Temperature and Deposition Time Effect on Properties and Kinetics of CdSe and CdS_{0.25}Se_{0.75} Films Deposited by CBD

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Received: June 06, 2016; Revised: May 04, 2017; Accepted: May 21, 2017

CdSe and CdS $_{0.25}$ Se $_{0.75}$ thin films were grown by the Chemical Bath Deposition technique at different temperatures (50-90°C) and deposition times (5-180 min). Both kinds of films are polycrystalline, constituted by nanostructured clusters of particles. CdSe films consist in a mixture of cubic and hexagonal phases (4-8 nm crystal size), whereas only the hexagonal phase is observed in the CdS $_{0.25}$ Se $_{0.75}$ ones (6±1 nm crystal size). A decrease on the CdSe films density was observed due to the sulfur introduction into the crystal lattice. The composition of the ternary films is affected by both temperature and deposition time. The Band gap values (E $_{\rm g}$) are affected by temperature, atomic composition and deposition time, decreasing from 2.09 to 1.93 eV, showing a quantum confinement effect mainly in the CdSe films. The films thickness, ranging from 30 to 600 nm, increases as a function of temperature and deposition time. Photoluminiscence signal is improved after thermal treatment, evidenced by the radiative broad bands observed at 1.84 and 2.20 eV.

Keywords: Nanostructured films, Semiconductors, Kinetics of deposition

1. Introduction

II-VI semiconductor compounds as thin films have been studied over the past decades. They can be prepared by several techniques such as laser ablation, spray pyrolysis, thermal evaporation, and chemical bath deposition (CBD), among others¹⁻⁵. CBD films are obtained by spontaneous precipitation in alkaline medium, occurring when the ionic product exceeds the solubility product, by heterogeneous and homogeneous reactions taking place on the substrate and in the bulk solution respectively6; deposition occurs even at low temperatures and short times. This technique allows a close control on the film properties. CBD has been used to deposit several semiconductors including chalcogenide materials such as ZnSe, ZnS, CdS, CdTe and CdSe⁶⁻¹⁰. The need to develop new nanomaterials, expand their applications and improve their physical properties motivated the synthesis of complex ternary and quaternary compounds such as CdSSe7,11-14, CdZnSSe7 and CoZnCdS15. Nanostructured CdSe thin films have been extensively studied and used in optoelectronic, photoelectrochemical and non-linear optics applications. The formation of ternary CdS_{1,y}Se_y solid solutions improves the physical properties of the binary CdSe. Tailoring the CdS_{1-x}Se_x composition (x) allows the enlargement of its response range in the visible spectrum, widening its applications. Notable achievements have been reported on the synthesis and characterization of CdS, Se thin films by several techniques, most of them focused on the improvement of the optical, electrical and structural properties by modifying the composition. However, neither the kinetics of deposition nor the effect of temperature and time on the chemical nature of the films have been reported. In previous works, we reported the experimental procedure and the optimal Cd:S:Se bath atomic ratio to obtain CdS_{1.x}Se_x films with specific compositions^{11,16}. In the present study, the synthesis of CdSe and CdS $_{0.25}$ Se $_{0.75}$ films carried out varying deposition time and temperature is reported, analyzing the effect of the variables and the introduction of sulfur ions into the CdSe crystal lattice on the structural, morphological and optical properties of the obtained films. Additionally, to understand the basic kinetics of the heterogeneous reaction, the growth rate, thickness and atomic composition were correlated with time and temperature. Low temperature photoluminescence measurements of CdS_{0.25}Se_{0.75} were also performed to determine exciton recombination and/or free to bound transition.

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2. Experimental

2.1 Deposition

CdSe and CdS, Se, films were deposited onto Corning glass by the Chemical Bath Deposition (CBD) technique according to the procedure reported elsewhere¹. 0.1M CdCl₂, 0.1M CS(NH₂), and 0.1M Na₂SeSO₃ solutions prepared from analytical grade reagents were used as precursors. Deposition temperature was set at 50, 75 and 90°C. Alkaline pH of the bath was kept at 10.5 by adding 4M NH₄OH; an excess of ammonia is required to avoid the formation of Cd(OH)₂¹⁷. $0.2M\ NH_4Cl$ was used only for $CdS_{0.25}Se_{0.75}$ growth. To promote the homogeneity of the films, the precursors were pre-heated at the deposition temperature prior to be mixed. To obtain CdS_{0.25}Se_{0.75} films it is necessary to employ an excess of Se16, therefore a 1:0.25:1.31 Cd:S:Se precursors ratio was employed. On the other hand, for the CdSe films the Cd:Se precursors ratio was kept at 1:1, as indicated in the literature^{1,11,18}. The influence of deposition time (5 to 360 min) on atomic composition, thickness and growth rate of the films was analyzed. Two atmospheres, vacuum (TT) and CdCl, rich (TT CdCl₂), were tested in order to improve the photoluminescence signal of the grown samples. Photoluminescence of CdS_{0.25}Se_{0.25} films was measured from room temperature to 10K.

2.2 Films characterization

Structural properties were studied by X-ray diffraction (XRD) employing a Bruker Advanced diffractometer (Cu $K_a=1.5406\text{Å}$) operating in grazing angle (0.3-2°) configuration. The surface morphology of the films was observed with a SEM JEOL JSM6701F equipped with an Energy Dispersive Spectroscopic (EDS) module. Optical absorption was measured using an UV-Vis spectrometer Perkin-Elmer Lambda35. Photoluminescence (PL) measurements were carried out by exciting with a He-Cd laser (442 nm), focused on the sample through a spherical lens; for the CdSe samples, a HeNe laser (633 nm, 1.9 eV) was also used. The outcoming radiation from the film was focused on a 1403-SPEX double monochromator and detected with a RCA-C31034 photomultiplier coupled to a photon counter, thermoelectrically cooled to improve the signal-noise ratio. The detected PL spectra were corrected for the spectral response of the system. A Sloan Dektak Profilemeter was used to measure the thickness of the samples.

3 Results and Discussion

3.1 Structural and morphological properties

As it is known, CdSe films crystalize in hexagonal^{2,3}, cubic ^{4,8,18} or a mixture of both phases^{1,11}. Films deposited

by using several techniques are polycrystalline in nature¹⁻³. Figure 1a shows the XRD patterns of CdSe thin films grown at 50, 75 and 90 °C during 15 and 120 min. Due to the thin films obtained and the low crystalline quality of the samples, the substrate contribution for the films grown at 50 and 75 °C during 15 min is observed. As growth time and temperature increase, crystalline quality improves and four peaks become well defined, corresponding to the (100), (002), (110) and (112) planes of the hexagonal phase (JCPDS file No 653436). Additionally, these reflections, excepting that observed around 24.21°, match the (111), (220) and (311) planes of the cubic phase too (JCPDS file No 882346). According to these results, films could have a mixture of both phases. Films show preferential orientation on (002) and (111) planes as previously reported in literature^{4,5,18}. A small shift on the peaks position to higher angles from those corresponding to the JCPDS files, observed in all films, can be associated to the presence of strains. In Figure 1b, two diffraction peaks can be elucidated on the CdS_{0.25}Se_{0.75} samples grown at 15 min, not observed in the corresponding CdSe XRD pattern. This result can be due to the higher thickness and better crystalline quality of the films, indicating a faster and more orderly crystallization rate in the case of the CdS_{0.25}Se_{0.75} samples. As expected, the peaks are slightly shifted to higher angles $(2\theta=0.2^{\circ})$ due to the introduction of S into the crystal lattice of CdSe, resulting in the ternary solid solution formation. As reported in literature for CdS_{1-x}Se_x^{12-13,19}, CdS_{0.25}Se_{0.75} films are polycrystalline with hexagonal phase showing preferential orientation on the (002) plane related to the JCPDS files No 50072. However, considering the similarity in the unit cell packing of cubic zinc blende and hexagonal wurtzite structures, the cubic phase contribution in these films could not be disregarded, as reported by Xie et al 12. In all cases, time and temperature increase both thickness and crystalline quality of the films, but there is no evidence of their influence in the films strain. According to the crystal size values of the samples, estimated with the Scherrer's equation using the full width at half maximum (FWHM) of the (111) and (002) planes, temperature does not affect the CdS_{0.25}Se_{0.75} films (6±1 nm crystal size in all cases); regarding the CdSe films, the crystal size value slightly increases as temperature is increased, with estimated values of 4, 6 and 8 nm for the films grown at 50, 75 and 90 °C respectively.

SEM micrographs of CdSe and CdS_{0.25}Se_{0.75} films are shown in Figure 2. Semispherical nanostructured clusters that grow with time and temperature constitute both kind of materials; the average cluster size increase from 50 to 600 nm; in despite of temperature, size distribution is wider at short deposition times. CdSe films are dense and homogeneous from the beginning of deposition, indicating that nucleation and growth occur simultaneously¹⁷. More ordered and defined clusters are observed for ternary films, the low density indicates slow deposition rate that can be attributed to the introduction of S in the lattice; the micrographs for the films

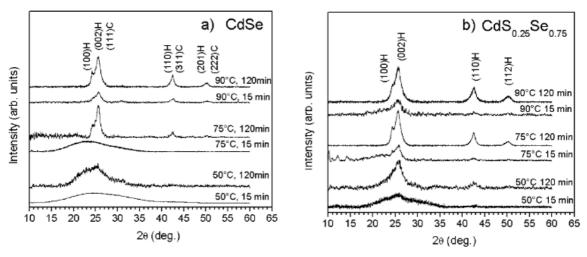


Figure 1. XRD spectra of a) CdSe and b) CdS_{0.25}Se_{0.75} films grown during 15 and 120 min at different temperatures.

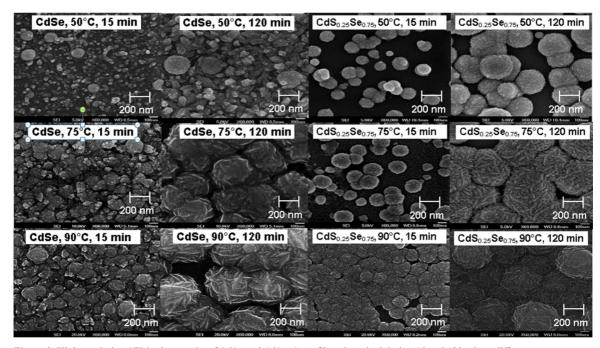


Figure 2. High-resolution SEM micrographs of CdSe and CdS_{0.25}Se_{0.75} films deposited during 15 and 120 min at different temperatures.

deposited during 15 min at 50 and 75°C show few clusters, that give rise by growth and coalesce to the denser films observed at 120 min. These results indicate that the XRD peaks definition observed in Figure 1b is due to the higher crystalline quality of the CdS_{0.25}Se_{0.75} films deposited at 15 minutes and not to their thickness, compared to CdSe. At the longest deposition time (120 min), the resulting films are denser, with similar morphology and narrower cluster size distribution than those obtained at shorter deposition times for all temperatures tested.

EDS analysis reveals an average 1.2:1 Cd:Se atomic composition for all the CdSe samples, suggesting that films possess Se vacancies at all time and temperature deposition

conditions. In Figure 3 the variation of Cd, S and Se atomic composition of CdS_{0.25}Se_{0.75} samples prepared at 50 (a), 75 (b) and 90°C (c), as a function of deposition time is presented. The composition was calculated assuming that S+Se =1 in all the samples. As can be observed, the atomic composition behavior with time is similar for all temperatures. Even though the S:Se molar ratio is 0.25:1.31 in the bath solution (75% Se excess), precipitation starts (5 min) with a S excess, which decreases to reach an almost constant value, strongly suggesting that a S rich CdSSe solid solution is first obtained and that the S²-substitution by Se ions is taking place subsequently, as reported in literature for CdS₁. Se_x ternary solid solutions^{14,16}. The expected composition,

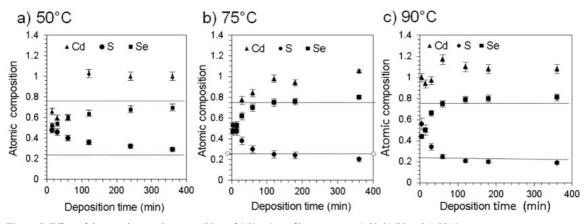


Figure 3. Effect of time on the atomic composition of CdS_{0.25}Se_{0.75} films grown at a) 50, b) 75 and c) 90°C.

CdS_{0.25}Se_{0.75}, is obtained at 120 and 60 min for 75 and 90 °C respectively. For films prepared at 50°C, the expected composition is not attained even at 360 min, indicating that the sulfur substitution process is strongly accelerated by temperature. The Cd ion coefficient increases with both time and temperature, reaching a close to 1 constant value.

3.2 Optical properties

Optical properties of the CdSe and CdS_{0.25}Se_{0.75} films were analyzed through absorption and photoluminescence studies. Figure 4a shows the absorption spectra of films deposited at 50, 75 and 90°C during 120 min, which were normalized with the highest signal in order to improve the comparison. A well-defined absorption edge is observed for all films, showing that films have good optical properties. Absorption edges of CdSe and CdS_{0.25}Se_{0.75} films shift to red as a function of temperature. However, the addition of S to CdSe alloy provokes a blue shift of the absorption

edge. Considering that both CdSe and CdS_{0.25}Se_{0.75} are direct band gap semiconductors, band gap values were estimated using the $\alpha hv = A(hv - E_{\rho})^{1/2}$ equation, where α is the absorption coefficient, A is a constant and n=1/2 for allowed direct transitions. The E_g value is obtained by extrapolation to α =0 in the $(\alpha h)^2$ vs h plot (Figure 4b)¹¹ ^{12,20}. As expected, E_a decreases according to temperature but increases with the formation of the ternary compound. The estimated CdSe E_a are 2.02, 1.96 and 1.90 eV for films grown at 50, 75 and 90°C respectively. These values are higher than E_o for the bulk material (1.74 eV) because of the small crystal size of the samples, as calculated from XRD (from 4 to 8 nm), whereby a quantum effect is predictable $^{12,20\text{-}22}$. Regarding $CdS_{0.25}Se_{0.75}$, the estimated E_a values are 2.09 (50°C), 1.98 (75°C) and 1.93 eV (90°C). The difference between the experimental and the theoretical value for the ternary compound (1.91 eV from Vegard's Law) is attributed to the small crystal size (6 nm)²² of the samples. The effect of the deposition

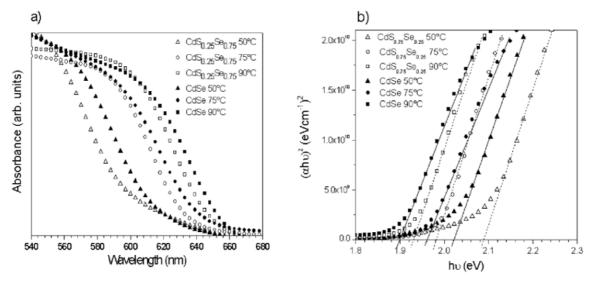


Figure 4. a) Absorbance spectra and b) plot of $(\alpha h \upsilon)^2$ vs $(h\upsilon)$ of CdSe and CdS_{0.25}Se_{0.75} films grown during 120 min at different temperatures.

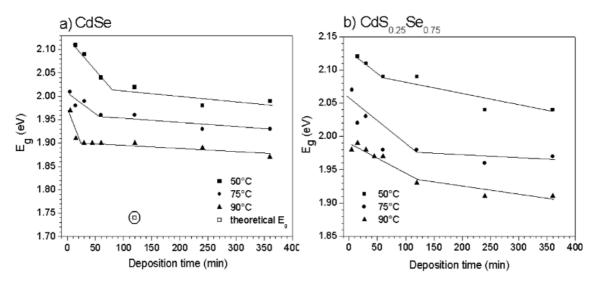
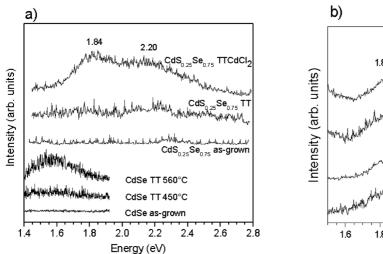


Figure 5. Energy band gap, Eg, of a) CdSe and b) CdS_{0.25}Se_{0.75} films grown at different deposition time and temperature.

time on the E_g value for CdSe and CdS $_{0.25}$ Se $_{0.75}$ films at different temperatures is depicted in Figure 5a and 5b respectively. In both cases, E_g decreases as a function of deposition time, until reaching a constant value for all temperatures. In the case of CdSe films, the decrease can be related to crystal size, which slightly diminishes too. However, as the crystal size for the ternary compound films is almost constant (6 nm), the reduction of E_g in this case can be related to the change in the composition, as observed in Figure 3.

Figure 6a shows the room temperature photoluminescence results for the as-grown and the thermal-treated (TT) CdSe and CdS_{0.25}Se_{0.75} films. As it can be seen, no signal for the as-grown CdSe samples was detected. Moreover, after the thermal annealing at 450°C, a broad band centered

around 1.55 eV appears, it becoming better defined after annealing at 560°C. The PL signal at room temperature is significantly improved at annealing the CdS_{0.25}Se_{0.75} sample with CdCl₂ at 400°C; the spectrum shows two radiative broad bands, one at the low energy side, with a maximum around 1.84 eV and the second centered at 2.20 eV approximately. A similar spectrum has been already reported by Perna et al.²³, corresponding to a CdS_{0.2}Se_{0.8}, sample grown by laser ablation. Usually, those bands are related to deep levels, attributed to either sulfur or selenium vacancies, or else to non-radiative extrinsic defects due to structural disorders of the alloy. Figure 6b depicts the PL signal behavior with temperature corresponding to the CdS_{0.25}Se_{0.75} sample grown during 120 minutes. The large linewidth and the peak position of the high energy



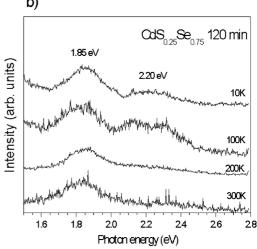


Figure 6. a) Room temperature PL spectra of as grown and thermal treated (TT) CdSe and CdS0.25Se0.75 films and b) PL spectra of CdS0.25Se0.75 films measured at different temperatures, $10 \le T \le 300$ K.

band observed at low temperature suggest that it is not due to exciton recombination. No noticeable shift of the bands can be observed. The high energy band could be assigned to transitions arising from native impurity levels, such as free to bound or donor-acceptor recombination.

3.3 Kinetics of deposition

The thickness of all the CdSe and CdS_{0.25}Se_{0.75} films as a function of time and temperature are presented in Figure 7a and 7b, respectively. A typical time dependent S-shape curve is only observed in the CdSe films grown at 50°C as it occurs in just a few minutes¹⁷ it is rarely observed. In all other cases the thickness increase at a fast initial rate and the profiles show that the growth regime is taking place over six hours. It is clear that the introduction of S in the

bath does not affect the thickness of the films, thus the kinetics of both CdSe and CdS_{0.25}Se_{0.75} deposition is very similar. However, as already observed in Figure 2, ternary films deposited at short time (15 min) and low temperature (50°C) are less dense than binary films grown at the same conditions, thus nucleation of CdS_{0.25}Se_{0.75} is slow and growth is extremely fast. The growth rate was estimated as the ratio between thickness (nm) and deposition time (min), Figure 8 presents the effect of time on growth rate of CdSe (a) and CdS_{0.25}Se_{0.75} (b) films. Growth rate strongly diminishes as a function of time and temperature, going from 10 to 1 nm/ min in average, for binary and ternary films. Therefore the initial rate and the thickness notable increase with temperature strongly indicates that the kinetics of the film formation is controlled by the chemical reactions taking place in both ternary and binary systems.

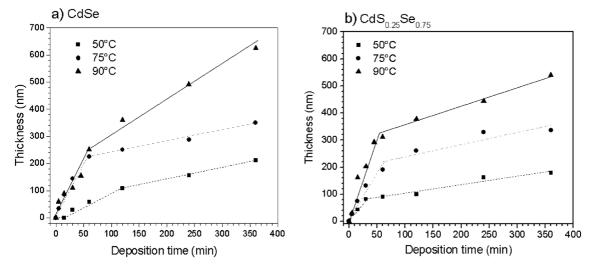


Figure 7. Thickness of a) CdSe and b) CdS_{0.25}Se_{0.75} films deposited at different time and temperature.

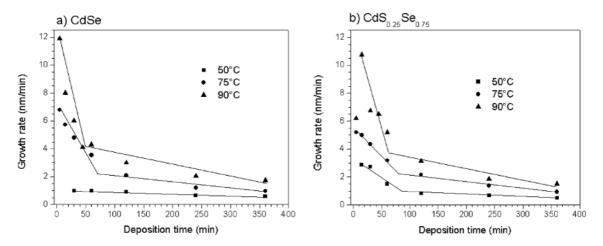


Figure 8. Growth rate variation of a) CdSe and b) CdS_{0.75}Se_{0.75} films as a function of deposition time and temperature.

4. Conclusions

Nanostructured CdSe and CdS_{0.25}Se_{0.75} thin films have been grown by CBD varying deposition time and bath temperature. CdSe films properties are modified by the solid solution formation with the S ion added to chemical bath; better quality crystallization in hexagonal phase is promoted, E_a is increased but density of the films is diminished and no PL improvement is detected. Ternary films composition, x, depends on time and temperature while Cd:Se ratio of binary samples is not affected by these parameters. Temperature and time deposition promote high crystalline quality and the decrease of band gap values; concerning CdSe films this reduction is related to crystal size and in the case of CdS_{0.75}Se_{0.75} films it is associated to the composition change. Room temperature PL of CdS_{0.25}Se_{0.75} films is observed after annealing with CdCl₂, two broad bands associated to cadmium or selenium vacancies and to structural disorder are observed. Low temperature PL of CdS_{0.25}Se_{0.75} films indicates free to bound or donor-acceptor recombinations. The kinetics of the film formation is controlled by the chemical reactions taking place in both ternary and binary systems.

5. Acknowledgments

This work was supported by IPN-SIP contracts 20151801, 20161872 and 20161876. E.A.S.R. thanks the CONACYT and IPN for PhD and BEIFI grants.

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