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## The Optical Properties of CIGS Thin Films Derived by Sol-Gel Dip Coating Process at Different Withdrawal Speed

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### Abstract

The copper indium gallium diselenide Cu(In,Ga)Se<sub>2</sub> (CIGS) thin-films deposited on soda lime silica glass substrates were dip-coated five times and annealed at 180°C. The advantages of CuIn(Ga)Se<sub>2</sub> thin films were its wide compositional tolerance, high conversion efficiency, flexibility, low cost of materials and high optical absorption in the visible spectrum. The effect of the withdrawal speed, on the optical properties of the CIGS thin films derived by sol-gel process detailed clearly in this study by transmission and reflection measurements with controlling the withdrawal speed. The prepared CIGS thin films had p-type conductivity. The significant blue shift of absorption edge as well as tuning of optical band gap was observed with the withdrawal speed. The CIGS thin films at four different withdrawal speeds were such as 60, 120, 200 and 300 mm min<sup>-1</sup> prepared from colloidal suspensions to control the nature of nanospheres in the CIGS texture, because the colloidal solution was utilised as a template to control the particle shape.

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## 1. Introduction

Copper indium gallium diselenide (CIGS) thin films are formed p-type and direct bandgap semiconductor which have light absorption coefficient ( Krunk, 1999) and high photoelectric conversion efficiency used as an absorber layer in the solar cells ( Guillemoles et al., 2000). CIGS thin films are deposited by various methods as sputtered stacked elemental layer, rapid thermal processing, electrodeposited stacked elemental layer, rapid thermal processing, coatings of nano-particles precursor layer (non-vacuum), selenization with  $H_2Se$ , magnetron sputtering in Se atmosphere, screen printing of nanoparticles, co-evaporation and doctor-blade ( Brémaud, 2009). Co-evaporation method is the best method for the CIGS thin films (Mickelsen and Chen, 1980; Dimmler et al. 1996; Fredric et al., 1993) but it has got environmentally and economically disadvantages instead of that sol-gel method is both low cost and environmentally friendly. Beside, (Kaelin et al., 2005) and (Ahn et al., 2010) exhibit that the solution based process by using chemicals (metal-nitrates and chlorides), solvents (basic alcohols) and heat treatment medium (Se vapor) which cost-effective and environmentally friendly combinations like our study.

Thin film thickness depends on the withdrawal speed and there is a general relation between the thickness and withdrawal speed in Fig.1. Sol-gel dip coating technique is an economic method for low temperature annealing process of thin films.

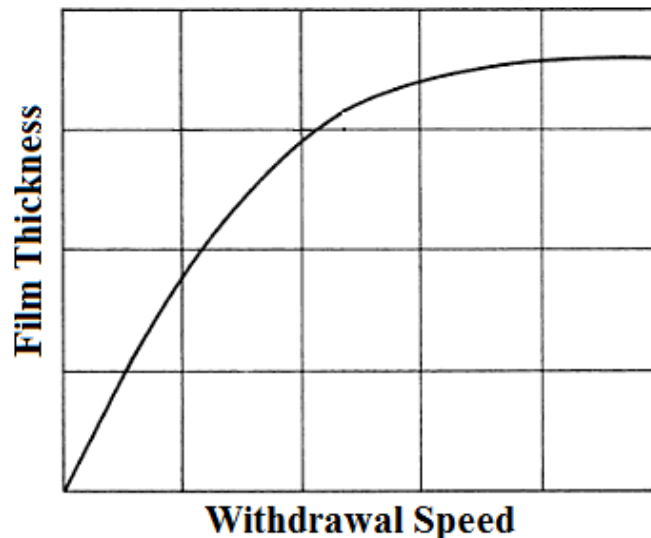


Fig.1. Relation between the thickness and withdrawal speed.

The effect of the withdrawal speed, on the optical properties of the CIGS thin films derived by sol-gel process detailed clearly in this study. This study presents some information on the optical properties by controlling the withdrawal speed. The significant blue shift of absorption edge as well as tuning of optical band gap was observed with the withdrawal speed. The CIGS thin films at five different withdrawal speed were prepared from colloidal suspensions to control the nature of nanospheres in the CIGS texture, because the colloidal solution was utilised as a template to control the particle shape. This study contributes to the field of the optical properties of CIGS thin films produced by the sol-gel method to reduce the cost of the production and to control the chemical composition on the surface of films in atomic scale.

## 2. Methodology

### 2.1. Research Goal

In this survey we aim to identify the effect of the withdrawal speed on the optical and electrical properties of the CIGS thin films by measuring transmission and reflection.

### 2.2. Production of CIGS Thin Films

CIGS thin-films were produced by sol-gel dip coating technique to apply this technique on large areas such as glass substrates. Prior to deposition, all of the substrates were sonicated in acetone and alcohol for 10 min, rinsed in distilled water for 10 min and then dried in still air. CIGS solution was prepared via the sol-gel route employing Diethanolamine (DEA,  $\text{CH}_2\text{CH}_2\text{OH}$ )<sub>2</sub> and hydrochloric acid were added to the solution as the stabiliser. The solution consisted of absolute ethanol, as the solvent material. Copper nitrate hydrate ( $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ; 99.999 %), indium nitrate hydrate ( $\text{In}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ; 99.999 %) and gallium nitrate hydrate ( $\text{Ga}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ ; 99.9 %) were used as the starting material. Followed by the addition of an ethanol solution (20 mL) with terpineol (Fruka, 14 g) and ethyl cellulose (Aldrich, 0.75 g) (Park et al. 2011).

### 2.3. Analyses and Results

The rise of withdrawal speed was very important to change the optical properties of the CIGS thin films. Fig.2. illustrates the transmittance (T%) of the CIGS thin films at four different withdrawal speeds such as 60, 120, 200 and 300  $\text{mm min}^{-1}$ . There were the changes in reflectance (R %) (in Fig. 3.) and absorbance (A %) (in Fig. 4) of the thin film coated due to the increase of withdrawal speeds. The optical transmittance of the CIGS thin film on the soda-lime-silicate glass decreased with the rise of the withdrawal speed of the substrate from the solution in Fig.2. There was a slight change at the reflectance of the thin film with the rise of the withdrawal speed in Fig. 3. Besides, the absorbance of the CIGS thin film improved at the ultraviolet range of the electromagnetic spectrum in Fig. 4.

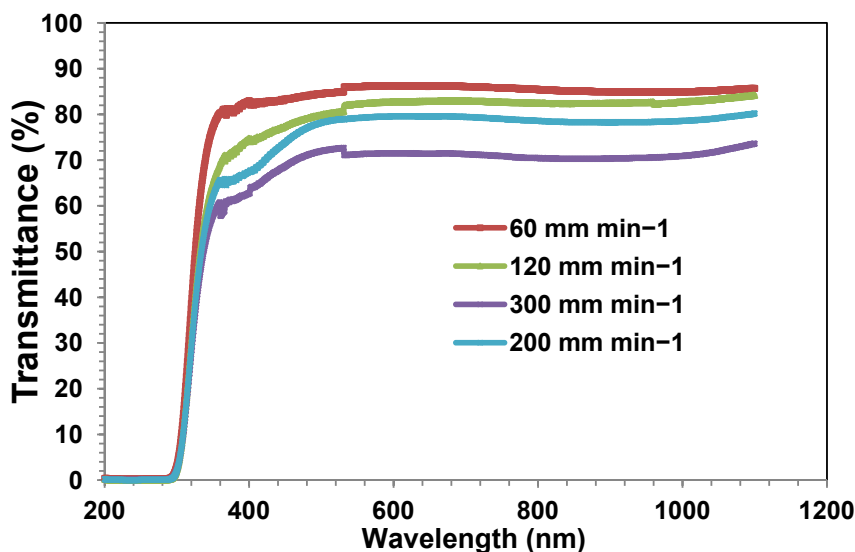


Fig.2. The changes of T % of the CIGS thin films at different withdrawal speeds.

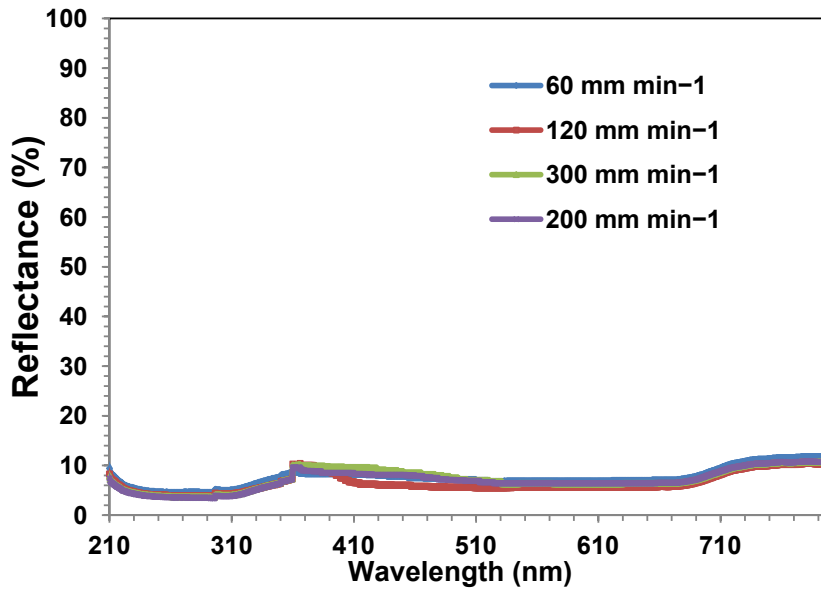


Fig.3. The changes of R% of the CIGS thin films at different withdrawal speeds.

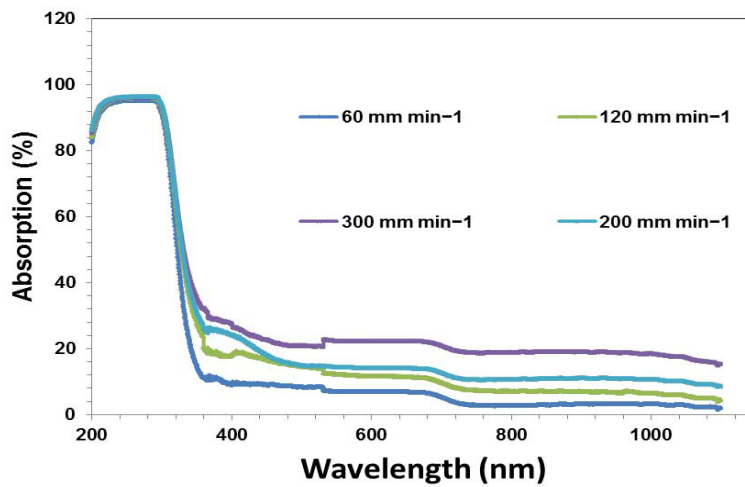


Fig.4. The changes of A% of the CIGS thin films at different withdrawal speeds.

The absorption coefficient ( $\alpha$ ) and the optical band gap ( $E_g$ ) of the CIGS thin films, can be calculated from the transmission spectrum in Eq. 1 and Eq. 2 (Green, M.A., 1982).

$$\alpha = \ln\left(\frac{I_0}{I}\right) \tag{1}$$

$$\alpha h \nu = A(h\nu - E_g)^{1/2} \tag{2}$$

where  $d$  is the thickness of the film and  $I$  is the transmitted light intensity,  $A$  is a constant,  $h\nu$  is the photon energy and  $E_g$  is the optical energy gap. The linear fit of  $(\alpha h\nu)^2$  vs.  $h\nu$  allows us to get the value of  $E_g$ . The allowed direct band gap was determined at the sol-gel derived CIGS films by sol-gel dip coating process in Fig. 5.

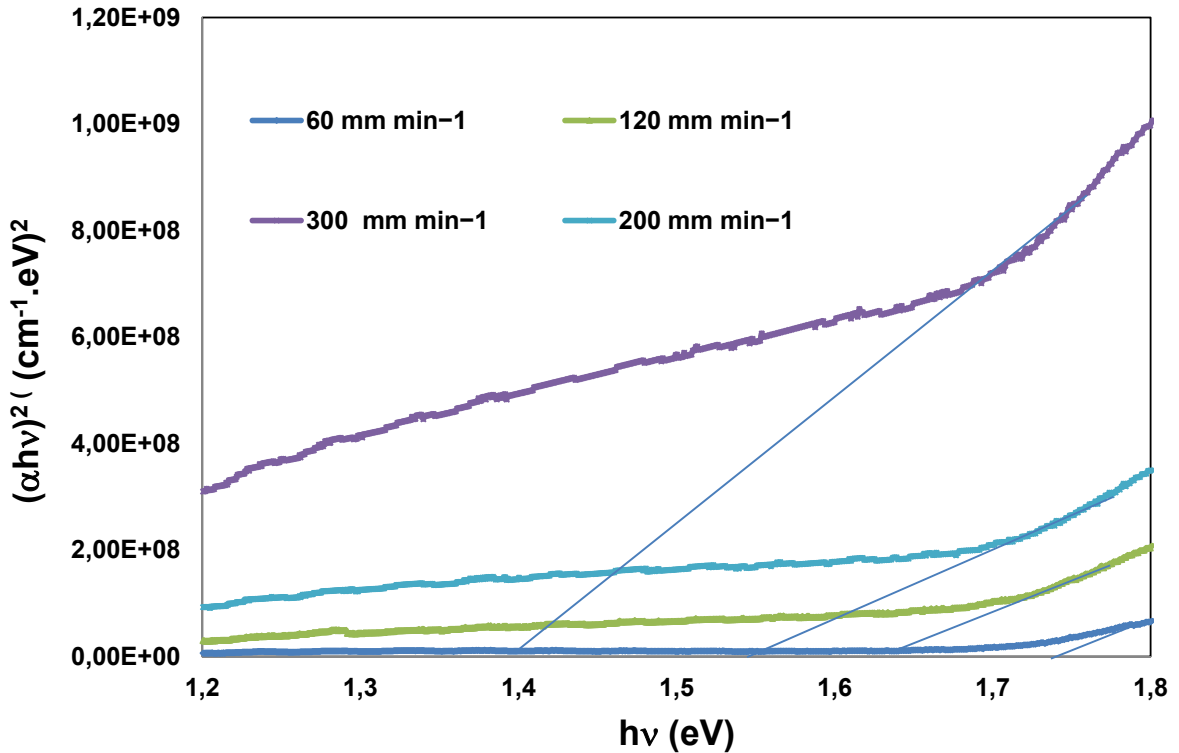


Fig.5. The changes of the optical band gap of CIGS film.

### 3. Conclusion

The optical transmittance of the CIGS thin film decreased with the increase of the withdrawal speed of the soda-lime-silicate glass substrate from the solution. There was the allowed direct band gap for all of the CIGS films produced on the substrates at different withdrawal speed. The energy band gap of the CIGS film was effected by the increase of the withdrawal speed of the glass substrate. The increase of the withdrawal speed of the substrate from the solution caused to decrease the optical band gap of the thin film depending on the improvement of the thin film thickness.

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