one smooth colloid.

In summary, bulk and surface of CaF_2 are metallized under low energy electron irradiation in a similar process of defect production, aggregation and ripening yielding a narrow distribution of metal colloids. The different crystal structure and the lower dimensionality of the diffusion at the surface is manifested in the oblate shape of the colloids and their bigger size which is due to a higher mobility of defects. Additionally, on the surface complete metal colloids may move while in the bulk material transport is only due to diffusion of point defects. It is obvious from Figure 1 that the electron beam interferes with the developing colloids at higher temperatures. At 450 K the electron beam increases the concentration of F-centers which are already mobile and causes a broadening of the colloid size distribution towards larger colloids compared to the distribution after irradiation at 150 K and subsequent heating to 450 K. Also, on the surface the mobility of defects and, possibly, the mobility of metal colloids is enhanced by the electron beam as shown by the fact that the SFM images of the early metallization stage (Figure 3) represent a frozen state of ripening.

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