Quantum Confinement and Crystalline Structure of CdSe Nanocrystalline Films

A. Rivera-Márquez (a), M. Rubín-Falfán (a), R. Lozada-Morales (a),
O. Portillo-Moreno (b), O. Zelaya-Angel[1]) (c), J. Luyo-Alvarado (c),
M. Meléndez-Lira (c), and L. Baños (d)

(a) *Posgrado en Optoelectrónica, FCFM-BUAP, Puebla, México*

(b) *Facultad de Ciencias Químicas, BUAP, Puebla, México*

(c) *Departamento de Física, Centro de Investigación y de Estudios Avanzados , P. O. Box 14-740, México 07360 D.F.*

(d) *Instituto de Investigación en Materiales, UNAM. México D.F.*

Nanocrystalline CdSe films were grown onto glass substrates by the chemical bath method. Different constant deposition temperatures (T_d) were employed in the range 4–65 ºC. Average grain size (GS) increased monotonically with T_d, reaching saturation at ~65 ºC. The GS values were in the interval 5–16 nm. At low T_d values (4–15 ºC), the structural phase was hexagonal wurtzite (W), for intermediate values, a wurtzite and zincblende (ZB) mixture of phases was found, and at high T_d (65 ºC) only cubic ZB phase was present in the layers. The variation of the bandgap as a result of the structural phase change and quantum confinement is studied.

1. Introduction

Semiconductor quantum dots play an important role in nanostructure physics and have great potential for valuable technical applications [1, 2]. Quantum confinement phenomenon in CdSe is one of the most studied subjects due to the good characteristics of this material for the understanding of the physical properties of nanometer size structures [1]. Several papers have been published on the preparation of CdSe quantum dots (QDs) in wurtzite (W) [3, 4], zincblende (ZB) [5] and both, W and ZB [6] crystalline structures. W and ZB are stable and metastable phases, respectively, of CdSe at normal conditions. Other works study the differences in physical properties of W and ZB structured QDs [7]. Comparison of CdSe properties between W and ZB phases have long been matter of research [8–10]. The analysis of the process of the structural phase transformation W ↔ ZB in crystals and polycrystalline films of CdSe started in the early 60s [11] and has been periodically studied until now [10, 12–14]. Phase transition from W to rock salt (RS) lattice in compressed CdSe-QDs has been widely studied in the last decade, and it is worthwhile to mention the work developed by Herhold et al. [15]. The CdSe QD W ↔ ZB phase transformation at constant normal pressure has produced so little attention that only two works have been found reporting, in one of them, experimental findings [6] and in the other one, theoretical results [7]. In this work, we are concerned with the characterization of the structural transformation W ↔ ZB of CdSe QDs, prepared on glass substrates employing the chemical bath de-

---

[1]) Corresponding author; e-mail: ozelaya@fis.cinvestav.mx

position (CBD) method, and changing the deposition temperature (T_d) from 4 to 65 °C. In this T_d-range, at low (high) temperatures, W (ZB) arises as the dominant crystalline structure of the layers deposited. Gradual mixtures of W-ZB are obtained at intermediate T_d values. Alike experimental results reported for microcrystalline CdSe-ZB → W structural transformation [10], where the forbidden energy band gap (E_g) value moves between two extreme points passing by a minimum value as consequence of the phase change, in the present case, E_g in CdSe-QDs diminishes from 1.98 to 1.83 eV going also through a minimum value (E_g = 1.80 eV), before reaching the final datum 1.83 eV. However, for CdSe microcrystalline thin films the ZB → W transformation is promoted by thermal annealing in Ar + Se$_2$ ambient [10]. The path, in this last case, is so important, since the reversible transformation cannot occur at normal pressure, i.e., by thermal annealing the W → ZB transformation does not occur. In the present work, we propose that the E_g-shift in our CdSe-QDs from 1.83 eV at T_d = 65 °C to 1.98 eV at T_d = 4 °C is originated, partially, by quantum confinement effects when the radius R of nanocrystallite goes over the interval from 15.4 to 5.4 nm when T_d diminishes (the CdSe excitonic radius is 5.6 nm [16]), and partially due to the changes in E_g provoked by the W → ZB crystalline-structure transformation of QDs [10].

2. Experimental

The CBD method used to grow the CdSe layers was described elsewhere [17]. The substrates employed were glass-slides, which were cleaned by immersing them into an aqueous solution of K$_2$Cr$_2$O$_7$, diluted in concentrated HCl, during 24 h. Afterwards, they were rubbed using distilled water and free Na detergent, rinsed in deionized water and then blow-dried using filtered clean air. The CdSe films were grown using the following deionized-water solutions: 0.1 M potassium hydroxide (KOH), 0.01 M cadmium chloride (CdCl$_2$), 0.5 M ammonium nitrate (NH$_4$NO$_3$) and 0.01 M selenourea (CSe[NH$_2$]$_2$). The solutions were mixed and taken to the programmed T_d for CdSe deposition. Growing time was in the range 0.25 h (T_d = 65 ± 2 °C) to 24.0 h (T_d = 4 ± 1 °C). Thickness (d) measurements were carried out in a Dektak II profilometer; the d values were in the range (200 ± 10) nm. The X-ray diffraction (XRD) spectra were obtained utilizing a Siemens D5000 diffractometer. The radius of the particle was determined employing the Debye-Scherrer formula, making corrections due to intrinsic instrumental broadening. Optical absorption spectra data were measured using a Unicam 8700 system over the 190–900 nm wavelength range, with an accuracy of $\Delta\lambda$ = ± 0.3 nm.

3. Results and Discussion

The gradual phase transformation from W to ZB or vice versa using different T_d values is illustrated in Fig. 1, which exhibits the evolution of the XRD patterns of samples. Lower temperatures than 0 °C were not possible to reach in our CBD system because of the freezing of aqueous solutions. The position of most featured peaks in the diffractograms were identified with W and/or ZB lattice structures of CdSe. Although a mixture of both W and ZB phases can be present in all the samples, an abrupt domination of W over ZB is observed in the range 4 → 30 °C. The XRD pattern at the bottom of Fig. 1 belongs to the CdSe layer grown at 65 °C after an annealing at 480 °C in Ar + Se$_2$ atmosphere, the triplet of the hexagonal structure is observed in the 2θ range of 24°–28°.

The diffractograms of CdSe layers grown from 4 to 30 °C are affected by preferred orientations, in such a way that the XRD-triplet is incomplete. By employing the De-bye-Scherrer formula to the different peaks in each spectrum of Fig. 1, the average radii of nanocrystallites were calculated. Corrections were made because of the instrumental broadening only. Figure 2 displays the dependence of R with T_d. It is evident that T_d strongly determines the size of the nanocrystallite. Lattice parameters of W and ZB nanostructured films become reduced when T_d diminishes, the volume of the unit cell (V_{uc}) should be, therefore, diminished. Lattice parameters were calculated from the interplanar distances defined by the experimental XRD peaks positions. The inset of Fig. 2 shows the dependence of the unit cell volume with T_d. Since the volume of the W unit cell is ideally defined to be one half of the ZB unit cell, the volume of hexagonal samples, in the inset of Fig. 2, is two times the real volume. This was made to have the same order of comparison. These results demonstrate that crystallites reduce their size, and on the other hand, there is a shrinkage of their lattice parameters when T_d goes to low values. An increase of the unit cell volume during the ZB → W phase transition at 300 °C for CdS thin films has already been reported [18], and it has also been observed in CdSe layers at 355 °C, in both cases by us. This experimental fact was explained through an increase of the Gibbs free energy of the lattice. Nevertheless, in
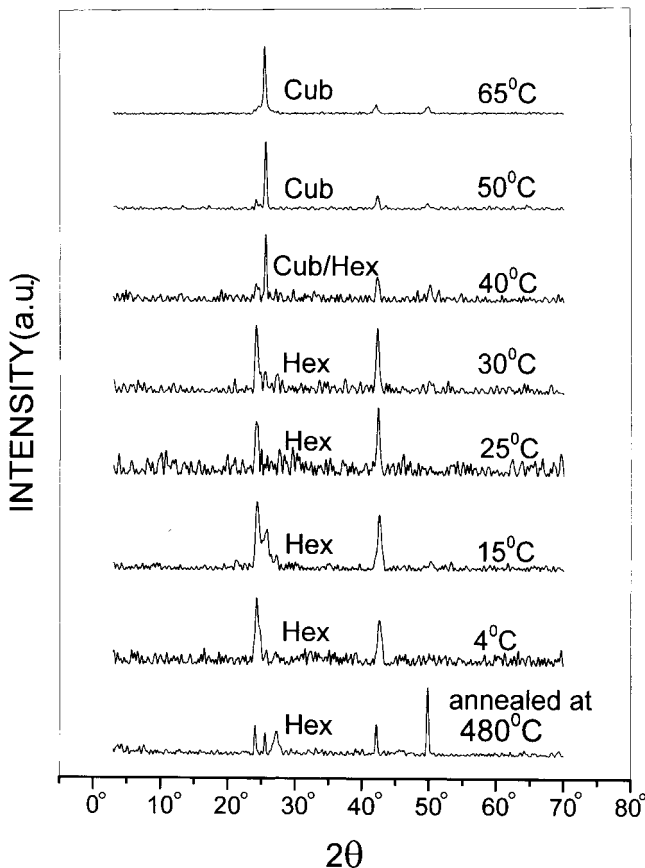

Fig. 1. X-ray diffraction patterns of CdSe films showing the evolution from wurtzite to zincblende structure for different deposition temperatures (T_d). The diffractogram at the bottom corresponds to the film deposited at 65 °C after thermal annealing at 480 °C in Ar + Se$_2$ atmosphere
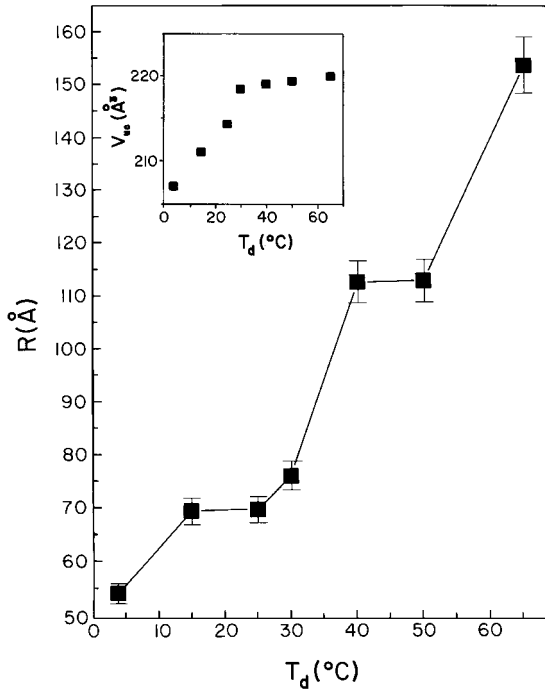
Fig, 2. Radius (R) of quantum dot versus deposition temperature (T_d). The inset exhibits the unit cell volume (V_{uc}) against T_d

the present situation, the shrinkage of the lattice parameters could indicate an extra positive pressure acting on the volume of our CdSe QDs. This pressure has been considered, by other authors [15], as originated by the surface tension because of the free surface of QD. It is worthwhile to remark that in the inset of Fig. 2, a significant decay of the QD-unit cell volume starts around R = 7.5 nm, close to the region where the material passes from a W-dominated to ZB dominated structure.

The E_g shift for different T_d values was calculated from optical absorption data. Figure 3 depicts the first derivative of the optical density [d(OD)/d($h\nu$)] as a function of the incident photon energy ($h\nu$). The relative minima in the spectra of the first derivative d(OD)/d($h\nu$) versus $h\nu$ graph define with excellent approximation the various critical points of the band structure [19, 20]. Figure 3 evidences, for three
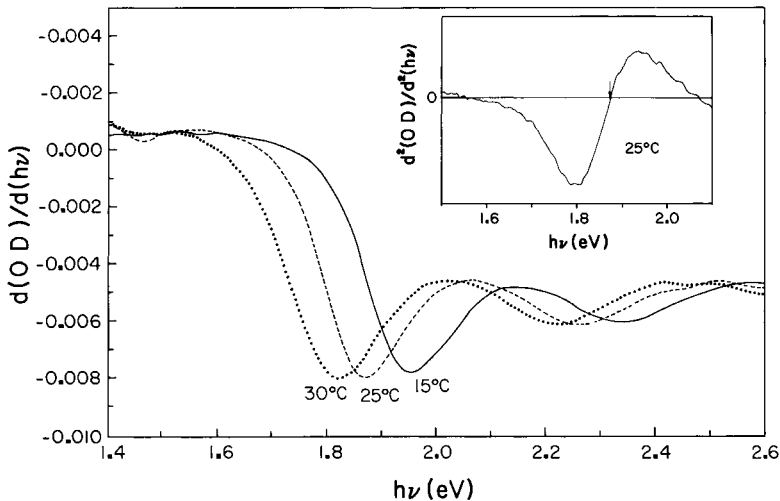

Fig. 3. First derivative of the optical absorption (OD) as a function of the photon energy ($h\nu$), for three different T_d values. The inset displays the second derivative of OD versus $h\nu$. The downward arrow points out the position of the E_g value for T_d = 25 °C

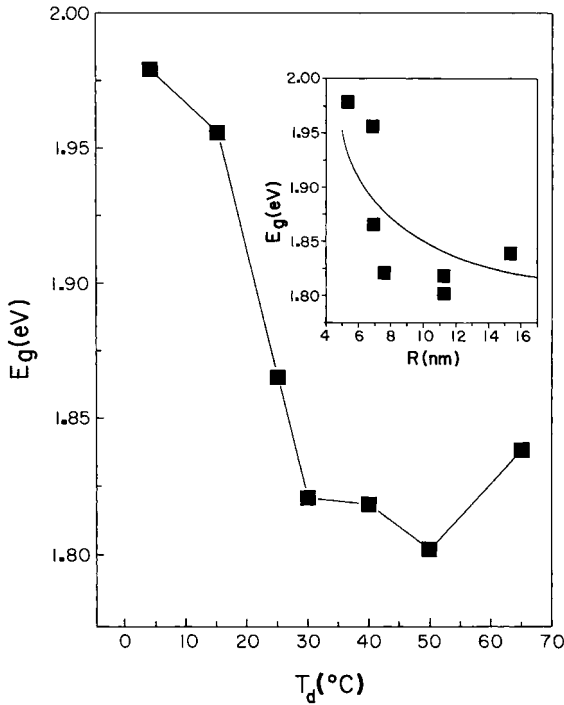Fig. 4. E_g as a function of T_d in the entire range of deposition temperatures. The inset shows E_g versus the QD radius (R), where squares are experimental points and solid line the Kayanuma's theoretical prediction

representative samples, the position change in the energy axis of E_g and $E_g + \Delta E_g$, being the spin–orbit splitting in the case of ZB-structures, and the spin–orbit plus the crystal field splitting for W-structures, respectively. The approximated equal separation between E_g and $E_g + \Delta E_g$, observed in Fig. 3 for the three samples, denotes a good proof of the size change in the lattice parameter of the QD crystalline structure. The inset in Fig. 3 shows the second derivative of OD plotted against $h\nu$. A more exact position of the critical point E_g in the $h\nu$-axis is defined by the crossing of the second derivative curve with the $h\nu$ axis, or rather the zero-position, which is there pointed out by the downward arrow.

The movement of E_g with T_d is displayed in Fig. 4. For $T_d = 4$ ºC, $E_g = 1.98$ eV was measured. This E_g value is higher than the bulk E_g value (1.83 eV), $E_g = 1.83$ eV is approximately the same E_g obtained in our measurements when $T_d = 65$ ºC ($R = 15.4$ nm). Figure 4 resembles the E_g versus T_a lineshape attained in the CdSe ZB $\rightarrow$ W transformation under thermal annealing (T_a) [10]. The ZB $\rightarrow$ W structural change, in this last case, is related with the minimum in the E_g versus T_a plot [10]. We think that in the case of Fig. 4, two mechanisms contribute to the E_g versus T_d behavior. The first one is the decrease in E_g when R rises; the second one is the lowering of E_g originated by the ZB $\rightarrow$ W transformation, similar to the decreasing of E_g owed to the ZB $\rightarrow$ W structural transition due to thermal annealing [10]. In the inset of Fig. 4, E_g against R is plotted. The solid line represents the theoretical prediction for CdSe outlined using the Kayanuma's effective mass approximation (EMA) theory [21]. The good concordance between theory and experiment by employing EMA in CdSe for large R values is well known [22]. As can be noticed in Fig. 4, E_g goes down faster than the theoretical values. We assume that the extra contribution of the ZB $\leftrightarrow$ W transformation produces a strong influence for an abrupt change in the E_g versus R plot, in comparison with a smoother E_g versus R prediction. A smooth decrease in the E_g versus R and in the E_g versus T_d plots observed in CBD-W-CdSe QDs, where W-phase is unchanged, has been just reported [3].

4. Conclusions

In summary, quantum confinement effects and phase transformation W $\leftrightarrow$ ZB in CdSe-QDs grown by CB, were proposed to explain the E_g versus R experimental result. The deviation of the functional dependence of E_g on R from the expected behavior is originated by the contribution of the ZB $\leftrightarrow$ W phase change, which affects the E_g values.

References

[1] D. J. Norris, A. Sacra, C. R. Murray, and M. G. Bawendi, Phys. Rev. Lett. **72**, 2612 (1994).
[2] R. G. Sun, Y. Z. Wang, D. K. Wang, T. L. Gustafson, and A. J. Epstein, Appl. Phys. Lett. **76**, 634 (2000).
[3] S. S. Kale and C. D. Lokhande, Mater. Chem. Phys. **62**, 103 (2000).
[4] Y. Xie, W. Z. Wang, Y. T. Qian, and X. M. Liu, J. Solid State Chem. **147**, 82 (1999).
[5] H. Cachet, H. Essaaidi, M. Froment, and G. Maurin, J. Electroanal. Chem. Interfacial Electrochem. **396**, 175 (1995).
[6] O. Yamamoto, T. Sasamoto, and M. Inagaki, J. Mater. Res. **13**, 3394 (1998).
[7] H. H. Von Grüber, Phys. Rev. (B: Condensed Matter) **55**, 2293 (1995).
[8] R. Ludeke and W. Paul, phys. stat. sol. **23**, 413 (1967), and references therein.
[9] M. M. Berezovskii and E. V. Makhnii, Phys. Solid State **38**, 358 (1996).
[10] O. Portillo-Moreno, R. Lozada-Morales, M. Rubin-Falfan, J. A. Perez-Alvarez, O. Zelaya-Angel, and L. Baños-Lopez, J. Phys. Chem. Solids **61**, 1751 (2000).
[11] C. J. M. Rooymans, J. Inorg. Nucl. Chem. **25**, 253 (1963).
[12] V. A. Fedorov, V. A. Ganshin, and Yu. N. Korkishko, phys. stat. sol. (a) **126**, K5 (1991).
[13] M. P. Kulakov and I. V. Balyakina, Sov. Phys. – Crystallogr. **35**, 871 (1990).
     I. V. Balyakina, V. K. Garman, M. P. Kulakov, G. I. Peresada, and V. S. H. Shektman, Izv. Akad. Nauk. SSSR Neorg. Mater. **28**, 2495 (1990).
     M. P. Kulakov and I. V. Balyakina, J. Cryst. Growth **113**, 653 (1991).
[14] A. Geddo Lehmann, M. Bionducci, and F. Buffa, Phys. Rev. B **58**, 5275 (1998).
[15] A. B. Herhold, C. C. Chen, C. S. Johnson, S. H. Tolbert, and A. P. Alivisatos, Phase Transit. **68**, 1 (1999).
[16] A. I. Ekimov, F. Hache, M. C. Schanne-Klein, D. Ricard, C. Flitzanic, I. A. Kudryavtsev, T. V. Yaseva, V. Rodina, and Al. L. Efros, J. Opt. Soc. Am. **10**, 100 (1993).
[17] J. L. Martinez, G. Martinez, G. Torres-Delgado, O. Guzman, P. del Angel, O. Zelaya-Angel, and R. Lozada-Morales, XXX J. Mater. Sci. Mater. Elect. **8**, 399 (1997).
[18] O. Zelaya-Angel, H. Yee-Madeira, and R. Lozada-Morales, Phase Transit. **70**, 11 (1999).
[19] B. G. Potter Jr. and J. H. Simmons, J. Appl. Phys. **68**, 1218 (1990).
[20] L. Katsikas, A. Eychmüller, M. Giersig, and H. Weller, Chem. Phys. Lett. **172**, 201 (1999).
[21] S. V. Gaponenko, in: Optical Properties of Semiconductor Nanocrystals, Cambridge University Press 1998 (p. 41).
[22] R. Garuthara and G. Levine, J. Appl. Phys. **80**, 401 (1996).