

Preparation and characterization of CdS nanocrystallites in nafion

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Abstract. Perfluoroethylene sulfonic acid polymer (NAFION) films are subjected to ion exchange in the medium of aqueous solutions of cadmium acetate, followed by ammonia passivation. The films are then treated with hydrogen sulfide gas for prescribed times. X-ray powder diffraction data of these samples have been analyzed for estimating the sizes of the nanocrystallites. The optical absorption spectra of the samples show an absorption edge beginning at 525 nm for the largest size clusters. A broad absorption band appears with a maximum around 410 nm–440 nm in the smaller size clusters.

Keywords. Quantum dots; semiconductors; CdS; nanocrystallites; nafion.

1. Introduction

Remarkable quantum confinement effects have been observed in semiconductor quantum dot materials such as CdS doped glasses prepared by melt quenching and sol-gel techniques (Ekimov and Efor 1988; Reifeld and Minti 1994). Nanosize CdS crystallites in the ionic polymer nafion (perfluoroethylene sulphonic acid) have been previously reported (Wang *et al* 1990). The microcrystallites are prepared by ion exchange in cadmium acetate solution and subsequent treatment with hydrogen sulfide gas. The crystallite size in these structures depend on the initial Cd^{2+} ion concentration in the solution. The crystallite sizes can be varied by annealing the sample for different time durations (Wang *et al* 1990). It was reported that size characterization of the sample becomes difficult as the particle size decreases below 4 nm. Here we report the preparation of CdS nanocrystallites of different sizes less than 2 nm in nafion film and their characterization through XRD and optical absorption.

2. Experimental

Nafion films of thickness 0.18 mm are cleaned in boiling 70% nitric acid for 30 min and then repeatedly washed in boiling water till the pH of the water bath is neutral. The film is then soaked in 0.5 M aqueous cadmium acetate solution for time durations varying from 8 to 20 h. The film is dried under vacuum for 1 h and exposed to ammonia gas for 30 min and again dried under vacuum for 1 h. The film is then treated with hydrogen sulfide gas for 15 to 20 min followed by drying under vacuum to yield CdS nanocrystallites.

The XRD is taken by step scanning with a step width of 0.02° and 10 sec integrating time. A profile fitting program (PROFIT) (Toraya 1985) is used to deduce the full width at half maximum (W). The fitting takes into account the amorphous background, the presence of $K_{\alpha 1}$, $K_{\alpha 2}$ X-ray lines, asymmetry in the Bragg peaks and tail decay rates of

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the peaks. The overall goodness of the fit is determined by the reliability index defined by

$$R = \left\{ \frac{\sum_{i=1}^N w_i [y(x_i)_{\text{obs}} - y(x_i)_{\text{calc}}]^2}{\sum_{i=1}^N w_i y(x_i)_{\text{obs}}^2} \right\}^{1/2}, \quad (1)$$

where $y(x_i)_{\text{obs}}$ are the observed ordinates for the angle x_i , $y(x_i)_{\text{calc}}$ are the values calculated. w_i are the weightages of the points taken in proportion to the relative heights. N is the number of data points in the fit.

The best fit corresponding to the minimum value of R is used. The crystallite size is determined by using the Scherrer's formula (Cullity 1978) for the mean diameter of the particle

$$D = \frac{\lambda}{W \cos(\theta)}, \quad (2)$$

where θ is the Bragg angle, λ the wavelength of the X-rays. The optical absorption spectra of the samples are recorded by a Hitachi U3400 Recording Spectrophotometer.

3. Results and discussion

Four sets of samples were prepared by varying the duration of the ion exchange process. These are denoted by S1, S2, S3 and S4. Figure 1 shows the XRD pattern containing the Bragg diffraction peaks due to the cubic phase β -CdS as well as a diffuse wide maximum due to the amorphous polymer matrix. The profile calculated by the PROFIT is also shown (continuous curve). The input value of the amorphous peak

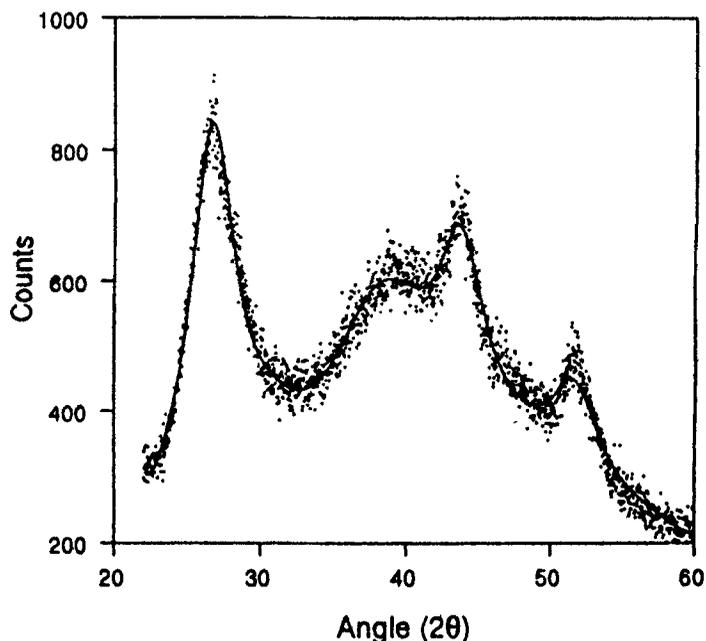


Figure 1. XRD of CdS in nafion.

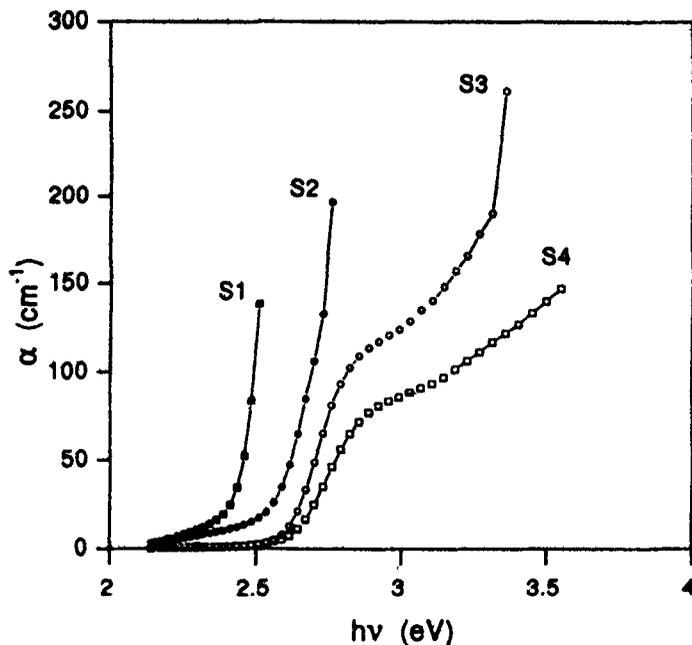


Figure 2. Optical absorption spectra of CdS in nafion.

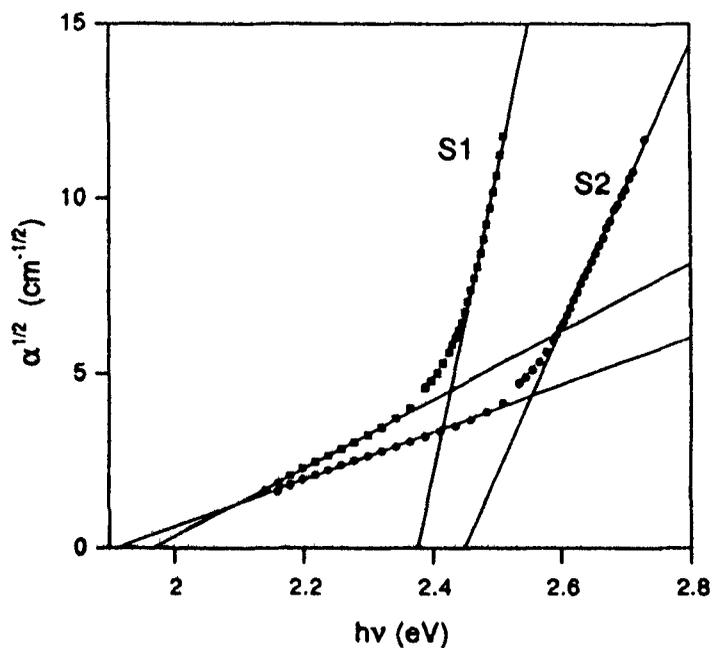


Figure 3. Plot of $\alpha^{1/2}$ vs $h\nu$.

width is varied systematically to minimize R . Samples S1, S2 (ion exchange duration 20h and 14h respectively) correspond to the mean diameters of 6 nm and 2 nm respectively.

Figure 2 shows the optical absorption spectra of the four samples. Analyzing the tail and absorption edge in the case of S1 and S2 we find that it corresponds to an indirect allowed band to band transition (Smith 1961) (figure 3) with a band gap energy (E_g) 2.17 eV and 2.18 eV and phonon energy 0.20 eV and 0.27 eV for S1 and S2, respectively. The absorption spectra of the samples 3 and 4 show a broad absorption band with a maximum around 410 nm–440 nm. These bands are presumably due to excitonic transitions as interpreted in an earlier work (Wang *et al* 1990).

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