

ARAŞTIRMA MAKALESİ/RESEARCH ARTICLE

DEPOSITION, STRUCTURAL AND OPTICAL PROPERTIES OF THE CdZnSSe FILMS

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ABSTRACT

CdZnSSe films have been produced by the spray pyrolysis method on to the glass substrates kept at various substrate temperatures and with varying Se contents. The X-rays diffraction spectra of the films have shown that the films produced are polycrystalline and hexagonal in structure. The films have exhibited direct band gap characteristics with the band gap values lying in the range between 2.82-2.97eV.

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

CdZnSSe FİLMLERİNİN ELDE EDİLMESİ, YAPISAL VE OPTİKSEL ÖZELLİKLERİ

ÖZ

CdZnSSe filmleri püskürtme yöntemi ile cam tabanlar üzerine farklı Se miktarları ve farklı taban sıcaklıklarında elde edilmişlerdir. X-ışını kırınım desenleri filmlerin hekzagonal ve polikristal yapıda olduklarını göstermektedir. Filmlerin yasak enerji aralığının direkt bant geçişli olduğu ve değerlerinin 2,82-2,97eV arasında değiştiği belirlenmiştir.

Anahtar Kelimeler: Bileşik yarıiletkenler, Püskürtme, X-ışını kırınımı, Yasak enerji aralığı.

1. INTRODUCTION

II-VI compound materials are almost the first that have been used on an industrial scale for the production of semiconductors and related devices. They are used as cathode-ray tube screen materials, electroluminescent devices, ultraviolet responsive pigments, flash detectors and even as photoconductors and solar cells (Al-Ani et al., 1993). Direct band semiconductors with high absorption coefficients are favourite candidates for solar cells because of their potential to minimise material cost by their use in polycrystalline form and their ease of fabrication (Sahu, 1995). Wide band gap CdS has been used as the window material in heterojunction solar cells together with several narrow band gap semiconductors such as Cu₂S, InP, CuInSe₂, CdTe, etc (Mathew et al., 1995). ZnSe and CdS are excellent luminescent materials and offer promising applications

in devices operated in the visible region (Venugopal et al., 1996b). ZnSe and CdS are II-VI compounds, with cubic zincblende and wurtzite structures with direct bandgaps of 2.67 and 2.42eV, respectively, are found to be very promising materials for optoelectronic devices and heterojunction solar cells. In view of the potential applications of ZnSe and CdS, ZnSe_{0.5}CdS_{0.5} alloy films are suitable for various electronic devices (Venugopal et al., 1995).

II-VI compound semiconductors have been prepared by a variety of techniques, which include spray pyrolysis, ion beam deposition, molecular beam epitaxy growth (Ray et al., 1998). One of the prospective procedures used to prepare semiconductor thin films is the method of chemical spray pyrolysis. This method is widely used for the large-scale production, cost and simplicity of operation.

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Spray pyrolysis is basically a chemical deposition technique in which fine droplets of the desired material solution are sprayed onto a heated substrate (Afifi et al., 1995). The first time SnO₂ films were made by Mochel in 1951 by spraying a SnCl₂ solution in air (Fahrenbruch, 1977). The deposition of II-VI semiconductors by the spray pyrolysis technique was first investigated by Chamberlin and Skarman. They deposited several of the sulfides and selenides in their work on photoconductors (Chamberlin and Skarman, 1966).

In this study the preparation techniques as well as the structural and optical properties of the CdZnSSe films have been investigated for different Se contents at various substrate temperatures.

2. MATERIALS AND METHODS

2.1. Sample Preparation

CdZnSSe films have been produced by the spray pyrolysis method. The spray pyrolysis set up is shown in Figure 1.

An aqueous solutions of 0.01M of CdCl₂.H₂O, ZnCl₂, (NH₂)₂CS, H₂NC(=Se)NH₂ containing the necessary elements in compound had been used as the solution. Equal volume of CdCl₂.H₂O and ZnCl₂ solutions, appropriate amounts of (NH₂)₂CS and H₂NC(=Se)NH₂ solutions were mixed and sprayed on to the glass substrates at different substrate temperatures. Optical microslide glass plates (1x11x26mm³) are used as substrates. The temperature of substrate was controlled by an Iron-Constantan thermocouple. The flow rate of the solution during spraying was adjusted to be 2.6mlmin⁻¹ and kept constant throughout the experiment. The normalised distance between the spray nozzle and the substrate is 29cm. N₂ was used as the carrier gas. The other deposition conditions are given in Table 1. After deposition, the films were allowed to cool to room temperature. The film thickness was estimated by weighing method. Colour of the films was observed to change from dark yellow to light yellow with increase in Se atomic fraction.

Table 1. The Deposition Conditions of Cd_{0.73}Zn_{0.27}S_{1-x}Se_x Films.

Films	Substrate Temperature (°C)	Deposition Time (min)	Films Thickness (µm)
Cd _{0.73} Zn _{0.27} S	275	80	1.21
Cd _{0.73} Zn _{0.27} S _{0.8} Se _{0.2}	225	60	0.65
Cd _{0.73} Zn _{0.27} S _{0.8} Se _{0.2}	275	110	0.72
Cd _{0.73} Zn _{0.27} S _{0.8} Se _{0.2}	300	75	0.86
Cd _{0.73} Zn _{0.27} S _{0.6} Se _{0.4}	275	120	0.76

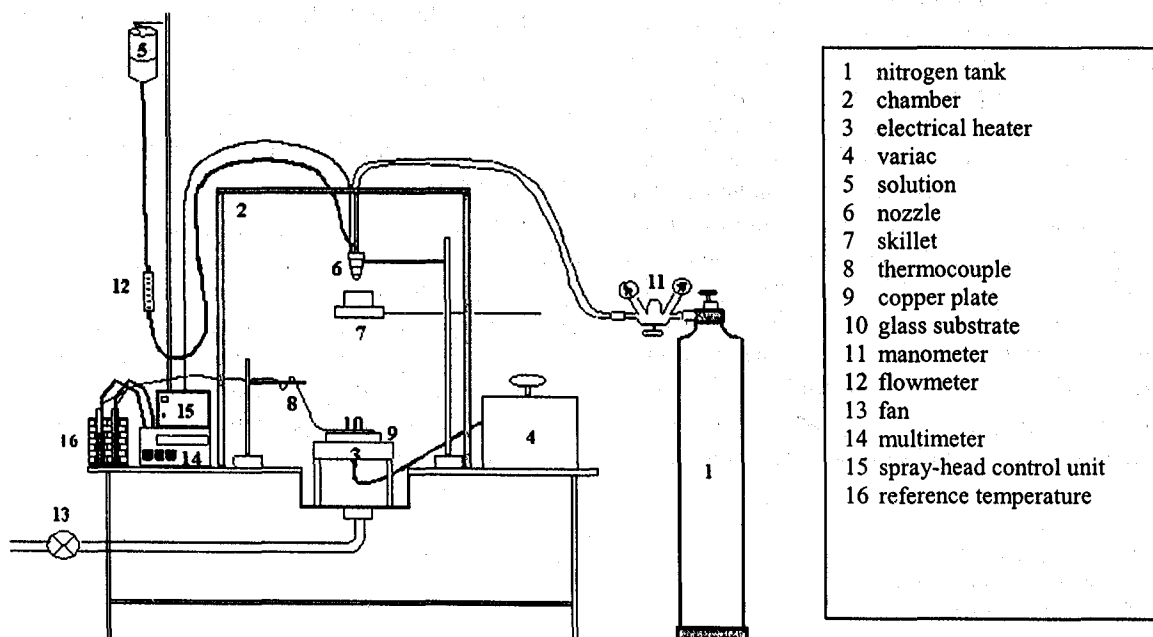


Figure 1. Schematic of The Spray Pyrolysis System Used for CdZnSSe.

2.2. Measurements

Structural studies of the films were carried out by the XRD technique using a RIGAKU RINT 2000 Series X-Ray Automatic Diffractometer with $\text{CuK}\alpha$ radiation ($\lambda=1.5404\text{\AA}$). The scanning angle 2θ was varied in the range of $20\text{-}60^\circ$.

Optical absorption studies of the films at room temperature were recorded in the wavelength range $200\text{-}900\text{nm}$ in a SHIMADZU UV-2101 PC UV-VIS Scanning Spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. XRD Analysis

Although the solution to be sprayed constitutes the required elements as $\text{Cd}_{0.5}\text{Zn}_{0.5}\text{S}_{1-x}\text{Se}_x$, XRD results have exhibited the peaks of $\text{Cd}_{0.73}\text{Zn}_{0.27}\text{S}_{1-x}\text{Se}_x$ compounds. Hence, the results and discussions would be based on the semiconducting compounds related to the XRD results.

X-ray diffraction spectra of $\text{Cd}_{0.73}\text{Zn}_{0.27}\text{S}_{0.8}\text{Se}_{0.2}$ films prepared at different substrate temperatures are shown in Figure 2, as it is seen that $\text{Cd}_{0.73}\text{Zn}_{0.27}\text{S}_{0.8}\text{Se}_{0.2}$ film produced at 300°C substrate temperature has a better crystallinity.

X-ray diffraction spectra of $\text{Cd}_{0.73}\text{Zn}_{0.27}\text{S}_{1-x}\text{Se}_x$ films prepared at 275°C substrate temperature with Se ($x=0.0, 0.4$) contents are shown in Figure 3. The X-ray

peaks corresponding to the 2θ diffraction angle were identified and compared with that of standard values from the JCPDS data file (JCPDS file reference number Card no: 150105, 160869, 210829, 361451, 371463, 400835, 400836).

X-ray diffraction studies showed that all the films were found to be polycrystalline. From Figure 3, it is evident that the $\text{Cd}_{0.73}\text{Zn}_{0.27}\text{S}_{1-x}\text{Se}_x$ films exists in hexagonal (wurtzite) structure. This agrees with previous works of Venugopal et al. (1995), Vijayalakshmi et al. (1994), Venugopal et al. (1996a), Chu et al. (1992), Gupta et al. (1977), Ray et al. (1998), Chaudhari et al. (1992), Afifi et al. (1995), Mathew et al. (1995), Lewis et al. (1986), El-Sherif et al. (1996).

3.2. Optical Analysis

For a large number of semiconductors, in either crystalline or amorphous forms, the dependence of the absorption coefficient, α , upon the photon energy $h\nu$, for optically induced transitions is in the form

$$\alpha n_0 h\nu = (h\nu - E_g)^n \quad (1)$$

where E_g is the band gap of the material, n_0 is the refractive index, and n is the exponent. The exponent n determines the type of electronic transitions causing the absorption from the valence band to the conduction band and can take the values $1/2$ and $3/2$ for direct allowed and direct forbidden transitions respectively, 2 and 3 for indirect allowed and indirect forbidden transitions, respectively (Mott and Davis, 1971).

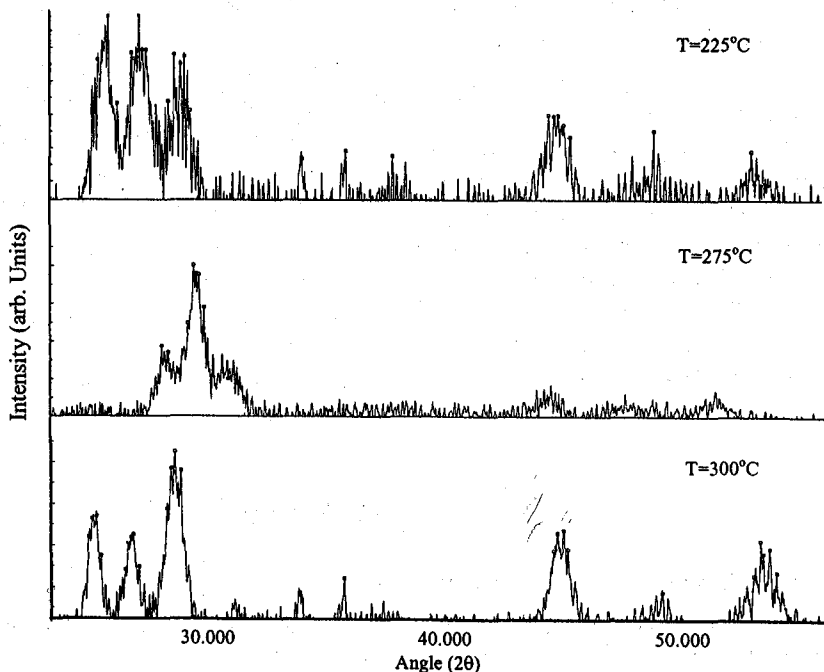


Figure 2. XRDs of $\text{Cd}_{0.73}\text{Zn}_{0.27}\text{S}_{0.8}\text{Se}_{0.2}$ Films for Different Substrate Temperatures.

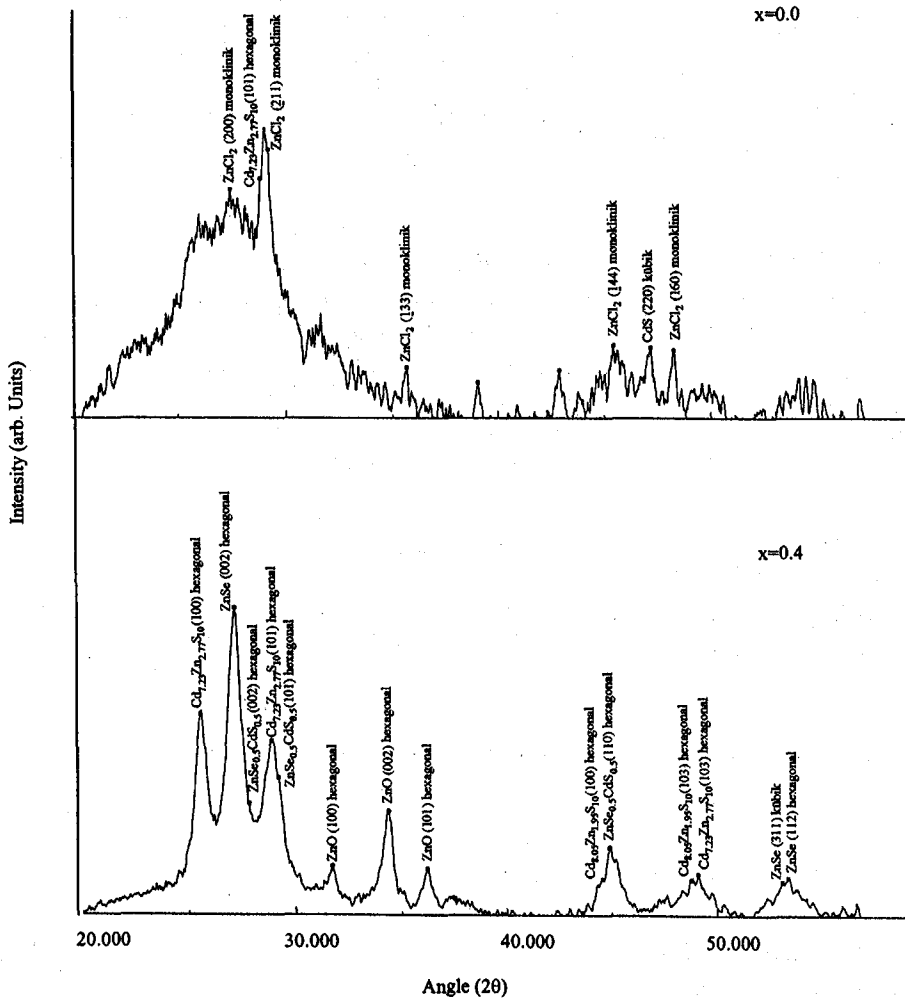


Figure 3. XRDs of $\text{Cd}_{0.73}\text{Zn}_{0.27}\text{S}_{1-x}\text{Se}_x$ Films for Different x Compositions Deposited at 275°C Substrate Temperatures.

Optical absorption studies of the $\text{Cd}_{0.73}\text{Zn}_{0.27}\text{S}$, $\text{Cd}_{0.73}\text{Zn}_{0.27}\text{S}_{0.8}\text{Se}_{0.2}$ and $\text{Cd}_{0.73}\text{Zn}_{0.27}\text{S}_{0.6}\text{Se}_{0.4}$ films have been carried out in the wavelengths range between 350-500nm and are shown in Figures 4a, 5a, and 6a. The values of the energy band gap can be estimated from the extrapolation to zero absorption in the $(\alpha h\nu)^2$ versus $h\nu$ plots which are shown as the inset in the figures. The optical band gaps were in the range 2.82-2.97eV and given in Table 2. It is seen that the energy band gap decreased with Se concentration. This is in good agreement with the reported values (Ray et al., 1998; Vijayalakshmi et al., 1994; Venugopal et al., 1995; Venugopal et al., 1996a; Venugopal et al., 1996b; Feng et al., 1993).

4. CONCLUSION

$\text{Cd}_{0.73}\text{Zn}_{0.27}\text{S}_{1-x}\text{Se}_x$ films have been deposited by the spray pyrolysis method on to glass substrates. X-ray diffraction studies have revealed the polycrystalline and hexagonal structure of $\text{Cd}_{0.73}\text{Zn}_{0.27}\text{S}_{1-x}\text{Se}_x$. It is hardly

possible to produce a compound semiconductor with a desirable stoichiometric ratio by the spray pyrolysis method. Peaks of different compounds were determined through the X-ray diffraction spectra of $\text{Cd}_{0.73}\text{Zn}_{0.27}\text{S}_{1-x}\text{Se}_x$ films. From the XRD results it is seen that Cd:Zn ratio varies in the range 3:1 to 4:1, whereas this ratio is 1:1 in the solution.

Optical absorption studies showed the band gap value to be 2.82-2.97eV. The band gap varied nonlinearly with Se. Despite the fact that the band gap values were not affected by lower Se concentrations, it seems that increasing the Se contents will have a profound effect on E_g .

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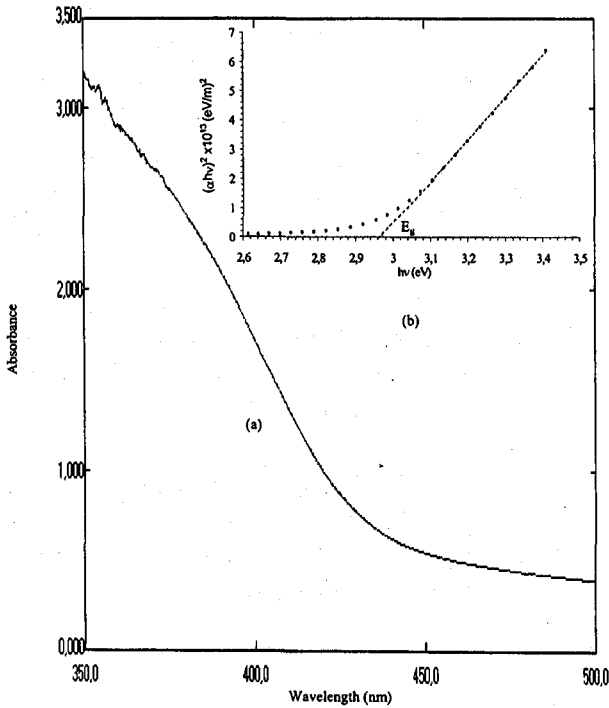


Figure 4. a) Optical Absorption Spectra of $Cd_{0.73}Zn_{0.27}S$ Film at Room Temperature
 b) Variation of $(\alpha hv)^2$ versus $h\nu$ of $Cd_{0.73}Zn_{0.27}S$ Film Deposited at $275^\circ C$ Substrate Temperatures.

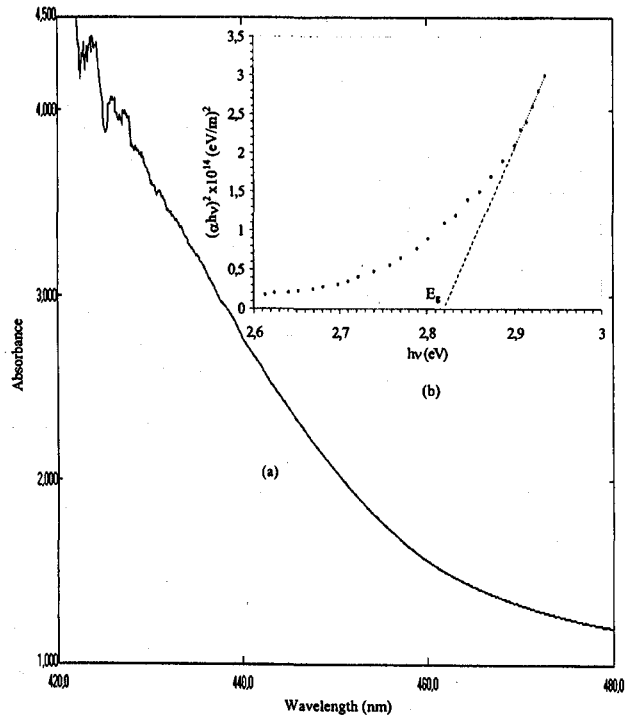


Figure 6. a) Optical Absorption Spectra of $Cd_{0.73}Zn_{0.27}S_{0.6}Se_{0.4}$ Film at Room Temperature
 b) Variation of $(\alpha hv)^2$ versus $h\nu$ of $Cd_{0.73}Zn_{0.27}S_{0.6}Se_{0.4}$ Film Deposited at $275^\circ C$ Substrate Temperatures.

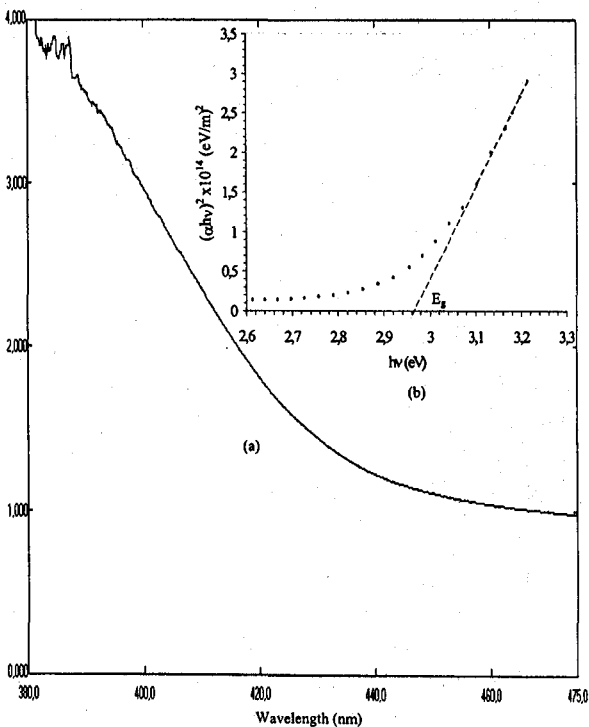


Figure 5. a) Optical Absorption Spectra of $Cd_{0.73}Zn_{0.27}S_{0.8}Se_{0.2}$ Film at Room Temperature
 b) Variation of $(\alpha hv)^2$ versus $h\nu$ of $Cd_{0.73}Zn_{0.27}S_{0.8}Se_{0.2}$ Film Deposited at $275^\circ C$ Substrate Temperatures.

Table 2. Band Gap Values of $Cd_{0.73}Zn_{0.27}S_{1-x}Se_x$ Films for Different x Compositions.

Films	E_g (eV)
$Cd_{0.73}Zn_{0.27}S$	2.97
$Cd_{0.73}Zn_{0.27}S_{0.8}Se_{0.2}$	2.96
$Cd_{0.73}Zn_{0.27}S_{0.6}Se_{0.4}$	2.82

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