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Optical Properties of $CuInS_2$ Films Produced by Spray Pyrolysis Method

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ABSTRACT

$CuInS_2$ semiconductor films have been produced by the spray pyrolysis method on to the glass substrates kept at different substrate temperatures. Optical characteristics of the $CuInS_2$ films have been analyzed using spectrophotometer in the wavelength range 400-900nm. The optical band gap energy has been obtained from the plot of $(\alpha h\nu)^2$ vs $h\nu$. The absorption spectra of the films showed that this compound is a direct band gap material and gap values varied between 1.51-1.80eV, depending on the substrate temperatures.

Key Words: Compound semiconductors, Spray pyrolysis, Absorption spectra, Energy band gap, Substrate temperature.

SPRAY PYROLYSIS YÖNTEMİYLE ELDE EDİLEN $CuInS_2$ FİLMLERİNİN OPTİK ÖZELLİKLERİ

ÖZET

CuInS2 yarıiletken filimleri püskürtme yöntemiyle cam tabanlar üzerine farklı taban sıcaklıklarında elde edilmiştir. $CuInS_2$ filimlerinin optik karekterizasyonları dalgaboyu 400-900nm aralığında spektrometre kullanılarak analiz edilmiştir. Yasak enerji aralığı $(\alpha h\nu)^2$'nin $h\nu$'ye göre grafiğinden elde edilmiştir. Filimlerin absorpsiyon spektrumlarından bu bileşiğin direkt bant aralığına sahip olduğu ve taban sıcaklığına bağlı olarak yasak enerji aralığının 1.51-1.80eV arasında değiştiği görülmüştür.

Anahtar Kelimeler: Yarıiletken bileşikler, Püskürtme yöntemi, Absorpsiyon spektrumu, Yasak enerji aralığı, Taban sıcaklığı.

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1. INRODUCTION

The development of contemporary, sophisticated technologies which increase the quality of human life is closely related to the semiconducting materials. The science and technology of semiconducting thin films have a crucial role in high-tech industry. Thin film of semiconducting materials are applicable in the field of microelectronic, optical electronic, in communication technologies, as well as in energy generation and conservation strategies, etc.(Pejova et al., 2003, 381-388).

$CuInS_2$ is one of the I-III-VI_2 type semiconductors which crystallizes in the chalcopyrite or sphalerite structure (Ortega-Lopez and Morales-Acevedo, 1998, 96-101). It has direct band gap of 1.3-1.5eV, high absorption coefficient ($10^5 cm^{-1}$) (Pathan and Lokhande, 2004, 11-18). An environmental viewpoint, $CuInS_2$ does not contain any toxic constituents that makes it suitable for terrestrial photovoltaic applications (Krunks et al., 1999, 125-130).

A variety of techniques have been applied to deposit CuInS2 thin films, such as single source evaporation, coevaporation from elemental sources, sulfurisation of metallic precursors (Antony et al., 2004, 407-417), diffusion of Cu and S into InxS precursor, electrodeposition and spray pyrolysis (Ortega-Lopez and Morales-Acevedo,1998, 96-101; Krunks et al., 2000, 61-64; Kijatkina et al., 2003, 105-109; Oja et al., 2004). Spray pyrolysis is an attractive method for large area thin films production because it is a low-cost and easy to make process (Ambia et al., 1994, 6575-6580; Zouaghi et.al., 2001, 39-46; Oja et al., 2004).

In this study, preparation techniques as well as the optical properties of the $CuInS_2$ films have been investigated at various substrate temperatures.

2. MATERIALS AND METHODS

$CuInS_2$ films have been produced by spraying the aqueous solution of 0.01M of $CuCl_2$ $.2H_2O$, $InCl_3$ and $(NH_2)_2CS$ in a 1:1:2 (by volume) onto the microscope glass substrates ($1x10x10mm^3$, $1x10x13mm^3$ and $1x13x26mm^3$) at different substrate temperatures of 225, 250 and 275°C. The substrate temperature was maintained to within ±5°C. Prior to deposition, the substrates were cleaned in acetone.

For the spray pyrolysis we used a system similar to that shown in Fig. 1. Spray pyrolysis is basically a chemical process, that is the spraying of the solution onto a substrate held at high temperature, where the solution reacts forming the desired film (Br.Patent 632256, 1942; Chamberlin and Skarman, 1966, 86-89; Lampkin, 1979, 406-416; Afify, et al., 1991, 152-156; Falcony, et al.1992, 4; Zor et al., 1997, 1132-1135; Aksay, 2001,147-156; Nunes et al., 2002, 281-285). The spray rate was measured by a flowmeter. The flow rate of the solution during spraying was adjusted to be about $2.5 ml min^{-1}$ and kept constant throughout the experiment. The normalized distance between the spray nozzle and the substrate is 29cm. Nitrogen was used as the carrier gas. The temperature of the substrate was controlled by an Iron-Constantan thermocouple. The thickness of the films were measured using the weighing- method. The other deposition conditions are given in Table 1.

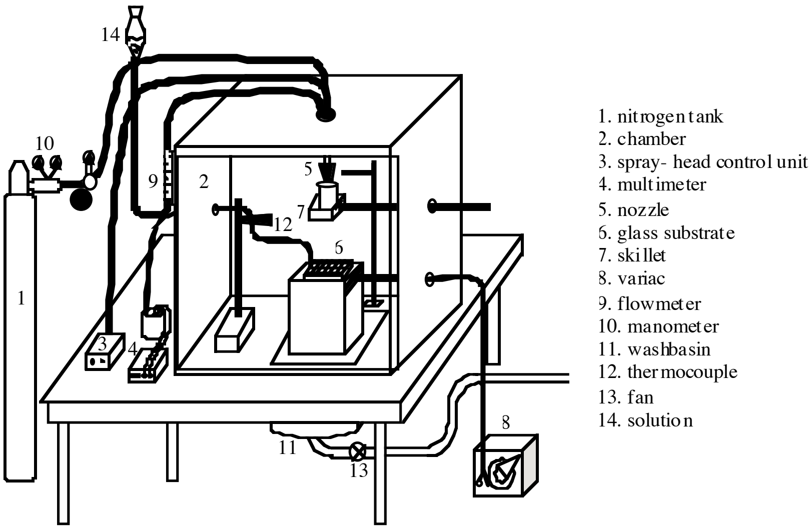


Figure 1. Schematic of the spray pyrolysis system.

Table 1. The deposition conditions of $CuInS_2$ films.

Film	Substrate Temperature (°C)	Nitrogen Gas (bar)	Flowmeter-rate (mLmin^{-1})	Spray Distance (cm)	Deposition Time (min)	Films Thickness (μm)
	225±5	0.2	2.5	29	55	1.59
$CuInS_2$	250±5	0.2	2.5	29	55	1.43
	275±5	0.2	2.5	29	55	1.39

Optical absorption spectra of the films at room temperature were recorded on a SCHIMADZU UV-2101 and UV-2401 Scanning Spectrophotometer in the wavelength range 400-900nm.

3. RESULTS AND DISCUSSION

3.1. Optical properties

3.1.1. Transmittance measurements

The optical band gap of the material has been determined from the transmittance (T) vs. wavelength (λ) plot shown in Fig.2. The fundamental absorption, which corresponds to electron excitation from the valence band to the conduction band, can be used to determine the nature and value of the optical band gap. The film produced presented at lower temperature (225°C) lower transmission. The film prepared at 250°C presented higher transmission compared to the ones produced at other temperature.

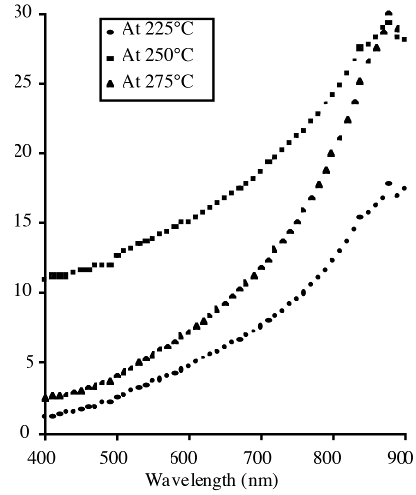


Figure 2. Transmittance spectra at various temperatures for $CuInS_2$ films.

3.1.2. Absorption coefficient

The absorption coefficients α of the films have been calculated from the experimentally measured values of A and T according to the following relation

$$T=(1-R)^2 \exp(-A)=(1-R)^2 \exp(-\alpha t) \quad (1)$$

where R is the reflectance, T the transmittance, A the absorbance and t the film thickness(El-Zahed, 2001, 641-646, 95-104; Kanan et al., 2003, 328-332; Bouzidi et al.,2002, 141-147).

The optical absorption coefficient α is determined using the relation

$$\alpha = (2.303 / t) [\log(1 / T)] \quad (2)$$

where t is the thickness of the film and T is the transmittance (Benramdane et al., 1997, 119-123; El-Zahed et al., 2003, 19-27; Padiyan et al., 2004, 8-14). We have calculated the absorption coefficient for $CuInS_2$ films having the estimated thickness values that varied between 1.39-1.59μm. Absorption coefficient spectra versus the wavelength are presented in Fig.3.

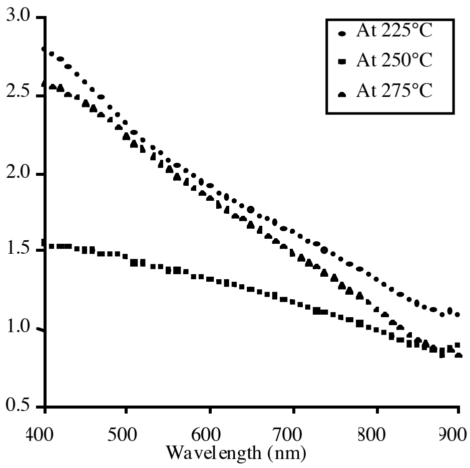
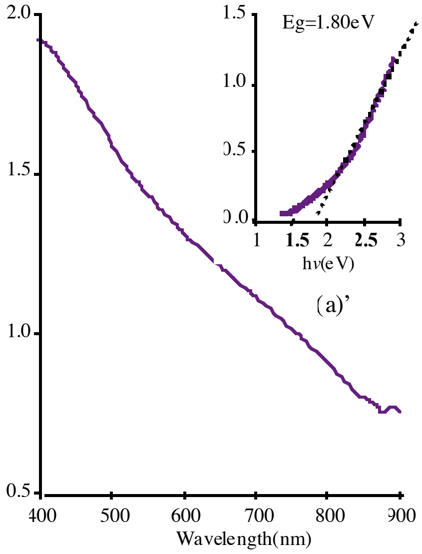
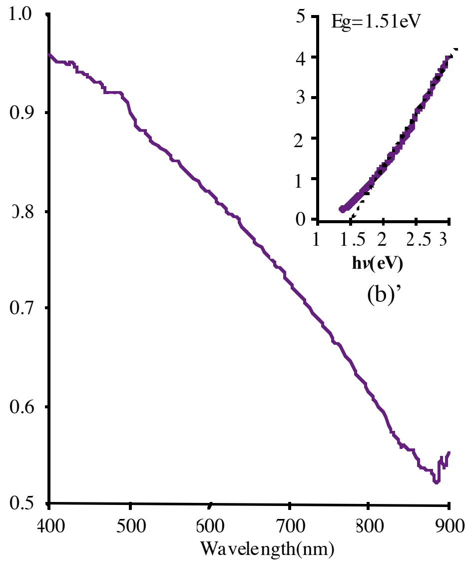


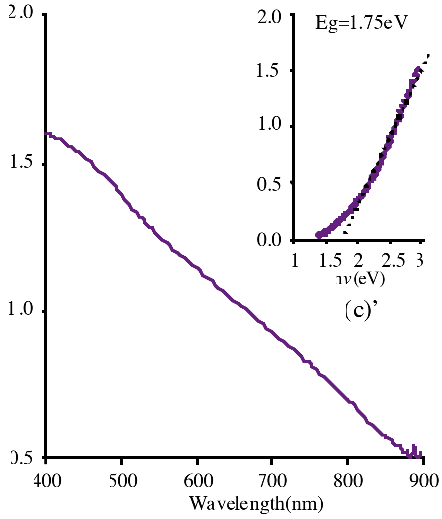
Figure 3. The relation between absorption coefficient (α) vs wavelength (λ) for $CuInS_2$ film at different substrate temperatures.



(a)



(b)



(c)

Figure 4. At room temperature (a) 225±5°C, (b) 250±5°C, (c) 275±5°C optical absorption spectra and , (a)' ,(b)', (c)' the plot of $(\alpha h\nu)2$ versus hν of $CuInS_2$ films.

3.1.3. Determination of the gap energy

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

$$(\alpha h()^{1/n} = constant(h\nu - E_g) \quad (3)$$

where $h\nu$ is the incident photon energy, α is absorption coefficient, and the exponent n depends on the type of transition. n=1/2, 2, 3/2 and 3 corresponding to allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions respectively (Pankove, 1971; 35-40; Mott and Davis, 1971, 238-239).

Optical absorption studies of the CuInS2 films have been carried out in the wavelengths range between 400-900nm and are shown in Figures 4a, 4b, and 4c. 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. This compound is a direct band gap material with values of 1.80eV at 225±5°C, 1.51eV at 250±5°C, and 1.75eV at 275±5°C substrate temperature as derived from the insert graphs. From substrate temperatures ranging from 225°C to 250°C, a decrease in band gap values was observed except but for 275°C. A possible cause for this effect may be carrier degeneracy in $CuInS_2$ due to defect in the crystalline lattice (Ortega-Lopez and Morales-Acevedo, 1998; 96-101). From these observations, the influence of both the film thickness and substrate temperature on Eg values is clearly evident. This is in good agreement with the reported values (Aksay, 1996, 1-99; Sıham and Eid, 1997, 171-179; Ortega-Lopez and Morales-Acevedo, 1998; 96-101; Krunks et al., 1999; 125-130; Kanzari and Rezig, 2000, 335-340). Similar observations have been made by some authors regarding the variation in band gap values in chalcogenide thin films (Acosta et al., 2004, 11-20; Lalitha, 2004, 187-189; Padiyan et al., 2002, 51-58). This decrease in energy band gap was attributed to variation of stochiometry (Velumani et al., 2003, 347-358). In the present study, the decrease of optical band could be attributed to the presence of unsaturated defects, which increase the density of localized states in the band gap and consequently decrease the optical energy gap (El-Zahed et al., 2003, 19-27).

4. CONCLUSION

Films of $CuInS_2$ onto glass substrate at different substrate temperatures, ranging from 225°C to 275°C, have been prepared using a spray pyrolysis method. The optical studies reveal that these films has a direct band gap and the band gap energy varies from 1.80 to 1.51eV with substrate temperature. It is observed that the band gap decreases with the increase of the substrate temperature. The determined optical parameters are in good agreement with previously reported results on similar films. In conclusion, spray pyrolysis method for the production of thin solid films is a good method for the preparation of thin films suitable for scientific studies and for many applications in technology and industry.

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