

ARAŞTIRMA MAKALESİ/RESEARCH ARTICLE

STRUCTURAL AND OPTICAL PROPERTIES OF $Cd_{0.22}Zn_{0.78}S$ FILMS PRODUCED BY SPRAY PYROLYSIS METHOD

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ABSTRACT

$Cd_{0.22}Zn_{0.78}S$ semiconductor films have been produced by the spray-pyrolysis method at different substrate temperatures, and their structural and optical properties have been investigated. X-ray diffraction spectra of the films showed that they are hexagonal and formed as $Cd_{0.22}Zn_{0.78}S$ polycrystalline structure. The absorption spectra of the films showed that this compound is a direct band gap material and gap values varied between 2.72eV and 2.90eV.

Key Words: Compound semiconductors, Spray pyrolysis, X-ray diffraction spectra, Absorption spectra, Energy band gap.

PÜSKÜRTME YÖNTEMİ İLE ELDE EDİLEN $Cd_{0.22}Zn_{0.78}S$ FİLMLERİNİN YAPISAL VE OPTİKSEL ÖZELLİKLERİ

ÖZ

Püskürtme yöntemi ile farklı taban sıcaklıklarında elde edilen $Cd_{0.22}Zn_{0.78}S$ yarıiletken filmlerinin yapısal ve optiksel özellikleri incelenmiştir. X-ışını kırınım desenlerinden, elde edilen filmlerin polikristal ve hegzagonal $Cd_{0.22}Zn_{0.78}S$ yapıda oldukları saptanmıştır. Absorpsiyon spektrumu ölçümlerinden filmlerin direkt bant geçişli olduğu ve yasak enerji aralıklarının 2,72eV ile 2,90eV arasında değiştiği belirlenmiştir.

Anahtar Kelimeler: Yarıiletken bileşikler, Püskürtme yöntemi, X-ışını kırınım desenleri, Absorpsiyon spektrumu, Yasak enerji aralığı.

1. INTRODUCTION

There has been considerable interest in the field of thin film semiconductors for the use in solar cell devices. Films of $Cd_xZn_{1-x}S$ have been found extensive applications in various optical, electronic and optoelectronic devices. Also the $Cd_xZn_{1-x}S$ films have become the subject of considerable interest due to the possibility of using these films in solar cells (Kumar et al., 1998). $Cd_xZn_{1-x}S$ films have been prepared using various methods, which include spray pyrolysis (Feigelson et al., 1977; Chynoweth and Bube, 1980; Uplane et al., 1996), ion beam deposition (Kuroyanagi,

1994), molecular beam epitaxial growth (Karasawa et al., 1991), solution growth (Padam et al., 1988), chemical vapor deposition (Chu et al., 1991), evaporation (Torres and Gordillo, 1992), chemical bath deposition (Dona and Herrero, 1995, Yamaguchi et al., 1999), screen printing method (Kumar et al., 1998), and dip technique (Ray et al., 1998; Karanjai and DasGupta, 1987).

The deposition of II-VI semiconductors by the spray pyrolysis method was first produced by Chamberlin and Skarman (Chamberlin and Skarman, 1966). In the present work, $Cd_{0.22}Zn_{0.78}S$ films are pro-

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duced by this method which is the spraying of the aqueous solution of the reactants onto a hot substrate. Compared to other methods, spray-pyrolysis has the following advantages; (1) simple and continuous operation, (2) economical, (3) uniform particle size distribution, (4) controllable size, and (5) controllable anion and cation concentrations or dopants (Zor et al., 1997; Kim et al., 2002). Other advantages of the spray-pyrolysis method are that it can be adapted easily for production of large-area films, and to get varying band gap materials during the deposition process.

In this paper, we report the details of preparation, structural and optical properties of $\text{Cd}_{0.22}\text{Zn}_{0.78}\text{S}$ films.

2. MATERIALS AND METHODS

$\text{Cd}_{0.22}\text{Zn}_{0.78}\text{S}$ films have been produced by spraying the aqueous solution of 0.05M of $\text{CdCl}_2 \cdot \text{H}_2\text{O}$, 0.05M of ZnCl_2 , and 0.05M of $(\text{NH}_2)_2\text{CS}$ in a 1:1:2 (by volume) onto the microscope glass substrates ($11 \times 26 \text{mm}^2$ and $11 \times 6 \text{mm}^2$) at different substrate temperatures of $250 \pm 5^\circ\text{C}$, $275 \pm 5^\circ\text{C}$, $300 \pm 5^\circ\text{C}$.

The details of the spray pyrolysis set-up is shown in Figure 1. The spray rate was measured by a flowmeter. The flow-rate of the solution during spraying was adjusted to be about 3.5mlmin^{-1} and kept constant throughout the experiment. Nitrogen was used as the carrier gas. The nozzle was kept vertically above the substrate plate at a distance of 28cm. During the spraying process the substrates were heated by electrically heating the copper plate. Substrate temperature was

Table 1. Substrate Temperature, Deposition Time and The Thickness of $\text{Cd}_{0.22}\text{Zn}_{0.78}\text{S}$ Films.

Substrate Temperature ($^\circ\text{C}$)	Deposition Time (min)	Film Thickness (μm)
250 ± 5	60	6.10
275 ± 5	45	7.21
300 ± 5	35	4.14

controlled by means of Iron-Constantan thermocouple. The films obtained was yellow in colour with good adhesion onto the surface. The thicknesses of the films were measured using the weighing-method. Substrate temperatures, deposition times and the thicknesses of these films are given in Table 1.

The crystal structure of $\text{Cd}_{0.22}\text{Zn}_{0.78}\text{S}$ films was characterized by RIGAKU RINT 2000 Series X-Ray Automatic Diffractometer using $\text{Cu:K}\alpha$ radiations ($\lambda_{\text{K}\alpha} = 1.5405 \text{Å}$). A range of 2θ from 20° to 60° was scanned, so that all possible diffraction peaks could be detected.

Optical absorption spectra of the films at room temperature were recorded on a SHIMADZU UV-2101 PC UV-VIS Scanning Spectrophotometer in the wavelength range 200nm-900nm.

3. RESULTS AND DISCUSSION

X-ray diffraction spectra of the deposited films have been given in Figure 2. The peaks with the Miller indices given belong to the $\text{Cd}_{0.22}\text{Zn}_{0.78}\text{S}$ (JCPDS file

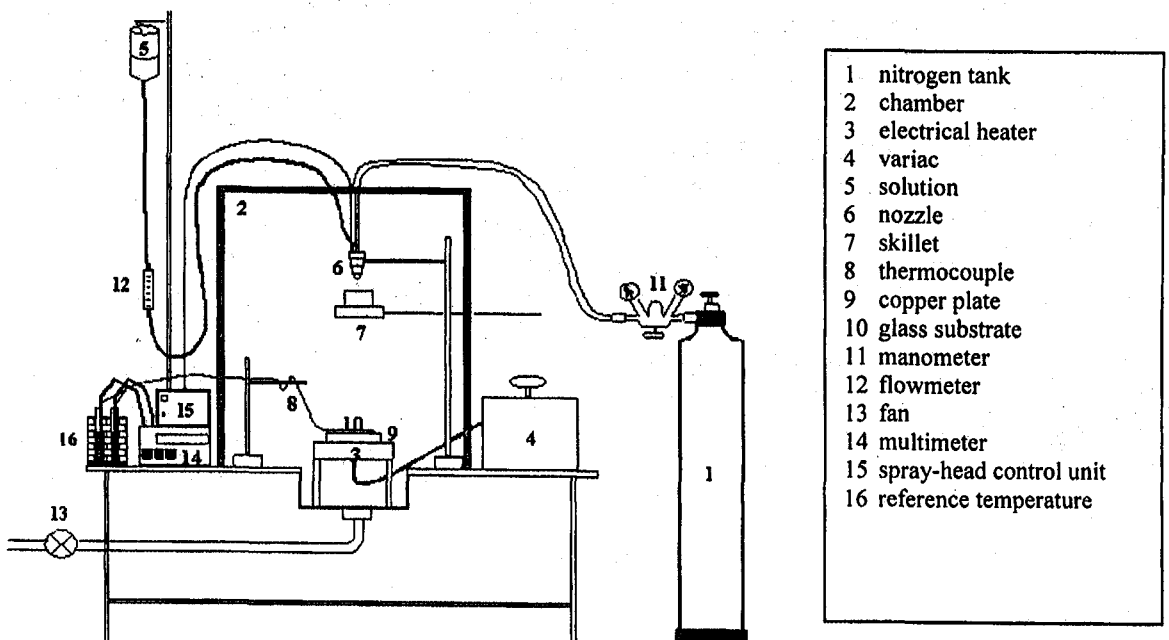


Figure 1. Schematic Diagram of The Spray Pyrolysis Set-up Used in Present Work.

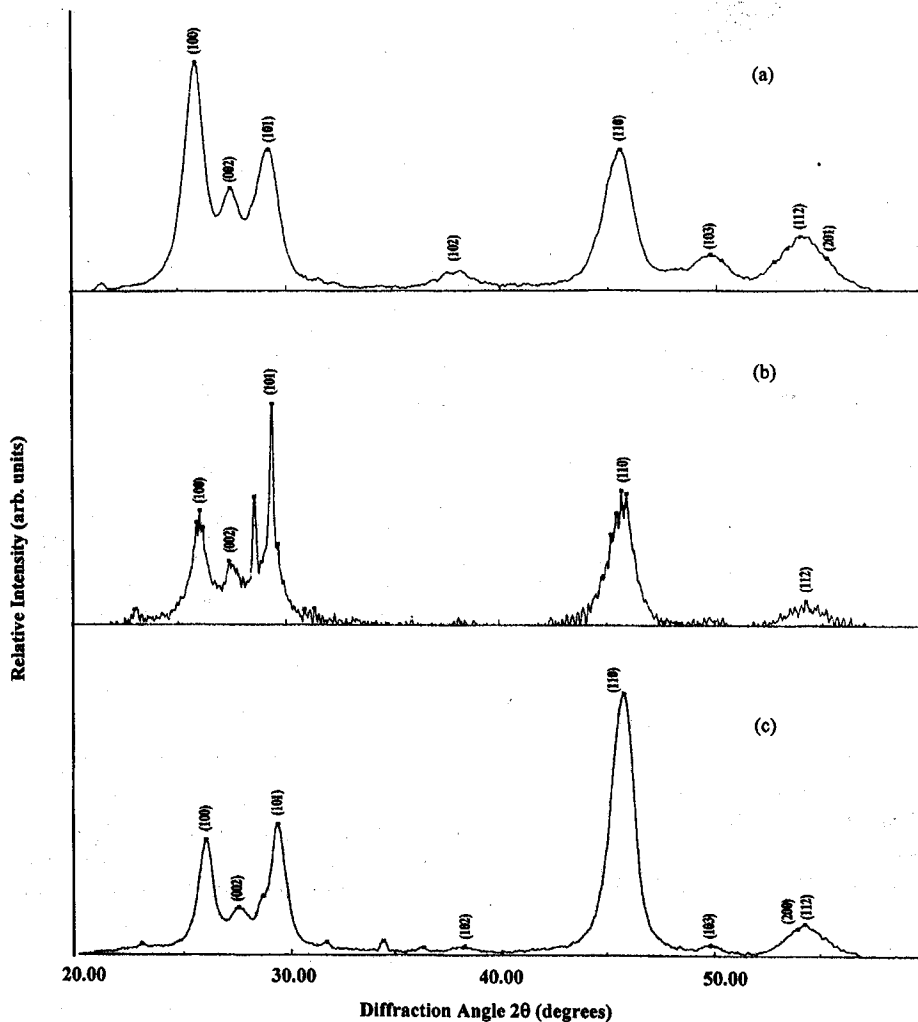


Figure 2. X-ray Diffraction Spectrum of $\text{Cd}_{0.22}\text{Zn}_{0.78}\text{S}$ films at (a) $250\pm 5^\circ\text{C}$, (b) $275\pm 5^\circ\text{C}$, and (c) $300\pm 5^\circ\text{C}$ Substrate Temperatures.

reference number Card no: 351469) compound semiconductor in hexagonal form. Of these three spectra, the peaks are more clear and sharper in (b) than (a) and (c), which represent higher crystallinity at $275\pm 5^\circ\text{C}$ substrate temperature. The peak at $2\theta=28.540^\circ$ in Figure 2b most probably belongs to the $\text{Cd}_{0.8}\text{Zn}_{0.2}\text{S}$ (JCPDS file reference number Card no: 400835) hexagonal structure that this type of formation of Cd, Zn, and S is possible (Çağlar and Zor, 2002).

The hexagonal structure and x-ray diffraction spectra of these films agree with the former studies (Brinkman, 1988; Ray et al., 1998; Yamaguchi et al., 1999).

The optical band gap, E_g , for the as-deposited films were calculated on the basis of the fundamental absorption using the well-known relation

$$\alpha h\nu \approx (h\nu - E_g)^n \quad (1)$$

where $h\nu$ is the incident photon energy, α is absorption coefficient, and n depends on the nature of band transi-

tion; $n=1/2$ and $3/2$ for direct allowed and direct forbidden transitions, and $n=2$ and 3 for indirect allowed and indirect forbidden transitions, respectively (Pankove, 1971). The optical band gap of these films have been determined from a plot of $(\alpha h\nu)^2$ versus photon energy $h\nu$.

Figure 3, 4, and 5 show the absorption spectra and the insert graphs show the plot of $(\alpha h\nu)^2$ vs $h\nu$ for $\text{Cd}_{0.22}\text{Zn}_{0.78}\text{S}$ films produced at $250\pm 5^\circ\text{C}$, $275\pm 5^\circ\text{C}$, and $300\pm 5^\circ\text{C}$ substrate temperatures, respectively. The steps observed in the absorption spectra are due to the spectrophotometer. Therefore, correction curve is drawn onto the each absorption spectrum. This compound is a direct band gap material with values of 2.85eV at $250\pm 5^\circ\text{C}$, 2.90eV at $275\pm 5^\circ\text{C}$, and 2.72eV at $300\pm 5^\circ\text{C}$ substrate temperature as derived from the insert graphs. Energy band gap values of these films agree with previous studies (Feigelson et al., 1977; Agnihotri and Gupta, 1979; Padam et al., 1988; Torres and Gordillo, 1992; Kuroyanagi, 1994; Dona and Herrero, 1995; Kumar et al., 1998; Ray et al., 1998).

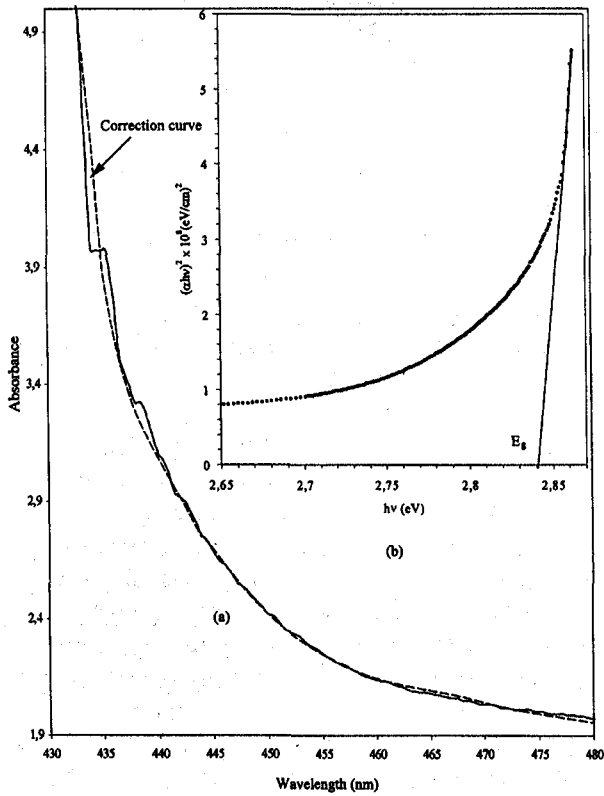


Figure 3. At Room Temperature, (a) Optical Absorption Spectra and (b) The Plot of $(\alpha hv)^2$ vs hv of $Cd_{0.22}Zn_{0.78}S$ Film Produced at $250 \pm 5^\circ C$ Substrate Temperature.

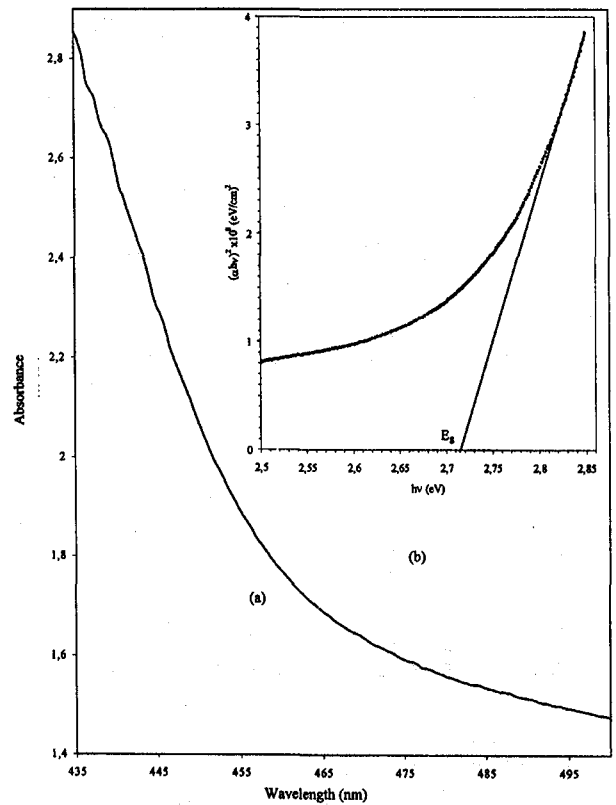


Figure 5. At Room Temperature, (a) Optical Absorption Spectra and (b) The Plot of $(\alpha hv)^2$ vs hv of $Cd_{0.22}Zn_{0.78}S$ Film Produced at $300 \pm 5^\circ C$ Substrate Temperature.

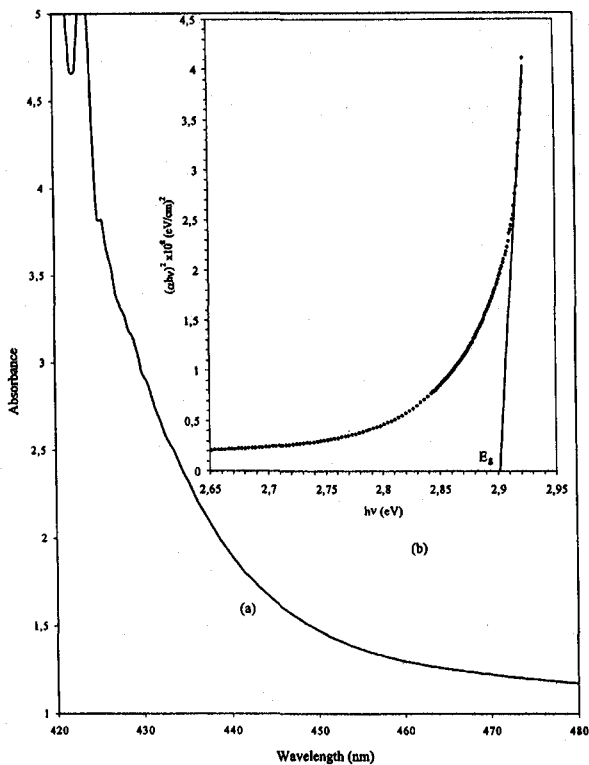


Figure 4. At Room Temperature, (a) Optical Absorption Spectra and (b) The Plot of $(\alpha hv)^2$ vs hv of $Cd_{0.22}Zn_{0.78}S$ Film Produced at $275 \pm 5^\circ C$ Substrate Temperature.

4. CONCLUSION

$Cd_{0.22}Zn_{0.78}S$ semiconductor films have been produced by the spray pyrolysis method at different substrate temperatures. The crystallinity and composition of deposited films were determined by the x-ray diffraction technique. To produce a semiconductor compound by means of this method is not straightforward process. For this reason, it is quite possible to get different phases. As a matter of fact, one-to-one ratio of Cd and Zn ions in the solution, became almost one-to-four in the resultant compound as $Cd_{0.22}Zn_{0.78}S$. These films have shown better crystallization at $275 \pm 5^\circ C$ substrate temperature. Polycrystalline nature of the film with hexagonal structure has been determined. The diffraction peaks of (100), (101) and (110) shifts toward the higher angles when the substrate temperature increases. These spray pyrolysed $Cd_{0.22}Zn_{0.78}S$ films show direct band gap values varied between 2.72eV-2.90eV. The variation of the band gap is most probably due to the formation of other phases and compounds.

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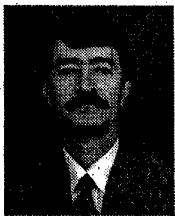
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