Effect of annealing temperature on the crystalline quality of chemically deposited CdSe films

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Chemically deposited CdSe thin films have been studied attending to their crystalline quality with the variation of annealing time and temperature. It was found that the as-grown films have cubic structure. These samples maintain their cubic structure if the annealing temperature does not exceed the temperature of phase transition. The analysis made by X-ray diffraction and Raman dispersion show that the samples annealed at temperatures less than the transition temperature increase their crystalline quality. The main increase on the crystalline quality was done in the first hour of treatment; remaining without variation for long time.

Keywords: CdSe; Chemical bath; Raman spectroscopy

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 [1,2,3]. Nair et al. [2] have shown that the as deposited CdSe films are amorphous and that after annealing at temperatures over 450^0 C the development the hexagonal wurtzite structure occurs. Portillo-Moreno at 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. 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 [3, 5]. 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.
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. The results sugest that the main increase on the crystalline quality was done in the first hour of annealing; remains unchanged for larger annealing time.

2. Experiment

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 ^{0}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 ^{0}C for 1hour, 16 hours, 30 hours and 46 hours ; II) at 300 ^{0}C for 1 hour, 5 hour and 93 hours; and at 450 ^{0}C for 1 hour. 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 $2\theta = 15^0$ to 85^0, with a step size of 0.05^0.
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 632.8-nm line of a He-Ne laser and the scattered light 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. Film homogeneity was verified by comparing the Raman spectra of different spots on the sample surface. Special care was taken to avoid sample damage due to laser heating effects.

3. Results and Discussions

Figure 1 shows the x-ray diffraction patterns of (a) as-grown, (b) annealed at 250 ^{0}C for 1 h, (c) annealed at 300 ^{0}C for 1 h and (d) annealed at 450 ^{0}C for 1 h. The as grown

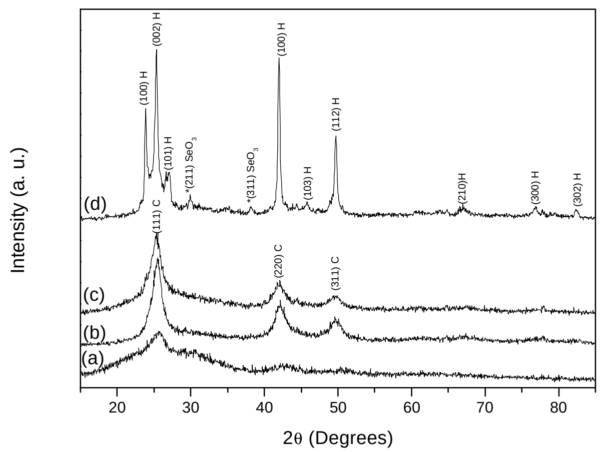

Figure 1. XRD spectra of the samples (a) as-grown, (b) annealed at 250 ^{0}C for 1 h, (c) annealed at 300 ^{0}C for 1 h and (d) annealed at 450 ^{0}C for 1 h.

sample (a) has very poor crystalline quality, and an improvement in the crystalline quality of the films after annealing is clearly seen. The AA samples below the transition temperature present cubic structure. A transformation of phase from cubic to hexagonal, in these samples, will be observed in the sample treated at 450 ^{0}C by the unfolding of the peak (111) into several typical peaks of the hexagonal structure that is an evidence that a transformation of phase is accounted. All peaks were indexed using the powder diffraction files (PDF), the number were 190191(cubic), 772307 (hexagonal and 221314 (SeO_3). We can see that the films had single phase, on the film annealed at 450°C we had peaks related with SeO_3, this can be due at the air used as the annealing atmosphere. An important remark is that the angular position of the (111), (220) and (311) plane for the cubic phase are practical the same that the (002), (100) and (112) for the hexagonal phase.

In order to compare the cristallinity of the annealed samples at different time, we fit a pseudo-voigt function of the peak corresponding to the plane (111) for each sample. We obtained the area of the peak and made the ratio of area of the annealed sample to area of as growth sample. These ratio give us the influence of the annealing in the crystallinity. Figure 2a and 2b show the variation of the ratio with the annealing time for the samples annealed at 250 °C and 300°C, we can see that the main increase was obtained at 1 hour of annealing, for longer time we did not obtain a variation. These results suggest that the main effect on the annealing was done in the first hour. The thermal treatment must improve the crystalline order of the films when the temperature is below that of the phase transition. However, the increase in the treatment time at that temperature does not have any significant effect.

Figure 3, shows the room temperature a Raman spectra of the CD-CdSe films: (a) as growth and annealed at 250 ^{o}C by (b) 1 hour, (c) 16 hours, (d) 30 hours and (e) 46 hours. 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

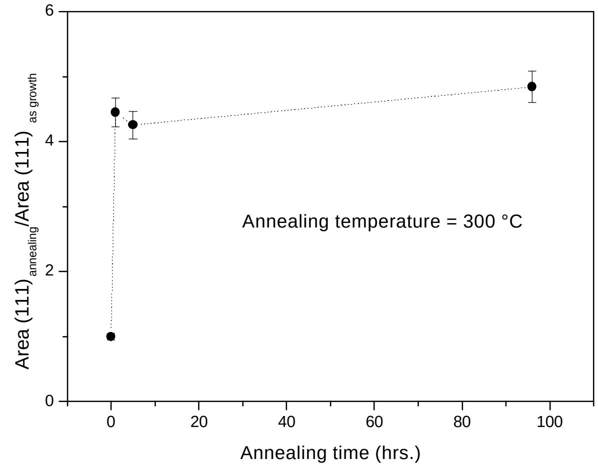

Figure 2a. Ratio between the Area of (111) plane of annealed sample and area of (111) plane of as growth sample; for annealing temperature of 250 °C and different annealing time

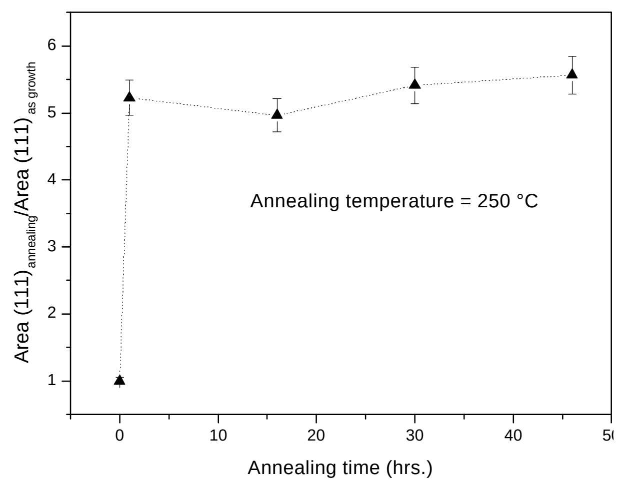

Figure 2b. Ratio between the Area of (111) plane of annealed sample and area of (111) plane of as growth sample; for annealing temperature of 300 °C and different annealing time

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 3LO overtone was clearly distinguishable. It is well known that the higher the intensity of the overtones, the better crystalline structure of the films. Therefore, we have plotted in Fig. 4 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 ^{o}C. From this graph it was possible to conclude that the crystalline quality of the films was improved starting with the first treatment for one hour and then, only a slight improvement in the quality of the films is obtained for samples annealed for longer periods of time. In other words, long annealing times do not have a significant effect on the crystalline quality of the films. These results are in good agreement with those obtained by X-ray diffraction analysis.

Nair 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

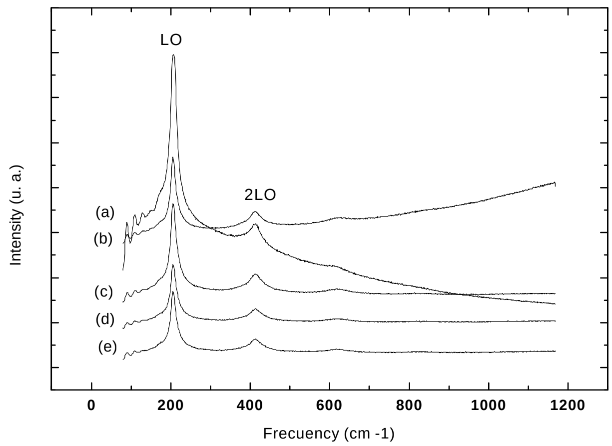

Figure 3. Raman spectra of CdSe samples (a) as-grown, (b) annealed at 250 ^{0}C for 1 h, (c) annealed at 250 ^{0}C for 16 h, (d) annealed at 250 ^{0}C for 30 h and (e) annealed at 250 ^{0}C for 46 h.

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.

4. Conclusions

It has been found that the CD-CdSe films grown with cubic structure. For annealing temperature below the critical the cubic phase is retained. The transformation of phase from cubic to hexagonal is development by an annealing temperature of 450 °C. From the X-rays 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 large annealing time.

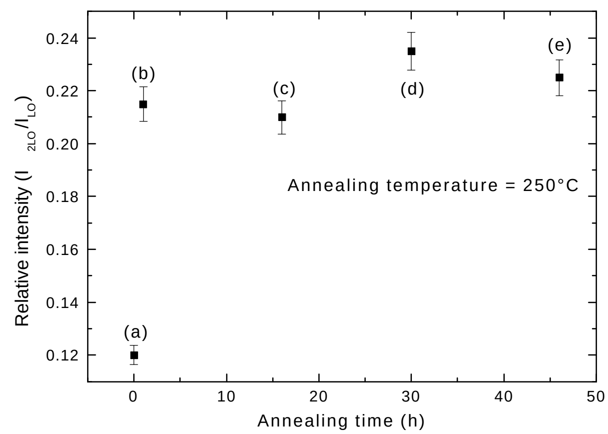

Figure 4. Relative intensity of the 2LO overtone with respect to that of the LO mode as a function of annealing time for the CdSe films.

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