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Effect of annealing temperature on the crystalline quality and phase transformation of Chemically Deposited CdSe films

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Polycrystalline CdSe thin films were grown on glass substrates by chemical bath deposition at 50 ºC. The samples were annealed in air atmosphere at different temperatures and characterized by X-ray diffraction and Raman spectroscopy. It was found that the as-grown films have cubic structure. These samples maintain their cubic structure for annealing temperatures between 60 ºC and 300 ºC. For annealing temperatures higher than 300 ºC we obtain a mixture of cubic and hexagonal phases. The analysis made by X-ray diffraction and Raman dispersion show that the samples annealed at temperatures under the phase-transition temperature increase their crystalline quality. In order to determinate the temperature for the complete transition of the cubic phase, we used the precipitated material obtained during the grown of the CdSe films. This material was annealed on air atmosphere between 300 °C and 500 °C with 50 ° intervals. The samples were measured by X-ray diffraction. The samples maintained the cubic structure if the annealing temperature is under 300 °C. For temperatures between 300 °C and 450 °C we found a mixture of cubic and hexagonal phase. For an annealing temperature of 500°C we obtain only the hexagonal phase.

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1 Introduction

Chemically deposited (CD) CdSe films have been widely studied, mostly for their use in photovoltaic solar cells and other applications. CD-CdSe films are reported to have cubic, hexagonal, and mixed crystal structures [1–3]. Nair et al. [2] have shown that the as-deposited CdSe films are amorphous and that after annealing at temperatures over 450 °C the development the hexagonal wurtzite structure occurs. Portillo-Moreno et al. [4] reported that the critical temperature of the transformation of cubic to hexagonal phase of CdSe films occur at 355±25 °C; obtaining the single hexagonal phase at 429 °C. Kale et al. [5] reported the influence of air annealing on the structural, optical and electrical properties of CD CdSe nano-crystallites. The CD-CdSe films have been widely studied attending to the quantum confinement effects that are manifested in these films due to the distribution of particle size that is possible to obtain. In many cases these samples present a surface-optic Raman mode that is used to characterize their quality, this mode is evident in samples with lower crystalline quality.The change of phase in CdSe has been matter of discussion among different authors [6] and until now, there is a lack of a conclusive study. A main problem for this question is the preferential orientation that the films present. In this work, the effect of annealing time and temperature over the crystalline quality of CD-CdSe films is reported. We characterized the CD-CdSe films by X-ray diffraction (XRD) and Raman Spectroscopy. In order of

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determinate the temperature for the complete transition of the cubic-to-hexagonal phase, we utilized the precipitated material obtained during the grown of the CdSe films. These material were annealed on air atmosphere and measured by X-ray diffraction.

2 Experimental details

The CdSe films were deposited from an aqueous solution of 0.027 M Na_2SeSO_3 , 0.027 M $CdCl_2$ and 50 ml NH_3 30% as complexing agent. The pH of the solution was adjusted by the NH_3. The substrates were 26 x 75 mm Corning glass microscope slides, boiled in chromic acid and bi-distilled water. The cleaned substrate was immersed into the freshly-prepared solution, and left for 72 hours at 50 °C. During the first 24 hours the vessel with the solution and the substrate was closed to avoid the evaporation of the solution. The chemical deposition technique is described elsewhere [1,5,6]. The as-grown (AD) films were washed with bi-distillated water, dried and then annealed in air atmosphere (AA): I) at 250 °C for 1 hour, 16 hours, 30 hours and 46 hours ; II) at 300 °C for 1 hour, 5 hour and 93 hours; and at 450 °C for 1 hour. The precipitated material obtained during the grown of the CdSe films was annealed on air atmosphere between 300 °C and 500 °C with 50°C steps. XRD measurements were carried out using a X ray diffractometer from Rigaku with Cu Kα (1.54 Å) radiation. The samples were scanned in the range 2θ from 15° to 85° with a step size of 0.050°. The Raman scattering experiments were carried out at room temperature in a Labram Dilor micro-Raman system, which was equipped with a confocal microscope. The sample was excited with the line of 632.8 nm from an He-Ne laser and the scattered light was analyzed with a CCD. The laser beam was focused onto the sample surface with the aid of a 50X objective, which yielded a laser beam spot of approximately 2 microns in diameter.

3 Results and discussion

Figure 1 shows the X-ray diffraction of the (a) as-grown film and the 1 hr, air annealed samples (b) at 250 °C, (c) at 300 °C and d) at 450 °C. The as-grown sample has very poor crystalline quality, and an improvement in the crystalline quality of the films after annealing is clearly seen as the annealing temperature increases. The AA samples below the transition temperature present cubic structure. The sample annealed at 450 °C is a mixture of cubic and hexagonal phases. The peaks were indexed using the powder diffraction files, the number were 19091 (cubic), 772307 (hexagonal and 221314 (SeO_3).

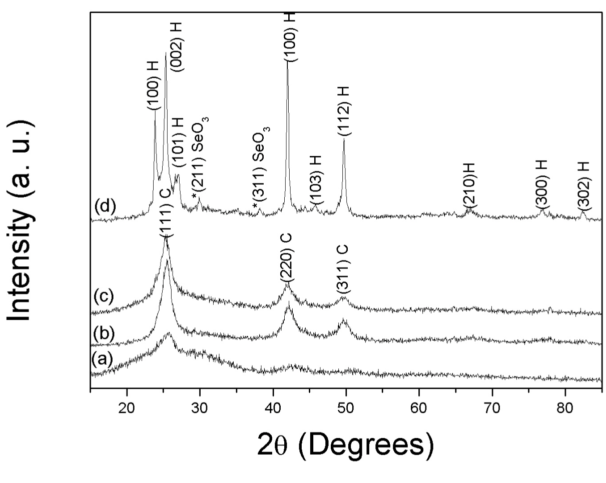

Fig. 1 XRD spectra of the samples (a) as-grown, (b) annealed at 250 °C for 1 h, (c) annealed at 300 °C for 1 h and (d) annealed at 450 °C for 1 h.

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In order to compare the crystallinity of the annealed samples at different times, we fit a pseudo-Voigt function of the peak corresponding to the plane (111) for each sample. From the fitted peaks was obtained the area of the peak and the ratio of the area of the annealed sample to the area of as growth sample was calculated. These ratio gives the influence of the annealing in the crystallinity. Figures 2a and 2b show the variation of this ratio with the annealing time for the samples annealed at 250 °C and 300 °C. From the figure can be seen that the main increase was obtained at 1 hour of annealing, for longer times noticeable changes were not observed. These results indicate that during the first hour of annealing the main effects are obtained. The thermal treatment improves the crystalline order of the films when the temperature is below the phase transition temperature but an increase in the treatment time at that temperature does not have any significant effect.

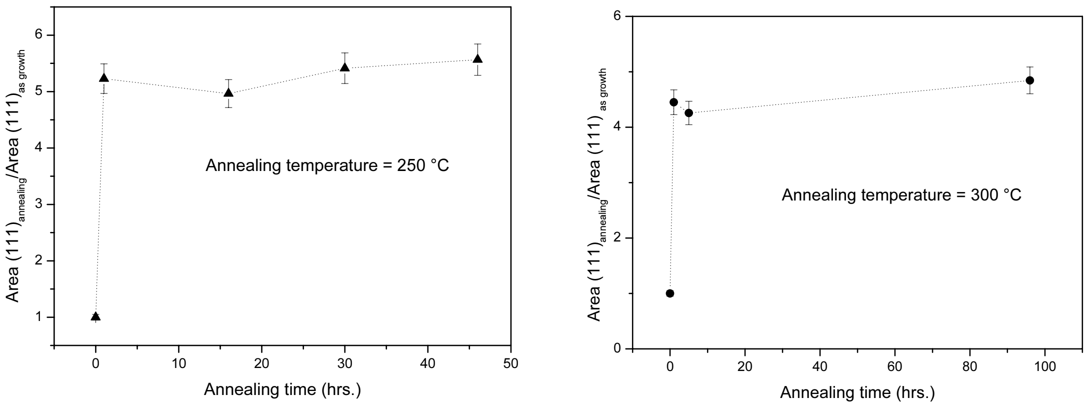

Fig. 2 Ratio between the area of (111) plane of the annealed sample and area of (111) plane of the as-grown sample; for annealing temperature of a) 250 °C and b) 300 °C for different annealing times.

We obtained the room temperature-Raman spectra of the CD-CdSe films: (a) as growth, and annealed at 250 °C by (b) 1 hour, (c) 16 hours, (d) 30 hours and (e) 46 hours. In the spectra the peak observed at around 207 cm^{-1} corresponds to the CdSe longitudinal optic phonon (LO). A common feature in the Raman spectra is the appearance of LO overtones. In the annealed samples it is possible to observe up to the fourth overtone, which is an evidence of the crystalline quality of the samples. In the case of the AD films, the 3 LO overtone was clearly distinguishable. It is well known that the higher the intensity of the overtones, the better crystalline structure of the films.

In order to asses this effect, in Fig. 3 is plotted the relative intensity ratio of the two most intense peaks (I_{2LO}/I_{LO}) as a function of annealing time for films annealed at 250 °C. From this graph it can be concluded that the crystalline quality of the films was improved starting with the first treatment for 1 hr and then, only a slight improvement in the quality of the films is obtained for samples annealed for longer periods of time. These results are in good agreement with those obtained by X-ray diffraction analysis. Rai et al. [3] have observed a surface-optic Raman mode for AD films. They observed that such mode disappears when the samples are annealed. In our case for both AD and AA films the SO Raman mode was not evident. This is also another indication of the good crystalline quality of our AD and AA samples.

In the Fig. 4 are presented the X-ray diffraction patterns of the annealed CdSe powders. It can be appreciated that the samples annealed between 300 °C and 450 °C present a mixture of cubic and hexagonal phases, and only the sample annealed at 500 °C is pure hexagonal form. The results indicate that the phase transition of CdSe begins between 250 °C and 300 °C and it is completed between 450 °C and 500 °C. More detailed studies on the transition temperature values are intended.

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4 Conclusions

Chemically deposited CdSe films had been studied by X-ray diffraction and Raman spectroscopy after air annealing. It has been found that the CD-CdSe films grow with cubic structure. The cubic-to-hexagonal transition begins between 250 °C and 300 °C and it is completed between 450 °C and 500 °C. From the X-ray diffraction patterns and the Raman spectra it was concluded that annealing at temperatures lower than the transition temperature produced better crystalline quality. The main increase on the crystalline quality was done in the first hour of annealing remaining without variation for longer annealing times.

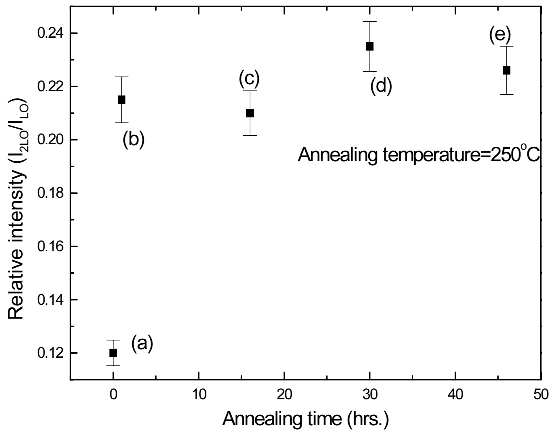

Fig. 3 Relative intensity of the 2LO/1LO ratio as a function of annealing time for the CdSe films.

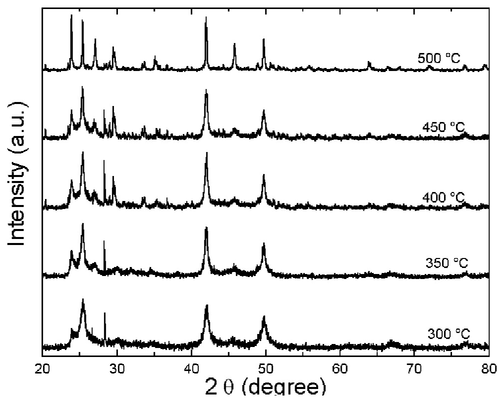

Fig. 4 X-ray diffractograms of the precipitated CdSe powder annealed at different temperatures.

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