SYNTHESIS AND CHARACTERIZATION OF COPPER ZINC SULPHIDE ($CuZnS_2$) THIN FILMS

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Abstract

The Copper Zinc Sulphide ($CuZnS_2$) films were fabricated with and without complexing agents (EDTA and TEA) by chemical bath deposition method. Incorporation of complexing agents provided the higher optical absorption, lower band gap energy, and smoother surface of $CuZnS_2$ thin films. In addition, varying the concentration of precursor solution (0.5 – 1.5 M) and dipping time (24 – 72 hrs) the optical property and surface topography of thin films were investigated. The concentration (0.5 M) and dipping time (48 hrs) provided the lower band gap energy of 2.0 eV and RMS surface roughness of 0.93 μm which are key requirements for light absorber layer in solar cells.

Keywords: $CuZnS_2$, chemical bath deposition method, complexing agents, band gap energy

Introduction

A solar cell or photovoltaic cell (previously termed "solar battery"), is an electrical device that converts the energy of light directly into electricity by the photovoltaic effect, which is a physical and chemical phenomenon. It is a form of photoelectric cell, defined as a device whose electrical characteristics, such as current, voltage, or resistance, vary when exposed to light. Solar cells are the building blocks of photovoltaic modules, otherwise known as solar panels. Solar cells are described as being photovoltaic, irrespective of whether the source is sunlight or an artificial light. They are used as a photo detector (for example infrared detectors), detecting light or other electromagnetic radiation near the visible range, or measuring light intensity. The operation of a photovoltaic (PV) cell requires three basic attributes: (1). the absorption of light, generating either electron-hole pairs or exactions. (2) the separation of charge carriers of opposite types. (3) the separate extraction of those carriers to an external circuit.

The thin films technology has attracted much attention because of its unique size dependent properties and applications in the optoelectronic

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devices, solar cell, sensors and laser materials. The preparation of copper zinc sulphide ($CuZnS_2$) thin film by chemical bath deposition technique is currently attracting a great deal of attention as the technique is relatively simple and cost effective, has minimum material wastage, does not need sophisticated instrument and vacuum and can be applied in large area deposition at low temperature. The chemical bath deposition method uses a controlled chemical reaction to deposit a thin film. In typical experimental approach, the substrates are immersed in solution containing the chalcogenide source, metal ion and complexing. Copper Zinc Sulphide ($CuZnS_2$) thin film has absorb highly in the UV and near infrared wavelength. $CuZnS_2$ thin film can only allow visible radiation to be transmitted through the glazing system into the building if these films are used in coating the glazing. $CuZnS_2$ thin films can be called solar transmitting films (STF) such as films can also be used to anti-reflect solar radiation falling on and passing through solar collector glazing onto absorber plates in photo-thermal solar energy devices. The application of $CuZnS_2$ thin film are good materials for glazing system, poultry buildings, anti-reflection coatings, eyeglasses and solar cells fabrication[1].

Experiment

In the elementary state of my work, cleaning process totally play a vital role which includes four steps from washing with detergent and ending at cleaning stage with Isopropanol Alcohol (IPA). Firstly, we cleaned the glass substrates with ultrasonic cleaner in distilled water. Subsequently, it was being washed with acetone and IPA in order to ensure the cleaning purpose that can affect to my research. In making solution setup, 5 ml of Zinc chloride ($ZnCl_2$) and 5 ml of Copper chloride ($CuCl_2$) were measured, transferred into the beaker. The mixture was stirred for 10 minutes after which 10 ml Thiourea $(NH_2)_2CS$ was added and stirred to have a homogeneous mixture. Addition of Thiourea formed a jelly – like solution, 5 ml of EDTA (Na_4 ($C_{10}H_{16}N_2O_8$)), 3 ml of TEA ($C_6H_{15}NO_3$) and 3 ml of Ammonia (NH_3) solution were added to the mixture. The solution was stirred for 15 minutes followed by addition of 20 ml of distilled water. The final solution was stirred to have a homogeneous mixture. The varying bath parameter is the deposition time. At 6 hours, the film had no deposit. They were allowed to stand for 12 hours after which deposition was noticed on the film. The remaining films were allowed to stand for 24 hours, 48 hours, 72 hours, The substrates were removed at the end of each time, dried in air at room temperature. They were then annealed at 672 K for 1 hour to obtain adherent copper zinc sulphide ($CuZnS_2$) transparent thin films.

Results and Discussions

The absorption spectrum of the Copper Zinc Sulphide ($CuZnS_2$) films were plotted Absorbance against wavelengths is presented in figure 1. The values are 0.39 at 300 nm for $CuZnS_2$ (with complexing agent) and 0.15 at 370 nm for $CuZnS_2$ (without complexing agent). The absorbance of copper zinc sulphide ($CuZnS_2$) thin film with complexing agents is higher than without complexing agents. This higher absorption may be due to the formation of more $CuZnS_2$ with better adhesion to the substrates under this condition.

The absorbance of the specimens plotted against wavelengths are presented in figure 2 It is observed that the spectral absorbance of the specimens vary with wavelength in similar manner, increasing rapidly from a value of about 0.20 at 280 nm to various maximum values of 0.4 at 355 nm for $CuZnS_2$ (0.5 M), 0.39 at 300 nm for $CuZnS_2$ (1.0 M) and 0.29 at 325 nm for $CuZnS_2$ (1.5 M) and then decreased to a minimum values of 0.27 at 550 nm for $CuZnS_2$ (0.5 M), 0.12 at 400 nm for $CuZnS_2$ (1.0 M) and 0.26 at 460 nm for $CuZnS_2$ (1.5 M). So, we can conclude that 0.5 M concentration of $CuZnS_2$ films gives the highest absorbance.

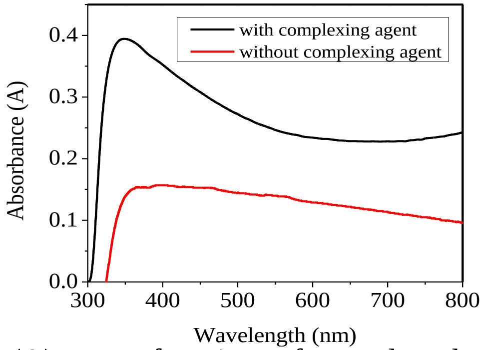


Figure 1: Absorbance (A) as a function of wavelength for Copper Zinc Sulphide ($CuZnS_2$) thin film

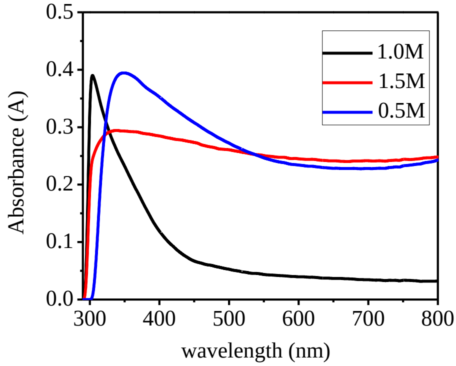


Figure 2: Absorbance (A) as a function of wavelength (nm) for Copper Zinc Sulphide ($CuZnS_2$) thin film for different concentrations

The changes of absorption of Copper Zinc Sulphide ($CuZnS_2$) film on different dip time are wondered. So, the absorption spectrum of the Copper Zinc Sulphide ($CuZnS_2$) films were plotted Absorbance against wavelengths is presented in figure 3. As shown in figure 3, we observed that 48 hours dip time $CuZnS_2$ film possessed the highest absorption peak while the 72 hours dip time $CuZnS_2$ film gave the lowest absorption peak. The absorption peak of 24 hours dip time $CuZnS_2$ film obtained the middle trend.

The graph of $(Ah\upsilon)^2$ against $h\upsilon$ are shown in figure 4. The band gap energy can be determined by extrapolation of $(Ah\upsilon)^2$ against $h\upsilon$. The band gap energy value of Coppr Zinc Sulphide ($CuZnS_2$) thin film for without complexing agent is 2.1 eV. As a result, we observed that the copper zinc sulphide ($CuZnS_2$) film without complexing agents provided the lower band gap energy than the copper zinc sulphide ($CuZnS_2$) films.

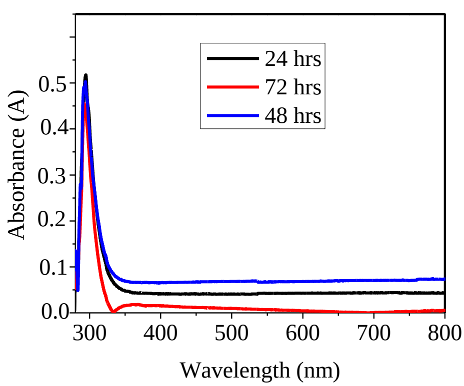


Figure 3: Absorbance (A) as a function of wavelength for Copper Zinc Sulphide ($CuZnS_2$) thin film for different dip time

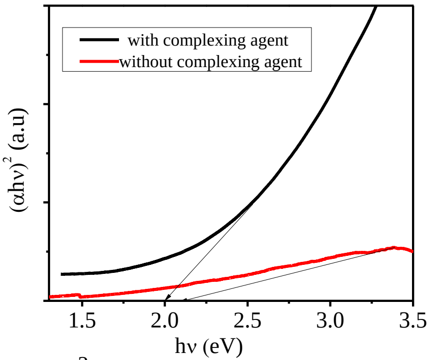


Figure 4: Plot of $(Ah\upsilon)^2$ vs hυ for Copper Zinc Sulphide ($CuZnS_2$) thin film

The graph of $(Ah\upsilon)^2$ against hυ are shown in figure 5. The band gap energy can be determined by extrapolation of $(Ah\upsilon)^2$ against hυ. $CuZnS_2$ (0.5 M) increasing from a value is 1.7 eV to various maximum values 2 eV, $CuZnS_2$ (1.0 M) increasing from value is 2.5 eV to 2.7 eV and $CuZnS_2$ (1.5 M) increasing from value is 1.5 eV to 2.4 eV. The direct band gaps were extrapolated from the graph at $\alpha^2 = 0$, and the values obtained are 2eV for $CuZnS_2$ (0.5 M), 2.7eV for $CuZnS_2$ (1.0 M) and 2.1eV for $CuZnS_2$ (1.5 M).

The graph of $(Ah\upsilon)^2$ against hυ are shown in Figure 6. The band gap energy can be determined by extrapolation of $(Ah\upsilon)^2$ against hυ. $CuZnS_2$ (24 hrs) increasing from a value is 2.4 eV to various maximum values 2.7 eV, $CuZnS_2$ (48 hrs) increasing from a value is 1.8 eV to various maximum values 2 eV and $CuZnS_2$ (72 hrs) increasing from a value is 1.7 eV to various maximum values 2.3 eV. The direct band gaps were extrapolated from the graph at $\alpha^2 = 0$, and the values obtained are 2.7 eV for $CuZnS_2$ (24 hrs), 2 eV for $CuZnS_2$ (48 hrs), and 2.3 eV for $CuZnS_2$ (72 hrs).

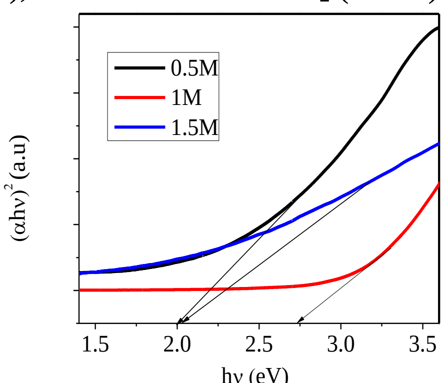


Figure 5: Plot of $(Ah\upsilon)^2$ vs hυ for Copper Zinc Sulphide ($CuZnS_2$) thin film

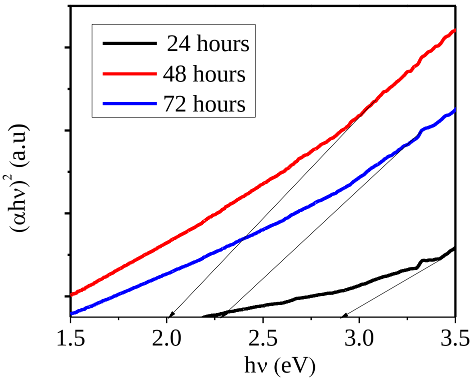


Figure 6: Plot of $(Ah\upsilon)^2$ vs hυ for Copper Zinc Sulphide ($CuZnS_2$) thin film

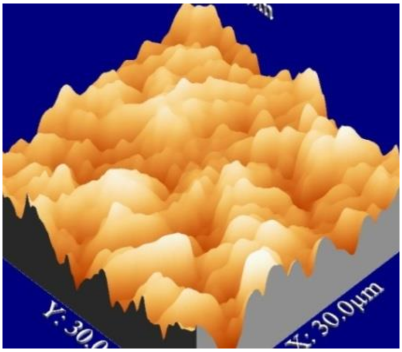
Table 1: Band gap energies the copper zinc sulphide ($CuZnS_2$) thin films

No	Type	Band Gap Energy (eV)	Reference Band Gap Energy (eV)
1	Without Complexing agents	2.1	2.0 - 2.7
	With complexing agents	2.0	
2	0.5 M	2.0	
	1.0 M	2.7	
	1.5 M	2.1	
3	24 hrs dip time	2.7	
	48 hrs dip time	2.0	
	72 hrs dip time	2.3	

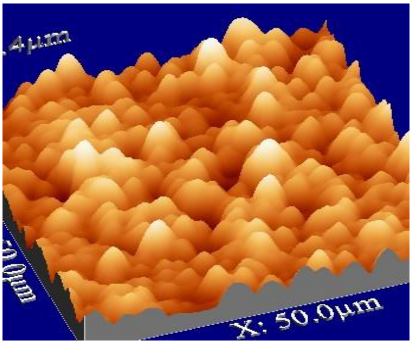
The topography of $CuZnS_2$ film was studied by using Atomic Force Microscope (AFM). The AFM images of the $CuZnS_2$ thin films grown on glass substrate are presented in Figure 7. Average roughness is the arithmetic average of the absolute values of the profile height deviations, within the sampling length. Root mean square average of the profile height deviations within the sampling length. The root mean square roughness value of $CuZnS_2$ thin films are 0.1714 μm for without complexing agent and 0.1321μm for with complexing agent.

The topography of $CuZnS_2$ film was studied by using Atomic Force Microscope (AFM). The AFM images of the $CuZnS_2$ thin films grown on glass substrate are presented in Figure 8. Average roughness is the arithmetic average of the absolute values of the profile height deviations, within the sampling length. Root mean square average of the profile height deviations within the sampling length. The root mean square roughness value of $CuZnS_2$ thin films are 0.1321 μm for (0.5 M), 0.2043 μm for (1.0 M) and 0.1691 μm for (1.5 M). The roughness value of $CuZnS_2$ film was measured over the scanning areas (50.0 μm × 50.0 μm). The root mean square roughness value of $CuZnS_2$ thin film is 0.2043 μm.

The topography of $CuZnS_2$ film was studied by using Atomic Force Microscope (AFM). The AFM images of the $CuZnS_2$ thin films grown on glass substrate are presented in Figure9. Average roughness is the arithmetic average of the absolute values of the profile height deviations, within the sampling length. Root mean square average of the profile height deviations within the sampling length. The root mean square roughness value of $CuZnS_2$ thin film are 173.70 nm for 24 hrs, 93.25nm for 48 hrs and 80.30 nm for 72 hrs. The average roughness value of $CuZnS_2$ thin film are 135.0 nm for 24 hrs, 71.5 nm for 48 hrs and 55.9 nm for 72 hrs. The roughness value of $CuZnS_2$ film was measured over the scanning areas (30.0 μm × 30.0 μm). The root mean square roughness value of $CuZnS_2$ thin film is 80.30 nm.

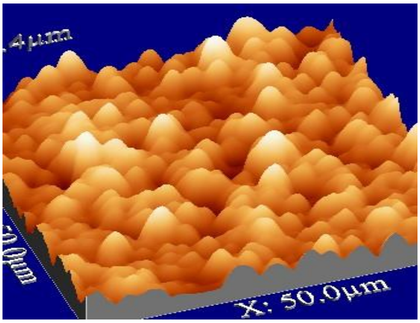


(a)



(b)

Figure 7: Atomic force microscopy images of Copper Zinc Sulphide ($CuZnS_2$) thin film (a) without complexing agent (b) with complexing agent



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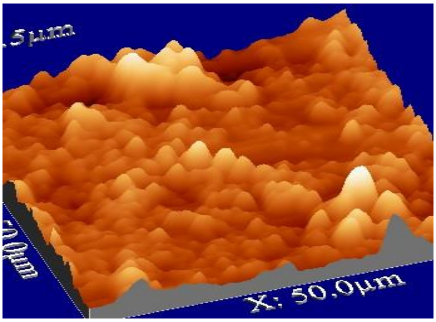

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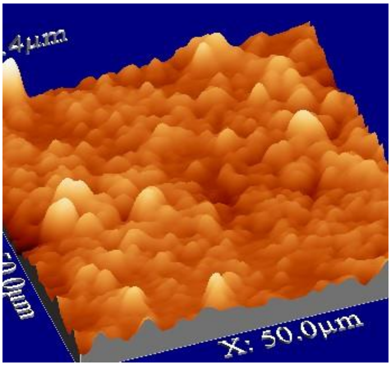
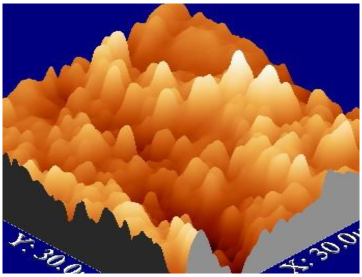


(c)

Figure 8: Atomic force microscopy images of Copper Zinc Sulphide ($CuZnS_2$) thin film for different concentration (a) 0.5 M (b) 1.0 M (c) 1.5 M



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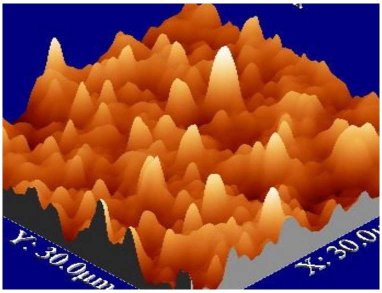

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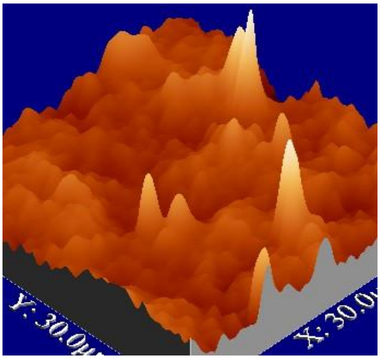

(c)

Figure 9: Atomic force microscopic images of Copper Zinc Sulphide ($CuZnS_2$) thin film for different deposition time (a) 24 hrs (b) 48 hrs (c) 72 hrs

Conclusion

The Copper Zinc Sulphide ($CuZnS_2$) films were fabricated with and without complexing agents (EDTA and TEA) by chemical bath deposition method. The $CuZnS_2$ film with complexing agents provided the higher optical absorption and band gap energy than that film of without complexing agents. Therefore, different concentration (0.5 M, 1.0 M, and 1.5 M) and different dip time (24 hrs, 48 hrs, and 72 hrs) were studied with complexing agents. 0.5 M $CuZnS_2$ film and 48 hrs dip time $CuZnS_2$ films gave the highest absorption and lowest band gap energies and smoother surface in each other concentration and dip times. The root mean square (RMS) roughness of $CuZnS_2$ films for different concentrations increased with increasing concentration while the root mean square (RMS) roughness of those films decreased with increasing the deposition time. The concentration (0.5M) and dipping time (48hrs) provided the lower band gap energy of 2.0eV and RMS surface roughness of 0.93μm which are key requirements for light absorber layer in solar cells.

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