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PHOTOCONDUCTIVITY STUDIES ON CDS FILMS GROWN BY CHEMCAL BATH DEPOSITION TECHNQUE

Hülya METİN[1], R. ESEN[2]

[1]Department of Physics, University of Mersin, 33342 Mersin, Turkey ,
[2]Department of Physics, University of Cukurova, 01330 Adana, Turkey

Abstract: CdS films were prepared by chemical bath deposition (CBD) at 60 °C without stirring. The optical properties of the films were seen to be dependent on the film thicknesses. The band gap energy obtained as 2.42 eV from the optical absorption measurements. The activation energy of the dark conductivity found to be 0.45 eV from the resistance measurements. Two different time constants were measured, one for fast decaying component and one for slow decaying component as 7.35 ms and 36.5 ms, for CdS films from the AC photoconductivity data.

***Keywords**:* CDB CdS; Optical properties; Photoconductivity

KİMYASAL DEPOLAMA YÖNTEMİ TEKNİGİYLE BÜYÜTÜLEN CDS FİLİMLERİNDE FOTOİLETKENLİK ÇALISMALARI

Özet: CdS filmleri 60 °C de karıştırmaksızın kimyasal depolama yöntemiyle hazırlandı. Filmlerin optiksel özellikleri filmin kalınlığına bağlı olduğu görüldü. Enerji aralığı optiksel soğurma ölçümlerden 2.42 eV olarak elde edildi. Karanlık iletkenliğinin aktivasyon enerjisi direnç özelliklerinden 0.45 eV olarak bulundu. AC fotoiletkenlik datalarından, CdS filmleri için iki farklı zaman sabiti 7.35 ms ve 36.5 ms, biri hızlı sönümleme bileşeni, diğeri yavaş sönümleme bileşeni olarak ölçüldü.

Anahtar kelimer: Kimyasal Depolama Yöntemi;CdS; Optiksel Özellikler; Fotoiletkenlik

1. Introduction

CdS thin films are used in commercial photocells and also as window material for CdS/CdTe solar cells continues as a subject of intense research in order to obtain cells with higher efficiencies. In this type of solar cell, fabrication of CdS films with low resistivity is very important because it helps to decrease the device sheet resistance to obtain the space and charge region in active zone, i.e., into CdTe film [1]. There are a number of reports on the properties of CdS in polycrystalline thick/thin films prepared by various techniques such as spray pyrolysis, electrodeposition, molecular beam epitaxy, chemical vapor deposition and chemical bath deposition. However, the basic problem with CdS is to obtain uniformity over a large area and stoichiometry. The chemical bath technique appears to be a relatively simple, inexpensive method to prepare a homegenous film with controlled composition. However, depending on the deposition conditions like pH of the solution, temperature, stirring, and time of deposition, the quality as well as the stoichiometry of the film differ and hence their structural and optical properties [2]. This technique, known as chemical bath deposition (CBD) is suitable for coating surfaces of any morphology and geometry. In particular, CBD is a low-cost and relatively simple technique for achieving good-quality cadmium sulphide CdS films. CdS/CdTe solar cells with very high efficiency have been obtained by growing the CdS layer using CBD [3]. Extensive research has been done on the deposition and characterization of Cadmium Sulphide (CdS) semiconducting thin films due to their potential applications in the area of electronic device fabrication.

Polycrystalline CdS thin films have good optical transmittance, wide band-gap and electrical properties suitable for their application to solar cell fabrication. CdS based solar cell structure exhibits better optical confinement towards higher efficiencies. Direct band-gap CdS thin films attracted much interest because of their preferred properties of intermediate band-gap, high-absorption coefficient, electron affinity, low resistivity and easy ohmic contact [4].

In this work thin films of CdS produced in different thicknesses. Their optical properties measured in the 300-1100 nm wavelength interval. Their AC photoconductivity properties are studied. The fast photoconductivity method is used with a white beam of light as the excitation source.

2. Experimental details

2.1 The deposition of the CdS thin films

CdS thin films have been deposited on glass substrate using CBD technique. The substrates used for deposition are commercial glass slides of 76 mm x 25 mm. Baths with concentrations $CdSO_4$ 1 M, thiourea 1.4 M, hydrazine 2.25 M, NH_3 %25, were used. Commercial glass slides, used as substrates, were cleaned in prophanol; ethanol and methanol ultrasonically, then etched in 5 % HF solution and finally, again washed with methanol ultrasonically. The glass slides were kept vertically in the beaker. The temperature of deposition process was 60 °C and the duration of deposition varied between 1-18 minutes. All of the solutions that were used in deposition were clear solutions without precipitation. The bath solution was held still without stirring. After the deposition, the CdS films were washed with methanol ultrasonically to remove the loosely adhered CdS particles on the film and finally dried in air.

3. Results and discussion

3.1 Optical properties of CBD CdS films

Optical properties of CdS films obtained by CBD were measured at room temperature by using Perkin-Elmer UV/VIS Lambda 2S spectrometer in the wavelength range 190-1100 nm. The spectral distributions of transmittance of the films with different thicknesses were determined and optical absorption coefficients were calculated using these data and thicknesses of the films.

3.1.1 3.1.1 The dependence of optical properties of the CBD CdS films on the thickness

We have produced a set of CBD CdS films which have three samples with the thicknesses of 0.40, 0.60, 0.80 μm. The variation of transmittance, optical absorption coefficient and square of the absorption coefficient as a function of incident photon energy are shown in Figs 1, 2 and 3 respectively. Interference fringes can be seen in Fig. 1. These values with the refraction index values are used to calculate film thicknesses. The transmittance (or absorbance) values are taken as the average of maximum and minimum values of these fringes. Examining the above figures we have found that thick films have lower α values at the forbidden gap region than thin CdS films. The Urbach tailing seems steeper in these films. Second difference between thick and thin films is that thinner films have high α values in the band-to band absorption region. This effect may be explained by proposing that thicker films have bigger crystallites (grains) so they are closer to the crystalline CdS, but bigger grain sizes gives results in larger unfilled inter-granular volume so the absorption per unit thickness is reduced.

The band edge steepness value was obtained by plotting α^2 versus E and taking the slope of the graph at the beginning of band-to-band absorption. The band edge steepness value B, takes lower values as thickness increases. The optical energy gap decreases with the increasing film thickness. All these thickness dependent properties are given in Table 1.

Table 1. Thickness dependent optical properties of CdS films

Thickness (μm)	Sharpness B(cm^{-2}/eV)	Energy Gap E_g (eV)
0.40	2.3x10^{10}	2.45
0.60	2.6x10^{10}	2.43
0.80	4.0x10^{10}	2.42

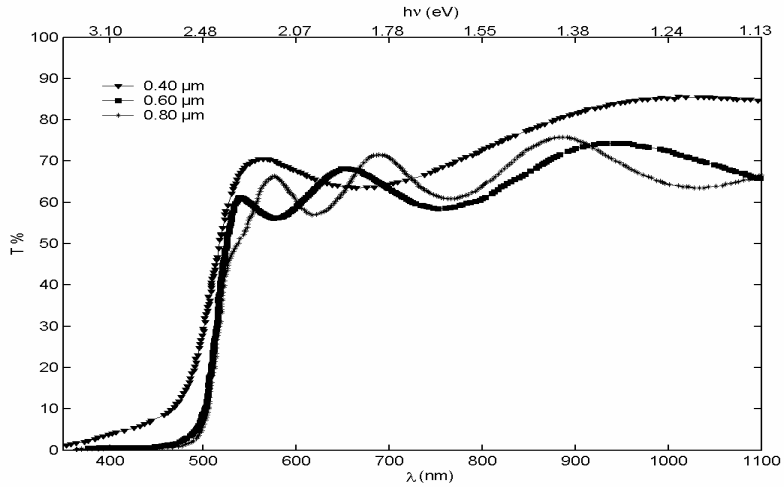

Fig.1. Optical transmittance spectrum of as-deposited CdS films with different thicknesses

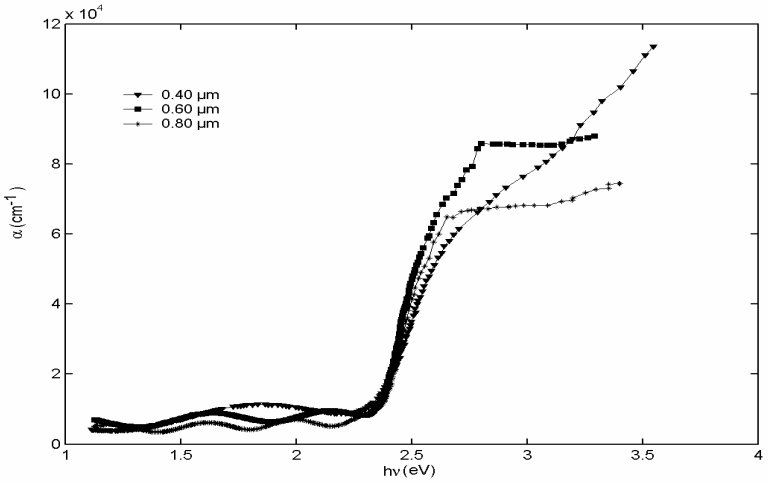

Fig.2. The α versus $h\nu$ graphs of as-deposited CdS film with different thicknesses.

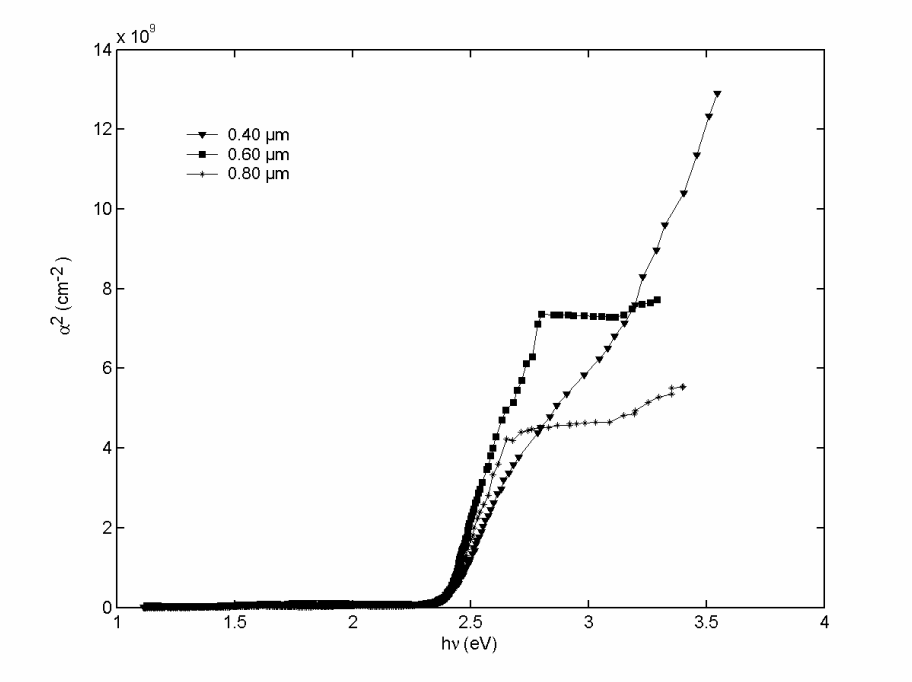

Fig.3. The α^2 versus $h\nu$ graphs of as-deposited CdS film with different thicknesses

3.2 The electrical properties of the CdS films

The dark conductivity of the CBD deposited CdS deposited films were measured using two planar indium electrodes in the temperature interval of (20°C-100°C). Fig. 4 is obtained from a 0.8 µm thick CdS film deposited at 60 °C. The room temperature resistivity was found to be $6x10^{10}$ Ω-cm. The high value of the room temperature resistivity can be attributed to the dislocations and imperfections of the films. The activation energy of dark conductivity was determined, using the relation

$$R = R_o \exp(E_a / kT) \tag{3}$$

and plotting $\ln(\frac{R}{R_o})$ v.s. 1000/T, where R in resistivity at temperature T, R_o is the resistivity at room temperature (293 °K), k is the Boltzmann's constant and E_a is the activation energy. The activation energy is found to be 0.45 eV (Fig.5). This value shows that Fermi energy is above the ($E_g/2$) level. The electrical conduction is controlled by the states near the conduction band. These values are in agreement with the previous works [5].

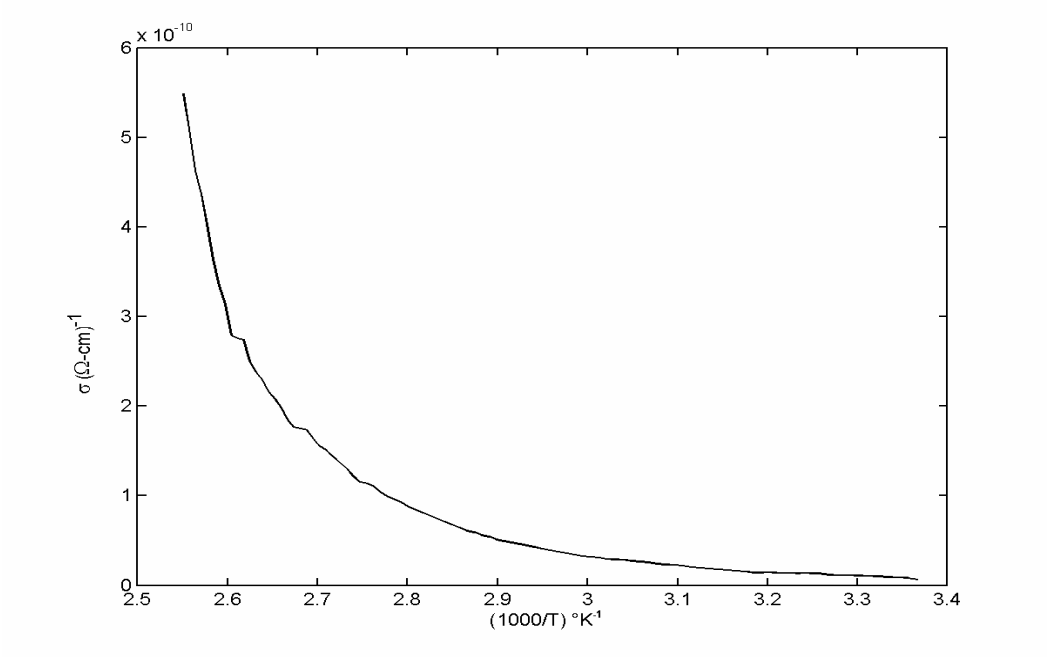

Fig. 4. Temperature dependence of the conductivity of CdS

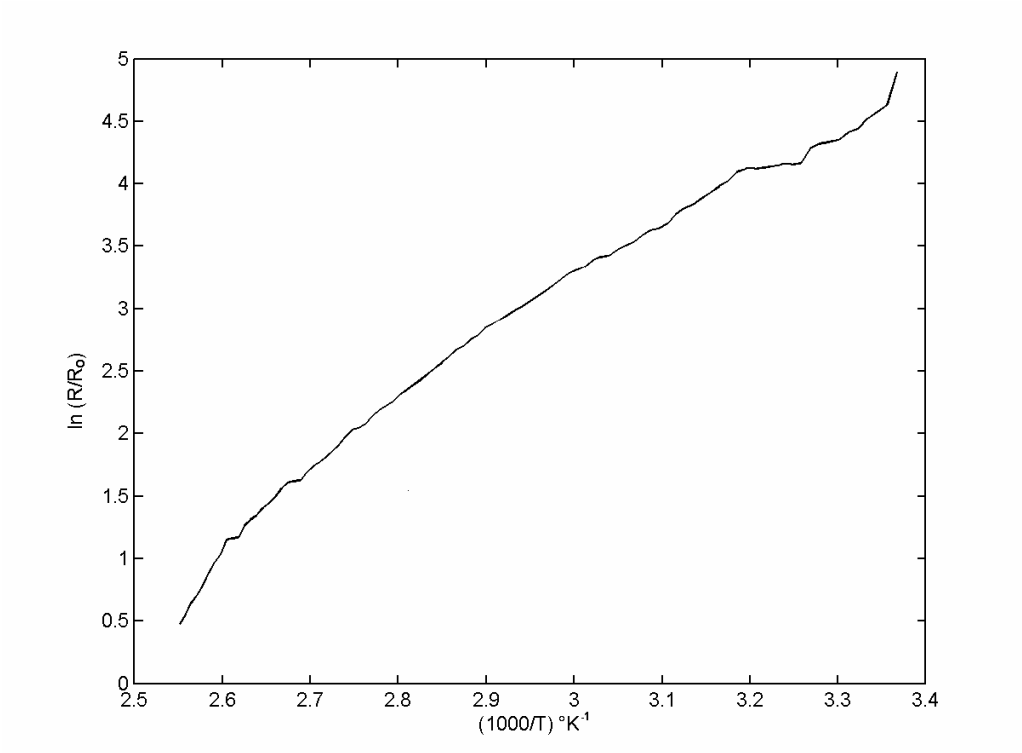

Fig. 5. The variation of $\ln(\frac{R}{R_o})$ as a function of inverse temperature of CdS

3.3 The fast component of the photoconductivity response of the CdS films by CBD

The photoconductivity measurements of the thin CdS film were made using the setup shown in Fig 6. In the experiment a white light beam produced by a 50 W quartz-halogen lamp was projected to the sample surface after passing trough a chopper. Three planar indium stripes with 2 mm and 4 mm gaps formed using a vacuum evaporator. A 9 V battery was used as a power source. A 560 kΩ resistor was connected in series to the battery and the sample and it was connected to the first channel of an oscilloscope with a frequency range of DC to 20 MHz. The output of the first channel connected to an A/D (analog-digital) converter. The data gathered with the computer using simple homemade software. The main source of noise in this experiment is the inductive/capacitive voltages on the metal parts due to the mains (50 Hz). The chopping frequency is selected as 13 Hz to minimize the harmonic of the line frequency. Using a battery instead of a power supply connected to main, using a Faraday Cage for the whole setup and also using a good grounding system were the precautions that were employed to minimize the electrical noise. Since the current trough the sample was in the order of a few ten nanoamps the signal to noise ratio (S/N) was still high in the experiment. It was in the order of 5/3.

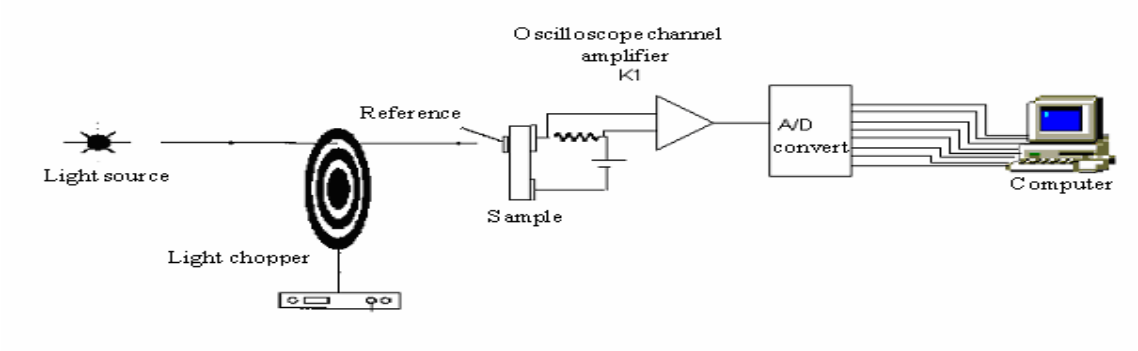

Fig. 6. The setup used for AC photoconductivity of the CdS thin films

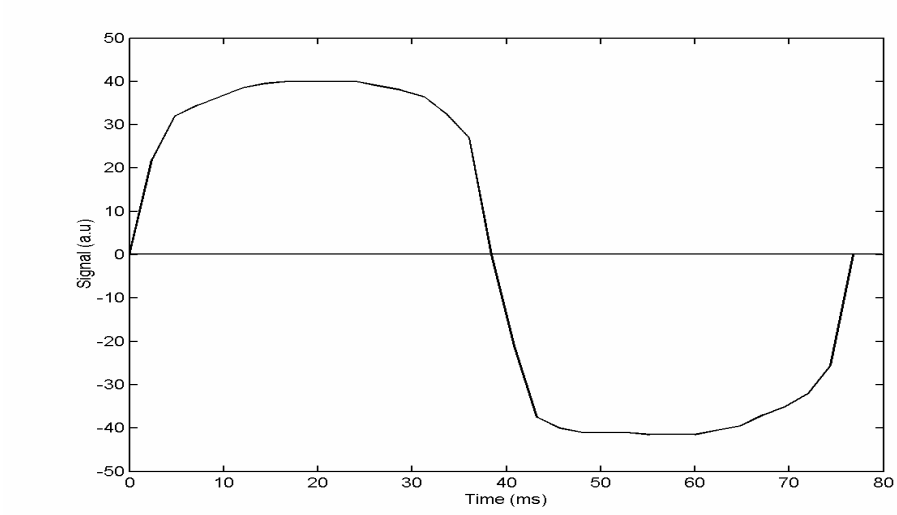

Fig.7. The AC photoconductivity response of a CBD thin CdS film

The photoconductivity response of CdS films is known to have very slow components in the order of tens of minutes [6]. The overall photoconductivity is the sum of all slow and fast components of the photoconductive

response. When a CdS film is illuminated the photo induced current carriers (here being electrons since the samples are slightly n type) can be expressed as

$\Delta n = n_1\tau_1 + n_2\tau_2 + n_3\tau_3 + n_4\tau_4 \ldots \qquad \tau_1 < \tau_2 < \tau_3 < \tau_4 < \ldots$

where Δn total is the number of photo-created current carriers, τ is life times, n's are their respective numbers. The CdS is rich of the recombination centers. A typical commercial CdS photocell has a rise time in the orders of 100 ms and a decay time of 300 ms as a total response of the above mentioned recombination sets [7]. We determined two of fastest lifetimes of our CdS samples from decay of the photocurrent. τ_1 is found to be 7.34 ms and τ_2 is found to be equal to 36.5 ms. Due to the noise in the system and the fact that some of the traps were not emptied when the next light pulse applied we were not able to determine precisely the other slow decaying lifetimes. The 75 percent of the photoconductive response is reached less than in 10 ms rise time, while roughly 85 percent decrease in the photocurrent is reached less then in 10 ms, in the decay phase.

4. Conclusions

CdS films, which were grown on glass substrate by CBD at 60 °C without stirring, showed good optical properties and adhered well to the substrates. Energy band gap value was found decreasing with increasing the thickness of the film. The band edge steepness *B* was also found to decrease with increasing thickness.

The time dependent photoconductive properties of CdS thin films by CBD method determined. Using pulsed white light excitation, the 75 percent of the overall response in rise phase is seen reached in less than 10 ms, while 85 percent of total response is reached in less than 10 ms in decay time. Many recombination levels are observed as expected from a polycrystalline, amorphous CdS films. The fastest two recombination times are determined from the decay of the photocurrent. τ_1 is found to be 7.34 ms and τ_2 is found to be 36.5 ms. The high level of signal to noise ratio (5/3) does not allow to determine the slower recombination time sets.

References

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