Environmental and In Situ SEM/TEM

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Observation of the transformation behavior of CdSe-Cr_2Se_3 nanoparticle composites by in-situ TEM techniques

M. Deng[1], V. Hrkac[1], K. Gerwien[2], B. Hesseler[2], F. Beiroth[2], V. Duppel[3], W. Bensch[2], L. Kienle[1]

[1]University of Kiel, Technical Faculty , Kiel, Germany
[2]Uinversity of Kiel, Institute of Inorganic Chemistry, Kiel, Germany
[3]Max Planck Institute for Solid State Research, Stuttgart, Germany

mden@tf.uni-kiel.de
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The synthesis of multinary nanomaterials is generally a complicated process due to occurrence of separation phenomena, e. g. the formation of mixtures containing binary compounds instead of ternary nanoparticles. Such limitation particularly applies when using soft chemical approaches for the syntheses, since low temperatures favor formation of metastable and inhomogeneous products. A few years ago we reported about a well-defined phase separation occurring during attempts to prepare ternary nanoparticles with composition $CdCr_2Se_4$ namely the formation of homogenously dispersed CdSe nanoparticles in an amorphous Cr_2Se_3 matrix [1]. Here we focus on the transformation behavior of CdSe-Cr_2Se_3 0-3 nanocomposites by external stimuli. Two pathways are selected for in-situ transmission electron microscopy (TEM) observations: i) High dose electron beam irradiation and ii) In-situ heating.i). Before an exposure with a high dose of electrons, the nanocomposite exhibited clearly a 0-3 microstructure, cf. the high resolution (HR)TEM micrograph in Figure 1a, top. The associated selected area electron diffraction (SAED) pattern in Figure 1a (bottom) shows strong Bragg reflections located on concentric rings besides diffuse rings of intensity. The diameter of these rings corresponds to the characteristic d-spacings of Cr_2Se_3 (diffuse rings) and CdSe (Bragg intensities) as labeled in the SAED pattern. After electron beam irradiation, the rings originating from the CdSe particles disappeared (Fig. 1b, bottom), and the remaining faint and diffuse intensities on concentric circles can be addressed to the unchanged Cr_2Se_3 matrix. At the previous positions of CdSe nanoparticles newly formed holes are clearly visible in the HRTEM micrograph (Figure 1b, top). Additionally, EDX spectra measured in the same region confirm the selective removal of the CdSe component. This finding was unexpected as the electron beam dose applied in the well known electron beam evaporation method [2] (used for synthesis of CdSe) is 10^{12} times higher than the dose selected for the TEM experiment.

ii) In the second in-situ experiment the dose of electrons was kept low, while the 0-3 nanocomposite was sequentially heated to 800 °C on a heating stage. Concerning CdSe a disappearance of the characteristic reflections in SAED was observed after reaching 550 °C. This result was confirmed by chemical investigations as no Cd could be detected after the heating procedure indicating an evaporation of the CdSe nanoparticles. The thermal evaporation temperature of CdSe in TEM significantly dropped in contrast to that of the conventional thermal physical vapor deposition. [3] Unlike the in-situ irradiation experiment and in contradiction to the phase diagram of bulk Cr_2Se_3 [4] the formation of poorly crystalline Cr after heating was detected. Figure 2(a) depicts a SAED pattern recorded on a region of the composite at 800 °C. The d-spacings of two broad diffuse rings in the SAED pattern can be assigned to (011), (112) planes of chromium (space group: Im-3m, bcc type). Moreover, structural studies performed at room temperature after heating showed also the presence of large crystalline Cr nanoparticles with an hexagonal symmetry (space group: $P6_3/mmc$, hcp type), as demonstrated in Figure 2b. This finding is in agreement with the commonly known phase diagram of Cr, featuring that the hcp type Cr is stable at room temperature, whereas temperatures above 100 °C favor the formation of bcc-Cr [5].

Another feature of the heating studies was the detected increase of the crystallinity of Cr_2Se_3 nanoparticles in comparison to the in-situ irradiation experiment. The d-spacings of the strong Bragg reflections arising in the SAED pattern of Figure 2a matches with literature values (space group: R-3) [6]. High resolution imaging supports these findings as presented in in the HRTEM micrograph and the FFT pattern of Figure 2c.

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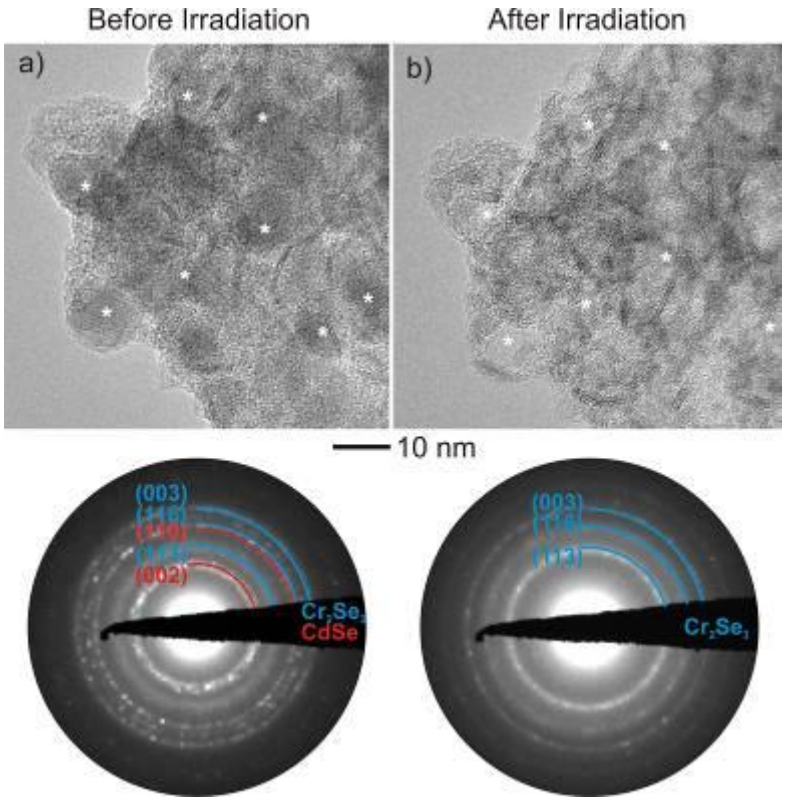

Figure 1. Comparison of HRTEM micrographs and SAED patterns recorded before (a) and after (b) in-situ transformation by exposure with a high dose of electrons evidence the removal of CdSe nanoparticles from the nanocomposite. The asterisks mark the positions of the CdSe nanoparticles present in the pristine material before the in-situ transformation.

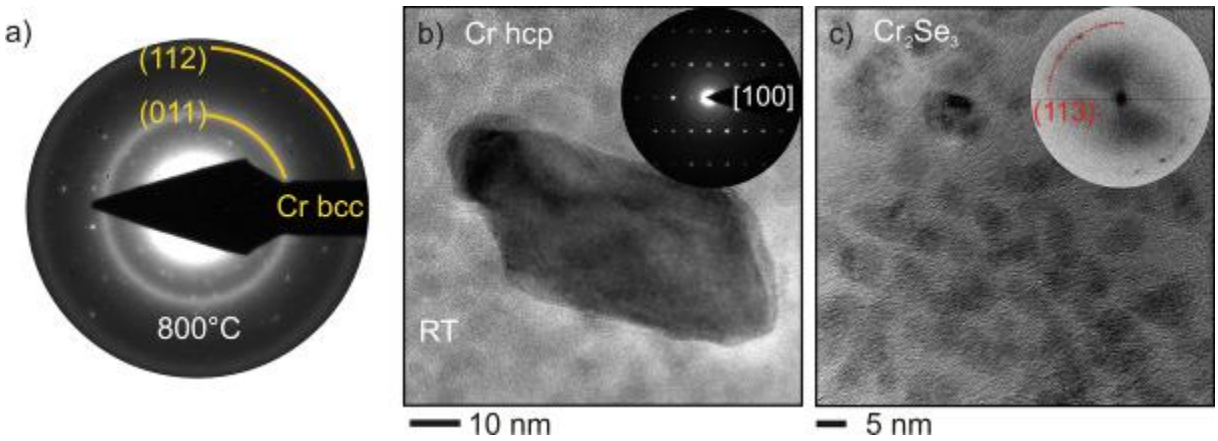

Figure 2. (a) SAED pattern after in-situ heating. (b) HRTEM micrograph of a Cr nanocrystal formed after heating with a corresponding SAED pattern as the inset. (c) HRTEM micrograph of Cr_2Se_3 particles after heating. Inset reveals the corresponding FFT.