

RAMAN AND PHOTOLUMINESCENCE STUDIES OF PURE AND
Sn-ENRICHED THIN FILMS OF CdS PREPARED BY SPRAY PYROLYSIS

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Thin films of CdS, pure and enriched with different concentrations of tin up to 6%, were prepared by the spray pyrolysis technique. All samples were prepared at the deposition temperature of 420 °C. The XRD diagnostic data of the investigated samples revealed the polycrystalline nature of the as-deposited samples. The main characteristic peaks of CdS appeared in both pure and enriched films prepared by all used methods. The enrichment of Sn has no effect on positions of the characteristic peaks. The observed effect of Sn enrichment is the change in peak broadening which increases with the increase of Sn concentration. The thickness values ranged from 0.65 up to 1.15 μm . The samples of pure CdS show a sharp absorption edge at about 2.43 eV. The absorption coefficient α of the investigated samples was calculated from transmission and reflection spectra. Photoluminescence measurements show red emission band of the as-deposited samples, which was quenched by Sn incorporation. This band is ascribed to the excess of Cd which was checked by the energy dispersive X-ray (EDX) spectrometry. Raman spectra of samples with different concentrations of Sn were studied. They show remarkable increase of intensity when increasing the film thickness and decreasing the Sn concentration.

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1. Introduction

CdS is one of the most studied materials with a band gap of about 2.43 eV [1–3]. It is an efficient window layer for the fabrication of solar cell structures due to its high transmittivity and low resistivity. Also, it is widely used because it yields the transparent SnO₂ conducting electrode needed in the measurements.

There are different ways to synthesize nano-crystalline CdS thin film such as chemical deposition, sol-gel, thermal evaporation, sputtering, spray pyrolysis (SP) technique, etc. [4–11]. The SP technique was used here because of its simplicity. It is known that nanocrystalline (1–5 nm) semiconductors exhibit the quantum confinement effect.

The previous reported photoluminescence (PL) spectra of CdS nanocrystallites, prepared by gas evaporation technique [12], show the peak position shifted to lower wavelength and the intensity of luminescence decreases with decreasing crystallite size. This is attributed to the fact that with decreasing crystallite size, the surface to volume ratio increases, leading to increase in surface band. The excited electron is captured by the surface of defect state before the occurrence of the direct radiative recombination, thereby, reducing the PL intensity. This result is in contrast to that observed by Agata et al. [13] in microcrystals also prepared by the gas evaporation technique. The red PL-peak intensity increases with decreasing crystallite size of the microcrystals. They have interpreted it as the transitions of electron trapped at surface states to the valence band as the microcrystalline size decreases. The volume to surface ratio increases leading to the increase in the intensity of the surface related band. Therefore, it is important to carry out the photoluminescence study to greater detail.

There are different ways to prepare nanocrystalline CdS. In the present work, we propose an approach to prepare nanocrystalline CdS thin film. It depends mainly on impeding of the growth of the initiated nuclei.

The structural studies, optical properties, SEM, FT-Raman shift and the photoluminescence [14,15] were used to elucidate the effect of Sn addition to pure CdS films.

2. Experimental

The as-deposited CdS thin films, pure and enriched to different concentrations of Sn were prepared by the spray pyrolysis process, using a home made spray system described elsewhere [16]. The used reactive solutions were an aqueous solution of 0.1 M CdS (prepared from 1:1 CdCl₂ and thiourea) and 0.1 M of an aqueous solution of SnCl₄. The Sn concentrations in CdS films were varied from 0.25% up to 6% by volume. The pure CdS samples were prepared at constant deposition temperature 420 °C, the deposition times were 15, 25 and 35 minutes, while the Sn-enriched samples were prepared at constant deposition temperature 420 °C and constant deposition time of 35 minutes.

The X-ray diffraction (XRD) patterns of the films were recorded with the Philips X-ray diffractometer PW/1710 having a Ni filter, and with monochromatised CuK α radiation of wavelength 0.15418 nm at 40 KV and 30 mA.

The scanning electron microscope (SEM) micrographs were made using JEOL JSM-T330 A scanning microscope at 2000 \times and 5000 \times , resolution 5 μ m and high tension of 25 kV.

Transmission (T) and reflection (R) spectra of the prepared samples were measured by normal incidence of light, using Jasco V-570 spectrophotometer, in the

wavelength range 0.2–2.5 μm , the blank substrate was the reference position. The absorption coefficient α of all investigated samples was deduced. The film thickness was calculated from the envelope of the transmittance spectra which have maximal and minimal interference extrema [18], also it is measured using the tally-step instrument with an experimental error of $\pm 3.5\%$.

FT-Raman spectrometer of the type BRUKER IFS 6/s, having a Nd-Yag laser of the wavelength 1064 nm as light source, was used in this investigation. The photoluminescence spectra of the investigated samples were measured using a room temperature photoluminescence setup. The exciting laser CW He-Cd laser (326 nm, 15 mW) was used as the excitation light source.

3. Results and discussion

The thickness of CdS films deposited at 420 °C was found to be 0.55, 0.85 and 1.15 μm , corresponding to deposition times of 15, 25 and 35 minutes, respectively. The effect of film thickness on the XRD diffraction patterns is shown in Fig. 1.

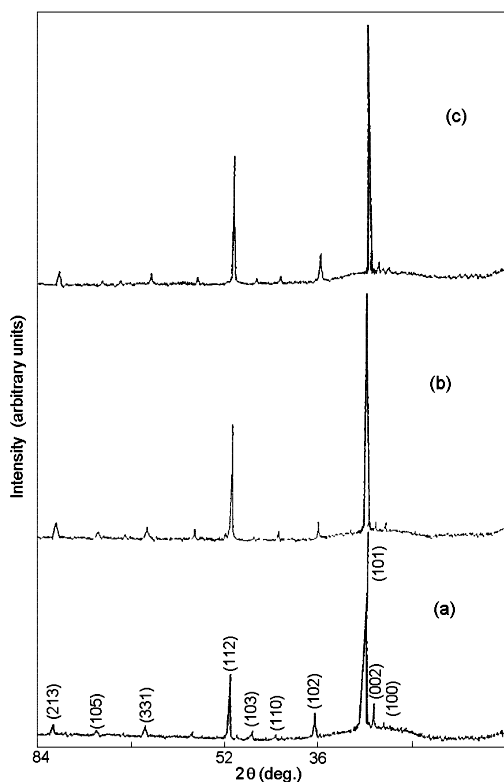


Fig. 1. XRD patterns of pure CdS thin films prepared at constant deposition temperature of 420 °C and different deposition times (a) 15 min., (b) 25 min. and (c) 35 min.

It is clear that the peak intensity increases as the film thickness increases. The XRD patterns of pure CdS film and that enriched with different concentrations of Sn prepared at constant deposition temperature 420 °C and constant deposition time of 35 minutes are shown in Fig. 2. The diffraction patterns in Figs. 1 and 2 show two intensive and sharp peaks at 2θ equal 52° and 28° which correspond to diffraction from (112) and (101) planes. They are the principle peaks of the CdS

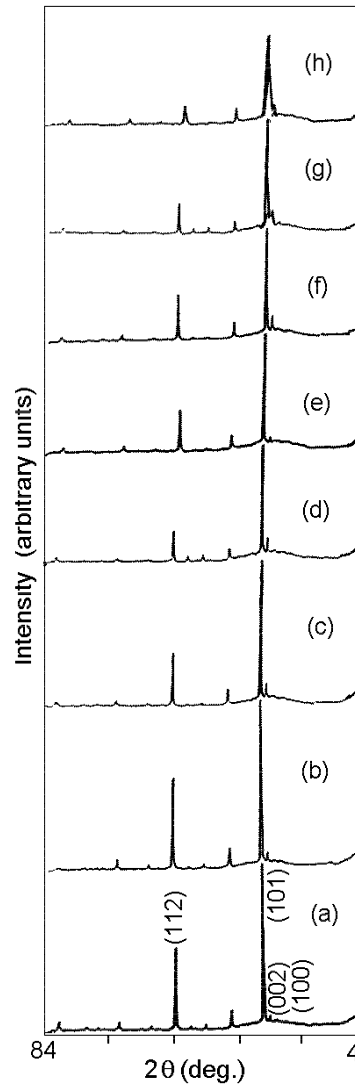


Fig. 2. XRD patterns for CdS thin films prepared at deposition temperature of 420 °C and deposition time of 35 minutes; (a) pure CdS, films enriched with (b) 0.25% Sn, (c) 0.5% Sn, (d) 0.75% Sn, (e) 1% Sn, (f) 1.5% Sn, (g) 4% Sn and (h) 6% Sn.

films. No change in the characteristic peak positions with increasing film thickness and concentration of the Sn enrichment was observed. This means that they retain the hexagonal structure of the pure CdS. No characteristic peaks corresponding to the enrichment element, Sn, or its oxides were detected in the XRD patterns. However, a decrease in the peak heights and an increase in the full width at half maximum (FWHM) were observed when increasing Sn concentrations [16], while an opposite trend was observed when increasing the film thickness. The decrease in peak heights as a result of Sn enrichment could be interpreted by its adsorption on the surface of growing CdS microcrystals which prevented it to grow larger along or perpendicular to the substrate. The observed induced change in the broadening due to Sn enrichment could be attributed to the induced strain and smaller-grown crystallites. The enrichment by tin atoms may impede the growth of nuclei of CdS crystallites which causes the formation of small crystallites.

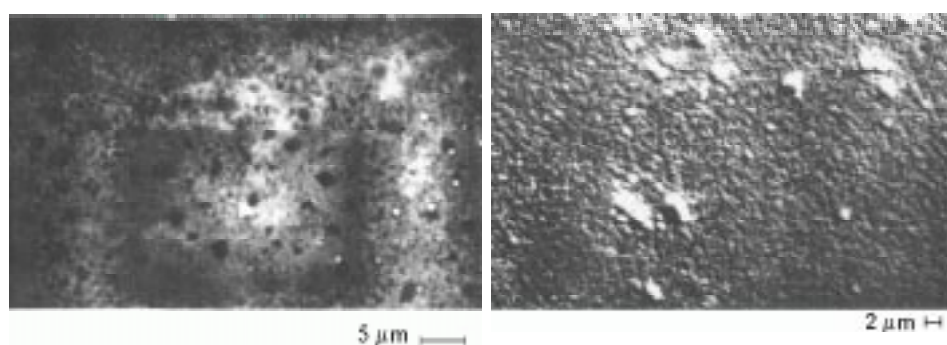


Fig. 3. SEM micrographs of CdS thin films prepared at constant deposition time of 35 minutes and constant deposition temperature of 420 °C, (a) film enriched with 6% Sn and (b) pure film.

The SEM micrographs for pure CdS film and that enriched with 6% of Sn, prepared at constant deposition temperature of 420 °C and constant deposition time 35 minutes, are depicted in Fig. 3. A marked difference can be noticed between the grain size of the films. In the case of pure film, one can identify the presence of larger grains on the surface under 2000 \times magnification. These grains are mainly formed for longer deposition times, when the solution contains a high concentration of the constituent formed by the parallel homogeneous precipitation reaction. As a consequence, the surface grains are due to the sticking of large aggregates on the surface. While very fine grains were observed under 5000 \times magnification in enriched films with 6% of Sn. The dark spots at the 6% concentration might be due to the phase separation of Sn precipitate (unreacted Sn) [18].

Figure 4 shows the optical transmission and specular reflection of light as a function of wavelength in the range 400 to 2500 nm for pure CdS thin film and films enriched to different Sn concentrations from 0.25% up to 6%. The average transmission values equal $85 \pm 7\%$ in the wavelength range 510 to 2500 nm for the different Sn concentrations. It is observed that both the transmission and reflection curves show interference patterns, and that the band gap of pure CdS is equal about

2.43 eV. The scale in the wavelength range 400 up to 800 nm was expanded for pure CdS thin film and film enriched to two different Sn concentrations of 1% and 6% as shown in the inset in Fig. 4 to clarify the changes if present. It is clear that the

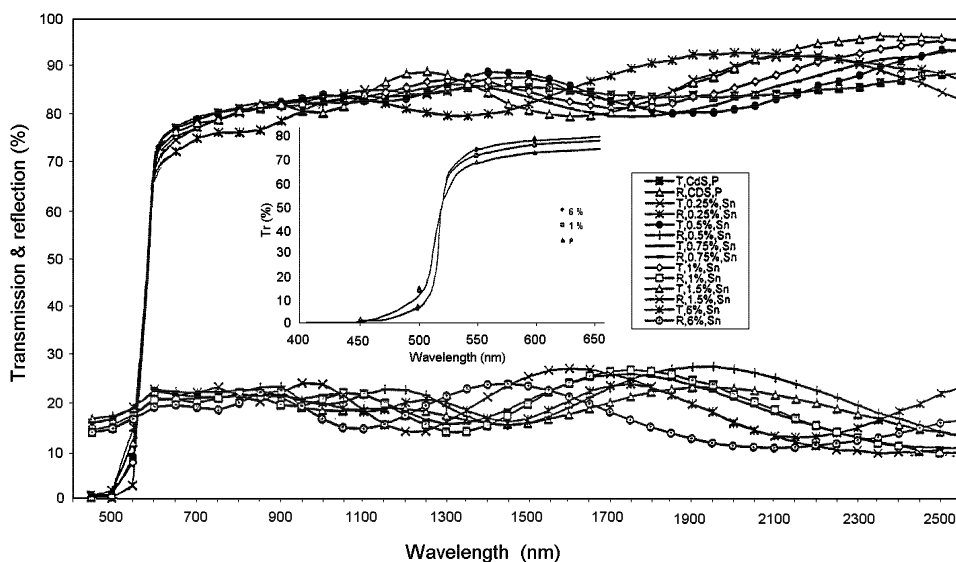


Fig. 4. Transmission (*T*) and reflection (*R*) spectra of as-deposited CdS thin film (*P*) and enriched with different concentrations of Sn from 0.25 up to 6%. The inset figure is of the expanded scale in the wavelength range 400 up to 800 nm.

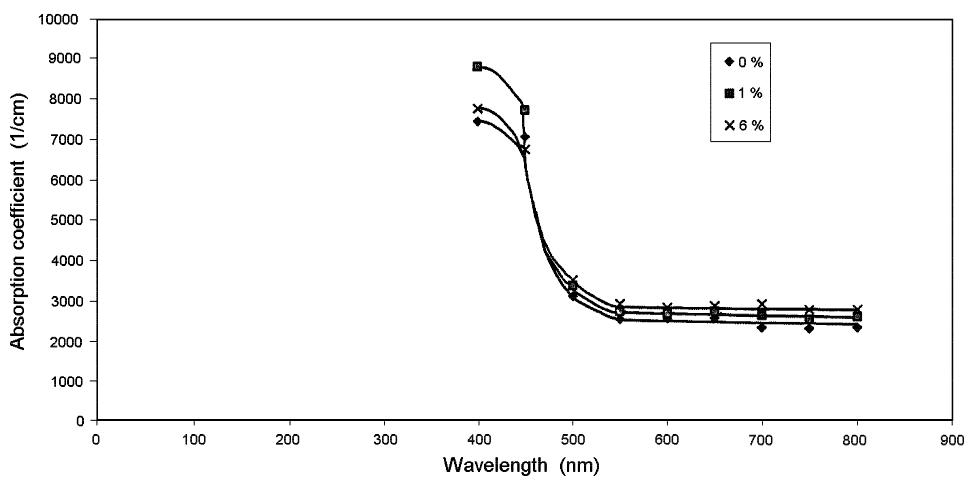


Fig. 5. The absorption coefficient as a function of the wavelength (nm) of pure CdS thin film and films enriched with 1% and 6% of Sn.

band gap shifted to a longer wavelength. Figure 5 shows the plot of the obtained values of the absorption coefficient α calculated from transmission and reflection measurements for pure and enriched films with two different concentrations of Sn of 1% and 6% as a function of the wavelength. It is seen that at short wavelengths, a steep decrease occurs in the absorption coefficient around the absorption edge (at E_g). It is found that by increasing the Sn concentration, α increases. The increase in α might be due to the increase of the surface roughness caused by Sn incorporation. This result is in agreement with results of Boer [19] who suggested that the creation of surface roughness gives rise to multireflections which capture the reflected radiation and enhance the absorptivity.

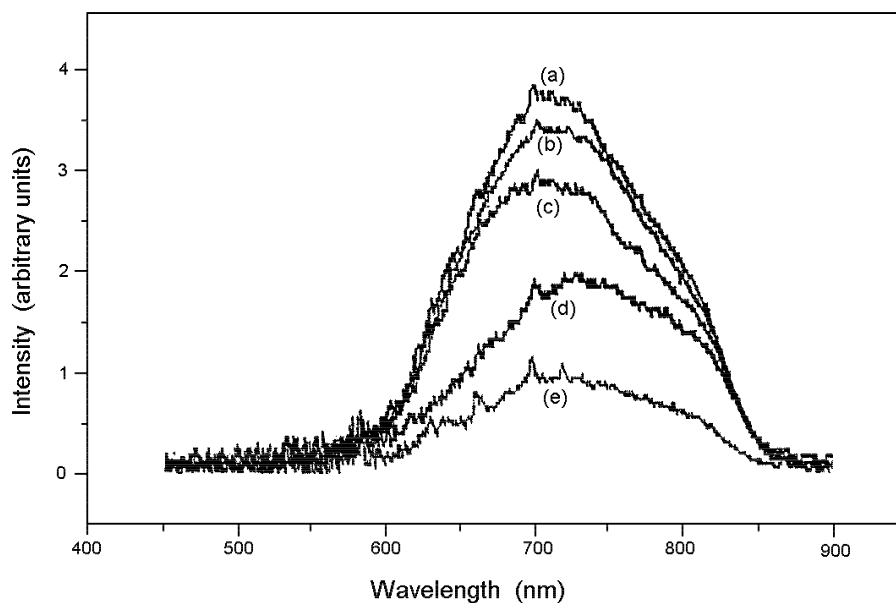


Fig. 6. Photoluminescence spectra of (a) pure CdS thin film, and CdS enriched with different Sn concentrations (b) 0.25%, (c) 0.50%, (d) 1% and (e) 6%, respectively.

The peak in the photoluminescence red emission spectrum centered at $\lambda \cong 698$ nm for the investigated CdS films prepared by spray pyrolysis technique is shown in Fig. 6. This red emission line, that is observed clearly even by naked eyes, can be identified with the excess of cadmium in the prepared thin film. The energy dispersive X-ray (EDX) manifests the excess of cadmium, where Cd to S ratio equals 52.66 : 47.34. The cadmium atoms are displaced to interstitial positions more easily than the sulfur atoms, because Cd has a smaller binding energy than S atoms in the CdS lattice. The excess of Cd leads to the increase of the presence of interstitial Cd atoms, i.e. there are large amount of defects which cause an important level of disorder [19–22]. Red PL was also observed for CdS samples with percentages of Sn of 0.25, 0.5, 0.75, 1.5 and 6%. This means that the observed red peak is mainly due to the excess Cd atoms. Generally, the peaks of the maxima show shift

toward the longer wavelength as the percentage of Sn increases. This shift may be attributed to the indirect recombination of the free electrons moving from the trap levels formed by the tin atoms to the holes in the valence band. These trap levels are in the energy gap and shift towards the valence band as the Sn atoms concentration increases. The maximum intensity of the PL seems to be decreased as the Sn percentage increases [12]. The decrease of the photoluminescence peak with the increase of Sn atoms could be explained by the electronic configuration of both Sn and Cd atoms. The $5S^2$ electrons of the excess Cd atoms are excited by laser and cause the PL peak. With Sn atom enrichment, their $5P^2$ sub-shell is completed at the expense of the $5S^2$ Cd atoms. Therefore, the number of electrons involved in the transition decreases as a result of the presence of Sn atoms. Thereby, the intensity of PL peaks at 698 nm decreased with increasing the Sn concentration and/or decreasing the crystallite size [21].

The dependence of the FT-Raman intensity on the different concentrations of Sn and different film thickness is shown in Figs. 7 and 8, respectively. The spectra were recorded over the wave number range from 250 up to 3500 cm^{-1} . Two distinct

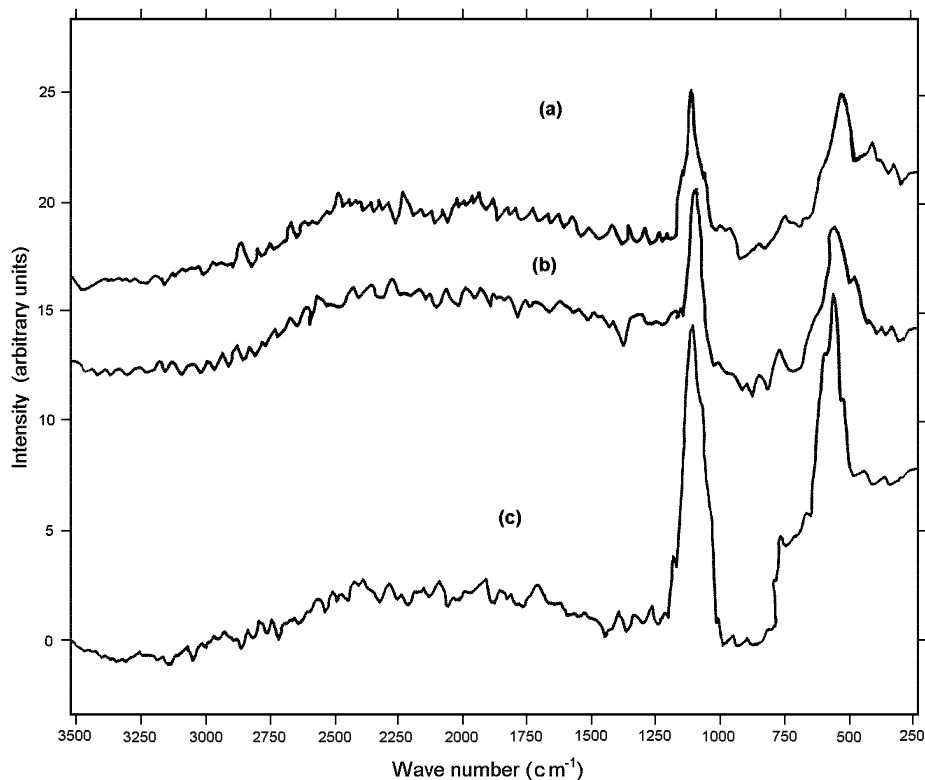


Fig. 7. FT-Raman spectra for pure CdS thin film and different deposition times of (a) 15 min., (b) 25 min. and (c) 35 min.

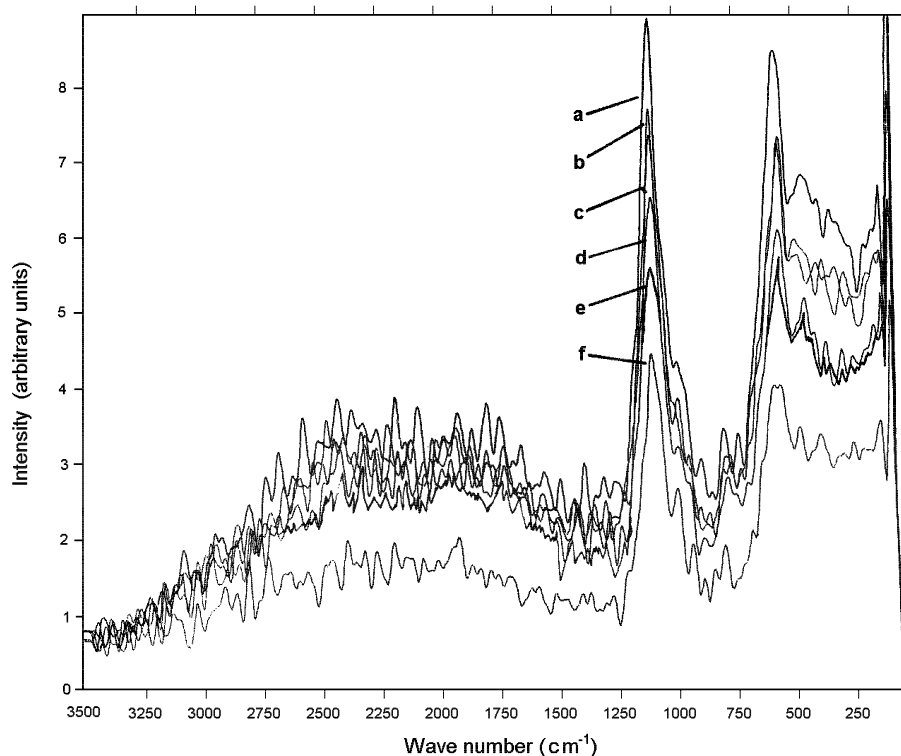


Fig. 8. FT-Raman spectra for (a) pure CdS thin film and the films enriched with different Sn concentrations (b) 0.50%, (c) 0.75%, (d) 1%, (e) 1.5% and (f) 6%.

features are present in all spectra. A sharp peak is observed at about 1100 cm^{-1} and a weaker one can be observed at 560 cm^{-1} . In Fig. 7, it is observed that by increasing the film thickness, the FT-Raman intensity increases. This may be a result of decreasing FWHM due to increases of the crystallite size [16]. The results in Fig. 8 seem to show that by increasing the Sn concentration, the FT-Raman intensity decreases. While we are unable to identify the surface roughness, the results are compatible with those obtained using PL, i.e., the intensity of Raman spectra were reduced by increasing the Sn concentration. The two FT-Raman features that appeared in CdS thin films at 1100 and 560 cm^{-1} are known to arise from the symmetry-dependent lattice dynamical oscillations. The presence of these two features is in agreement with the conclusions of the X-ray investigation of Ref. [22] which found that the films exhibited a large degree of preferred orientation similar to that seen here. An increase of the intensity in all of the Raman bands with both the decrease of Sn concentration and the increase in film thickness was observed, whereas the FWHM decreases and the crystallite size seems to increase in both

cases. It could be concluded that the crystallite size and the film thickness play an important role in modifying the Raman spectra.

4. Conclusion

The obtained data give evidence that the common values of the energy gap in pure CdS thin films are about 2.43 eV. This value does not change for different Sn concentrations except at 6% when it slightly decreases. The XRD study reveals an enhancement of crystallinity when increasing the film thickness. An opposite trend is obtained by the Sn enrichment of different concentrations, as a result of the decrease in crystallite size. That was confirmed by the surface morphology detected by SEM. The approach of adding foreign atoms with the aim to decrease crystallite size by impeding the growth of initial nuclei has been achieved, but to certain limits. FT-Raman spectra show an enhancement in their intensity due to both the increase of the film thickness and the decrease of Sn concentration. The photoluminescence results show red emission at $\lambda = 698$ nm in all pure and enriched films, which may be due to the excess of Cd that was detected by EDX. The Sn enriched atoms behave as a quencher for the observed PL peak. This is interpreted by the Cd and Sn electronic structures.

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RAMANOVI I FOTOLUMINESCENTNI SPEKTRI ČISTIH I KOSITROM
OBOGAĆENIH TANKIH SLOJEVA CdS PRIPREMLJENIH PRSKANJEM I
PIROLIZOM

Metodom prskanja i pirolize pripremali smo čiste i do 6% kositrom obogaćene tanke slojeve CdS. Sve uzorke smo pripremali na temperaturi polaganja od 420 °C. XRD spektri ispitivanih uzoraka pokazuju polikristaliničnu strukturu. Glavni karakteristični vrhovi CdS vide se i u čistim i u obogaćenim uzorcima pripremljenim primijenjenim metodama. Obogaćenje kositrom nema utjecaja na položaje karakterističnih vrhova. Međutim, javlja se proširenje vrhova koje se povećava pri povećanim koncentracijama kositra. Izmjerene i izračunate debljine slojeva su u skladu. Debljine slojeva bile su između 0.65 i 1.15 μm . Uzorci CdS pokazuju oštar apsorpcijski rub na oko 2.43 eV. Apsorpcijske koeficijente α ispitivanih uzoraka smo izveli iz transmisijskih i refleksijskih spektara. Mjerenja fotoluminescencije pokazuju crvenu emisijsku vrpcu koja trne dodavanjem kositra. Ta se vrpca tumači viškom Cd što smo potvrdili disperzivnom rendgenskom spektrometrijom (EDX). Proučavali smo i Ramanove spektre uzoraka s raznim koncentracijama kositra. Oni pokazuju snažan porast intenziteta za slojeve veće debljine i manje koncentracije kositra.