Barishal University Journal Part 1, 5(1&2): 15-26 (2018) ISSN 2411-247X

SYNTHESIS AND OPTICAL CHARACTERIZATION OF CZTS THIN FILMS FOR ABSORBER LAYER VIA SPIN COATING TECHNIQUE

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Abstract

The goal of the research was to make an excellent absorber layer for CZTS thin film. The CZTS solution was deposited onto glass substrate through spin coating technique with different rotation per min (rpm) and then the thickness was studied to determine the optimum condition of the thin films. Two sets of sample were prepared with different rpm 4500 and 5000 by a spin coater. The thickness of the CZTS thin films were measured by surface profilometer and all samples shows good rpm dependence thickness where the thickness decreases with increasing rpm. The optical properties of the films were studied with the help of Ultraviolet-Visible (UV-Vis) Spectroscopy. The optical band gap and Urbach energy were estimated from the measured absorbance data. The optical band gap as well as the Urbach energy increased with increasing rpm. The average optical band gap was found to be around 1.7 eV. Between two types of samples, CZTS sample of 4500 rpm shows good optical properties in comparison to another.

Keywords: Spin Coater, UV-Vis Spectroscopy, Surface Profilometer, Scanning Electron Microscopy.

Introduction

Cu_2ZnSnS_4 (CZTS) is a prominent low cost absorber layer to be used as a substitute of CIGS absorber layer in the thin film solar cells. CZTS thin films can lead to production of nontoxic thin film solar cells with high absorption coefficient. It is one of the most promising absorber layer materials for low-cost thin film solar cells due to its semiconducting properties such as p-type conductivity as well as the earth abundant and nontoxic constituent elements (Swami et al., 2013, Katagiri et al., 1997 and Atagiri et al., 2001). The low-energy consuming fabrication process is as impsortant factor is to be

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considered as the materials and their availability. The non-vacuum processes such as sol–gel spin coating (Maeda et al., 2011), chemical bath deposition (CBD) (Wangperawong et al., 2011) and electrochemical deposition (ED) (Scragg et al.,2010and Ennaoui et al., 2009), ink screen printing (Akhavan et al., 2012 and Woo et al., 2012), chemical spray pyrolysis (CSP) (Patel et al., 2013 and Shiyani et al., 2015) successive ionic layer absorption and reaction (SILAR) (Kim et al., 2016) have attracted much concentration in the context of thin-film deposition owing to their low manufacturing cost, simplicity and versatility.

CZTS thin film has a large absorption coefficient in the order of 10^4 cm^{-1} and has a direct band gap of around 1.5 eV, close to the optimal band gap for single-junction solar cells (Scragg, 2011). Katagiri et al., reported a promising conversion which has its efficiency of 6.77% in 2008 CZTS TFSC which was fabricated by co-sputtering technique using three targets of Cu, SnS, and ZnS followed by annealing in H_2S (Katagiri et al., 2008). IBM then improved the efficiency to 6.81% using a co evaporation process in 2010 (Katagiri et al., 2008). (Tanaka et al., 2009 and Katagiri et al., 2008) reported fabrication of CZTS TFSC via non-vacuum method. They used CZTS films prepared over 'Mo' coated glass substrates by sulfurizing precursors deposited by sol-gel technique as the absorber layer (Katagiri et al., 2008). The problem with sulfurizing spin coating precursors was that there was a lack of sulfur in the absorber layer even though sulfurization was carried out at a high concentration of hydro sulfur (Maeda et al., 2011).

In this research work, the CZTS thin films were deposited on soda lime glass substrate by the spin coating method, which is followed by sulfurization (Chung et al., 2013). The CZTS sol gel was prepared by using 2-methoxiethanol and MEA as solvent. The aim of this study is to see the change in optical properties of CZTS thin films with different rotation. The films were investigated by studying their optical properties and thus reveal the feasibility to fabricate a CZTS PV device by an inexpensive sol-gel process.

2. Experimental Details

2.1 Sample Preparation

In this experiment, soda lime glass (SLG) was used as substrates. The adhesion of thin film depends on the nature of the glass substrate. The glass on which the solution was deposited was cleaned by Ultrasonic Cleaner, after scrubbing by brush with the mixture of methanol and DI water. In ultrasonic bath the glass was cleaned by the following procedures: i) 10 minute with methanol, ii) 10 minute with acetone, iii) Again 10 minutes with methanol and finally, iv)15 minutes with de-ionized (DI) water. After weighting the sample by weight machine all the sample was taken into a beaker and dissolved it into its solvent. Then the resulted solution was stirred by magnetic stirrer (78-1 MAGNETIC STIRRER HOTPLATE, Made in CHINA) at 700° C for 30 minute. The solution was deposited on glass substrate after placing the glass substrate on spin coater (SPIN 150, made in GERMANY). The spin coating procedure was performed at a certain rpm. After depositing the sample on glass substrate at different rpm the sample was dried in electric oven (ED53, Made in GERMANY) for 30 minutes at 300°C for ensuring the presence of only metal without solvent. For sulfurization, the CZTS thin films were placed into a sealed test tube. To ensure the presence of sulfur, small amount of sulfur (S) was placed in close proximity of CZTS thin film. The sample was annealed into the furnace (KLS 10/12, Made in GERMANY) at 580°C for 1 hour. The whole processes were repeated twice with the variation of two different rpm, such as 4500 and 5000.

2.2 Characterization Technique

The surface profilometer has been used to measure the thickness of annealed CZTS thin films. The ultraviolet visible (UV-Vis) spectra of the as prepared thin films were recorded using a duel beam UV-Vis spectrophotometer (Shimadzu, UV-1601V, Japan) at room temperature in the transmittance as well as absorbance mode in the wavelength range (250–850) nm. A blank glass slide was used in this experiment as reference. The microstructure as well as surface morphology was observed using a scanning electron microscope (JEOL JSM-7600F).

3. Results and Discussions

3.1 Thickness Investigation

Table 1 represents the thicknesses of the CZTS thin films which were measured by using surface profilometer. Fig .1 represents the variation of film thicknesses of CZTS thin films with different rpm. It is found that the thickness of thin films decreases with the increasing of rpm.

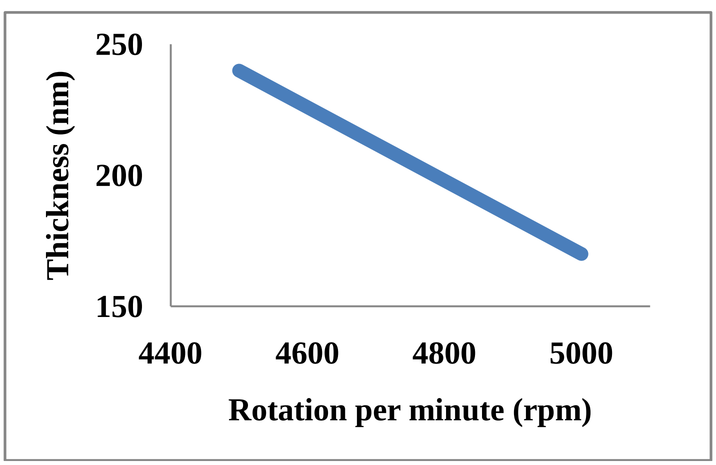

Fig. 1. Variation of thickness with rotation.

3.2 Optical analysis of CZTS thin films

3.2.1 Spectral distribution of the absorbance and transmittance

Fig. 2. shows the Absorbance versus wavelength (300 nm-800 nm) for two sets of CZTS thin films at different rotation (4500 rpm and 5000 rpm). From Fig. 2, it is seen that the maximum absorbance in the visible region (390-700) nm of the spectrum is 1.9 for 4500 rpm (240 nm) and 1.6 for 5000 rpm (170 nm) respectively. It is also seen that the absorbance decreases in the visible region with increase in wavelength for all cases. The maximum absorbance in the infrared (700 nm-1 mm) region of the spectrum is 1.2 and 0.95 for CZTS samples of 4500 rpm (240 nm) and 5000 rpm (170 nm) respectively. In this region the absorbance also decreases with rise in wavelength for all the samples. Comparing among these two samples it is seen that the absorbance for samples of 4500 rpm is higher than the other sample in the visible and infrared regions. Hence, it is concluded that CZTS thin film deposited 4500 rpm (240 nm) is good absorber layer. Since CZTS thin film is used as an absorber layer in thin film solar cell, so high absorption is required (Ito et al., 1988) and in this respect 4500 rpm spin coated CZTS thin film is much suitable for solar cell applications.

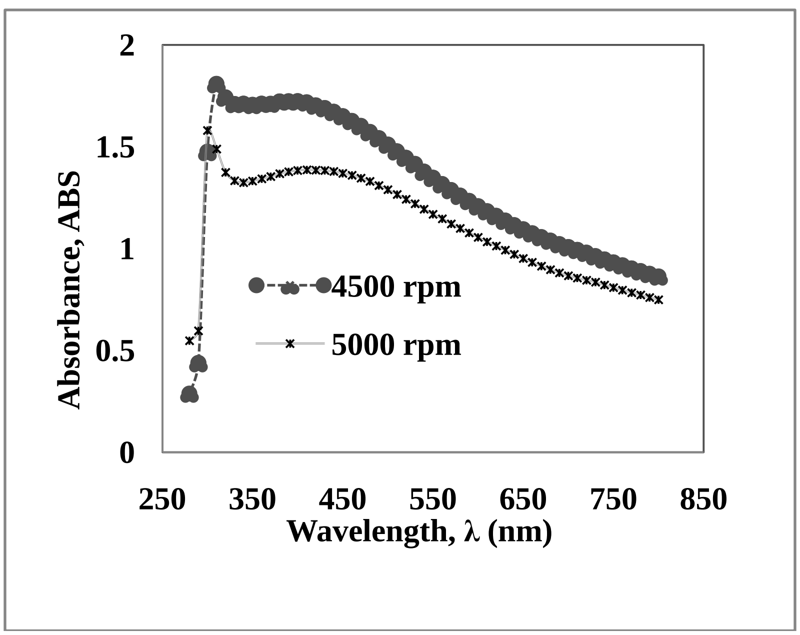

Fig. 2. Absorbance plot.

Fig. 3. shows the variation of transmittance with wavelength λ (nm) in the wavelength range (300-1100) nm for two CZTS thin film samples prepared at different rotation (4500

rpm and 5000 rpm). The minimum transmittances within the visible region of the spectrum (390-700 nm) were 3% and 8% for CZTS with 4500 rpm, 5000 rpm respectively. It is seen that the transmittance decreases with decreasing in light wavelength for all samples. In the Infrared region of the spectrum (700 nm-1 mm) CZTS for 4500 rpm shows 31% and 5000 rpm shows 33% maximum transmittances respectively. It is observed that the transmittance also decreases with decrease in wavelength in this region. From Fig. 3, it is noticed that the transmittance is lower for samples of 4500 rpm than the other sample in both visible and infrared region. Researchers have shown that low transmittance is desired (Ito et al., 1988) for CZTS thin films for absorber layer. Therefore, CZTS thin film deposited at 4500 rpm (240 nm) may be a good absorber layer for the lower transmittance in both visible and infrared region.

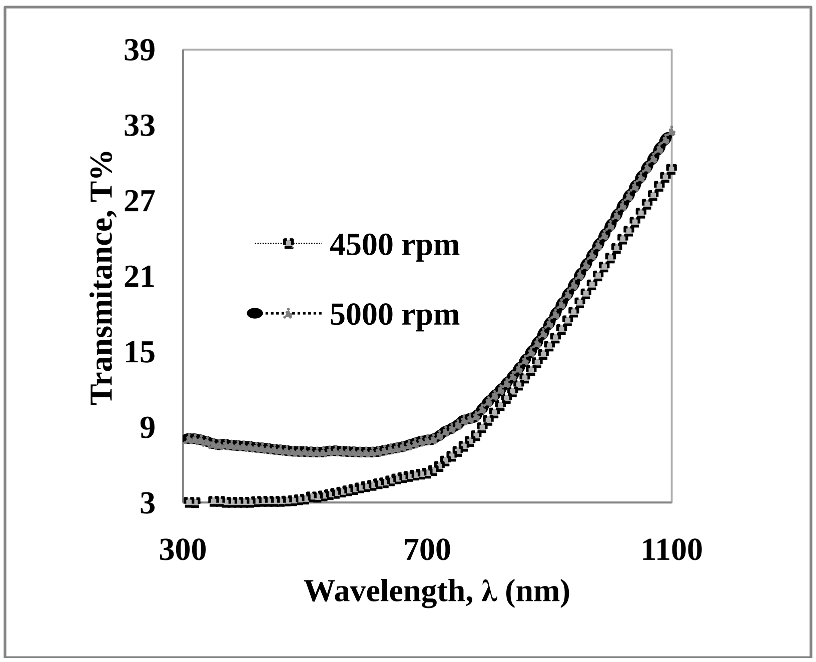

Fig. 3. Transmittance plot.

3.2.2 Optical band gaps and band edge sharpness determination

The absorption co-efficient α was determined from the absorbance data using the Lambert relation (Smith and Warren, 1966)

$$2.303A = \alpha d \quad (1)$$

So, $\alpha = 2.303\,(A/d)$

Where A is the absorption, and d is the thickness of the sample.

The plot of α as a function of photon energy hν for the CZTS thin films is shown in Fig. 4.

Fig. 4. presents the dependency of absorption coefficient on photon energy. It is seen that the absorption coefficient increases with increasing of photon energy in case of samples deposited at 4500 rpm and 5000 rpm.

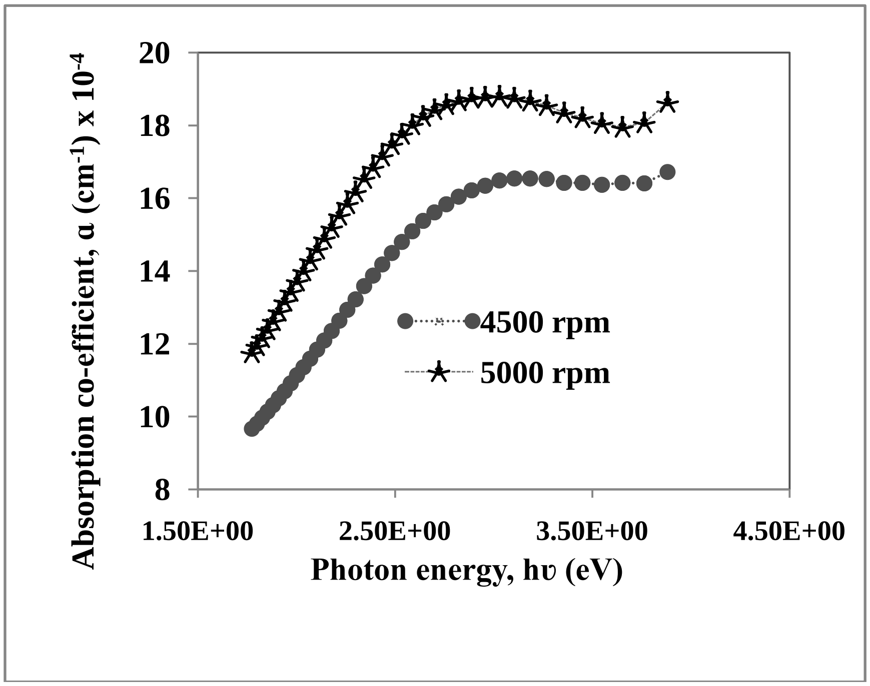

Fig. 4. Absorption co-efficient plot.

The optical transition involved in the thin films can be determined on the basis of the dependence of α on *hν* by using the Tauc relation (Tauc, 1912).

$$\alpha h\upsilon = B(h\upsilon - E_g)^n \qquad (2)$$

Where E_g is the optical energy gap between the bottom of the conduction band and the top of the valance band, the value of B is a constant and n is an index which can assume value of 0.5 for indirect transition and 2 for direct transition. Extrapolating the linear portion of the curve to $(\alpha h\nu)^2 = 0$ in the photon energy axis gives the values of band gap energy. In Fig. 5 $(\alpha h\nu)^2$ as a function of hν is plotted to obtain the E_g of the as deposited CZTS thin films. The E_g is determined from the intercept of the linear part of the curves extrapolated to zero α in the energy axis. The values of the E_g for as deposited CZTS thin films are tabulated in Table 1. It is found the band gap increases with increasing thickness of the film while that of with decrease in rpm.

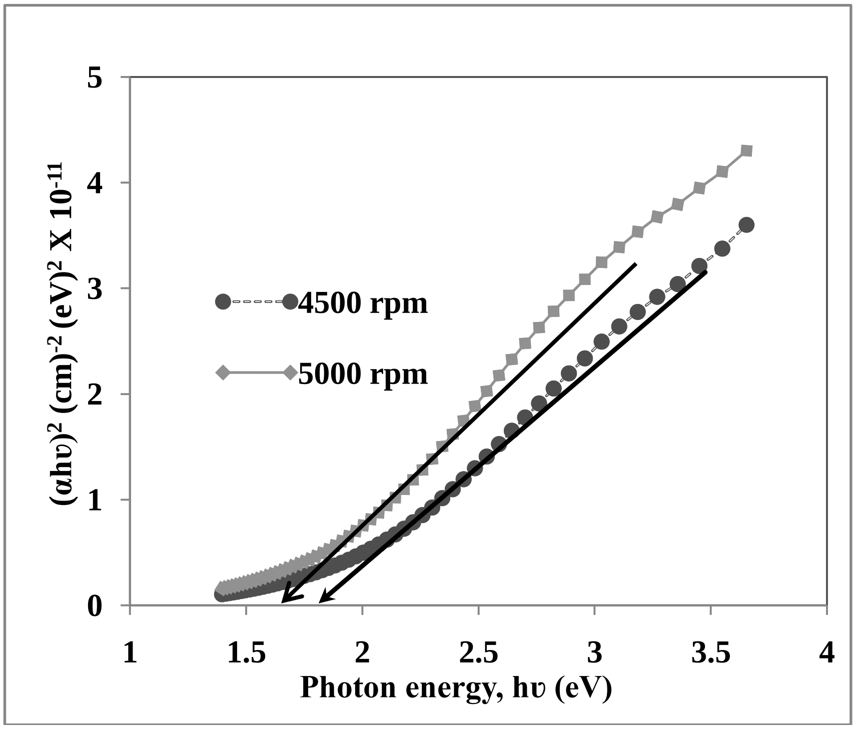

Fig. 5. Band gap energy plot.

Table 1. Band gap values for different CZTS samples.

Film thickness (nm)	Rotation per min min minute (rpm)	Band gap (eV)
240 nm	4500	1.8
170 nm	5000	1.6

It is observed that the film thickness of two different CZTS thin films decreases with increasing of rotation per minute (rpm) (from 4500 rpm to 5000 rpm). It is also found from Table 1 that the two types of CZTS thin films have band gap around 1.6 to 1.8 eV for different rpms. Here significant rpm (rotation per minute) dependence band gap is observed. 4500 rpm (240 nm) has yielded desired band gap of two different types of CZTS thin films as absorber layer for solar cell application. It has shown better thickness or rpm dependence. When a photon impinges on the surface of a PV device, there are three possible results. The photon may be absorbed by the material, reflected back into the atmosphere, or transmitted through the cell. If the photon is reflected or transmitted, a loss mechanism has occurred and the photon will not generate power. If the photon is successfully absorbed into the material, it may excite an electron from the valence band of the material to the conduction band and for photovoltaic operation electron-hole pair generation is required by the excitation of electron from the valence band to the conduction band (Mahr, 1962).

The energy of the photon relative to that of the band gap will determine the fate of the photon as it interacts with the material. If the energy of the photon is less than that of the band gap, the photon will not excite an electron into the conduction band. If the energy of the photon is exactly that of the material's band gap, the photon will excite an electron into the conduction band; if the photon has energy larger than that of the band gap, the photon will excite an electron, and the excess energy is wasted as thermal energy (Mahr, 1962).

The spectral dependence of α was studied at photon energies less than the energy gap of the films, i.e. in the region of the so called Urbach spectral tail, which characterizes the slope of the exponential edge and is expressed as (Urbach, 1953)

$$\alpha = \alpha_0 \exp(E/E_U) \tag{3}$$

Where, α_0 is a constant and E_U the Urbach energy. Thus, the plots of $\ln\alpha$ vs $h\nu$ should be linear whose slope gives Urbach energy (E_U), interpreted as the width of the tails of localized states in the band gap. An increase in the optical band gap of the amorphous thin films can be explained due to the decrease of the band tails in the gap. The $\ln\alpha$ vs $h\nu$ plots for the thin films at different rpm are shown in Fig. 6 and the corresponding values of E_U are also listed in Table 2.

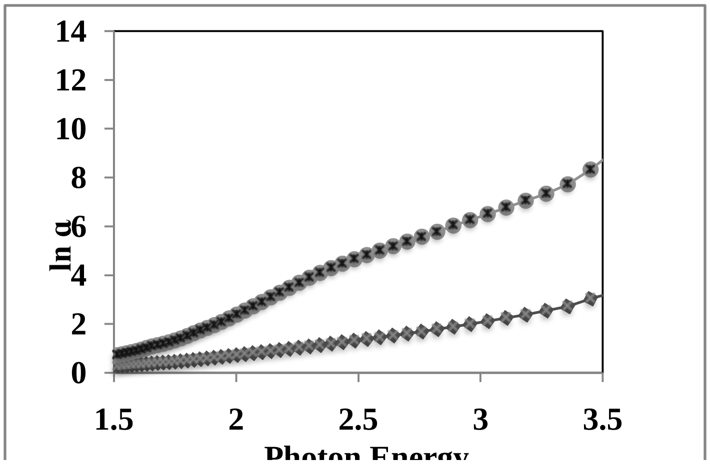

Fig. 6. Urbach plot.

Table 2. Variation of Urbach energy with thickness (rptation per min)

Thickness (nm)	Urbach energy (eV)	Thickness (nm)
240	3.6	240
170	2.08	170

3.3 Morphological analysis of CZTS thin films

The SEM micrographs displaying the surface morphology of CZTS thin films are shown in Fig.7. and 8., for the different rotations in this study.

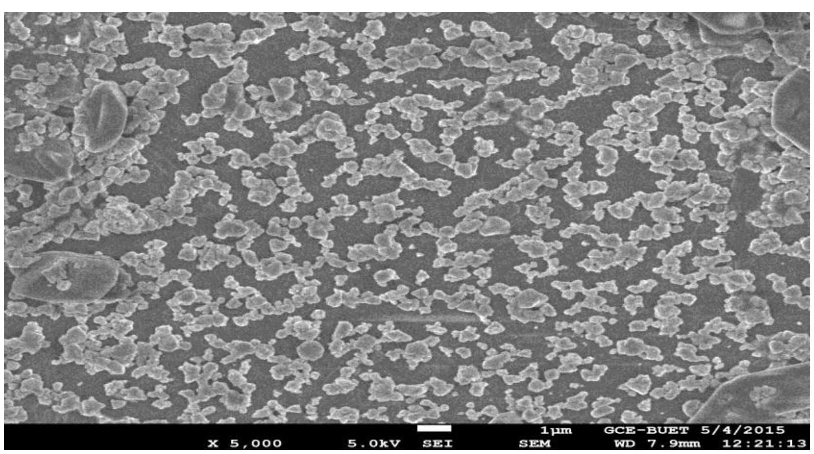

Fig. 7. SEM image for CZTS sample 4500 rpm.

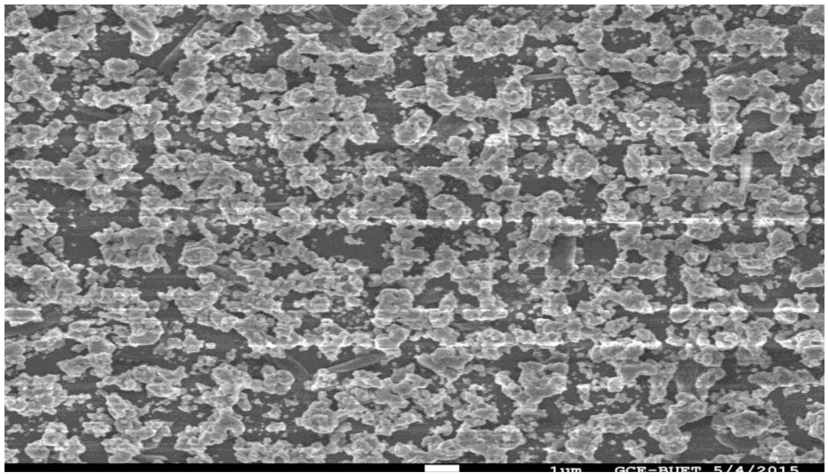

Fig. 8. SEM images of CZTS sample 5000 rpm.

Fig. 7. and Fig. 8. show the surface morphology of CZTS films using different rpm (rotation per min). The surface was not uniform with some granular agglomerates that were almost homogeneous in size throughout the thin film. It is seen that as the rotation or thickness changes some change in the type of granules. Fig.7. may shows particle type granules may be due to low rotation whereas Fig.8. for high rotation flowery type granules may be observed.

Conclusion

The CZTS thin films were deposited onto glass substrate successfully via spin coating technique at different rotation per min. The optical properties of the films were studied with the help of Ultraviolet-Visible (Uv-Vis) Spectroscopy. From this study we found that the better performance was found for the sample at 4500 rpm for its high absorbance and low transmittance. The optical band gap was found to be 1.8 eV for this film. The SEM image shows the non-uniform distribution of some granular agglomerates that was almost homogeneous in size throughout the thin film.

Acknowledgements

The author acknowledges Jahangirnagar University for giving the opportunity of research. Institute of Fuel research & Development (IFRD) centre, BCSIR, Dhaka for sample preparation, Pilot Plant and Process Development Center (PP and PDC), BCSIR, Dhaka for UV-Vis spectroscopy, Glass and Ceramic Engineering, Bangladesh University of Engineering and Technology (BUET), Dhaka for SEM and Institute of Electronics, Bangladesh Atomic Energy Commission, Dhaka for thickness measurement.

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