



STRUCTURAL AND OPTICAL PROPERTIES OF $\text{Cu}_2\text{ZnSnO}_4$ THIN FILM PREPARED BY DIP-COATING SOL-GEL

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Received 23-07-2013, revised 17-09-2013, online 27-09-2013

ABSTRACT

$\text{Cu}_2\text{ZnSnO}_4$ thin films were prepared by dip coating sol-gel method. Copper (II) acetate monohydrate, zinc (II) acetate dehydrate and tin (II) chloride dehydrate were used as the starting materials of the sol-gel method, ethanol and mono ethylamine were used as the solvent and the stabilizer, respectively. The phase structure and optical properties of the thin films were investigated by X-ray diffraction (XRD) and optical transmittance spectroscopy. The film prepared shows a good transmittance 83%-98% in the visible region, 2.16 refractive index and energy band gap about 2.3 eV.

Keywords: Dip coating; Sol-gel method; CuO, ZnO, SnO, $\text{Cu}_2\text{ZnSnO}_4$.

I. INTRODUCTION

CuO, ZnO, SnO three oxide semiconductor material have specific properties [1-16] for applications such as thin film, magnetic memory devices, integrated circuits, rectifiers, transistors, amplifiers, detectors, solar cell.

In recent years, SnO has received greater attention because it has a wide optical band gap of 2.7 eV to 3.2 eV, but in contrast to the n-type behavior of SnO_2 , SnO exhibits p-type conductivity [17]. SnO thin film has transmittance 95% in the visible region and a 2 to 2.4 refractive index value. These properties of SnO make it an interesting candidate for optoelectronic applications.

Copper oxide (CuO) is a p-type semiconductor with a band gap of 1.5 to 1.8 eV [18]. CuO thin film has transmittance of 20% in the visible region and it reaches 90% for the high wavelength of the visible region with 2 to 2.5 refractive index values. Its applications may be for catalysis, lithium-copper oxide electrochemical cells, solar cells, and gas sensors.

ZnO is a promising material for the use in ultraviolet or visible optoelectronic devices, because of its direct wide band gap in the range 2.5 eV to 3.2 eV. ZnO is naturally only n-type conduction due to a large number of native defects, such as oxygen vacancies and zinc interstitials [19]. ZnO thin film has transmittance of 99% in the middle of visible region and 2 to 2.4 refractive index values.

In this study mixture of TZCO (2CuO, ZnO, SnO) thin films has been prepared and examined to get a thin films with mixed properties from them. To prepare a thin film by dip coating the substrate is taken and immersed in the sol then it is pulled up with constant withdrawal speed so the sample gets five immersion steps, start up, deposition and drainage, evaporation, drainage as shown in figure (1) [3][11][12].

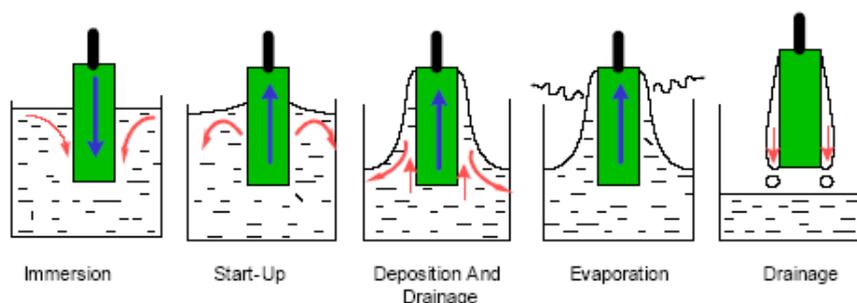


Fig. 1: Dip coating steps to get a thin film

II. EXPERIMENTAL PROCEDURE

0.044 mole/l of Copper (II) acetate monohydrate, 0.022 mole/l of zinc (II) acetate dehydrate and 0.022/1 mole of tin (II) chloride dehydrate were used as the starting materials of the sol-gel method, ethanol and mono ethyl amine were used as the solvent and the stabilizer, respectively, we add 5 ml from mono ethyl amine as stabilizer. The solution was stirred at 45 °C for an hour and soda lime glass substrates cleaned by ultrasonic waves then washed by acetone and distilled water respectively.

The solution was dip coated on soda lime glass substrates then pulled up at 2cm/min withdrawal speed then dried at 300 °C. The process was repeated five times then annealed at 400 °C for two hours.

III. RESULTS AND DISCUSSION

III.1. Structural properties for $\text{Cu}_2\text{ZnSnO}_4$ thin film prepared by sol-gel method

The XRD spectrums of the samples were recorded at room temperature using a Phillips PW 1480 Albaath university labs. Figure (2) shows the XRD Spectrum of $\text{Cu}_2\text{ZnSnO}_4$ thin film. The line (112) at $2\theta = 26.8^\circ$ is pointed to present of SnO, and the lines (002) at $2\theta = 35.5^\circ$, (111) at $2\theta = 38.9^\circ$ are pointed to present of CuO, and (101) at $2\theta = 36.2^\circ$ is pointed to present thin films of ZnO.

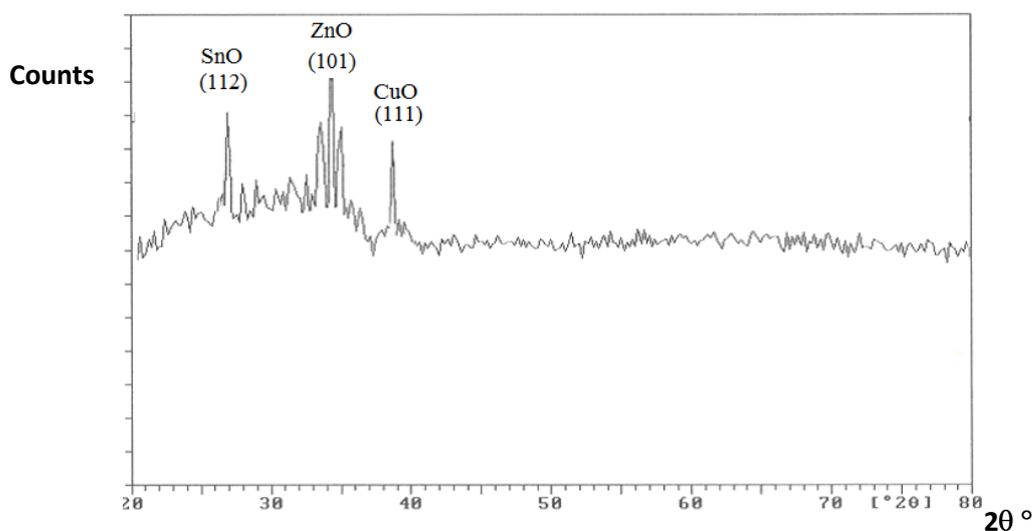


Fig. 2: $\text{Cu}_2\text{ZnSnO}_4$ thin film XRD Spectrum.

III.2. Optical properties for $\text{Cu}_2\text{ZnSnO}_4$ thin film prepared by sol-gel method

The optical transmittance was measured using a UV–VIS–NIR Jasco Scan spectrophotometer in the wavelength range from 190 nm to 2500 nm in Albaath University labs. Figure (3) shows the transmission spectrum as a function to wavelength for $\text{Cu}_2\text{ZnSnO}_4$ thin film by dip coating Sol – Gel. Figure (4) and figure (5) show the absorption and reflection spectrum respectively.

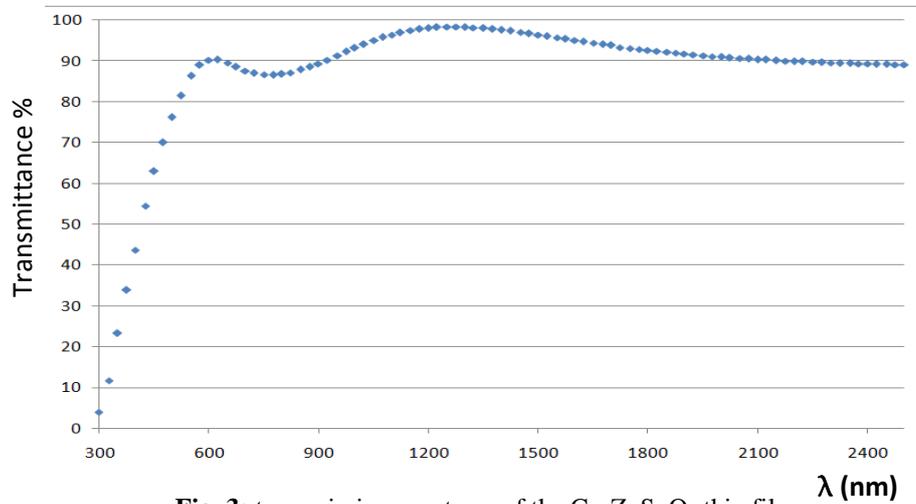


Fig. 3: transmission spectrum of the $\text{Cu}_2\text{ZnSnO}_4$ thin film

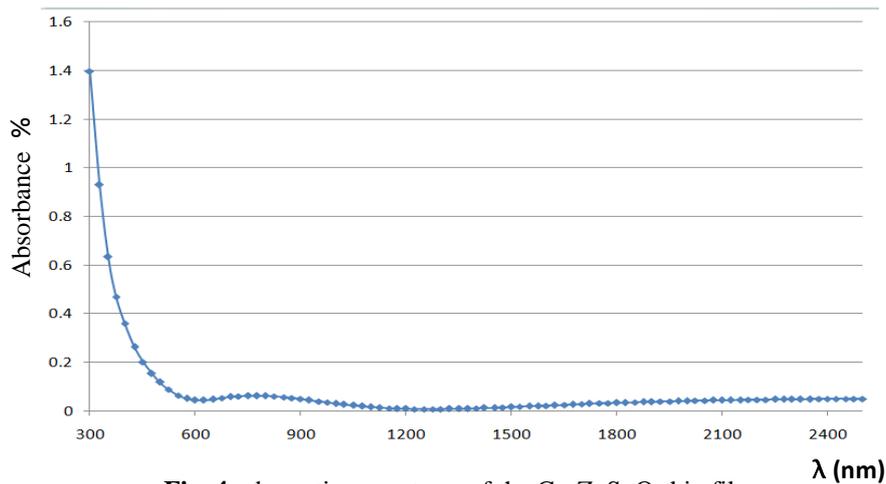


Fig. 4: absorption spectrum of the $\text{Cu}_2\text{ZnSnO}_4$ thin film

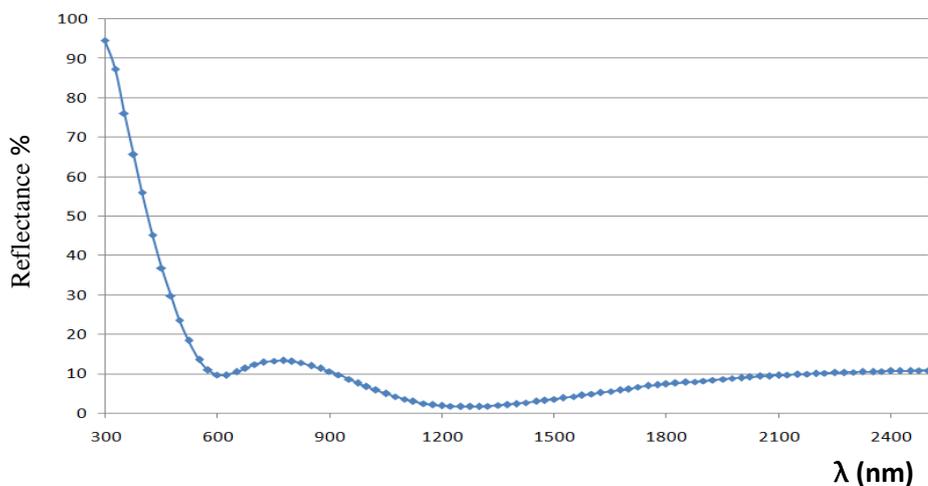


Fig. 5: reflection spectrum of the $\text{Cu}_2\text{ZnSnO}_4$ thin film

And with drawing the relationship between $(\alpha h\nu)^2$ as a function to energy ($h\nu$) we can determine the energy band gap of the direct allow transition for $\text{Cu}_2\text{ZnSnO}_4$ thin film by dip coating Sol-Gel as shown in Fig. 6.

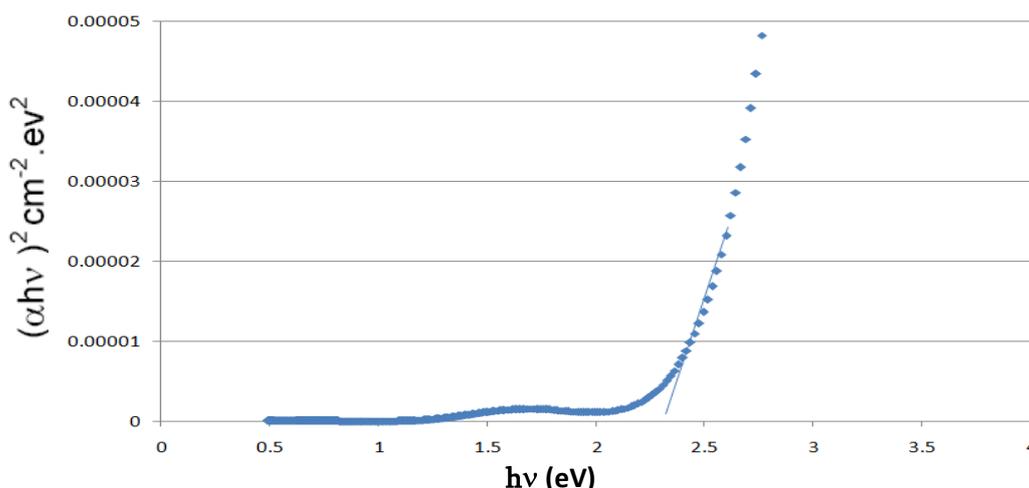


Fig. 6: energy band gap for direct allow transition for $\text{Cu}_2\text{ZnSnO}_4$ thin film

The thickness and refractive index of the $\text{Cu}_2\text{ZnSnO}_4$ thin film was calculated using Manifacier and Swanepoel method to determine the (n, d, α, k) starting from transmission spectroscopy and it was (192 nm) thickness and(2.16) for refractive index. Table1 summarizes the properties of CuO, ZnO, SnO, and $\text{Cu}_2\text{ZnSnO}_4$ prepared thin films.

Table 1: the properties of CuO, ZnO, SnO, and $\text{Cu}_2\text{ZnSnO}_4$ prepared thin films

Thin Film	Transmission (300-800)nm	Refractive Index	Energy Band Gap for allow Transition (eV)
CuO	20-90%	2-2.5	1.5-1.8
ZnO	95-99%	2-2.5	2.5-3.2
SnO	>95%	2-2.4	2.7-3.2
$\text{Cu}_2\text{ZnSnO}_4$	83-98%	2.16	2.3

IV. CONCLUSIONS

$\text{Cu}_2\text{ZnSnO}_4$ thin films were prepared by dip coating sol-gel method. Copper (II) acetate monohydrate, zinc (II) acetate dehydrate and tin (II) chloride dehydrate were used as the starting materials, ethanol and mono ethylamine were used as the solvent and the stabilizer, respectively. The solution was stirred at 45 °C for an hour and soda lime glass substrates cleaned by ultrasonic waves then washed by acetone and distilled water respectively. The solution was dip coated on soda lime glass substrates then pulled up at 2cm/min withdrawal speed then dried at 300 °C. the process was repeated five times then annealed at 400 °C for two hours. The film prepared has a good transmittance 83%-98% in the visible region and 2.16 refractive index and energy band gap about 2.3 eV.

So, we get a good thin film from mixed three oxides (CuO, SnO, ZnO) and get mixed characteristics from all. It has a good transmittance 83%-98% in the visible region and 2.16 refractive index and energy band gap about 2.3 e.V.

References

- [1] R. Wuerz, A. Eicke, M. Frankenfeld, F. Kessler, M. Powalla, P. Rogin, O. Yazdani-Assi, "CIGS thin-film solar cells on steel substrates", *Thin Solid Films* **517**, 2415–2418 (2009).
- [2] SeJinAhn, KiHyun Kim, KyungHoonYoon, "Cu(In,Ga)Se₂ thin film solar cells from nanoparticle precursors", *Current Applied Physics* **8**, 766–769 (2008).
- [3] W.abdullah, "Study of Electrical & Optical Properties of Thin Films Deposited by Sol-Gel methods (Technique)", Ph.D Thesis, Aleppo University 2006.
- [4] Sigeyuki Nakamura Akio Yamamoto, "Electrodeposited CuInS₂-based thin-film solar cells", *Solar Energy Materials & Solar Cells*, **75**, 81–86 (2003).
- [5] SeJinAhn, KiHyun Kim, KyungHoon Yoon, "Nanoparticle derived Cu (In, Ga)Se₂ absorber layer for thin film solar cells", *Colloids and Surfaces A: Physicochem. Eng. Aspects* **313–314**, 171–174 (2008).
- [6] Vijay K. Kapur, Ashish Bansal, Phucan Le, Omar I. Asensio, "Non-vacuum processing of CuIn_{1-x}Ga_xSe₂ solar cells on rigid and flexible substrates using nanoparticle precursor inks", *Thin Solid Films*, **431–432**, 53–57 (2003).
- [7] William W. Hou, Brion Bob, Sheng-han Li, Yang Yang, "Low-temperature processing of a solution-deposited CuInSSe thin-film solar cell", *Thin Solid Films* **517**, 6853–6856 (2009).
- [8] P. Saravanan, Sarfaraz Alam, G.N. Mathur, "A liquid-liquid interface technique to form films of CuO nanowhiskers", *Thin Solid Films* **491**, 168–172 (2005).
- [9] V.S. Gurin, A.A. Alexeenko, K.V. Yumashev, P.V. Prokoshin, S.A. Zolotovskaya, G.A. Zhavnerko, "Structure and optical properties of Cu_xO- and Cu_xSe doped sol-gel silica glasses", *Materials Science and Engineering C* **23** 1063–1067 (2003)
- [10] Xiaojun Zhang Dongen Zhang, Xiaomin Ni, Huagui Zheng, "Synthesis and optical properties of Cu₂O/SiO₂ composite films via gamma-irradiation route", *Materials Letters* **61**, 248–250 (2007).
- [11] Chien-Yie Tsay Kai-Shiung Fan, Sih-Han Chen, Chia-Hao Tsai, "Preparation and characterization of ZnO transparent semiconductor thin films by sol-gel method", *Journal of Alloys and Compounds* **495**, 126–130 (2010).
- [12] Lamia Znaidi, "Sol-gel-deposited ZnO thin films :A review", *Materials Science and Engineering B*, **174**, 318–330 (2010).
- [13] Christopher S. Dandeneau, Yu-Hong Jeon, Christopher T. Shelton, Tom K. Plant, David P. Cann, Brady J. Gibbons, "Thin film chemical sensors based on p-CuO/n-ZnO hetero contact", *Thin Solid Films* **517**, 448–454 (2009).
- [14] A. P. Rizzato, L. Broussous, C.V. Santilli, S.H. Pulcinelli, A.F. Craievich, "Structure of SnO₂ alcosols and films prepared by sol-gel dip coating", *Doped SnO₂ films for Solar Conf., Brasil May 2001*, **284**, pp. 61–67.
- [15] Gong Shuping Xia Jing, Liu Jianqiao, Zhou Dongxiang, "Highly sensitive SnO₂ thin film with low operating temperature prepared by sol-gel technique", *Sensors and Actuators B: Chemical*, **134**, 57–61 (2008).
- [16] M.alhamed, M.hasan, W.doubal "Characterization of thin films by determination of the optical constants (n,d, α,k)", *Aleppo university magazine (Syria)*, **50** (2006).
- [17] Abhirami K.M., Sathyamoorthy R., Matheswaran P, "Preparation Of SnO Thin Film By Thermal Evaporation", *National Conference on Developing Scenario in Applied Sciences and Communicative English Organized by Department of Science and Humanities, Kumaraguru College of Technology, Coimbatore* **49**, (2012).
- [18] Nguyen Duc Hoa, Sea Yong An, Nguyen Quoc Dung, Nguyen Van Quy, Dojin Kim., "Synthesis of p-type semiconducting cupric oxide thin films and their application to hydrogen detection", *Sensors and Actuators B* **146**, 239–244 (2010).
- [19] Hong Seong Kang, Byung Du Ahn, Jong Hoon Kim, Gun Hee Kim, Sung Hoon Lim, Hyun Woo Chang, Sang Yeol Lee, "Structural, electrical, and optical properties of p-type ZnO thin films with Ag dopant", *Appl. Phys. Letters* **88**, 202108 (2006).