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Annealing Effects on the Photoluminescence and Optical Properties of In-Doped CdS Films

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Keywords

In doped CdS;
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Abstract: Among the II–IV semiconductor compounds, CdS (band gap ~2.43 eV) have large applications as photoconductors, in semiconductor lasers, nonlinear optical devices and photovoltaic solar cells. In this work; In-doped CdS (CdS:In) films were fabricated on glass substrates by ultrasonic spray pyrolysis (USP) method. The obtained samples were annealed in air at 450 °C for two different times as 1 and 2 hours. Effects of annealing on the surface and optical properties of CdS:In films were investigated by atomic force microscopy (AFM), optical transmittance and the room temperature photoluminescence (PL) spectroscopy. Thicknesses of the films, refractive indices and extinction coefficient values were determined by spectroscopic ellipsometry technique using Cauchy–Urbach model. The optical transmittance spectra showed that the annealing process improves the optical transmittance in the visible region.

In katkılı CdS Filmlerinin Fotolüminesans ve Optiksel Özellikleri Üzerine Tavlamanın Etkileri

Anahtar Kelimeler

In katkılı CdS;
Fotolüminesans Spektrum
AKM

Özet: II-VI yarıiletken bileşikler arasında, CdS (band aralığı ~2.43 eV) fotoiletkenler, yarıiletken lazerler, nonlinear optik cihazlar ve fotovoltaik güneş pilleri gibi geniş uygulama alanlarına sahiptir. Bu çalışmada, In katkılı CdS (CdS:In) filmleri ultrasonik kimyasal püskürtme tekniğiyle cam tabanlar üzerine üretilmiştir. Elde edilen numuneler 450 °C'de iki farklı sürede tavlanmıştır. CdS:In filmlerinin yüzeysel ve optik özellikleri üzerine tavlamanın etkileri atomik kuvvet mikroskobu, optik geçirgenlik ve oda sıcaklığında fotolüminesans spektroskobisi alınarak incelenmiştir. Filmlerin kalınlıkları, kırılma indisi ve sönüm katsayısı değerleri Cauchy–Urbach modeli kullanılarak spektroskopik elipsometre tekniği kullanılarak belirlenmiştir. Optik geçirgenlik spektrumu tavlama işleminin görünür bölgede optik geçirgenliği arttırdığını göstermiştir.

1. Introduction

Because of the electronic and optical properties, II–VI compound semiconductors have been extensively investigated. CdS is an II–VI compound semiconductor which has an energy band gap of 2.42 eV at room temperature. It is extensively used in optoelectronic devices such as photoconducting cells, photosensors, transducers, laser materials, light emitting diodes, optical wave-guides and non-linear integrated optical devices. CdS thin films can be deposited using various techniques such as ultrasonic spray pyrolysis (USP) [Kaur, 1980, Martinuzzi, 1982, Ashour, 2003], chemical bath deposition (CBD) [Ximello-Quiebrasa, 2004], hydrothermal method [Sivasubramanian,2006], metalorganic chemical vapor deposition (MCVD) [Uda, 2003], pulsed-laser deposition [Ullrich, 2001], sol-gel spin coating[Thambidurai,2011], successive ionic layer adsorption and reaction (SILAR) [Sankapal, 2000], etc. Among all those methods, USP is simple, low cost, non-vacuum and suitable technique to prepare large area thin films [Ravichandran, 2008].

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The aim of this work is to observe the effect of annealing process on the surface and optical properties of the CdS:In films produced by ultrasonic spray pyrolysis technique.

2. Experimental details

CdS:In (%2 In doped CdS) films were deposited on heated microscope glass (Objekttrager, 1 cm×1 cm) substrates by USP technique at a substrate temperature of 300±5 ˚C. The substrate temperature was gauged with an iron-constantan thermocouple. The solution was sprayed onto pyrex glass substrates over 20 min. The solution flow rate was kept at 5ccmin^{-1} and controlled by a flowmeter. Deionised water was used as the solvent. The glass substrate was cleaned in ethanol and rinsed in deionised water. The starting spraying solution was mixed with a magnetic mixer to prevent sedimentation. The ultrasonic oscillator frequency was 100 kHz. The spraying solution consist of 0.1M $CdCl_2$ $2.5H_2O$, 0.1M $InCl_3$ and 0.1M thiourea $[CS(NH_2)_2]$ solutions. Produced films were annealed at 450˚C in air atmosphere for different annealing times (1 and 2 hours). The films were named as C2 (unannealed CdS:In), C21 and C22 depending on the annealing time.

Electrical resistivities of the films were taken by using Keithley 2601A Source Meter and four probe technique. SC620 Spectroscopic Ellipsometer was used to determine the ψ parameters, refractive indices (n) and thicknesses (d) of the films. Cauchy–Urbach dispersion model was used to fit the experimental ψ parameters. Cauchy –Urbach model may be used for samples with low absorption. So, measurements were fulfilled between 1200 and 1600 nm wavelength range where the films have low absorption.

Optical properties of the films have been characterized by investigating transmittance, absorbance and photoluminescence (PL) spectra. UV-2550 UV-VIS spectrophotometer was used to take transmittance measurements.

In order to obtain surface images, Park System XE-70 atomic force microscope (AFM) was used. The measurements were taken in non-contact mode, approximately 300 kHz frequency and 0.7 Hz scan rate in air at room temperature. All the images were taken from an area of 5μm×5μm. Also, root mean square (rms, Rq), average (Ra) and peak to valley (Rpv) roughness.

3. Results and Discussion

3.1. Optical Properties

The transmission and absorbance spectra were taken at room temperature to obtain information on the optical properties of the CdS:In thin films. The transmission spectra of the annealed CdS:In films are shown in Figure 1. Annealed CdS:In films showed higher transmittance as compared to deposited C2 sample.

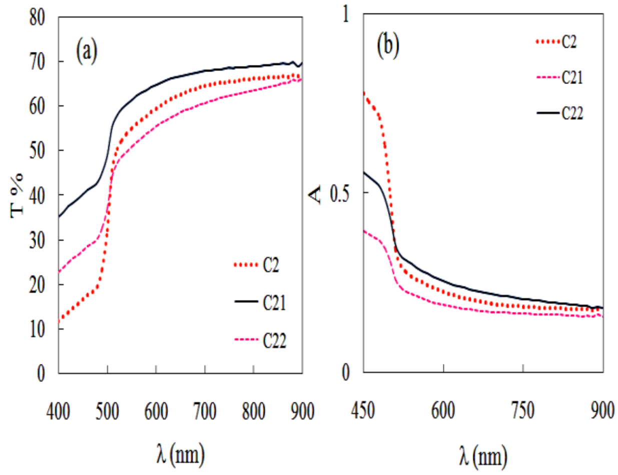

Figure 1. (a) The transmittance and (b) absorbance spectra of annealed CdS:In films(C2:unannealed CdS:In, C21:annealed at one hour CdS:In, C22: annealed at two hours CdS:In films)

Band gap values of all films have been determined by optical method using $(\alpha h\nu)^2 \sim h\nu$ plots given in Figure 2. In this method, the band gap values are obtained by extrapolating the linear portion of the plots of $(\alpha h\nu)^2$ versus $h\nu$ to $(\alpha h\nu)^2 = 0$. Annealing process caused that the band gap values decrease.

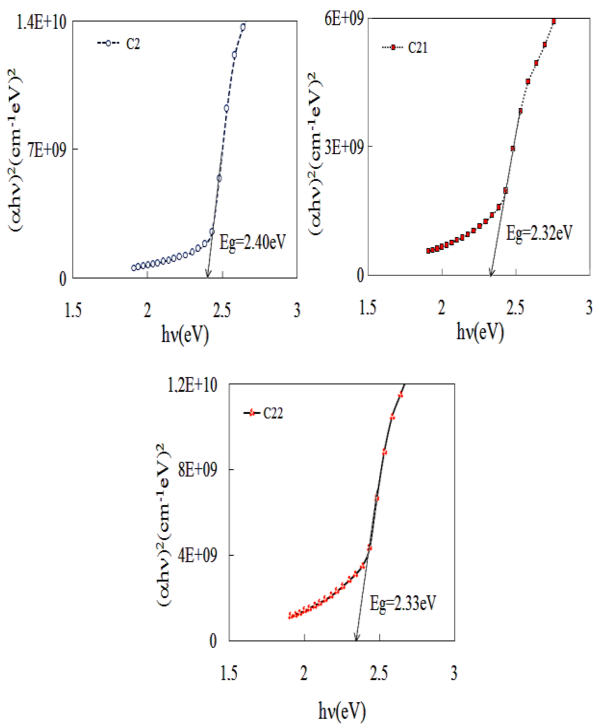

Figure 2. $(\alpha h\nu)^2 \sim h\nu$ plots of annealed CdS:In films

SE spectra of CdS:In films are shown in Figure 3. The optical response of the transparent or weakly absorbing CdS films can be described by a Cauchy–

Urbach dispersion relation. So, the experimental data were analyzed by using the Cauchy–Urbach model. An appropriate fit is found between the model and experimental data as shown in Figure 3.

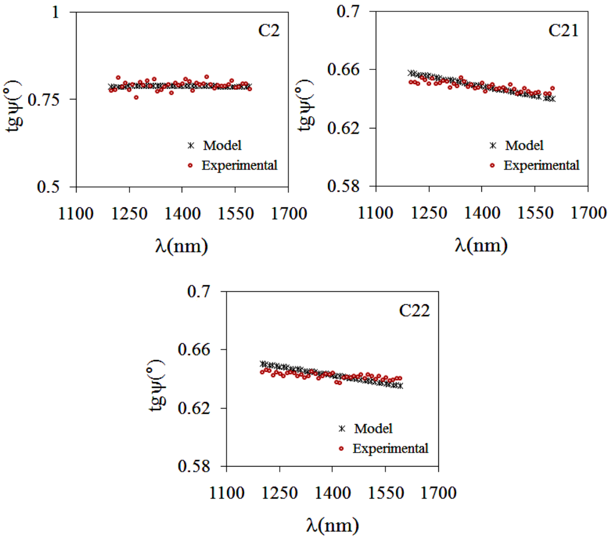

Figure 3. Spectroscopic ellipsometry spectra of CdS:In films

Thicknesses, refractive indices and extinction coefficients of all films have been determined using these tgψ spectra. The refractive index and the extinction coefficient spectra of CdS:In films are shown in Figure 4. It was determined from these figures that the refractive index decreases depending on annealing, while the extinction coefficient increases for C21 and C22 films.

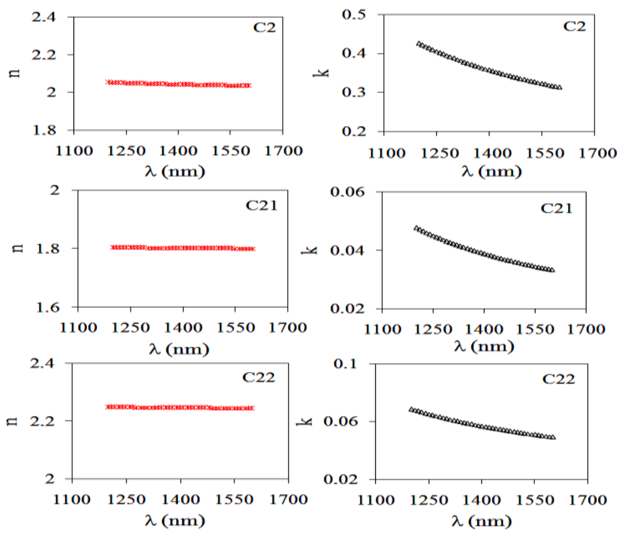

Figure 4. Refractive index (n) and extinction coefficient (k) spectra of annealed CdS:In films

Generally PL studies have been used to evaluate the defect structure within the band gap. The PL spectra recorded for annealed CdS:In thin films in the present study extend from 450 nm to 700 nm. (Figure 5). We think that the peak at 580 nm is associated with Cd^{2+} interstitials and the band at ≈690 nm is attributed to the complex defects including the cadmium vacancies. This result is consistent with the results obtained by Ravichandran et al. [Ravichandran, 2013].

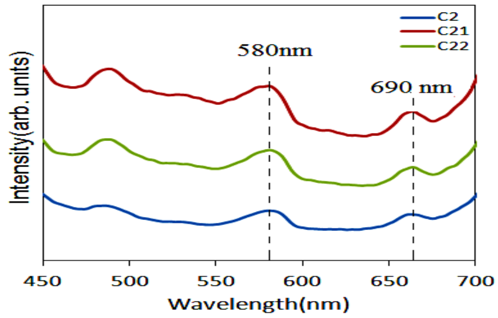

Figure 5. Room temperature photoluminescence spectra of the films

The influence of annealing on the PL spectra and other properties of CdS:In thin films was investigated in other research works [Ahmad, 2013], where it was found that annealing increases the intensity of the PL signal.

3.2. Surface Properties

AFM images of all films are shown in Figure 6. The atomic force micrograph of all the films showed a structure of hills and valleys with some voids. A granular structure with grains in different sizes is dominant for C21 films. White regions in this figure represent the formation of agglomerated grains one on the top of the other. For these white regions, we think that neighboring grains come together forming large clusters. It was determined from AFM images of all films that there are also black regions which represent the grain cavities on the film surface.

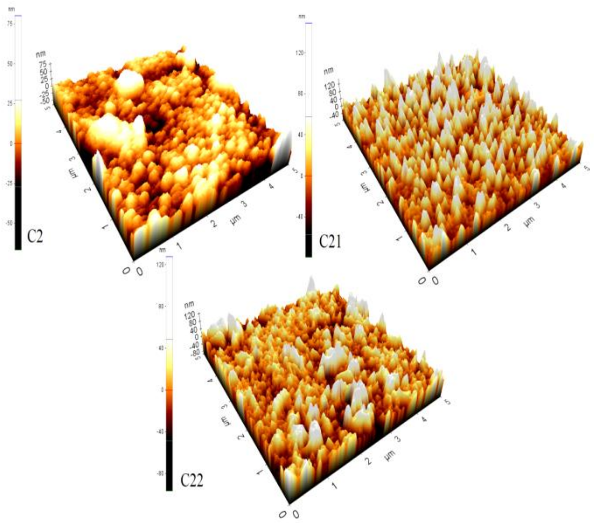

Figure 6. Three-dimensional (3D) AFM images of CdS:In films

Rq and Ra roughness values of CdS:In films are given in Table 1. It is clear that annealing process affected the roughness values of CdS:In films.

Table 1: Rq and Ra roughness values of CdS:In films

Film	Root mean square roughness(R_q) nm	Average roughness(R_a) nm
C2	29	22
C21	14	10
C22	15	12

3.3. Electrical Properties

Electrical resistivity values of annealed CdS:In films were determined by using four-point probe techniques and listed in Table 2. Annealing process caused electrical resistivity to decrease.

Table 2: The resistivity values of annealed CdS:In films

Film	Resistivity (Ω.cm)
C2	$8.64x10^{3}$
C21	$4.52x10^{2}$
C22	$2.35x10^{3}$

4. Conclusions

In this work, we report the effect of annealing on some physical properties of CdS:In films. Ultrasonic spray pyrolysis technique has been used to obtain the films. Optical characterizations of the films have been performed by spectroscopic ellipsometry and UV/vis spectrophotometer. First, experimental data has been fitted by Cauchy model and thicknesses and optical constants (*n* and *k*) of the films have been determined. Also, absorbance and transmittance spectra of the films have been investigated. Finally, band gap structure and values have been determined by optical method. The films exhibited a direct transition in the range 2.32-2.40 eV. These results suggest that CdS:In thin films should be further investigated for application towards the fabrication of solar cells. The surface properties were characterized by AFM.

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