The kinetics of CaF_2 metallization induced by low-energy electron irradiation

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Abstract

Results of experimental and theoretical studies on metal colloid growth after irradiation and subsequent heating of CaF_2 are presented. Samples at a temperature of 200 K were irradiated in UHV for 30 min with 2.5 keV electrons. After irradiation samples were heated at a rate of about 1 K/min and colloid formation was investigated by optical extinction spectroscopy. Colloid radii as well as the amount of metal were determined from a Mie scattering analysis. A steep rise in colloid size was observed between 260 and 270 K. The concentration of F centers not aggregated into colloids was below the detection limit for all temperatures. A microscopic theory of F and H center aggregation taking into account defect creation, interaction, diffusion, and annihilation of dissimilar defects is presented. Theory successfully reproduces the main experimental observations of small colloid formation at low temperatures during irradiation and the onset of colloid growth at a temperature where F centers become mobile. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The primary radiation defects in ionic solids – F centers (electron trapped by an anion vacancy) and H centers (interstitial halide atoms) – under intensive irradiation and at high enough temperatures are known to aggregate resulting in the formation of *metal colloids* and gas bubbles (see [1] and references therein). Metal colloid formation occurs via diffusion-controlled aggregation of F centers, the smallest aggregate centers $(F_2(M), F_3(R))$ with characteristic optical absorption bands, whereas large aggregates transform into metal colloids with a broad optical extinction band. Intensive experimental studies on the conditions of metal colloid formation were done for many alkali and alkaline-earth halides, including NaCl [2], LiF [3],

and CaF_2 [4]. In this paper we pursue earlier work [5] on colloids formed in CaF_2 upon irradiation with low energy electrons and photons and try to elucidate the process of colloid growth during annealing experiments in some detail.

2. Experimental procedure

Experiments were performed on single crystals of CaF_2 cleaved in air along their natural cleavage directions and then introduced into an ultra-high vacuum chamber. Crystals had dimensions of $20 \times 20 \times 5$ mm^3 and were mounted in a copper sample holder that could be heated to temperatures up to 650 K by resistive heater elements and cooled down to 200 K by a liquid nitrogen supply. The sample holder was designed as a frame allowing light transmission through most of the 4 cm^2 surface area. Transmission spectroscopy experiments were performed with monochromatized light from a Xe high pressure lamp and two photodetectors sampling a small fraction of the incident and the transmitted light. Absolute calibration for calculating the optical density of the irradiated sample was accomplished by reference measurements performed prior to electron irradiation and with the sample removed from the optical path. By this referencing procedure, extinction from the bare substrate and vacuum chamber windows as well as the wavelength dependent intensity of the light source was completely removed and spectra shown here solely represent changes in optical density introduced by electron irradiation. For the irradiation with low energy electrons we used an electron source providing a current density of 100 μA/cm^2 where the current was homogeneously distributed over a spot of 4×4 mm^2 at the sample surface. Optical transmission was measured in the center of this spot over about half of the area covered by the electron beam.

3. Experimental results

The aim of the present study was to quantitatively describe the size evolution of colloids prepared at low temperature during heating after

irradiation. Crystals were irradiated with 2.5 keV electrons for 30 min where the temperature during irradiation was kept constant at 200 K. After irradiation, crystals were heated at a rate of about 1 K/min and a series of consecutive spectra was taken to observe the time evolution of the optical extinction. A typical evolution is displayed in Fig. 1. Spectra were measured from 1.5 to 4 eV photon energy. Fig. 1 displays only the energy range up to 3 eV since we did not observe any significant features at higher photon energies.

A striking observation was that a measurable concentration of *F* centers (an *F* center absorption peak would be expected at 3.3 eV photon energy [6]) was not observed at any point of the evolution and also not in spectra obtained for other irradiation temperatures. At low temperatures we find a rather broad spectroscopic feature that cannot be assigned to any type of defect or defect aggregate but this band directly develops into a colloid band during heating. A common observation in optical spectra obtained during heating experiments is that the colloid peak undergoes a transformation in position and shape until it is stabilized at a certain temperature level. This transformation is a result of the temperature dependent change in colloid size; i.e. colloids grow until almost all have reached an equilibrium size that is stable with respect to moderate further heating or subsequent cooling. This phenomenon is commonly referred to as a process of colloid *ripening* following the initial stage of colloid *precipitation* [7]. During this
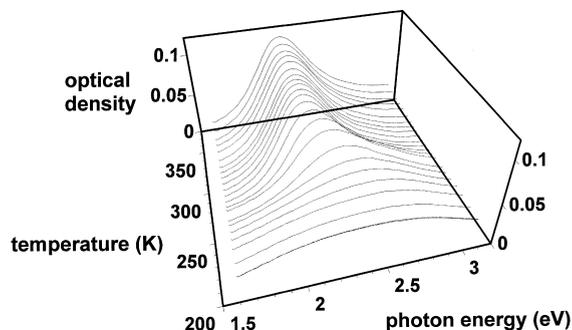
Fig. 1. Development of optical extinction spectra during heating of a CaF_2 crystal after electron irradiation (2.5 keV electrons) with a dosage density of 180 mC/cm^2 at a temperature of 200 K.

process large colloids grow on the cost of smaller ones by the exchange of F centers and within the finite time of experimental observation an initially broad distribution of colloid sizes is transformed into an ensemble of large equally sized colloids. Spectra as shown in Fig. 1 provide the possibility to extract quantitative information about size and density of colloids and their evolution with temperature.

Colloid bands can be predicted from the Mie theory for the extinction of light by spherical metallic particles [8]. Mie absorption bands were calculated by an algorithm suggested by Bohren and Huffman [9] where the pressure exerted on Ca colloids in CaF_2 was accounted for by a correction suggested by Orera and Alcalá [4]. We found that except for the very early stages of heating, experimentally observed spectra could well be fitted by Mie bands, indicating that it is justified to approximate colloids as spherical metallic particles and their size distribution is rather sharp. From the fitted curves we extracted the mean colloid radius and the areal density of metal and obtained a temperature series as shown in Fig. 2. The volume concentration of metal, i.e. the number of removed fluorine pairs per cm^3, can only be estimated at the present stage since the depth of the metallized volume is not precisely known. The areal colloid density given here denotes the amount of metal measured in cm^3 present in a column extending into the crystal with a unit cross-section of 1 cm^2. It is seen that the temperature of 250 K is
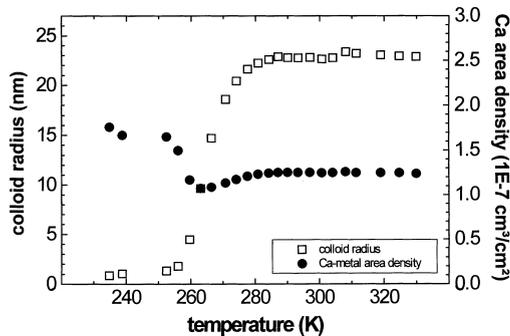
of critical significance for the ripening process and we interpret this step as due to thermal activation of F center movement. The ripening process is restricted to a rather narrow temperature interval and the colloid size does not change significantly above room temperature. The total amount of metal condensed in colloids is roughly constant. We regard the fluctuations observed below and in the ripening region as artefacts resulting from data analysis that is based on a narrow size distribution while we expect a broad range of colloid sizes in this temperature range. While the observation of ripening clearly indicates an exchange of F centers, the concentration of this species must be very low at any stage of the experiment since we do not detect F centers in our spectra. We performed simulations of combined spectra based on the Mie theory for colloids and modelling F centers by the Smakula formula [10]. In such spectra two absorption peaks appear and their relative intensities depend on the fraction of metal stored in free F centers compared to that condensed into colloids. This fraction was systematically varied in the model calculations and, knowing the detection sensitivity of our spectroscopic apparatus we can estimate that we should be able to detect a concentration of F centers corresponding to an amount of metal of less than 1% of that found for a typical Mie band.

4. Theoretical modelling

There exist several theories of the radiation-induced defect aggregation and colloid formation (see [11] and references therein). The most refined is a *microscopic* formalism treating elementary processes at atomic scale and using no fitting or uncertain parameters but several basic defect parameters like diffusion energies and interaction energies. An accurate, discrete-lattice theory of this kind has been developed recently [12] and applied to the F center aggregation in NaCl under irradiation [13]. This theory is used in the present study. In our calculations we consider the creation of H and F centers (generalized hereafter as defects A and B), with a dose rate p, and their recombination when during their migration defects approach each

Fig. 2. Mean colloid radius and areal metal density of calcium colloids in CaF_2 as a function of temperature derived by a Mie band analysis from the series of spectra shown in Fig. 1.

other to within the nearest neighbour (NN) distance. Defect interaction (interaction energies E_{AA}, E_{AB} and E_{BB}) is incorporated in our model via three types of NN attraction energies between the defects.

That is, the input parameters for colloid growth simulations are activation energies for diffusion and attraction energies between defects, as well as temperature and dose rate (which in present experiments is estimated as 10^{17} cm^{-3} s^{-1}). Activation energies for H and F centers in CaF$_2$ are assumed to be 0.46 and 0.7 eV, respectively, according to data available in literature [14]. The attraction energies determining H and F center attachment/detachment to/from similar-particle aggregates are not well known. Calculations of the elastic interaction between two nearest F centers in KBr yield an attraction energy of about 0.02 eV [15]. This value we also used in our calculations. For simplicity we assume that similar particle interactions are equal for different defects, $E_{int} = E_{AA} = E_{BB}$. We also neglect dissimilar particle interaction, i.e. $E_{AB} = 0$, since nearest neighbour F, H pairs are assumed to annihilate.

We calculate the time development of both defect densities (total concentrations) $n_B(t), n_A(t)$, as well as concentrations of single defects $n_\lambda^{(1)}$ (no other defects in nearest neighbour sites) and *dimer* defects $n_\lambda^{(2)}$ (two similar defects are nearest neighbours) where λ denotes A or B. Aggregates are characterized by the integral values of the number of particles N_A, N_B therein and their radii R_A and R_B.

First, we studied the kinetics of defect concentration growth during irradiation at low temperatures when the F centers are immobile but the H centers are moving either slowly (150 K) or are already quite mobile (193 K). Calculations show that at the end of 30 min irradiation the defect concentration grows still linearly with time; the saturation could be expected after two hours of irradiation only. The magnitude of the defect concentration 10^{20} cm^{-3}s^{-1} achieved, agrees reasonably well with experimental data shown in Fig. 2 when assuming a penetration depth of 10^3 Å for the 2.5 keV-electron [16].

The time development of the total H-aggregate concentration (n_A), single H and dimer H_2 centers

is illustrated in Fig. 3. Total concentrations of H centers almost coincide at the two temperatures; H concentration at 150 K irradiation temperature exceeds that at 193 K irradiation only for $t > 70$ min when irradiation is already switched off and the sample is heated by about 50 K. It is seen that the concentration of single H centers, $n^{(1)}$ at 193 K, decreases due to the growth of the dimer concentration, $n^{(2)}$, and the latter drops also at a certain time t_0 due to the growth of larger aggregates. The time t_0 decreases by 3 orders of magnitude when the irradiation temperature is increased by only 43 K.

F centers are immobile at such irradiation temperatures and their aggregation occurs only during sample heating after irradiation. Assuming a defect interaction energy $E_{int} = 0.02$ eV the size of F center aggregates (curve 1 in Fig. 4 (a)) and the mean number of defects therein (curve 2 in Fig. 4(b)) start to grow at 250 K, just when the F centers become mobile. This temperature is in good agreement with experimental data discussed in Section 3 as well as with the temperature of a rapid growth of M_A center concentration under pulsed electron irradiation of CaF$_2$ doped with Na, where this process also occurs through F center diffusion [17]. An increase of the interaction energy by 0.01 eV considerably shifts the colloid growth process to higher temperatures (curve 2 in Fig. 4(a)), since stronger attraction makes small aggregates more stable against ripening.
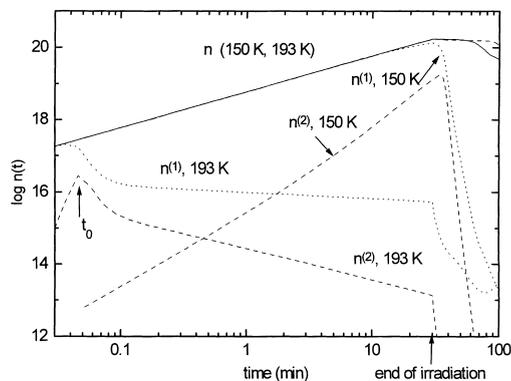
Fig. 3. Calculation of the H center aggregation with a dose rate of 10^{17} cm^{-3} s^{-1} during irradiation at 193 and 150 K. The curves and their labelling are explained in the text.
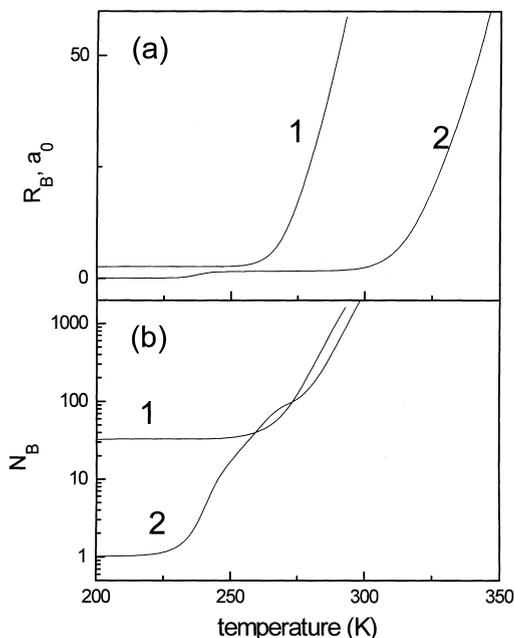
Fig. 4. (a) Heating-induced growth of the mean radius of F center aggregates, R_B, (in units of the F–F distance, i.e. 2.73 Å). (b) Mean number of particles inside each aggregate, N_B. Curves 1 and 2 in (a) are for defect interaction energies of 0.02 and 0.03 eV, respectively. In (b) curves 1 and 2 are for the activation energy for the radiation-enhanced F center diffusion of 0.4 eV and neglecting this effect.

Since colloid formation is experimentally observed at irradiation temperatures below the activation temperature for F center diffusion we propose aggregation during irradiation and that this process is characterized by a low activation energy.

To simulate such a *radiation-enhanced* process, we performed calculations for the F center effective activation energy of 0.4 eV under irradiation and usual energy of 0.7 eV after irradiation. Curve 1 in Fig. 4(b) demonstrates the formation of small stable F aggregates with a radius of several nm. These small aggregates transform into larger aggregates only at temperatures above the F center mobility edge (remember that the critical temperature depends also on the interaction energy (cf. curves 1 and 2 in Fig. 4 (a)).

A study of the dynamics of the total F center concentration as a function of the temperature shows that at 200 K only single F centers exist in a concentration close to 10^{20} cm^{-3} s^{-1}, whereas the concentration of dimers is smaller by 3 orders of magnitude. As temperature reaches that of the F center mobility, both concentrations drop by many orders of magnitude. However, the total F center concentration decreases insignificantly during heating up to 350 K, thus indicating that most of F centers have transformed now to large aggregates.

Acknowledgements

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