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Structural phase behavior in II–VI semiconductor nanoparticles

R. J. Bandaranayake, G. W. Wen, J. Y. Lin, H. X. Jiang, and C. M. Sorensen
Department of Physics, Kansas State University, Manhattan, Kansas 66506-2601

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Cubic structured CdS, CdSe, and CdTe, II–VI semiconductor nanoparticles have been synthesized using aqueous solution precipitation at room temperature. The “as-prepared” particles have a size of about 30 Å. Thermal annealing causes (a) an increase in particle size; (b) a structural transition from the cubic to the bulk, hexagonal structure for CdS and CdSe; and (c) no structural transition for CdTe. The unexpected cubic phase for small particles of CdS and CdSe may be due to either metastability or an equilibrium surface effect. The latter would imply a strong correlation between structure and the size and surface properties, and that there is a minimum size for hexagonal phase stability. © 1995 American Institute of Physics.

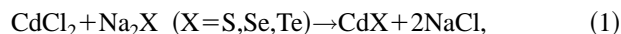
During the last decade, the physical properties of systems with reduced dimensionality have been an important and interesting subject.^{1–4} For semiconductor quantum dots (QDs), dramatic changes in their optical properties are expected when the dimension of the semiconductor approaches the Bohr radius of excitons, which sets the length scale for optical processes. There has been a considerable amount of research effort directed towards the understanding of the recombination dynamics of excitons in II–VI semiconductor QDs.^{5–8} This is partly due to the fact that excitonic transitions in II–VI semiconductor QDs are very suitable for investigating the effects of quantum confinement in these materials. Additionally, the II–VI semiconductor QDs have the potential for applications in areas such as nonlinear optical devices and fast optical switching devices.

So far, for the II–VI semiconductor materials less attention has been paid to the effects of reduced dimensionality and size on the material structure. For the bulk materials it is well known that CdS and CdSe have highly stable, hexagonal, wurtzite phases from room temperature to the melting point, while bulk CdTe has a cubic structure.⁹ Particulate, II–VI semiconductor QDs can be obtained by embedding particles in a glass matrix from melting.¹⁰ More recently CdS, CdSe, and CdTe particles capped with tri-*n*-octylphosphine/tri-*n*-octylphosphine oxide have been prepared by reacting organometallic reagents in the coordinating solvents at 300 °C.¹¹ Both these methods have produced CdX (X=S,Se,Te) nanoparticles (or quantum dots) all with the hexagonal phase, including CdTe, which is cubic in the bulk. In contrast, novel epitaxial techniques such as molecular beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD) have produced 2D structures including strained-layer superlattices of CdSe/CdS with a mixture of both cubic and hexagonal phases.¹² CdS polycrystalline thin films of the cubic phases have also been obtained by chemical bath deposition.^{13,14} Presently, the processes for obtaining the cubic phase for CdS and CdSe as well as the evolution from one phase to the other are not yet well established. Complete understanding and control over the structural properties of low dimensional systems including QDs are needed, as they may hold the key to many future applications.

In this letter, we report experimental results on the synthesis of CdS, CdSe, and CdTe, II–VI semiconductor QDs

based on a chemical method using aqueous solution precipitation at room temperature.

The synthesis of CdX (X=S,Se,Te) QDs was achieved by reacting Na₂X (X=S,Se,Te) with a mixture of Cd²⁺ ions in an aqueous medium at room temperature. The chemicals used for this process were of highest purity available from Aldrich Chemical Co. De-oxygenated aqueous solutions of Na₂X (X=S,Se,Te) and CdCl₂ of molarity 0.25 M were prepared from Na₂S·9H₂O, Na₂Se, Na₂Te, and CdCl₂. The stoichiometry of the reaction was



and reacted under Ar. Precipitation occurs instantaneously to form particles of CdX (X=S,Se,Te). The precipitates were sonicated for about 10 min to break large agglomerations of the precipitates. The precipitates were then washed with deoxygenated water, filtered, and dried in a desiccator under Ar. Subsequent thermal annealing was carried out under Ar. X-ray diffraction (XRD) measurements were utilized to determine the mean crystal size and structure.

Figure 1 presents the XRD spectra, normalized to the maximum line intensity, of CdS QDs including the “as-prepared” ($T=24$ °C) QDs and four thermally annealed samples. Examination and intercomparisons of spectra obtained at different annealing temperatures lead to four conclusions. First, the as-prepared samples are crystalline as seen by broad XRD features at three prominent lattice planes of these materials rather than amorphous which would yield only a very broad single nearest neighbor peak near the (111) line. Similar nonamorphous particles were made by Murray *et al.*¹¹ Second, the XRD pattern clearly reveals that the “as-prepared” CdS QDs have a cubic structure, as indicated by a single peak in the angular region between 20° and 30° in conjunction with the absence of the (103) and (102) peaks at about 48° and 37°. Third, the single peak in the angular region between 20° and 30° evolves to a three peak pattern with increasing annealing temperature T_a , which, in conjunction with the appearance of the (103) and (102) peaks, indicates a change in the crystalline structure from a cubic to a hexagonal phase. This structural transition occurs at an annealing temperature between 300 and 400 °C. Fourth, the XRD spectral linewidth decreases with increasing annealing temperature, indicating an increase in the crystallite size with

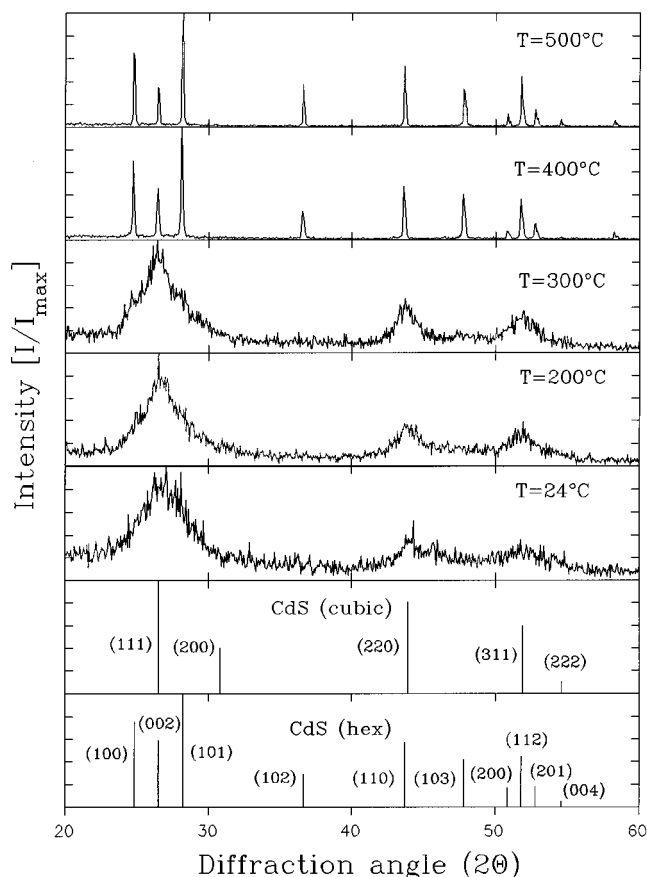


FIG. 1. X-ray diffraction spectra of the “as-prepared” and thermally annealed CdS QDs. Each annealing was carried out for a time period of 2.5 h in an Ar atmosphere. Included are also the corresponding line spectra of the bulk hexagonal and metastable cubic structures of CdS provided by the JCPDS (Joint Committee on Powder Diffraction Standards) database.

increasing T_a . We also present the XRD spectra of the “as-prepared” and thermally annealed CdSe QDs in Fig. 2. Similar features have been observed in CdSe as in CdS. However, the structural transition occurs at a lower annealing temperature, i.e., below 200 °C for CdSe compared with above 300 °C for CdS.

In Fig. 3, we present the XRD spectra of the CdTe QDs. In contrast to CdS and CdSe, thermal annealing causes only a variation in size for CdTe. The structure of the CdTe QDs remains cubic.

The mean crystallite diameter, d , can be determined from the linewidth of the XRD spectra by the Scherrer formula¹⁵

$$\langle d \rangle = \frac{0.94\lambda}{B \cos \theta_B}, \quad (2)$$

where λ is the x-ray wavelength, B is the full width at half maximum of the diffraction peak (radian), and θ_B is the half angle of the diffraction peak on the 2θ scale. When determining the QD sizes, the (110) diffraction peak near 45° or 42° was used for CdS or CdSe, respectively, to avoid convolution of three different peaks near 27° for the intermediate annealing temperatures. The dependence of QD size on the annealing temperature is shown in Fig. 4. Figure 4 indicates that our synthetic technique allows us to make QDs in the order of 30 Å (as-prepared) and vary the size to values near the

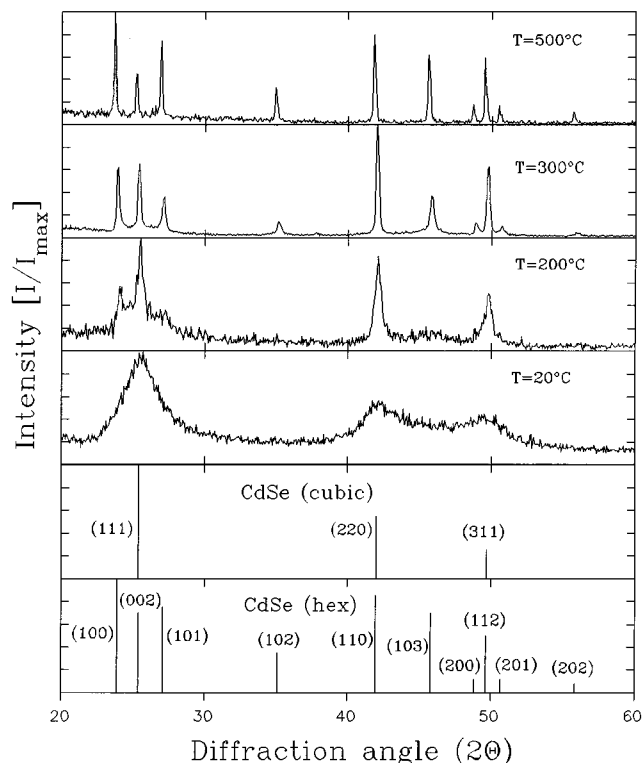


FIG. 2. X-ray diffraction spectra of the “as-prepared” and thermally annealed CdSe QDs. Included are also the corresponding line spectra of the bulk hexagonal and metastable cubic structure of CdSe provided by the JCPDS database.

bulk by subsequent annealing. An interesting feature shown in Fig. 4 is that the growth rate of size with annealing temperature is smallest for CdS. This behavior may be understood in terms of the material’s cohesive energy as indicated by the melting temperatures of CdS, CdSe, and CdTe which are 1750, 1350, and 1011 °C, respectively. Therefore, CdS QDs sinter more slowly under annealing than CdSe and CdTe.

There are two possible explanations for the phase behavior we have observed. First, the cubic structure of the “as-prepared” QDs is a nonequilibrium, metastable phase. This is reasonable given the method by which they were produced: rapid nucleation and growth from a supersaturated solution. The rapidity of similar precipitation reactions has been proposed to explain the creation of amorphous particulates of otherwise crystalline materials.¹⁶ The cubic structure may result from its closer similarity to a roughly spherical nucleus, expected at the initial instant of nucleation, than the hexagonal structure. Stacking fault energies of 13 and 14 meV/atom for CdS and CdSe,¹⁷ respectively, indicate the free energy difference between the cubic and hexagonal structure is small, again supporting metastability. If metastability is the proper explanation, then annealing temperature allows activation of the structure to the lower energy, stable, hexagonal phase.

The second possibility is that the cubic structure is the equilibrium phase for CdS and CdSe particles with a free surface. This would be due to surface effects which can dominate the properties of small particles (~50% of all the

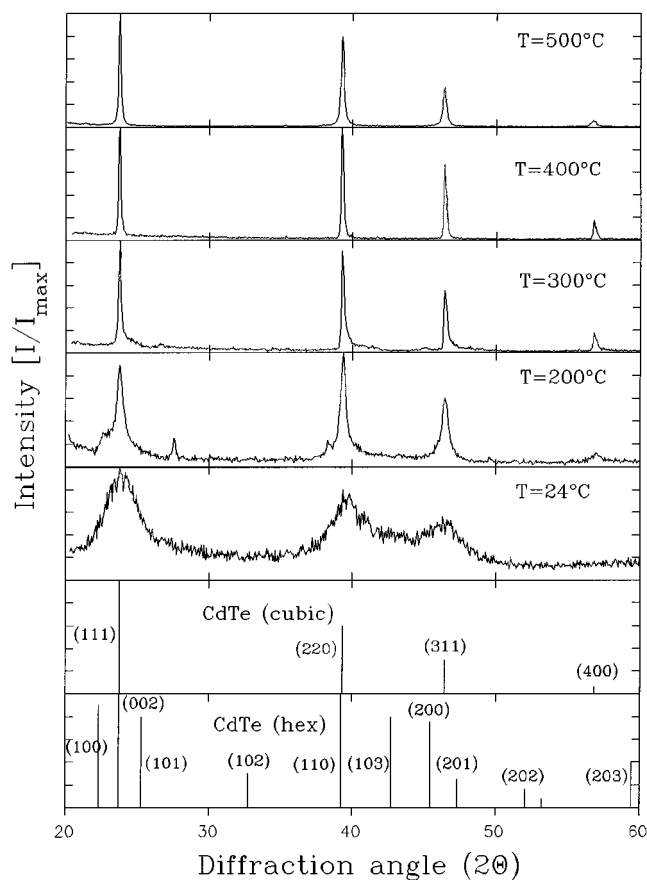


FIG. 3. X-ray diffraction spectra of the “as-prepared” and thermally annealed CdTe QDs. Included are also the corresponding line spectra of the cubic and hexagonal structures of CdTe provided by the JCPDS data base. The small peak in the angular range between 25° and 30° appearing in the 200 °C annealed QDs is due the presence of NaTe₃ in the starting material, which disappears at higher annealing temperatures.

atoms are on the surface of a 30 Å particle). This implies that the structural transition at elevated temperatures is caused by sintering, since it increases the size, hence the relative influence of the surface decreases so that the bulk, hexagonal structure can occur. This mechanism is supported by the observation that the sizes of CdSe and CdS QDs at which the structural transition occurs are about the same, ~150 Å, as indicated by arrows in Fig. 4. The importance of surface effects is demonstrated by the mixed cubic and hexagonal phases seen in 2D superlattices thought to be a result of mismatch induced strain between the CdS or CdSe and the substrate.¹² We also speculate that the small CdS and CdSe particle in glasses¹⁰ or strongly ligated with organophosphines¹¹ have different surface properties than our free surface particles and hence a different structure as well.

In conclusion, CdS, CdSe, and CdTe semiconductor QD have been synthesized using aqueous solution precipitation. Our synthetic technique allows us to make “as-prepared” QDs of the cubic structure with diameter of about 30 Å and vary the size to values near the bulk by subsequent annealing. Thermal annealing also causes a structural transition from the cubic to the hexagonal structure of the bulk for CdS and CdSe; however, no structural change is observed for

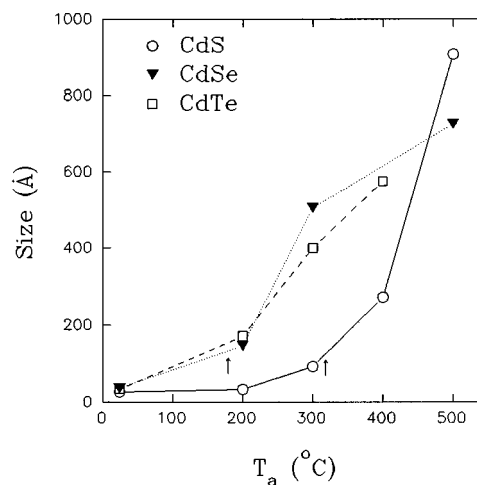


FIG. 4. The mean crystallite size of the QDs plotted as a function of annealing temperature T_a . Arrows indicate the temperatures at which the transition from the cubic to hexagonal structure occur in CdS and CdSe, which correspond to a mean QD size of about 150 Å.

CdTe. The cubic structure of CdS and CdSe for QD may be due to metastability or an equilibrium surface effect. The later explanation implies that for CdS and CdSe there is a correlation between the QD's size and structure, indicating a minimum QD's size for the formation of the hexagonal structure.

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