

**Experiment title:**

Study of the surface quality and crystal structure of CdS and ZnS nanoparticles in polymeric films.

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Report:

Nowadays the synergy among different disciplines in the field of nanotechnology is giving much impulse to hybrid organic/inorganic nanocomposites to tailor functional properties. A class of hybrid nanocomposites can be obtained by combining polymeric materials and inorganic nanoparticles. Nanoparticles of metals, oxides, semiconductors are among the most studied inorganic nanometric materials because of their peculiar electronic [1], optical [2] and catalytic properties [3] due to quantum-size effects. Our interest towards nanoparticle/polymer nanocomposites is motivated by the application that such materials can have in the field of organic electronics [4,5]. In particular, we study cadmium sulphide (CdS) nanoparticles grown directly within a polymer matrix by means of thermolysis of metal bis-thiolate precursors $\text{Cd}(\text{SR})_2$, where R is the organic part of the molecule [6]. The precursor is added to the polymer in solution and a polymeric film is successively obtained by spin coating the solution. As a polymer we have employed the cyclic olefin copolymer topas, which is highly transparent, water resistant, and suitable for different lab-on-chip systems. Thermal treatment of the bulk precursor/polymer system causes the decomposition of the precursor and the aggregation of the Cd and S atoms into CdS nanoparticles within the polymer. We found that the nanoparticle size and aggregation depend upon the annealing conditions, namely temperature and duration of the treatment [7].

In our experiment at ID01 (#CH2475) we studied the growth of CdS nanoparticles for different annealing conditions both ex-situ and in-situ. Grazing incidence diffraction (GID) and grazing incidence small angle scattering (GISAXS) experiments were performed on precursor/polymer films spin coated on Si/SiO₂ substrates. A small furnace mounted on the diffractometer was used, with the sample in primary vacuum ($\sim 10^{-1}$ mbar). The incident beam energy was kept at 12 KeV. While during the ex-situ experiments the crystalline signal from the particles was weak and hardly detectable, the in-situ studies have given very different results. GISAXS measurements were performed from room temperature up to 300°C by using a CCD camera. The initial features due to the Bragg diffraction from the precursor (Fig.1a) change by effect of the temperature (Fig.1b and 1c). At 150°C diffraction peaks arranged in hexagonal symmetry were observed in the GISAXS pattern, corresponding to an inter-particle distance of about 2.7nm, comparable with the particle size. This peculiar diffraction pattern becomes very well defined at 170°C, as shown in Fig. 1b. Our

interpretation of these results is that at this temperature the CdS nanoparticles are close packed and regularly arranged in an hexagonal 3D lattice with lattice parameter of 2.7nm.

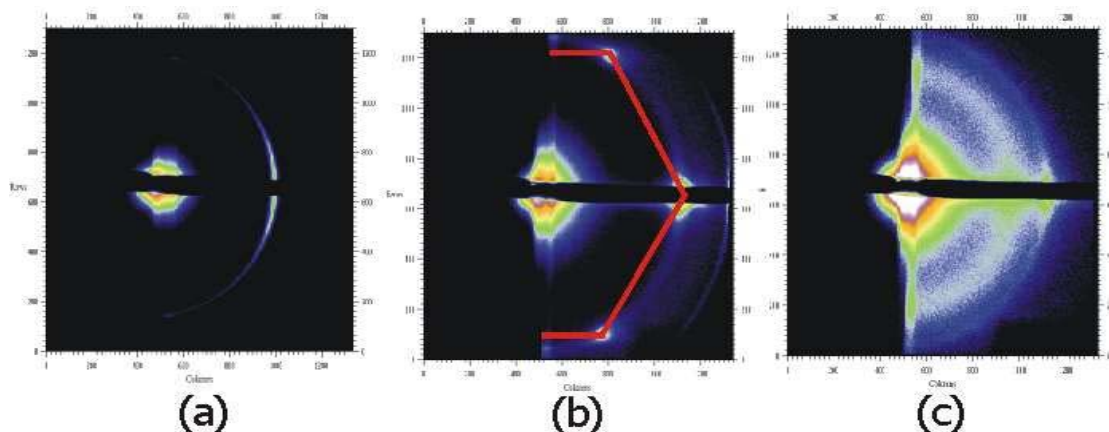


Figure 1. In-situ GISAXS 2D images of a Cd(SR)₂/topas film at room temperature (a), 170°C (b) and 300°C (c).

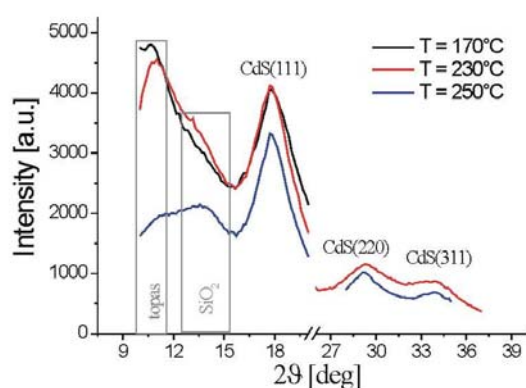


Figure 2. In-situ GID curves measured on a Cd(SR)₂/topas film at 170°C, 230°C and 300°C.

Further analysis are needed to corroborate the hypothesis. Such ordered state disappears for annealing above 220°C. GID measurements were performed in the annealing temperature range 170-250°C, after the formation of the particle array detected by GISAXS (Fig. 2). We used an incident angle of 0.08°, well below the critical angle ($\alpha_c = 0.15^\circ$) to enhance the scattering signal from the nanoparticles. Unexpectedly, already at 170°C we observe very pronounced crystalline peaks from cubic CdS corresponding to 2 nm size crystals, as shown in Fig. 2. With increasing temperature, the CdS Bragg peaks become more intense and sharper, while the topas amorphous peak intensity (at $2\theta = 10.7^\circ$) decreases.

This indicates that the polymer deteriorates at high temperatures, as shown in the curve at 250°C where the peak due to the SiO₂ layer becomes more evident. The important result is that a temperature of 170°C is sufficient for the CdS nanoparticles to form in thin polymeric films, while in the bulk system a temperature of 200°C is needed. Moreover, with respect to the ex-situ experiments, we observe a very strong crystalline signal from the CdS particles, which might indicate that an oxidation of the particles had occurred. In order to understand the particle growth and the oxidation effects, we need to investigate further the crystal growth of CdS nanoparticles by measuring GID *in-situ* and at temperatures below 170°C since GISAXS indicates that the nanoparticles organise themselves in an hexagonal lattice already at 150°C. Reducing the annealing temperature prevents the degradation of the polymer matrix and represents an important issue for the device realisation. We believe that the device performance can be greatly improved if the growth and dispersion of the nanoparticles within the polymer matrix are carefully controlled since the very first stages of the CdS formation.

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