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Potentiostat Electro-Deposited Cuprous Oxide and Cupric Oxide Thin Films for Photovoltaic Use

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ABSTRACT

To withstand the rising demand for energy while fuel and chemical energy are becoming rare, the development in the production of solar energy has become a necessity. There is a variety of solar cells; among them, thin-film photovoltaics is more popular because of low-cost production and good-efficiency. Nowadays, copper oxide has become popular to make thin film layers like CZTS, CIGS, etc. Unfortunately, the efficiency of these thin films is less than 20%. In order to obtain better efficacy, an investigation of the layers of thin films is needed. This research discussed the properties of copper and its oxides. In case of making the thin film layers, potentiostat electro-deposition was the chosen method where bath composition of $CuSO_4.5H_2O$ solution, temperature, time, potential difference were the variable parameters. The best-deposited layers were obtained in 0.2 M concentration, 40 minutes, -0.5 V potential difference and 65^oC. Hence, physical properties like thickness and hardness, and characterisation properties like X-ray diffractometry (XRD), scanning electron microscopy (SEM), UV-Vis spectrometry are observed to compare cupric oxide (CuO) and cuprous oxide (Cu_2O) thin films. CuO thin film shows better stability and rigidity than the Cu_2O thin film. But the thin film layer of cuprous oxide illustrates good homogeneity and nodular form. From the test mentioned above data, band gap has been measured for each deposited film, and the CuO thin film layer is raked out having a better band energy gap than the Cu_2O thin film layer.

Keywords: Photovoltaic; thin film; potentiostat electro-deposition; band energy gap.

INTRODUCTION

Conventional crystalline silicon has been used to make solar cells, but they are cost efficient. As a result, people are uninterested in using silicon-based solar panels. In case of reducing cost, thin film photovoltaic cell introduces us with a great posterior. Nowadays, organic synthesised perovskite materials are using to make a high-efficient absorber layer for solar usage [1, 2]. But the process of making organic photovoltaic is complex so that, the total production cost is high.

On the contrary, thin film solar cells, such as CZTS (copper-zinc-tin-sulfur) and CIGS (copper-indium-gallium-sulfur/selenium), can be easily fabricated. So, the overall production cost is lower than the perovskite solar cells [3]. The cost mainly depends on the materials that are used to manufacture the absorber layer. In order to develop the

matrix of different materials of the photovoltaic, rare earth metals and less available materials like cadmium, indium, selenium, titanium, and tellurium can be used to fabricate thin film solar cell. Different oxides such as ZnO, CuO etc. and sulfides such as CdS, ZnS, Cu-In-S, are also used to make thin films. The most popular thin film absorber layers of photovoltaics are CIGS and CZTS. The available CZTS and CIGS solar cells in the market offer a total efficiency of 9.5% and 15% respectively. But the best efficiency achieved in the laboratories is 20% for the CIGS solar cells and 14% for CZTS solar cells. The photovoltaic-efficiency depends on the band gap of material because the band gap is dependent on the absorbance of the oxide or sulfide layers of the thin film [4]. According to "Shockley-Queisser limit", the best efficiency 33.7% for CZTS can be achieved while the band gap will be 1.4 eV [5, 6]. So, there is a huge chance to improve today's CZTS photovoltaics absorber layers. In order to achieve higher efficiency, the mixed layer of oxides and sulfides of copper, zinc, tin were fabricated with various type of deposition methods (such as, chemical vapor deposition, physical vapor deposition, sputtering, atomic layer deposition, ion beam, laser melting, fused deposition modelling etc.) and different thickness [7, 8].

In recent research, the higher efficiency has been observed using a potentiostat electro-deposition method for making the thin film layers of oxides [9, 10]. Likewise, the CZTS or CIGS thin-film photovoltaic can be developed by electro-deposition method because it's easy production procedure and cost-saving method. Now, the primary element of CZTS or CIGS thin-film photovoltaics is copper or deposited copper oxide which plays a vital role for measuring the band energy gap of the absorber layer. Copper is a divalent element and so it has two types of oxide: cuprous oxide (Cu_2O) and cupric oxide (CuO). Therefore, in the case of making CZTS or CIGS solar cell, each of the copper oxides possesses different characterization properties and band energy gap as well as shows different efficiency. This research targets to develop and analyse the characteristics of Cu_2O and CuO thin films and to draw a comparison between them according to the stability, homogeneity, efficacy, absorbance and band energy gap.

EXPERIMENTAL PROCEDURES

Material and Method

From 1839 when Alexandre Edmond Becquerel first observed the photovoltaic effect, scientists are trying to catch more energy and in the journey of acquiring energy one thing should be kept in mind that is the cost of production. There are several parts of a photovoltaic cell; among them, the absorber layer is one of the most costly parts. In this research, electrochemical deposition has been chosen because of its easiness, flexibility and quickness. To be more specific, potentiostat electro-deposition was done [2, 11]. The potentiostat method was selected, and a constant current density was supplied. Three electrode system was consolidated where the reference electrode was Ag+/AgCl electrode; the other electrodes were copper. Looking forward to using the cheap and available material, copper and its oxides were chosen for the research. Copper is not only cheap but also non-toxic, good absorber of visible light and most importantly copper is a perfect material for potentiostat electro-deposition [12].

The solution for the research was $CuSO_4.5H_2O$ and 5% Nital was used for etching. Four parameters (bath composition, temperature, potential difference and time) were altered and other parameters (current density, pH value, electrocatalyst, heating rate etc.) remained unchanged. For temperature control, a heat bath was used using magnetic

stirring. Then the substrates were used in three electrode system as shown in Figure 1. Different bath composition (0.1 M, 0.2 M, 0.3 M, 0.4 M, 0.5 M) of $Cu_2SO_4.5H_2O$ were used to deposit Cu_2O and CuO thin films. For both the oxides, best-deposited films were observed in 0.2 M and 0.3M bath composition. Thus further investigation continued with Cu_2O and CuO thin film deposited from 0.2 M and 0.3 M baths. Table 1 shows the different parameters experimented in this work.

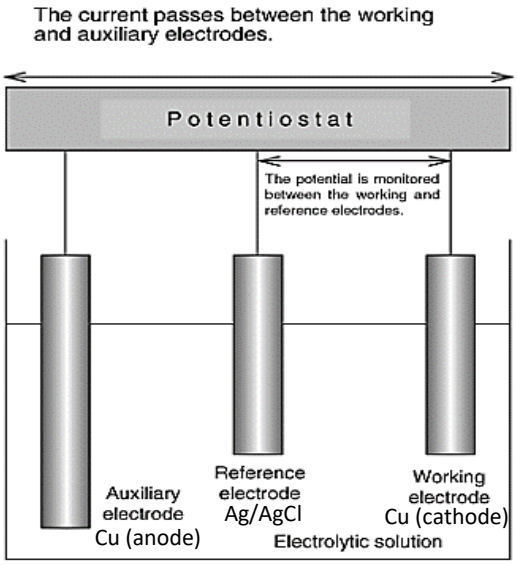


Figure 1. Schematic diagram of experimental setup.

Hardness and Thickness Measurement

Hardness properties were measured by micro-indentation. Shimadzu microhardness testing machine was used at Vickers hardness scale. The load was 100 Kg-f (0.98 KN) and duration of load applying time was 10 to 15 seconds. After deposition, thickness was measured by the metallographic image. For the metallographic testing, samples are cut into small pieces and mounted in Bakelite plastic. Then, the sample is polished by the emery papers of 120, 180, 320, 600, 800, 1200 and 1500 respectively and finally in the spinning polisher. Then the microstructures were taken to measure the thickness. But the film thickness was similar and perfect thickness could not be measured. So, to get more accurate thickness measurement, the ultrasound sensor machine was used. This machine can evaluate the real thickness of the thin films.

Characterisation Test

After getting the good deposited thin film of CuO and Cu_2O, some characterization tests were done such as scanning electron microscopy (SEM) to observe the sample's surface topography and composition, x-ray diffractometry (XRD) to determine the phases present in the deposited films, UV- vis Spectrometry to determine the absorbance of the deposited films at the wavelength range of 200-1100 nm. The SEM image processing was done by SEM JSM-6490 version 1.0 machine. The pixel size was 0.00002 and the computer software was Micron Maker Sum. Images observed in 10000, 20000 and 30000 magnification. X-ray diffractometry test was done by "RIGAKU Ultima IV X-ray

diffractometer". Band-gap was calculated according to the absorption measured by UV spectrophotometer absorbance at a fixed recording absorption spectrum.

Table 1. Variable parameters.

Bath Composition (M) $CuSO_4.5H_2O$	Potential difference (V)	Time (min)	Temperature (°C)
0.2	-0.4	35	60
			65
			70
		40	60
			65
			70
	-0.5	35	60
			65
			70
		40	60
			65
			70
0.3	-0.4	35	60
			65
			70
		40	60
			65
			70
	-0.5	35	60
			65
			70
		40	60
			65
			70

RESULTS AND DISCUSSION

Micro-Hardness Measurement

The observed values of Vickers hardness test of Cu_2O and CuO thin deposited films respectively, are listed in Table 2 and Table 3 respectively. From the data, it is inferred that CuO film shows a greater hardness than Cu_2O film. In parallel, greater hardness indicates high stability. Therefore, CuO is more hard and stable than that of Cu_2O. The interatomic bond between the atoms of copper and oxygen enhances significantly in CuO through electro-deposition technique. In electrodeposition, the copper (II) ion exerts two electrons which are occupied in pairing with the oxygen ions. Copper (I) ion exert one electron and two of these ions tried to be connected with one single ion of oxygen. The bond strength of Cu_2O is less than the bond strength of CuO. So, it is highly important to use CuO instead of Cu_2O in case of making an absorber layer for copper-based thin film solar cell.

Table 2. Micro-hardness of Cu_2O thin film.

Concentration $CuSO_4.5H_2O$ (M)	Voltage (V)	Temperature (◦C)	Hardness (HV)
0.2	-0.4	65	26.23
0.3	-0.4	60	63.46
0.2	-0.5	65	48.45
0.3	-0.5	60	78.77

Table 3. Micro-hardness Values of CuO thin Film

Concentration $CuSO_4.5H_2O$ (M)	Voltage (V)	Temperature (◦C)	Hardness (HV)
0.2	-0.4	65	47.81
0.3	-0.4	60	163.96
0.2	-0.5	65	84.01
0.3	-0.5	60	126.91

Thickness Measurement

It is inferred from Table 4 and Table 5 that the films were not deposited uniformly. So, a variety of thickness was observed. Moreover, average thickness values of CuO thin film is higher than the Cu_2O thin film. Therefore, CuO deposited thin film gives a more stable coating than that of Cu_2O thin film. The atomic structure of Cu_2O is larger than the atomic structure of CuO. From the thickness data, it is clearly observed that the layer of Cu_2O is less than the layer of CuO. That means, less amount of Cu_2O atoms are present in the layer of Cu_2O and a higher number of atoms are present in the CuO layer which makes the compact and hard layer of CuO.

Table 4. Coating Thickness of Cu_2O Film

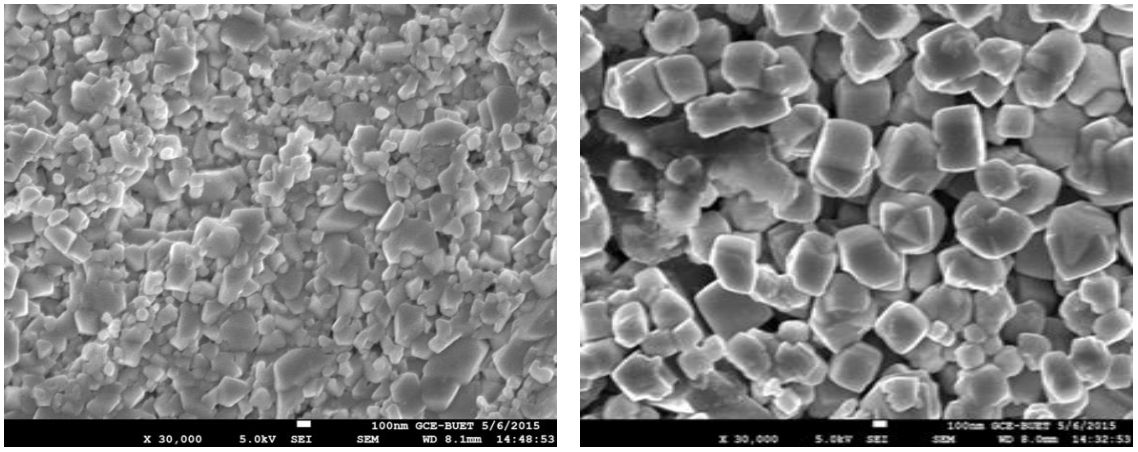
Concentration $CuSO_4.5H_2O$(M)	Voltage (V)	Temperature (◦C)	Average thickness (µm)
0.2	-0.4	65	2.58
0.3	-0.4	60	6.52
0.2	-0.5	65	3.24
0.3	-0.5	60	5.8

Table 5. Coating thickness of CuO Film

Concentration $CuSO_4.5H_2O$ (M)	Voltage (V)	Temperature (◦C)	Average thickness (µm)
0.2	-0.4	65	7.4
0.3	-0.4	60	18.44
0.2	-0.5	65	3.625
0.3	-0.5	60	5.0

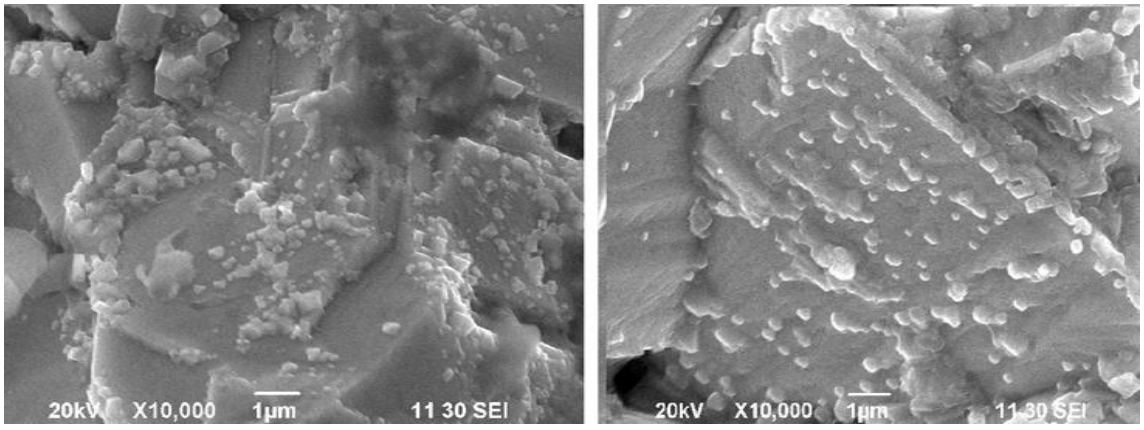
Characterisation of Thin Film

Electron microscopy results are shown in Figure 2 and Figure 3; which represent the SEM images of Cu_2O thin film and CuO thin film. From the figures, it is depicted that Cu_2O film has good grain refinement and homogeneity than that of CuO film. It is also observed that the particles of Cu_2O are loosely bonded. On the other hand, the particles of CuO surface has densely collaborated with each other. For, different bath composition, CuO always possessed better surface roughness and good planarity.



(a) (b)

Figure 2. SEM images of Cu_2O thin film; (a) deposited from 0.2 M bath composition, (b) deposited from 0.3 M bath composition.

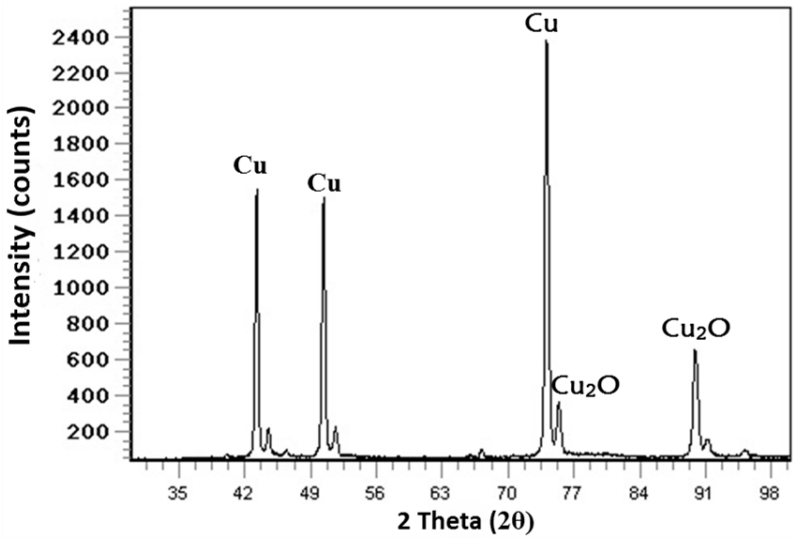


(a) (b)

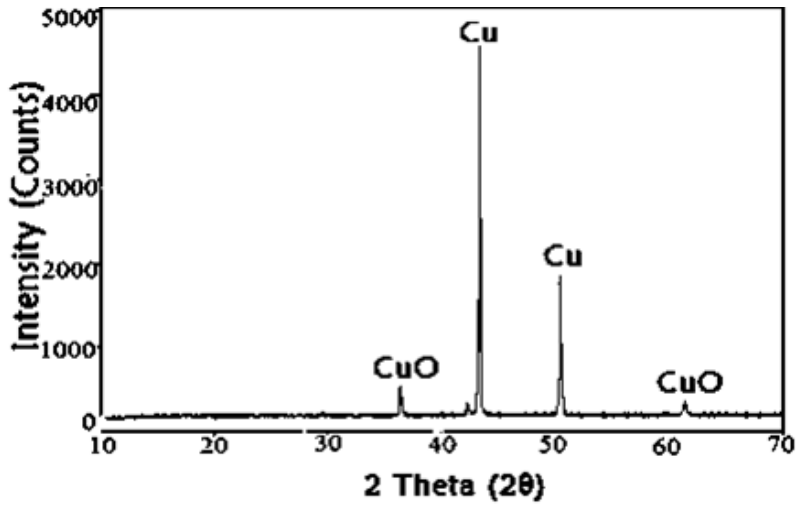
Figure 2. SEM images of CuO thin Film; (a) deposited from 0.2 M bath composition, (b) deposited from 0.3M bath composition.

Figure 3(a) and 3(b) depicts the results of X-ray diffractometry of Cu2O and CuO thin films, respectively. The intensity versus 2θ graphs shows the evidence of thin films. The intensity peaks of the films assure the penetration of X-ray through the film to the substrate. The Cu peaks were observed because of the substrate copper metal, and the oxides ensured the presence of the thin film absorber layer. Moreover, the peaks illustrated the existence of crystallinity of the thin film. There is no intermetallic phase is

observed from the XRD analysis. There are no peak broadening phenomena observed in the XRD graphs, that means no non-uniform lattice strain was formed [13, 14]. From the intensity values, it is empirically observed that the Cu_2O has higher weight percentage in the sample than the CuO. Thus, the thinner layer of Cu_2O has a higher mass than the thicker layer of CuO.



(a)

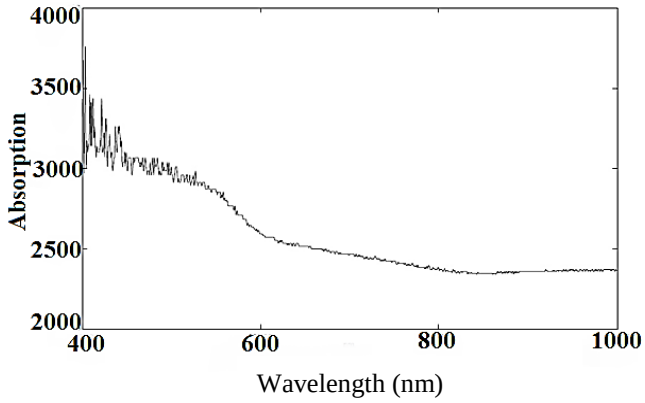


(b)

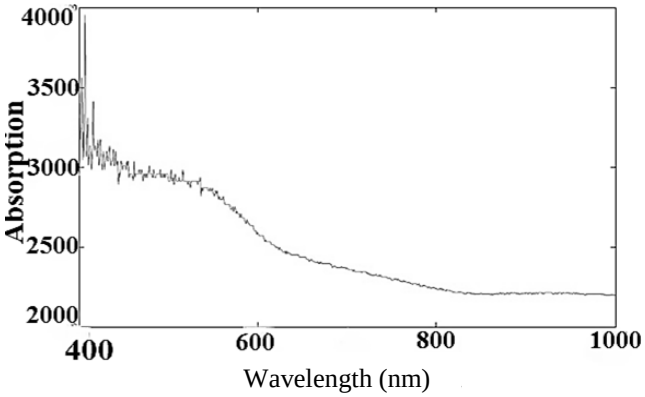
Figure 3. XRD scan of (a) Cu-Cu_2O and; (b) Cu-CuO thin film.

Absorption of ultraviolet ray according to the wavelength, was measured by UV-Vis spectrometry. The graphical representation of the measured data is illustrated in Figure 4(a) and 4(b). From the data values, the band gap was calculated by absorption energy-related formulas [15]. Moreover, Figure 5(a) and 5(b) are illustrated to measure the band gap value. Here, absorption coefficient $\alpha = 2.303$ A/d where planks constant, h = 6.626×10^{-34} light velocity, c = 3 x 108 ms^{-1}, wavelength= λ, absorbance =A, thickness= d. This graph is depicted by the average values of different parameters like bath composition, potential difference, time and temperature. From these graphs, the band gap measured for the Cu_2O thin film is 0.5 eV, whereas the band gap for CuO thin film is 0.9

eV. The Shockley–Queisser limit and from this graph, it is found that 0.9 eV gives more efficiency than 0.5 eV band gap [5, 16]. Therefore, CuO thin films give more efficiency than that of Cu_2O thin films.

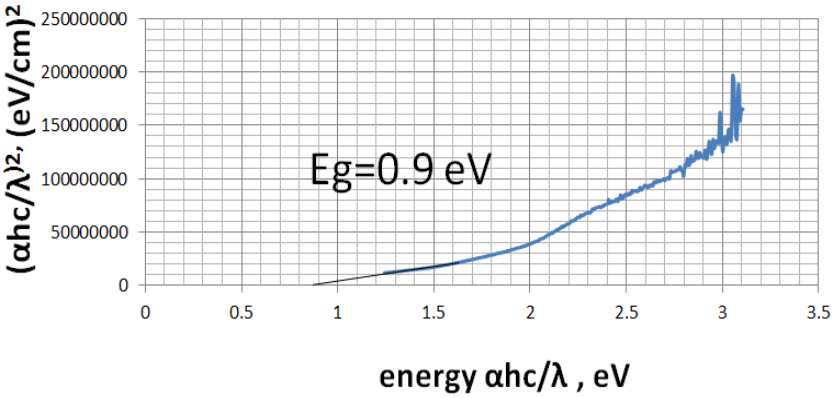


(a)

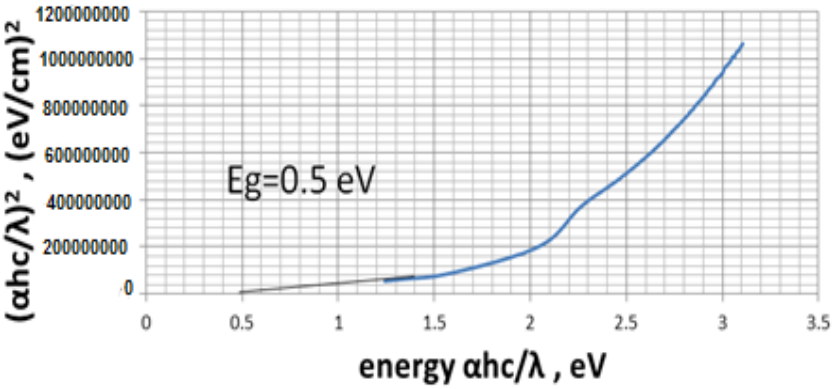


(b)

Figure 4. UV-Vis spectrometry graph of deposited (a) Cu_2O and; (b) CuO thin film.



(a)



(b)

Figure 6. Band gap measured for (a) CuO (b) Cu_2O thin film.

CONCLUSION

This heuristic research targets to achieve a better thin film of copper oxides. From characterisation tests and measurement of physical properties, a constructive comparison established. Focusing on stability and rigidity, Cu_2O thin film shows less effective than CuO thin film. On the contrary, the grain refinement and uniformity of grain size of Cu_2O thin film is very good. But cupric oxide (CuO) thin film does not depict positively in this case. The most important thing is the efficacy of the thin films as the absorber layer of the photovoltaic cell. Therefore, using CuO thin film in preparation of CZTS may create a novel future in the field of the photovoltaic cell. Not only CZTS photovoltaics but also this study may have a great impact on the other thin film solar cell which has a thin layer of the copper. This research study also opens a wide door of future materials research for the absorber layer made by very cheap inorganic materials. The upcoming era of inexpensive and non-toxic solar cells will have a stunning beginning by using copper oxide layers. The comparison between the oxides will also help in qualitative assessment for the thin films. This qualitative analysis has been opened a new road to investigate the conventional models and materials of thin films. This unique study indicates a useful technique to improve conventional thin films. In future, several oxides and sulphides of different metals can be observed to mitigate the future demands of highly efficient low-cost solar devices.

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