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XRD RAMAN AND Uv-vis SPECTROSCOPICAL ANALYSIS OF NANOSTRUCTURED CdS:Li FILMS

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ABSTRACT

CdS and CdS:Li films were produced by means of ultrasonic spray pyrolysis (USP) method by spraying on glass substrates heated up to 340±5 °C. LiCl in three different rates was added into the preliminary solution while producing the CdS:Li films. The effect of Li on the structural and optical characteristics of the CdS film was analyzed. XDR spectra showed that the crystallization degree decreases while lithium is 15% and increases when lithium rate increases. The crystallite sizes were calculated to be in the range of 60-85 nm. SEM photographs showed that the contribution of Li changed surface appearances of films and their particle size. All films exhibited the Raman peaks centered 298 and 590 cm⁻¹ and the peak profiles were almost symmetric. The optical band gap and Urbach energy values of these films were determined. The maximum transmittance was found to be almost 80% for the visible region. LiCl which was added to the preliminary solution changed the optical characteristics of CdS film.

Keywords: Li doped CdS film; XRD; Raman; Optical properties

1. INTRODUCTION

In the first quarter of the 21st century, perspective of people for energy resources changed. The effects such as extinction of fuel and other fossil fuels, environmental pollution and global warming made it necessary to search renewable energy resources. As a result of this search, solar cells were invented for wide use of solar power in daily life. Solar cell is a p-n junction which directly converts sunlight into solar power. Production of solar cells is partially easy and their field of use has been gradually expanding due to their characteristics as they are long-life devices if they are used properly; they do not require high temperatures for high efficiency, they have smaller size compared to the power they supply, they are not harmful on the environment and they can easily be moved. The basis of inorganic solar cells is the semiconductor thin film technology. Consequently, analyzing optical, electrical and structural characteristics of semiconductor thin films used mainly in the solar power systems and electronic and optoelectronic (light emitting diodes) circuit elements have become more important parallel to technological developments.

CdS as one of the II-VI group compounds is commonly used as the glazing material for (In,Ga)Se₂ and CdTe photovoltaic solar cells due to its band structure and 2.4 eV optical band gap [1–5]. It is also applied in light emitting diodes (LED), photodetectors and thin film transistors and it is considered as n-type semiconductor due to its sulfur deficiency [6]. A variety of deposition techniques are used to deposit CdS films of desirable optical, electrical and structural properties; such as chemical bath deposition [7], thermal evaporation [8], screen printing [9], spray pyrolysis [10–12], etc. Among these techniques, ultrasonic spray pyrolysis (USP) method is a simple and economical one which does not require complex tools and vacuum, allows producing films with wider surface space and doped with different elements at the same time. The films obtained by this technique have polycrystalline structure. Study on the thin film technology for solar cells shows that based on the film applications, device quality CdS thin films can be produced by combining various dopant impurities while the film is being produced [13, 14]. While, doping III, group elements of the periodic

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table, such as Al, In and etc., cause changes on resistance and flaw density and doping alkali metals causes changes on optical characteristics of CdS material [15-17]. In the literature, the studies conducted on the effects of doping alkali metals on structural, optical, vibrational and superficial characteristics of CdS material are limited and the effects of doping Li on the structural and optical properties of CdS films produced by spray pyrolysis method have been reported, rarely. The doping materials and ratios are the parameters for determining the structural and optical properties of the CdS films produced by spray pyrolysis method. For this reason, LiCl in three different rates was used as the doping material and the effects of Li concentrations on structural and optical characteristics of CdS material were analyzed in this study.

2. EXPERIMENTAL PROCEDURE

CdCl₂ H₂O (0.05M), H₂NCSNH₂ (0.05M), LiCl (0.01M) aqueous solutions were used for producing CdS and CdS:Li films. The precursor solutions were produced by mixing these solutions in the rates mentioned in Table 1. 100 ml solution in total was previously sprayed on the glass substrates heated up to 340 °C. By means of a Fluke 62 max infrared thermometer, substrate temperature was kept constant at 340±5 °C. The distance of the ultrasonic spray head to the substrate was almost 30 cm. The flow rate of solution was adjusted to be 5 ml min⁻¹ and 0.2 kg cm⁻², respectively during spraying under control of flow meter and carrier gas pressure. Carrier gas used in this process was nitrogen. XRD measurements were conducted for determining the produced crystallization levels and phases. These measurements were conducted by using a CuK α ray with $\lambda=1,541$ Å wavelength and BRUKER D8 Advance X-ray diffractometer. The XRD pattern was scanned in 2θ range of 20°-70°. The films were mounted on rotating sample holders (at 15 rpm). Surface images were obtained by using a ZEISS Ultra plus model scanning electron microscope (FESEM)). Raman measurements were conducted at 50-3500 cm⁻¹ range by Bruker Senterra Dispersive Raman system (with He-Ne laser) at a wavelength of 632.8 nm. Optical absorption and reflectance spectrum of the films were measured in 200-900 nm wavelength range by using Shimadzu 2450 UV model spectrometer.

Table 1. Precursor solutions of the CdS and CdS:Li films

<i>Film</i>	<i>CdCl₂ H₂O (ml)</i>	<i>LiCl (ml)</i>	<i>H₂NCSNH₂ (ml)</i>
CdS	50	---	50
CdS:Li (15%)	35	15	50
CdS:Li (25%)	25	25	50
CdS:Li (35%)	15	35	50

3. RESULTS AND DISCUSSIONS

3.1. X-ray Diffraction Pattern of the Film

The crystallinity and the preferred crystal orientation of the films were analyzed by the XRD method. Figure 1 shows the diffraction patterns of pure the CdS and the Li doped CdS films. X-ray diffraction patterns of the films were measured in $20^\circ \leq 2\theta \leq 70^\circ$ range. It was observed from the XRD diffraction patterns that the films had polycrystalline structure. Crystallization degree decreased while lithium was 15% and increased when lithium rate increased. Orientations of crystal planes were in hexagonal form and the CdS structure and at (100), (002), (101), (102) (110), (103) and (112) directions (JCPDS 041-1049). Preferential orientation of the CdS, which was (101), changed for Li 25% and Li 35% film as (002). Changes occurred in the intensity of the main peaks were scribed to the rotation of some crystalline grains during the preparation processes. The same phenomena have been observed for Li doped CdS thin films, produced by sol-gel spin-coating technique reported by [18]. The peak for Cd

was observed in addition to the lithium doped diffraction patterns of the films (JCPDS: 03-065-3363). From these diffraction patterns, the crystallite sizes were calculated by means of Scherrer formula [19] and the CdS for Li 15%, Li 25% and Li 35% films and found respectively as 76 nm, 60 nm, 50 nm and 65 nm.

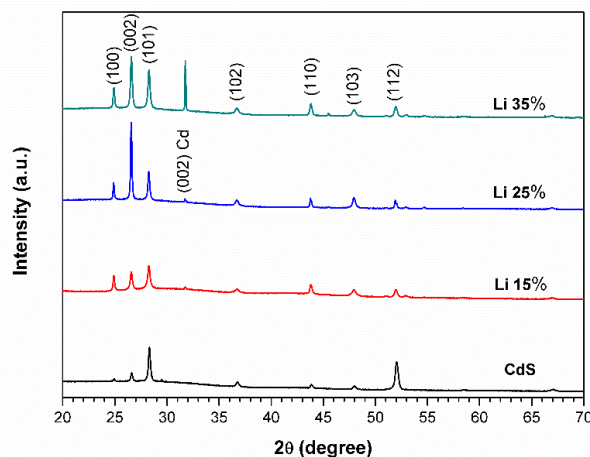


Figure 1. XRD spectra of the CdS and CdS:Li nanostructured films

Surface images were taken by 100 000 \times magnification (Figure 2). When, the surface images of the films were analyzed, it was observed that the Li doping caused changes on surface appearances and particle sizes. The particle sizes on the surfaces of Li 15% and Li 25% films were not very distinct. It was evaluated that the spandrel particles were dominant on the surface of the CdS film and the spandrel particles became round when preferential orientation began changing as a result of Li doping. Particle sizes are consistent with the crystallite sizes found from the XRD results. An idea about the particle size is obtained from the SEM photograph and it helps to determine the range of particle size.

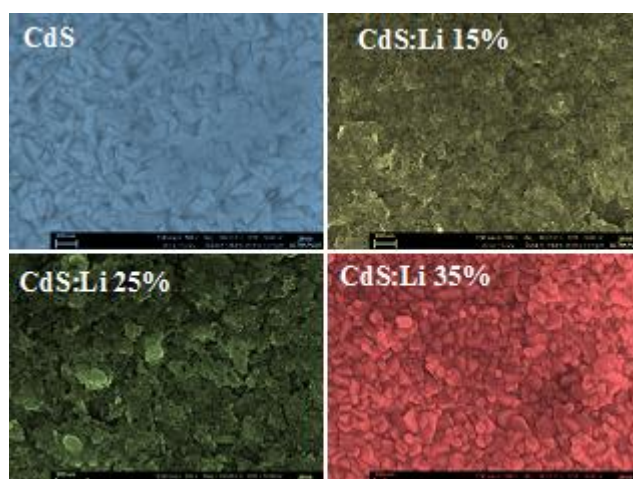


Figure 2. SEM images of the CdS and CdS:Li nanostructured films

3.2. Raman Spectroscopy

Theoretical foundations of Raman spectroscopy has been laid in 1930s, however because of the equipment needed for capturing the weak Raman signal and the problems related with laser technology, the studies on extending this technique have been continued up to now. Raman scattering

can be used for characterizing a structure in crystal form [20]. Figure 3 shows the room temperature the Raman spectra of the films. Two distinct active Raman modes were observed on the spectra.

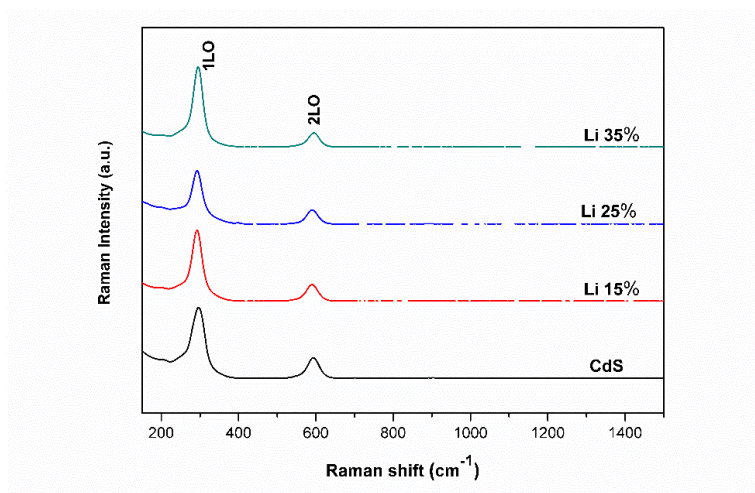


Figure 3. Raman spectra of the CdS and CdS:Li nanostructured films

The peaks observed around 298 cm^{-1} and 590 cm^{-1} belong to bulk CdS vibration mode [5]. There are changes in strengths of peaks. Raman strengths are mostly proportional to the concentration of active particles. Asymmetric formation of peaks makes you think there are defects in the structure. As it is seen from Figure 4, it is observed that the bulk CdS lattice vibration mode which had been seen at 298 cm^{-1} shifted to a lower part. Shifts increase as the particle size decreases. Peaks may shift to lower values for thin films by diminishing particle size and the effect of phonon formation [21]. The particle sizes of films can be compared by matching individual positions of peaks of CdS films.

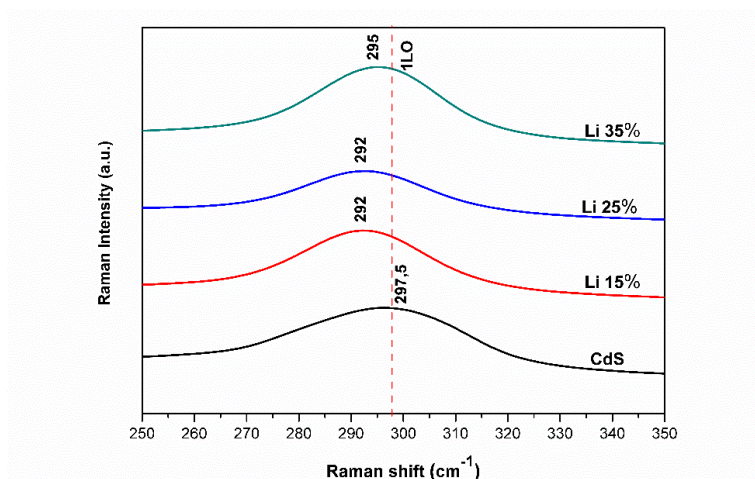


Figure 4. Raman spectrum shift of the CdS and CdS:Li nanostructured films

3.3. UV-Visible Studies

Traveling of the light reflecting and penetrating through the thin film is different than its traveling in normal medium. Reflection and diffraction of light through a film are based on magnitudes such as film thickness, refraction index and extinction coefficient. In Figure 5, the transmittance spectra of the films against wavelengths are seen. As it is seen from the figure, transmittance value in the visible region ($\lambda = 500\text{ nm}$) increased from 55% maximum and 87% in the near infrared region ($\lambda = 900\text{ nm}$). The highest transmittance value belongs to CdS: Li 15% film. Also for high-Li-containing films,

transmittance values decreased and reflectance values increased in the visible region. This might be due to the influence of various factors such as structural parameters, carrier concentrations and defects.

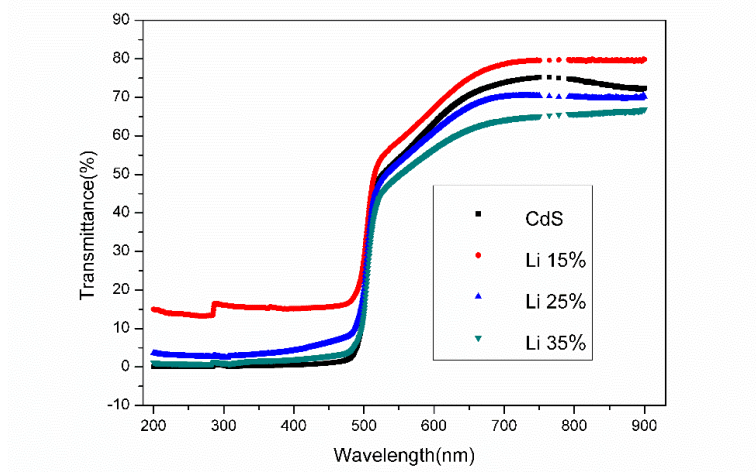


Figure 5. The transmittance spectra of CdS and CdS:Li nanostructured films

The reflectance spectra of films are seen in Figure 6. Increasing reflectance values were observed as the doped Li amount increased. One of the optic factors, the extinction coefficient (k) is extremely important for determining the optical characteristics of the materials to be used in solar cells. Extinction coefficient of a material is based on its absorption values. The extinction coefficient values were determined by means of the (1) expression [22].

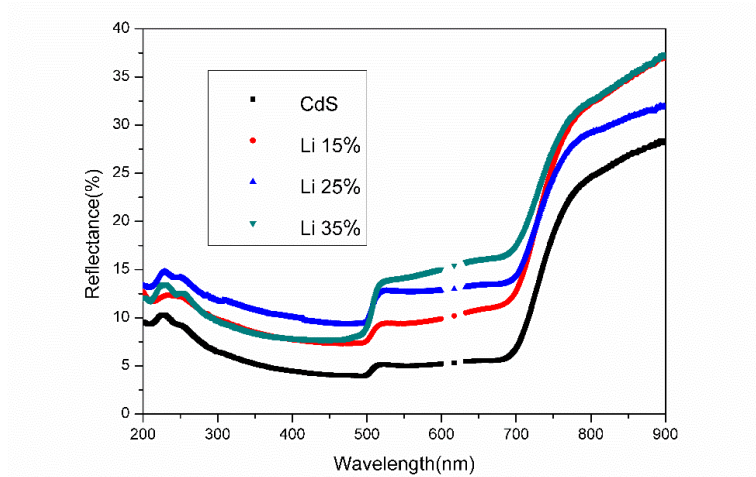


Figure 6. The reflectance spectra of CdS and CdS:Li nanostructured films

$$k = \frac{\alpha\lambda}{4\pi} \quad (1)$$

The change of extinction coefficients of films based on wavelength can be seen in Figure 7. In the visible region ($\lambda = 475$ nm), extinction coefficients of films are in between 0,03 and 0,07. Minimum value belongs to CdS: Li 15% film and in relation to this, the transmittance value of the CdS: Li15% film in this region is the highest. Several studies show that optical absorption of a semiconductor does not increase smoothly and very fast in the optical band gap. But in many materials, the optical

absorption spectrum starts near the limit that it should. The cause of this is band tails. Band tails on the edge of bands can be found in all crystal or amorphous structures. Static stresses and defects are the factors that play an effective and leading role in the formation of these tails. Furthermore, temperature change has an impact through its dynamic effect. If, lower dynamic effects are ignored, Urbach rule under static effect is;

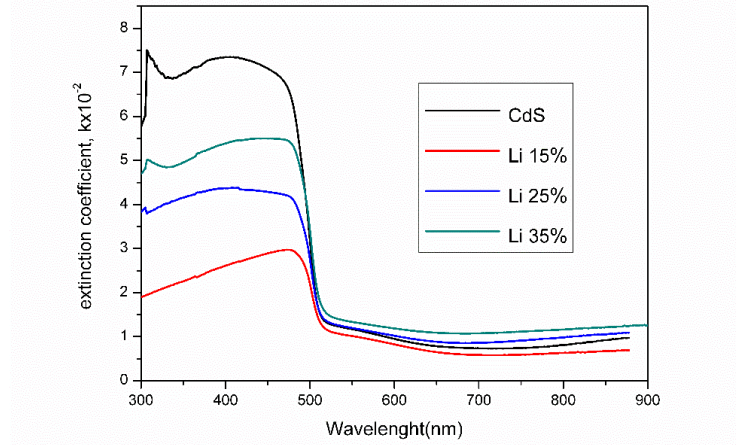


Figure 7. Variation of extinction coefficient of the films with wavelength

$$\alpha = \alpha_o \exp\left(\frac{E}{E_U}\right) \quad (2)$$

given by the equation above [23] and Urbach parameter E_U ;

$$E_U = \left(\frac{d(\ln \alpha)}{d(h\nu)}\right)^{-1} \quad (3)$$

can be found by the equation above. For calculating Urbach parameters, the $\ln(\alpha) \sim h\nu$ graphic was drawn as seen from Figure 8.

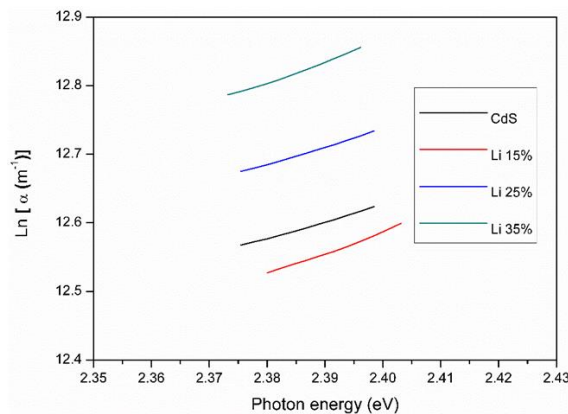


Figure 8. The Urbach plots of the CdS and CdS:Li films

Urbach parameters calculated by means of the Equation (3) are given in Table 2. Band tails, in any semiconductor, crystalline or amorphous structure narrow the optical band gap and cause an increase in the absorption spectrum. As shown in Table 2, the optical band gap (E_g) also tends to decrease with

Li doping due to the increase in its carrier concentration [24,25]. A shift higher wavelength side in the absorption edge towards lower band gap is noticed in all Li doped CdS thin films [18].

Table 2. E_g and E_U values of the CdS and CdS:Li films

	<i>CdS</i>	<i>CdS:Li (15%)</i>	<i>CdS:Li (25%)</i>	<i>CdS:Li (35%)</i>
E_g (eV)	2.415	2.413	2.405	2.395
E_U (meV)	596	546	769	911

4. CONCLUSIONS

Polycrystalline CdS films were established on glass substrates by producing CdS and Li in three different rates. XRD and Raman spectroscopy practices were used for determining the crystallization quality and phase contents of these films which were produced by means of Spray Pyrolysis method. XRD results show that lithium which was added into the spray solution in various rates, influenced the crystallization rates of films and preferential orientation, which had been (101) for the CdS film, was changed as (002) for Li 25 and Li 35 films. Two apparent active Raman modes of bulk CdS were observed around 298 cm^{-1} and 590 cm^{-1} . Lattice vibration mode observed in Li containing films around 300 cm^{-1} shifted to a lower part. Optical measurements show that the highest transmittance value belongs to CdS: Li 15% film. Increasing reflectance values of films and changing Urbach energy values were observed, as a result of increasing Li rate in the preliminary solution.

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