Türkiye Teknoloji ve Uygulamalı Bilimler Dergisi
Turkish Journal of Applied Sciences and Technology
dergipark.gov.tr/tubid

ISSN: 2528-8652
2017, 1(2): 79-85

RESEARCH ARTICLE / ARAŞTIRMA MAKALESİ

The Influence of Layer Number on Properties of Cu_2ZnSnS_4 Films

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ARTICLE INFO / MAKALE BİLGİSİ
Received / Geliş Tarihi: 03.09.2017
Accepted / Kabul Tarihi: 27.10.2017

Keywords:
Cu_2ZnSnS_4
Sol-gel
Optical Properties

ABSTRACT

In present study, Cu2ZnSnS4 thin films were deposited via single-step sol-gel spin coating process. The effect of layer number on the structural, morphological and optical properties was investigated. XRD results showed that 7 layered film had crystal structure but other films had amorphous structure. 7 layered film grown at (112) preferential orientation and it had another peak of (200). AFM analysis indicated that any particle on surface of 3, 4 and 5 layered films was not observed and the particle structure was observed for 6 and 7 layer films. The crystallite sizes for 6 layer films were very small, but 7 layer films had both small and big particles on its surface. This particle structure was not homogenous for the film surfaces. From UV-VIS studies, optical band gap of 3, 4, 5, 6 and 7 layered films were found to be 1.88 eV, 1.82 eV, 1.73 eV, 1.68 eV and 1.48 eV, respectively. This result indicates that 7 layered film is very suitable for solar cell as an absorber layer.

Cu_2ZnSnS_4 İnce Filmlerin Özelliklerine Tabaka Sayısının Etkisi

ÖZET

Bu çalışmada, Cu2ZnSnS4 ince filmler tek-adımlı sol-jel döndürerek kaplama yöntemi ile büyütülmüştür. Yapısal, yüzeysel ve optik özelliklere tabaka sayısının etkisi araştırılmıştır. XRD sonuçları 7 tabakalı filmin kristal yapıda olduğunu ve diğerlerinin amorf olduğunu göstermiştir. 7 tabakalı film (112) tercihli yönelimde büyümüştür ve film ayrıca (200) kristal yönelimine de sahiptir. AFM analizi ile 3, 4 ve 5 tabakalı filmlerin yüzeylerinde herhangi bir parçacığın oluşmadığını ve parçacık yapısının 6 ve 7 tabakalı filmler için oluştuğu gözlenmiştir. 6 tabakalı filmdeki paracıklar çok küçük olmasına karşın 7 tabakalı filmlerin yüzeyinde nano-boyutta küçük ve büyük ebatlarda parçacıklar gözlenmiştir. Bu parçacık yapısı film yüzeyleri için homojen değildir. UV-VIS çalışmalarından 3, 4, 5, 6 ve 7 tabakalı filmlerin optik bant aralıkları sırasıyla 1,88 eV, 1,82 eV, 1,73 eV, 1,68 eV ve 1.48 eV olarak bulunmuştur. Bu ise 7 tabakalı filmin güneş pillerinde soğurucu tabaka olarak kullanımı için uygun olduğunu göstermektedir.

Anahtar Kelimeler:
Cu2ZnSnS4
Sol-jel
Optik özellikler

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1. Introduction

Recently, there is an increasing interest in thin film photovoltaic materials due to energy requirements and low production costs (Chory et al., 2010). Cu_2ZnSnS_4 (CZTS) is an emerging solar light absorber (Riha et al., 2011) and it has excellent thermal, chemical, electronic, optical and mechanical properties in addition to less environmental damaging and cost effectiveness candidature (Moholkar et al., 2011). Cu_2ZnSnS_4 is one of chalcogenide-based semiconductors such as $CuInSe_2$ (CIS), $CuGaSe_2$ (CGS), $Cu(In,Ga)Se_2$ (CIGS), Cu_2ZnSnS_4 (Cu_2ZnSnS_4) and CdTe, and it has the similar to kesketerite structure of CIGS. In these materials, indium and selenium are replaced with zinc and tin metals and sulphur, respectively. Controlled substitution of S with Se practically allows band gap tuning approximately from 1.5 to 1.0 eV (Tanaka et al., 2007). Although those of CIGS, CIS, CGS and CdTe are composed of toxic (Se, Cd), expensive (In and Ga) (Tanaka et al., 2009) and rare elements (In, Ga and Te) (Shinde et al., 2012), this quaternary compound does not contain toxic elements and expensive rare metals as mentioned above (Jeon et al., 2011). Cu_2ZnSnS_4 is a kid of p-type direct band gap semiconductor with a band-gap value of between 1.4-1.5 eV (Sarswat and Free, 2011; Kumar et al., 2010) and with a large absorption coefficient in the order of 10^4 cm^{-1} which make it a suitable absorption layer for applications in thin film solar cells (Kumar et al., 2010; Yeh et al., 2009; Ito and Nakazawa, 1988; Nakayama and Ito, 1996*)***.** Many researchers have prepared Cu_2ZnSnS_4 thin films by many techniques such as chemical bath deposition (CBD) (Wangperawong et al., 2011), electroplating (with sulfurization) (Araki et al., 2009), single-step electrochemical deposition (Jeon et al., 2011; Pawar et al., 2010) and two-step electrochemical deposition (with annealing at sulfur atmosphere) (Scragg et al., 2009), co-evaporation (Tanaka et al., 2006), microwave-assisted solution method (Shin et al., 2012), pulsed laser deposition (PLD) (Moholkar et al., 2011; Sunn et al., 2011), chemical successive ionic layer adsorption, reaction (SILAR) (Shinde et al., 2012), DC magnetron sputtering (Fernandes et al., 2009), spray pyrolysis (Kamoun et al., 2007) and sol-gel spin coating techniques (Tanaka et al., 2007).The sol-gel spin coating technique is attractive due to its easy manipulation of the samples, ability to prepare high quality thin films in large scale, simplicity, safety, low cost of apparatus**,** and deposition of high purity (Tanaka et al., 2007). At the sol-gel technique, Cu_2ZnSnS_4 thin films generally have been grown in two stages, initially sol-solutions of metal salts have been deposited on substrate and then they have been annealed at sulfur atmosphere (Tanaka et al., 2007; Tanaka et al., 2009; Sarswat and Free, 2011; Maeda et al., 2011; Moritake et al., 2009). But, at a few studies, Cu_2ZnSnS_4 films directly have been synthesized from sulfur-containing sol-solutions in single-step (Yeh et al., 2009; Minlin et al., 2011; Fischereder et al., 2010; Yakuphanoglu, 2011). In present study, single-step sol-gel technique has been used to synthesize Cu_2ZnSnS_4 thin film with different layer numbers on glass substrates from sulfur-containing sol solution. We investigated also the effect of layer number on structural, morphological and optical properties of Cu_2ZnSnS_4 films.

2. Materials and Methods

In the present work, Cu_2ZnSnS_4 thin films were deposited on glass substrates by single-step spin coating sol-gel method. The experimental chart for deposition of films is given Fig.1. Sol-solutions for Cu_2ZnSnS_4 precursors were prepared from 0.2 M copper (II) acetate monohydrate [$Cu(CO_2CH_3)_2.H_2O$], 0.1 M zinc (II) acetate dehydrate $Zn(CH_3COO)_2.2H_2O$], 0.1M tin (II) chloride dihydrate [$SnCl_2.2H_2O$] and 0.8 M thiourea [$SC(NH_2)_2$]. The thiourea concentration chosen (0.8 M) is more than the stoichiometric requirement (0.4 M) because of compensation for the loss of sulfur during sol-gel drying and annealing (Kumar et al., 2010). 2-methoxyethanol [$C_3H_8O_2$, 2-MTE] and monoethanolamine [C_2H_7NO, MEA] were used as solvent and stabilizer, respectively. The molar ratios of metal ions to MEA were maintained at 1:1. The sol solutions were stirred at 50 ^oC for 24 h to obtain a clear and homogenous solution. The glass substrates were cleaned with acetone and methanol and distilled water by using an ultrasonic cleaner, rinsed in de-ionized (DI) water and dried by nitrogen gas flow. In the spin coating process, the resultant solution was dropped on glass substrate, which was rotated at a speed of 3000 rpm for 25 sec by using a spin-coater. The as-coated film was sintered at 200 ^oC for 5 min to evaporate solvent and remove the organic sediments and then spontaneously cooled to the room temperature. This procedure was repeated for 3, 4, 5, 6 and 7 times. Finally, they were annealed in air at 250 ^oC for 30 minutes.

The crystalline properties were investigated by using a Rigaku Miniflex II x-ray diffractometer (XRD). The diffractometer reflections were investigated at room temperature and the values of 2θ were altered between 15^o and 80^o. The incident wavelength was 1.5418 Å. The surface characters of films were examined with atomic force microscope (AFM fabricated by Nanomagnetics-Instrument). AFM images were obtained in tapping mode, in 512x512 resolutions and with 1 μm/s of scanning speed. The optical absorbance of the thin films were recorded in spectral region of 300-1000 nm at 300 K using a UV-VIS spectrophotometer (Perkin-Elmer, Lambda 40) which works in the range of 200-1100 nm and has a wavelength accuracy of better than ±0.3 nm.

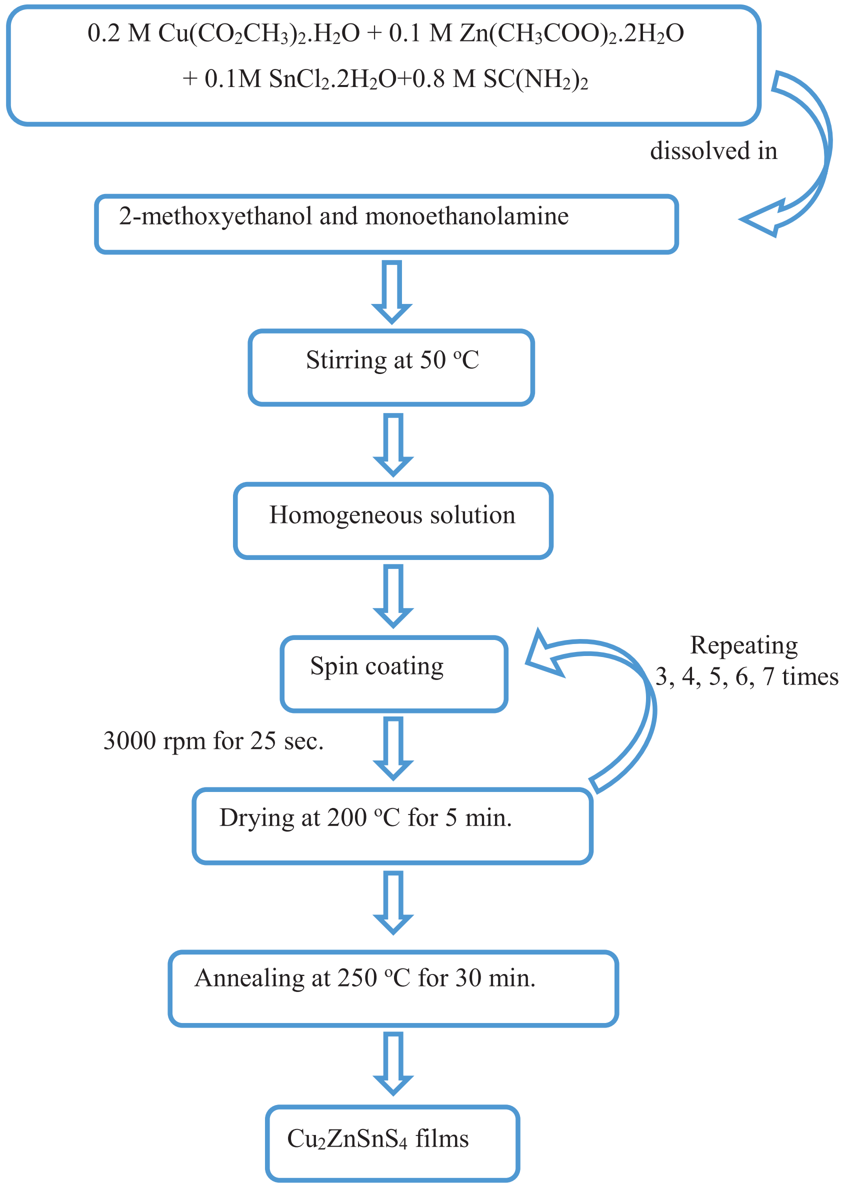

Figure 1. Experimental chart for deposition of Cu_2ZnSnS_4 films

3. Results and Discussions

The structural properties of films were investigated by X-ray diffraction (XRD). The XRD graph of the Cu_2ZnSnS_4 films has been shown in Fig.2. As can be seen from this figure, 3, 4, 5 and 6 layered films are nearly amorphous but 7 layered film has polycrystalline structure and the planes of (112) and (200) have been observed and these peaks are characteristic for the 'kesterite' tetragonal structure of Cu_2ZnSnS_4 (JCPDS card no:26-0575). The peak of (112) is preferential orientation and this was also observed in earlier studies (Tanaka et al., 2007; Sarswat and Free, 2011).

The surface morphology of Cu_2ZnSnS_4 thin film grown on glass substrates was investigated by atomic force microscopy (AFM). The AFM images of films were shown in Fig. 3. As can be seen from Fig. 3a-b-c, any particle on the surfaces of 3, 4 and 5 layered films is not seen, which indicates that a film was not completely formed. This result is also observed by XRD as amorphous structure. There are some particles on the film surface of 4 and 5 layered films and these particles can be Cu_2ZnSnS_4 grains. When the number of layer is 6, a lot of small nano-sized particles appear on the film's surface but these particles are not enough for crystallinity. As increasing the number of layer up to 7 (in Fig. 3e), there are small and big nano-sized particles on film surface, the sizes of particles change between about 50-500 nm and their distribution is not homogenous on the surface. As can be seen from fig. 3e and 3f, the shape of nano-particles resembles to triangular structure. The surface roughness of 3, 4, 5, 6 layered films was not determined but the surface roughness of 7 layered film was determined as 5.26 nm.

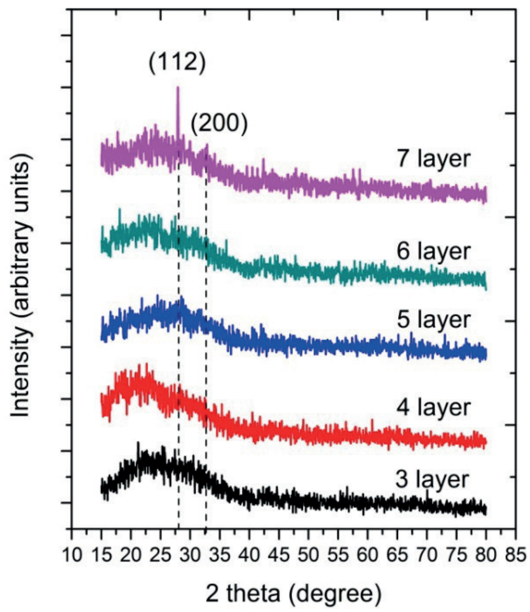

Figure 2. The XRD patterns of the films

The optical properties of the films at different layers number were investigated by UV-Vis spectrophotometer. Fig. 4a shows absorption spectra of films and the absorption of 3 layered film is continuously increasing with an increase in layer number. The absorption (absorbance, A) of an optical medium is given with $A = 0.434\alpha l$. α is absorption coefficient and l is the length of absorbing medium. In the present study, the film thickness which refers to l, increases with increasing layer number and absorption increases.

The optical band gap of Cu_2ZnSnS_4 thin film was obtained by the following relation

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

Where hν and A are photon energy and the constant, respectively. Fig. 4b shows a plot of $(\alpha h\nu)^2$ *versus photon* energy (hν) for Cu_2ZnSnS_4 thin film. Eg values are determined by plotting $(\alpha h\nu)^2$ vs. hν and extrapolating of the linear region of the plot to zero absorption ($(\alpha h\nu)^2 = 0$).

As seen in Fig. 4b, the band gap values of 3, 4, 5, 6 and 7 layered Cu_2ZnSnS_4 thin films were found to be 1.88 eV, 1.82 eV, 1.73 eV, 1.68 eV and 1.48 eV, respectively. The band gap values of films decrease with increasing layer number and it is close to the optimum value needed for solar energy conversion, which this suggests that the grown Cu_2ZnSnS_4 thin film is quite suitable for photovoltaic applications for 7 layer. The band gap value of 1.48 eV is almost in agreement with the previously reported values (Yeh et al., 2009; Kamoun et al., 2007; Maeda et al., 2011)

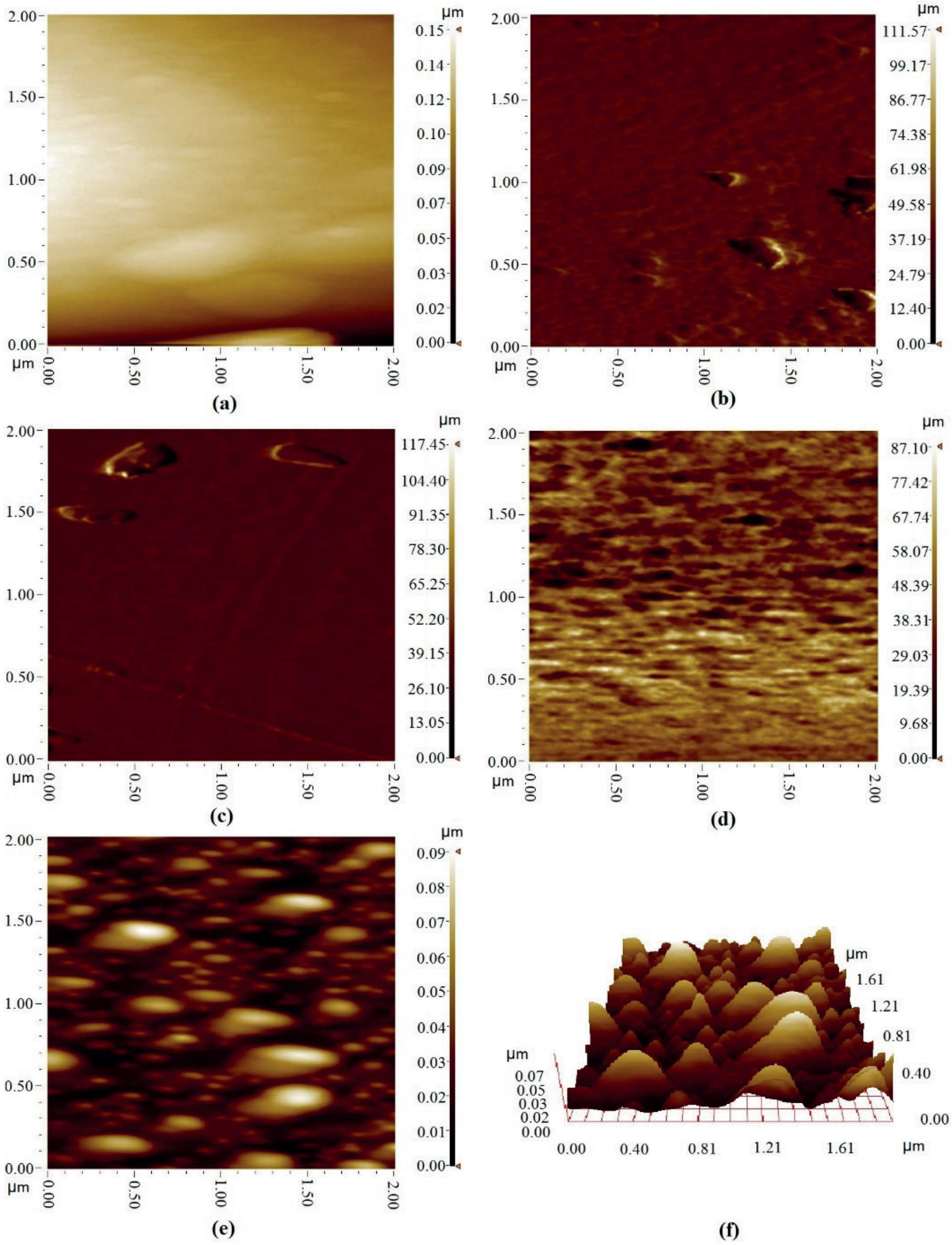

Figure 3. The AFM images of films; (a) 2D image of 3 layered-film, (b) 2D image of 4 layered-film, (c) 2D image of 5 layered-film, (d) 2D image of 6 layered-film, (e) 2D image of 7 layered-film, (f) 3D image of 7 layered-film

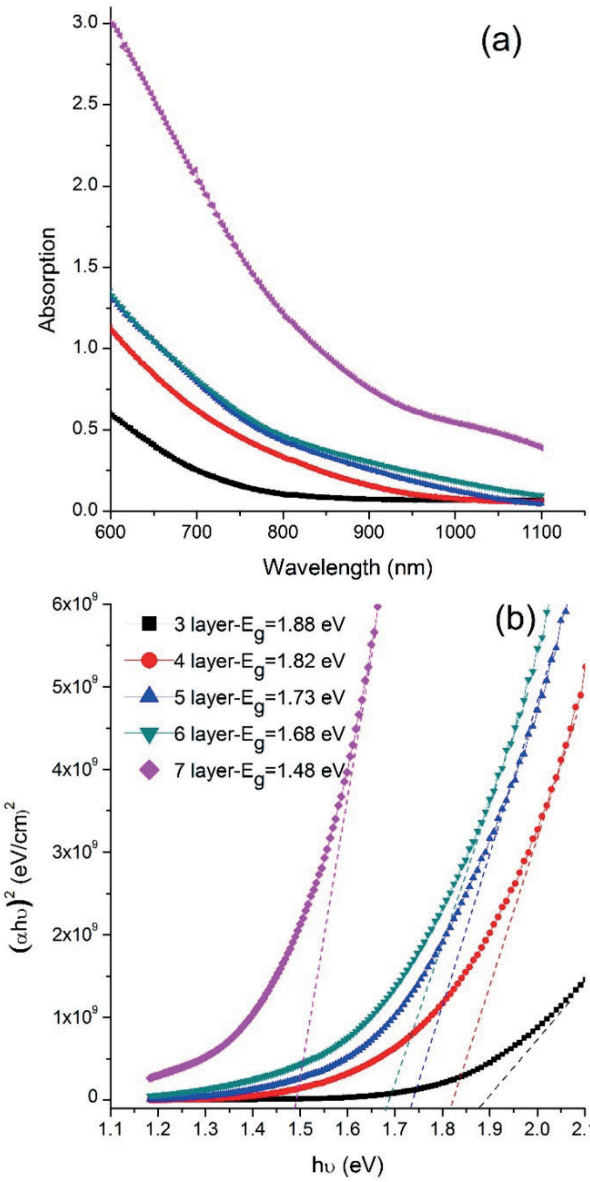

Figure 4. (a) The absorption graphs of films, (b) Eg value plots of films

4. Conclusions

This work reports a single-step deposition of Cu_2ZnSnS_4 thin films with sol-gel spin coating process. The influence of layer number on the crystalline, morphological and optical features of Cu_2ZnSnS_4 films was examined by XRD, AFM and UV-VIS spectrophotometer. The crystal structure was only observed for 7 layered-film with (112) preferential orientation. The nano-particles were determined on the surfaces of 6 and 7 layered films and these particles had non-homogenous distribution. The optical band gap of 3, 4, 5, 6 and 7 layered films were determined to be 1.88 eV, 1.82 eV, 1.73 eV, 1.68 eV and 1.48 eV, respectively. The results obtained from present work suggest 7 layered-film can be used in solar cells as an absorber layer.

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