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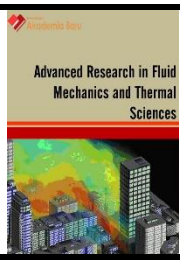

Investigation of Sulfurization Time Duration Process Effects on Thermally Evaporated CZTS Absorber Layer for Photovoltaic Application

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ABSTRACT

In this study, Cu_2ZnSnS_4 (CZTS) thin films were deposited onto Mo coated soda lime glass (SLG) substrates using thermal evaporation deposition method. Stoichiometric CZTS powder (99.95%) is used as the source material. All the deposited samples were then sulfurized at different time from 10 minutes to 50 minutes at 580°C. The characteristics of the sulphurized films were investigated. Overall, the result showed a potential CZTS's existence although several secondary phases also being detected.

1. Introduction

At present, world vitality energy utilization is exceedingly relying upon the non-sustainable power source, which are essentially petroleum derivatives like coal, oil, gaseous petrol and atomic vitality. Very nearly 70% of the vitality being devoured by created nations is relying upon these sustainable power sources. The fundamental disservice for non-sustainable power source is that the volume of sources is diminishing throughout the century because of an expansion in the human populace. For instance, the oil saves on the planet are at present draining and it is assessed would be exhausted in an additional 50 years' time frame. The route for more renewable energy produce to meet the continuous growing world's energy demand has prompted the scientific community to focus their research activities on renewable energy field for example on the possible materials and structure

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suitable for photon energy's capture. Among the candidates of the solar cells, thin film solar cells especially inexpensive, abundant and nontoxic material copper-zinc-tin-sulphide (CZTS) based solar cell is a promising type of solar which can be realized as high efficiency and low cost solution for electricity generation. It has been years now since Cu_2ZnSnS_4 (CZTS) was introduced in the field of solar photovoltaic cell and the popularity is still growing. CZTS has direct-band gap, high absorption coefficient, p-type conductivity. Moreover, it is abundant, non-toxic and inexpensive, which promotes it as a promising candidate for absorber layer in thin film solar cell [1]. There were many ways to growth an CZTS absorber layer for photovoltaic application such as co-evaporation [2,3], RF sputtering [4], RF sputtering and vapor phase sulfurization [5], hybrid sputtering [6], reactive sputtering [7], electro plating and sulfurization [8,9], nanoparticles [10,11], and spray pyrolysis [12,13]. Among all, thermal based vacuum method was reported to be one of the applicable methods [14]. This longest standing tradition of depositing technique basically involved three basic important steps which were heating of source and then change to vapour based on thermodynamics theory, transportation of the vapour from the source boat to the substrate according to kinetic theory of gases and condensation of the vapour on the substrate by condensation phenomena. Even without sulfurization process, whereas only post deposition annealing process at 300°C for 40 min, Shi *et al.,* had obtained 0.36% efficiency of photovoltaic (PV) device deposited in high vacuum thermal evaporation chamber using synthesized CuS, ZnS and SnS powder precursors prepared by hydrothermal method [15]. Furthermore, sulfurization process can improve the crystallization of deposited CZTS films by looking at its crystallite size and density number of the preferred orientation and also to eliminate the secondary phases that were highly anticipated to occur when dealing with quaternary compound like CZTS [16, 17]. As reported by Amal *et al.,* binary secondary phases start to initiate between 250 and 350°C of sulfurization temperature followed by the intermediate ternary compound. Then CZTS began to appear at 400°C and finally all the secondary phases will disappear gradually between 500°C and 550°C. To date, the highest efficiency of 8.4% was reported for CZTS solar cells by thermal evaporation in a vacuum system equipped with Knudsen-type source of elemental Cu, Zn, Sn, and S and post-deposition annealing procedure done at 570°C [18]. By going through only annealing process of CZTS samples, a good structural quality films can be obtained together with suitable optical and electrical properties [15]. Furthermore, by extending the process to sulfurization can improve the performance of the films. The crystallization of sulfurized CZTS films was reported to be in the best state at sulfurization temperature ranging from 500 to 550°C where the secondary phases will disappear slowly [17]. In this work, we present the result for the effect of sulfurization time duration process on CZTS deposited films.

2. Methodology

Growth of the compound was in the sequential deposition of CZTS by thermal evaporation method followed by sulfurization process. Soda lime glass with dimension of 75 mm long, 25 mm width and 2mm thick were used as substrates and it was cleaned using ultrasonic bath using methanol and acetone for 10 minutes followed by methanol again and finally deionized water for 15 minutes. For the deposition of back contact, sputtering target of 99.95% of Mo was used. The pressure in the sputtering chamber was set at 5 x 10-3 Pa as base pressure and 1.7 Pa as working pressure. The sputtering power was set at 100 Watt and the sputtering time was 1 hour at room temperature with 2 sccm flowing of purified Ar (99.99%) as the working gas. As for the deposition of CZTS absorber layer, it is illustrated in Figure 1. Using a powder stoichiometric CZTS source and with the use of tungsten boat as the heating element, the deposition was done by applying current gradually increased until the source were fully evaporated. Distance between boat and substrate

holder was set to 5 cm. The chamber of vacuum thermal evaporator was set to background pressure of 5x10-1 Pa and the source powder of CZTS was evaporated using tungsten boat by applying current gradually increased until 45 A. This deposition process took place for about 20 minutes per cycle. The as-deposited precursors were then send for sulfurization process. The set-up of this sulfurization heat treatment process is shown in Figure 2. The deposited samples were put inside a wrapped crucible with the presence of sulfur chunk and placed in quartz tube furnace. The sulfurization process was done under a dynamic nitrogen gas, N_2 flowing at rate 80 sccm. The temperature inside the chamber was observed by a thermocouple for accurate reading and ramped up at 25°C/min until the desired maximum sulfurization temperature was attained. At this temperature, which was 580°C, the program was to hold the temperature for 10 minutes for the sulfurization process took place. This process was repeated for 4 others holding time namely 20, 30, 40 and 50 minutes respectively. These profiles are shown in Figure 3.

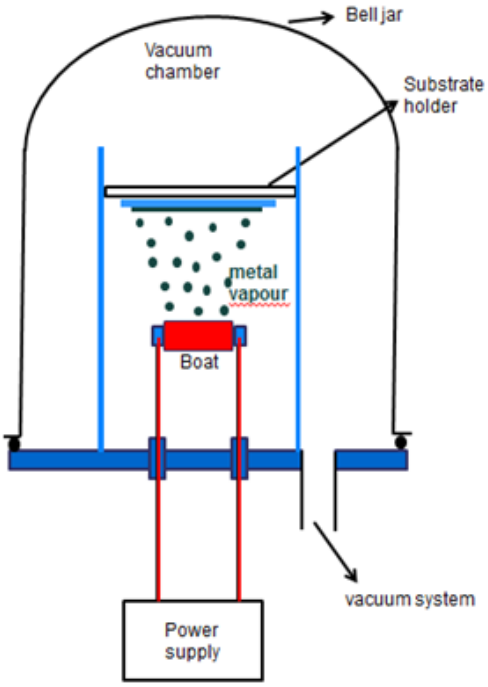


Fig. 1. Thermal Evaporation's deposition diagram

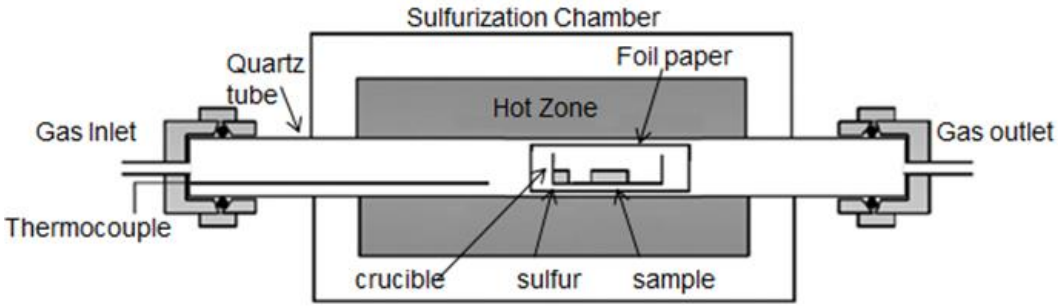


Fig. 2. Sulfurization chamber

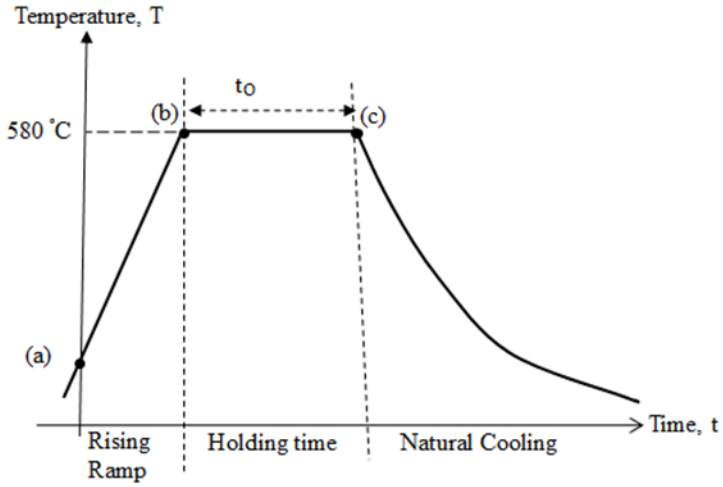


Fig. 3. Sulfurization profiles used for the CZTS growth

Point (a) is the initial temperature inside the furnace and point (b) is the desired sulfurization temperature. The time taken from (b) to (c) was set to various time, t_O, which were 10 to 50 minutes for the crystallization of CZTS took place. At the end of the process point (c), the furnace was let off for natural cooling with closed chamber approximately 6 hours' time. The characterization of the thin films were examined by X-ray diffraction (BRUKER aXS-D8 Advance) using Cu-Kα radiation wavelength, λ= 1.5408 Å with diffraction angles (2θ) ranging from 20O to 80O and 0.02O step size. As well as high resolution Raman spectroscopy equipped with Ar laser with an excitation wavelength of 325 and 514 nm. The morphology of the film was observed by scanning electron microscopy (SEM, Hitachi S3400-N, and Japan) with an operating voltage of 15 kV. The optical properties of the films were measured by UV-Vis beam spectrophotometry at room temperature and for carrier concentration by Hall Effect measurement systems, HMS ECOPIA 3000 with magnetic field of 0.57 T and probe current of 10 mA for all samples.

3. Result and Discussion

Characterization of the as deposited CZTS absorber layer was made. XRD and Raman Spectroscopy were used for structural analysis and phase identification. Figure 4 shows result of XRD and we can see that the films have a dominant peak with orientation (112) at 28.48O which corresponds to CZTS according to JCPDS card No. 01-075-4122. The second peak of CZTS occur at 47.57O and some secondary phases start developing started with SnS at 56.37O. It is anticipated that secondary phases such as ZnS and SnS to formed at less deposition time before CZTS formation at longer one. The cross section of the sample got from SEM (Figure 5) showed that the thickness of CZTS film deposited at 20 min (Figure 5(a)) and 40 min (Figure 5(b)) were in rising trend from 2.78 µm to 5.24 µm thick. Meanwhile, Figure 6 shows result of XRD of all the sulfurized film and can be conclude that same with as deposited film, it also have a dominant peak with orientation (112) at 28.48O but with more intensity.

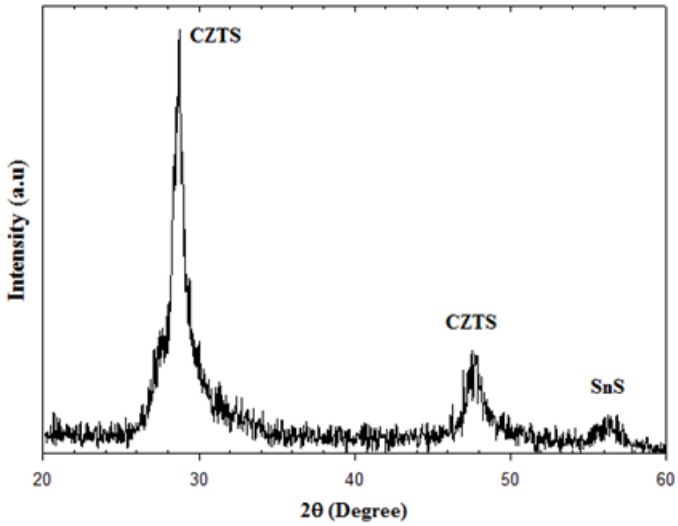
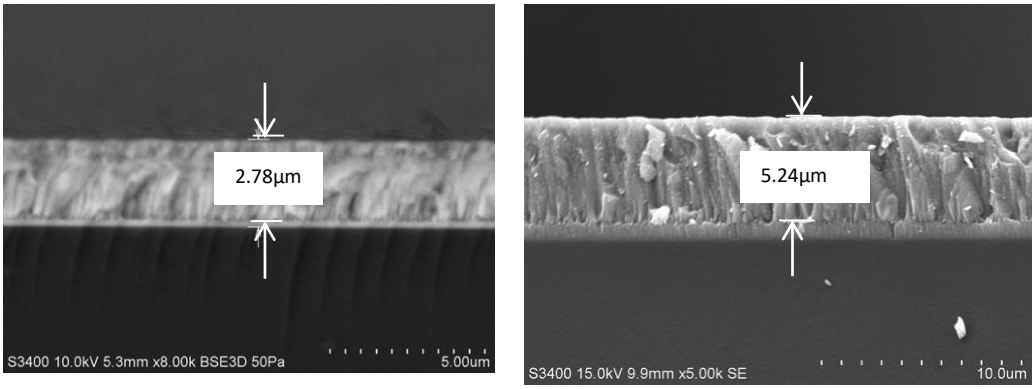


Fig. 4. X-ray diffraction patterns for as deposited CZTS (45A, 20min)



(a) (b)

Fig. 5. SEM images of the as deposited CZTS layer: (a) 20 minutes and (b) 40 minutes

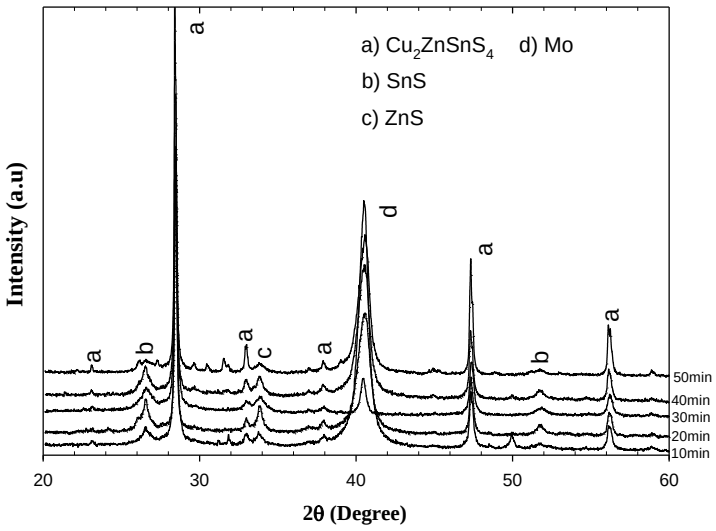


Fig. 6. X-ray diffraction patterns of the sulfurized films

The intensity of the peak was increasing with sulfurization time. Furthermore, it also revealed that Mo peak existed at all the films at 40.59O (JCPDS card No. 03-065-7442). As for secondary

phases, binary compound of SnS occur 2θ equal to 26.5O and 51.93O (JCPDS card No. 01-075-8260) and also ZnS at 33.9O (JCPDS card No. 01-073-6005). And the intensity of those respective secondary phases was decreasing with the increasing of sulfurization time. Characterization via Raman spectroscopy with laser power 514nm gives a Raman spectrum of Figure 7. It showed intensive peak observed on all the sulfurized films, the Raman peak was centered at 338 cm-1 that come from CZTS [5]. It was observed that most centered film was sulfurized at 30 min and all others were shifted slightly to the left of it. It explain that, samples sulfurized at 10, 20, 40 and 50 min were experiencing strain compared to the 30 min. Also width of the peak for all the sulfurized samples were almost the same showed that crystallization were not much different form one another. The surface morphology of the sulfurized CZTS thin film was observed by SEM as Figure 8. The surface of the film sulfurized for 10 minutes (Figure 8(a)) showed a smooth with small piece particle on top of it. Meanwhile for film sulfurized after 50 minutes, the grain become bigger showed that the crystallinity of the compound has improved with the elevated sulfurization time.

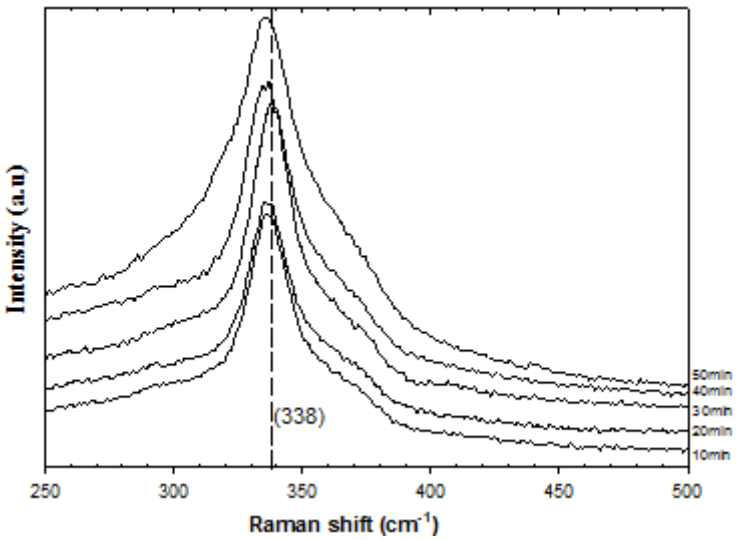


Fig. 7. Raman spectroscopy of the sulfurized films

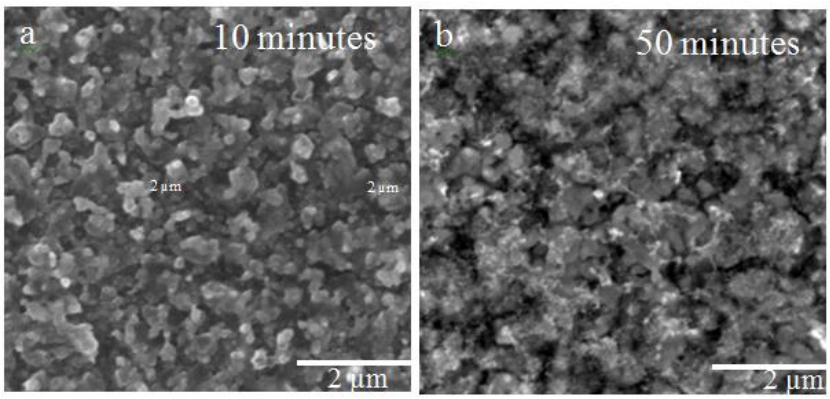


Fig. 8. SEM images of the sulfurized films at: (a) 10 minutes and (b) 50 minutes

For optical properties of the sulfurized film, observed from the transmission data conclude that the range of bandgap was between 1.440 eV to the maximum value of 1.573 eV as in Figure 9. From the Atomic Force Microscope (AFM), Figure 10 showed the image of the CZTS layer in 1 micrometre scale. It can be observed that the roughness changed over time.

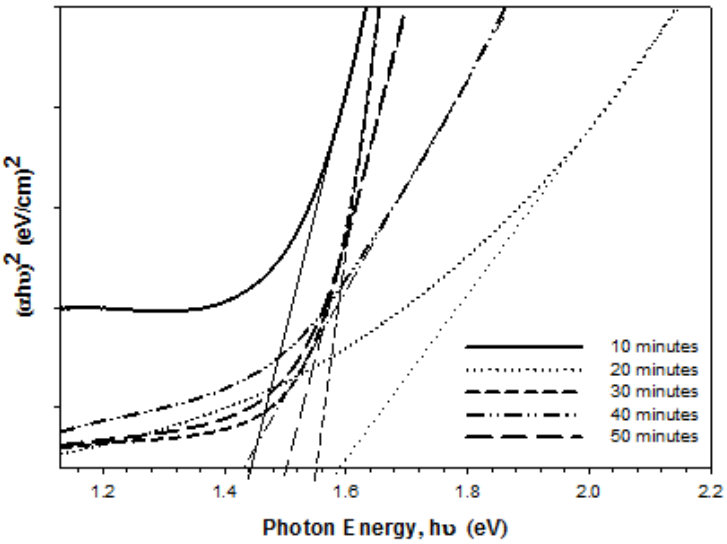


Fig. 9. Result of UV-Visible optical absorption measurement for the sulfurized films

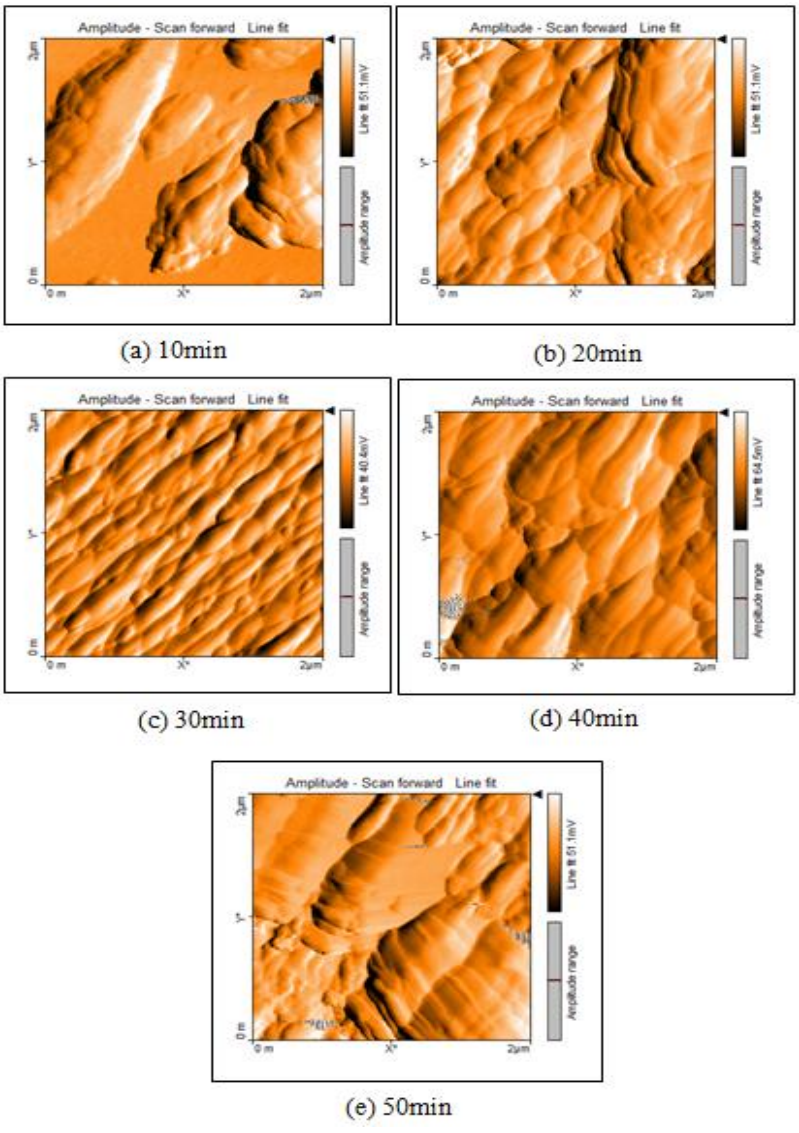


Fig. 10. AFM result for the sulfurized films

The root mean square (RMS) roughness for the sulfurized film were rising with more time heat provided to the samples but slightly shown a downward trend for 40 and 50 minutes as tabulate in Table 1.

Table 1
AFM surface roughness

Sulfurization time (min)	Surface roughness (nm), Sq
10	14.037
20	59.772
30	69.781
40	43.593
50	41.161

4. Conclusions

In this research, the main focus started with depositing Cu_2ZnSnS_4 single source compound powder through thermal evaporation onto SLG coated Mo. Furthermore, the as deposited Cu2ZnSnS4 films was growned then by sulfurization process with the effect of sulfurization time from 10 to 50 minutes were investigated. As the result, XRD peak indicated that secondary phases occur on all the films especially binary compound of ZnS and SnS. The less secondary phases occur at 30 minutes and it is being confirm by Raman spectra that an intense CZTS peak occur at 338 cm-1. For SEM it showed that the morphology become rougher and the bigger grain with time. It is similar to the RMS surface roughness observed by AFM. In term of thickness, it is anticipated that with more time, the thickness increased where it rise from 2.78µm for 20 min sample to 5.24µm for 40 min. Last but not least, UV-visible spectroscopy revealed the CZTS film to have band gap with maximum value of 1.573 eV.

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