International Journal of Advanced Engineering and Nano Technology (IJAENT)
ISSN: 2347-6389, Volume-2 Issue-2, January 2015

Electrodeposition and Characterization of Copper Oxide Thin Films for Solar Cell Applications

Abu Sadat Md. Sayem Rahman, Md. Anisul Islam, Kazi Md. Shorowordi

Abstract*— *Copper oxide thin films are being considered in thin film solar cells for its unique photovoltaic properties. Electrodeposition is one of the cheapest processes to deposit copper oxide thin films. In this study, copper oxide was electrodeposited on the copper substrate in an electrolyte bath containing 0.2M $CuSO_4.5H_2O$, 3M lactic acid and NaOH. A Potentiostat/Galvanostat with silver chloride electrode (Ag/AgCl) as a reference electrode was used for elctrodeposition. During deposition, the bath temperature and pH were maintained at 60^0C and 12-12.5 respectively. Copper oxide was deposited at different potentials and deposition time. The films deposited at different electrodeposition conditions were characterized by Scanning Electron Microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDS) and UV Spectrometer. From visual inspection it was found that copper oxide film is black and adherent on copper substrate. The SEM study revealed that copper oxide films became more compact and grain sizes of copper oxide films decreased at more negative potentials in deposition potential range. EDS analysis showed that percentage of oxygen in the copper oxide films increased with more negative potentials at the deposition potential range. It was found that with increase of time more adherent and uniform film thickness occurs. The variation of current density and thickness of copper oxide films with different deposition parameters were analyzed. The absorption spectrums which represent the optical properties were also correlated with the deposition parameters.

Keywords* —*Copper oxide; Electrodeposition; Solar cell; Film thickness; Optical absorbance.

I. INTRODUCTION

The worldwide growth of energy demand and exploitation of fossil fuel leads us to find out alternative sources of energy. Renewable energy or solar energy can be a good alternative source of energy to solve current energy demand. Solar cell is getting more and more popular in recent years for electricity generation. The worldwide electricity production from solar energy is expected to grow from 18 percent in 2007 to 23 percent in 2035 [6]. There are many semiconducting materials which have very good photovoltaic properties; among them copper oxides are very promising materials for low cost solar cell [12].

Photovoltaic community showed interest in Cu_2O to use as a solar cell material since mid seventies [13]. There are many advantages of Cu_2O, for example Cu_2O is non- toxic in nature, simple production process [12] and 9-11% theoretical solar efficiency [3]. However its practical solar efficiency is not so high. In past, practical electrical power conversion efficiencies of Cu_2O obtained by researchers were below 2% [14]. But in recent years efficiency of 2% has been reported by researchers [15].

Electrodeposition method of Cu_2O was first developed by Stareck [7]. It was also described by Rakhshani [8-11]. In his work, a method of simple processes of electrolysis was applied to produce Cu_2O. Electrodeposition process has many advantages, for example; it can be used to make back wall or front wall cells as well and also suitable for producing large area devices. Electrodeposition is a low temperature process. It is also possible to control film thickness, morphology and composition by adjusting electrical parameters and composition of bath solution [3]. However one major problem in electrodeposition process is the high resistivity (104 – 106 ohm-cm) of electrodeposited Cu_2O film [16].

In this work, thin films of copper oxides (Cu_2O, CuO) were made by using electrochemical deposition technique on copper substrates, using a three electrodes system. The three electrodes are anode, cathode and reference electrode. The controlling parameters in this work were operating voltage, p^H, concentration of bath solution ($CuSO_4$. $5H_2O$), operating time and temperature. The optical properties of deposited films were measured by Ultraviolet–visible spectroscopy. Optical absorbance of copper oxide films were also compared with different electrodeposition parameters.

II. EXPERIMENTAL

A. *Preparation of working electrode (cathode)*

Rectangular thin plates of copper, about 1mm thick, were first polished using different grades of emery papers. Then the electrodes were washed with distilled water to remove dust particles. After that electrodes were rinsed with 10% nitric acid (HNO_3) solution for two minutes. Electrodes were again washed with distilled water for very short time and readily transferred to the solution for electrodeposition.

B. *Electrodeposition of Copper oxide*

The electrodeposition of copper oxide was carried out with a three-electrode setup. A Potentiostat/ Galvanostat was used for this purpose. The reference electrode was Ag/AgCl electrode. Copper sheet was used as both working electrode and counter electrode (anode). In some experiments platinum (Pt) was also used as anode. The electrodeposition bath contains 0.2 M $CuSO_4{\cdot}5H_2O$ and 3 M Lactic Acid ($C_3H_6O_3$) solution [5]. The p^H of electrodeposition bath was adjusted to

Manuscript Received on January 2015.

Abu Sadat Md. Sayem Rahman, B.Sc. in Materials and Metallurgical Engineering, Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh.

Md. Anisul Islam, B.Sc. in Materials and Metallurgical Engineering, Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh.

Kazi Md. Shorowordi, Asst. Prof., Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology (BUET), Dhaka, Bangladesh.

around 12 by the addition of NaOH. During electrodeposition the bath temperature was varied from 60^{o}C to 40 ^{o}C [5]. The experiment was done at different deposition potentials, time, temperature, p^H and copper sulphate ($CuSO_4$. $5H_2O$) concentration (Table 1). The effect of these parameters on the properties of copper oxide film was observed.

Table 1: Electrodeposition parameters

potential (V)	Time (min)	Temperature (^{o}C)	pH	$CuSO_4$. $5H_2O$ concentration (M)
-0.45 to -0.65	10 -50	40-60	11.5-12.5	0.15-0.25

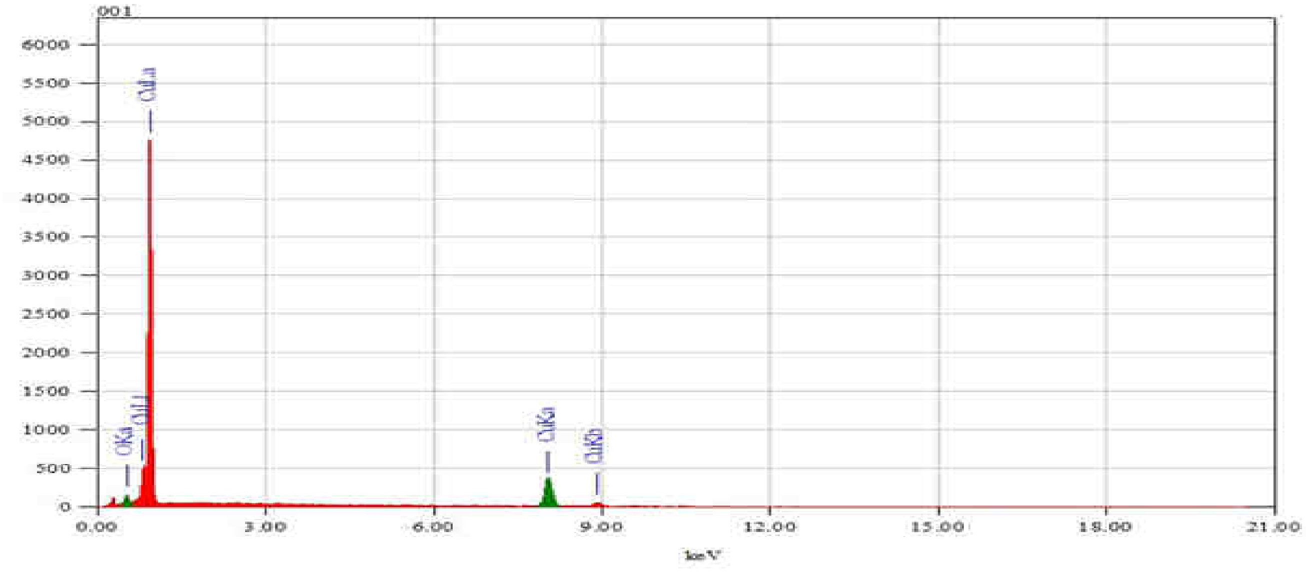
C. *Characterization*

JEOL JSM-7600F**,** Field Emission Scanning Electron Microscope (FESEM) was used to characterize the surface morphology and grain size of the electrodeposited sample. Energy dispersive spectroscopy (EDS) mode of the FESEM was used to characterize the amount of element present in the deposited film in mass percentage. The thickness of copper oxide films was measured by using Fischer, Durlscope mPoR. Data from at least five different spots on the coated surface was taken and measured the average of them and also calculated the standard deviation. Pharmaspec UV-VIS spectrophotom eter shimadzu was used to determine the absorbance of the samples at the wavelength ranges from 200 nm to 800 nm. The absorbance at wavelengths smaller than 400 nm was very noisy and because of this wavelength range from 400 nm to 700 nm was selected to make comparison. Copper oxides were prepared at different deposition potentials, time, temperature, p^H and $CuSO_4{\cdot}5H_2O$ concentration and all the samples were characterized by the aforementioned techniques.

III. RESULTS AND DISCUSSION

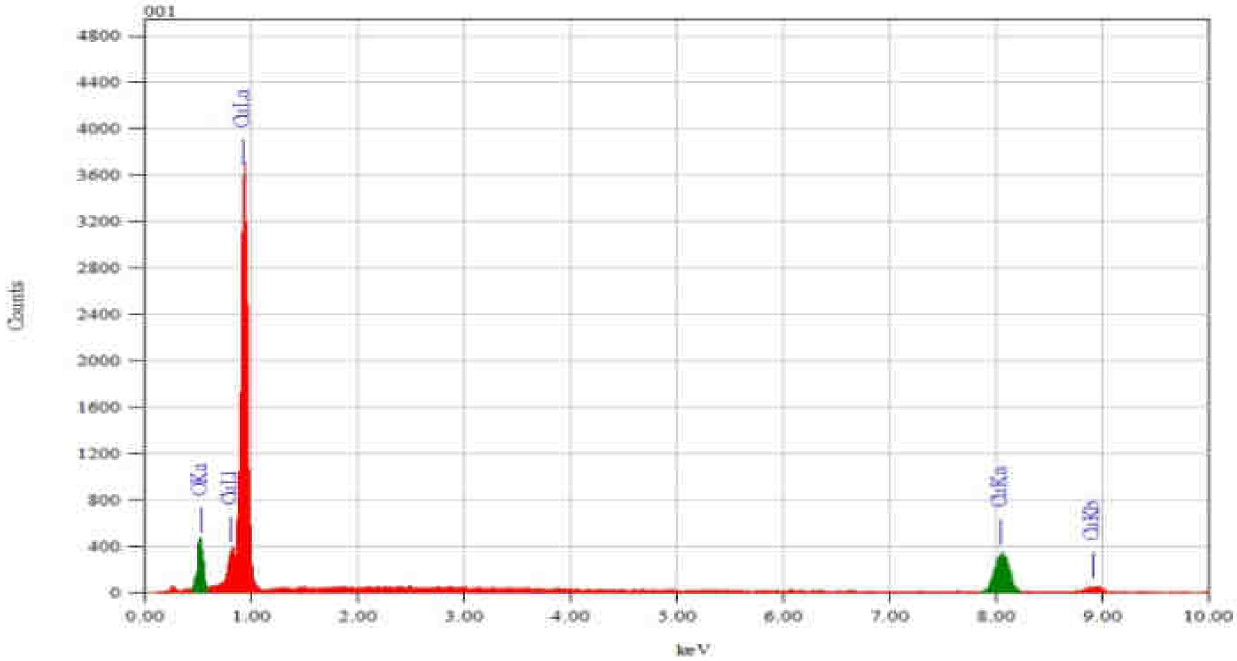
A. *Energy-dispersive X-ray spectroscopy (EDS)*

In order to determine percentage of different elements, EDS analysis was done on copper oxide films that were electrodeposited at different electrodeposition parameters. From the EDS analysis of the copper oxide which was electrodeposited with copper cathode and Pt anode, it was found that there was 99.09% of copper present in the sample, Fig. 1. Only 0.91% of oxygen was present. So we can say that it is almost entirely copper and no copper oxide is present. The electrodeposition potential is more negative (-0.65V), for this reason copper deposition occurred instead of copper oxide. From the EDS analysis of the sample deposited at -0.45V, it is found that there is 4.44% of oxygen present in the sample and 95.56% of copper, Fig. 2. It is also crystalline in structure. To become cuprous oxide it should have 11.18% of oxygen and this oxide film has only 4.44% of oxygen which is much less than the required amount. So it is not entirely cuprous oxide or cupric oxide. There is only a few amount of copper oxide is present in the sample. Copper oxide which was deposited at -0.50V consists of mainly 17.94 % of oxygen and 82.06 % copper, fig. 3. To become cupric oxide it should have 20.13% of oxygen. As the oxygen content of our sample is very close enough to the required amount of oxygen to become cupric oxide, we can say that it may be cupric oxide. The copper oxide which was deposited at -0.55V also contained 17.95 % of oxygen and 82.05 % copper, Fig. 4. As the oxygen content is very close enough to the required amount of oxygen to become cupric oxide, this copper oxide can also be considered as cupric oxide.



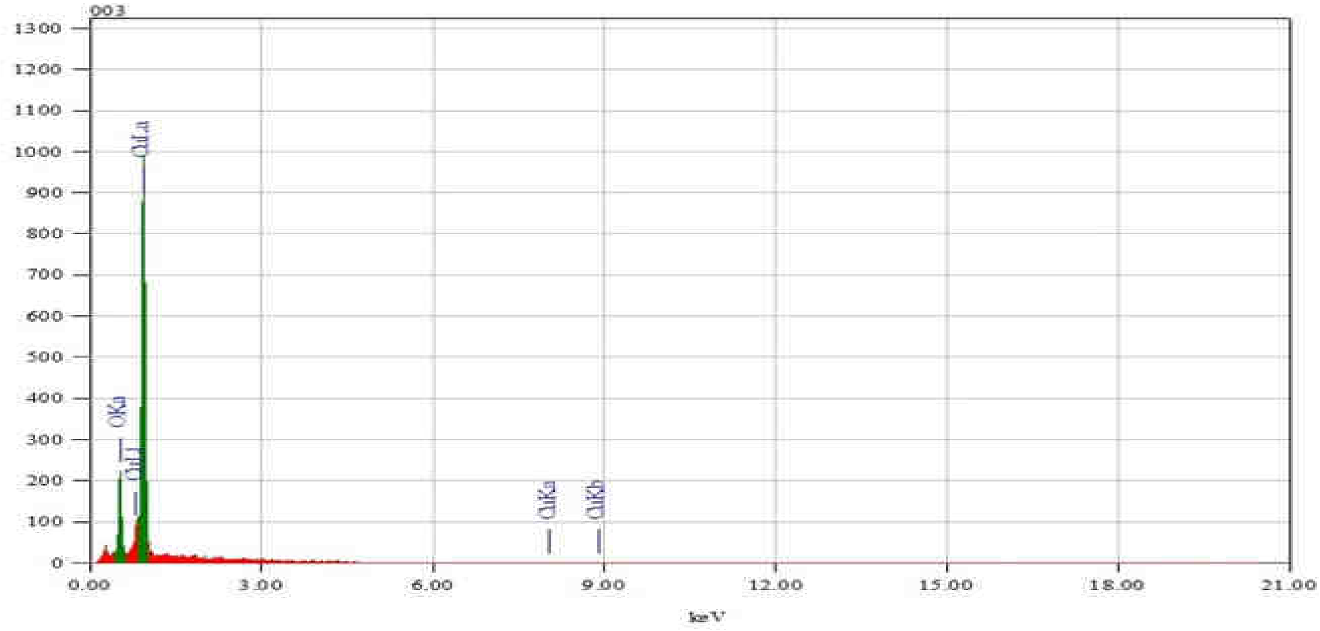
Element		(keV)	Mass%	Sigma	Atom%	Compound
O K		0.525	0.91	0.04	3.53	
Cu K	*	8.040	99.09	1.57	96.47	
Total			100.00		100.00	

Fig. 1: EDS analysis of the sample deposited with copper cathode and Platinum anode.



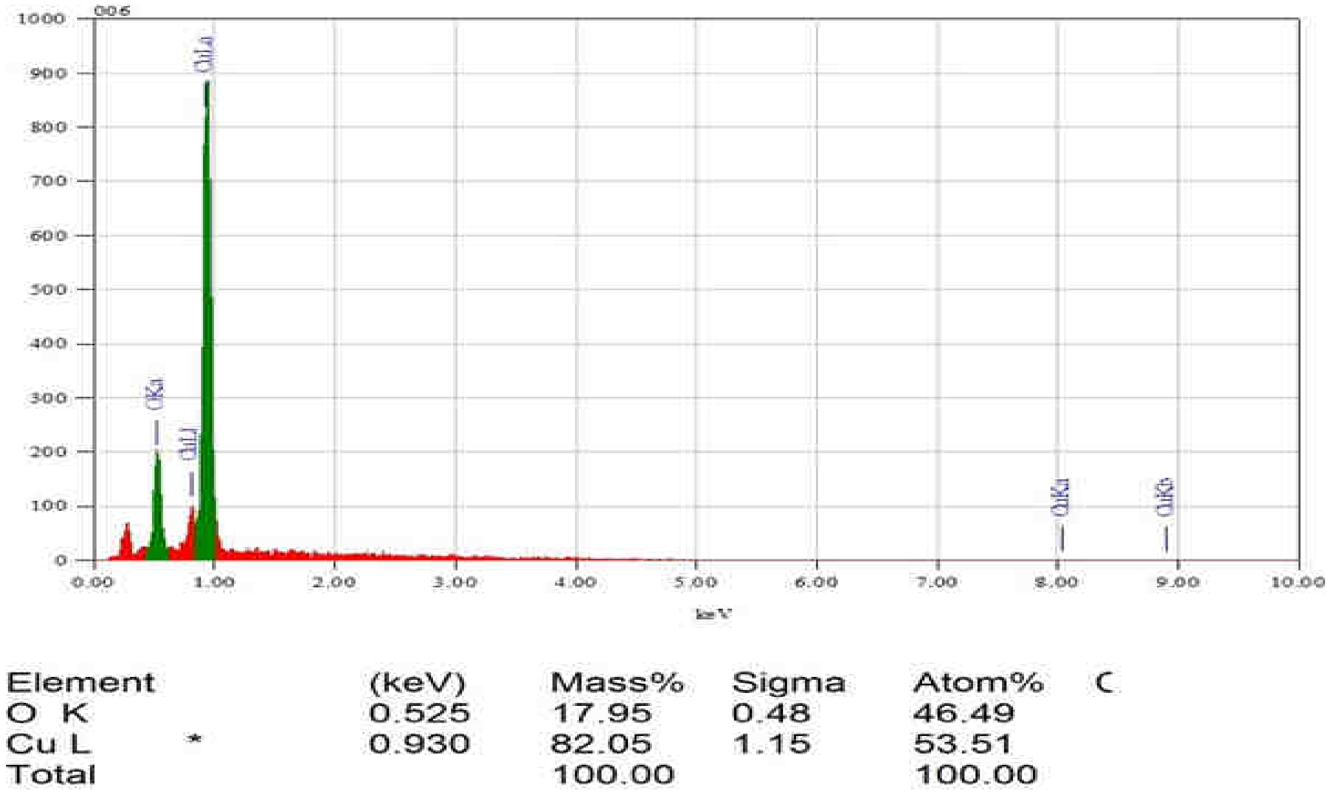
Element		(keV)	Mass%	Sigma	Atom%	Compound
O K	*	0.525	4.44	0.03	15.58	
Cu K	*	8.040	95.56	0.78	84.42	
Total			100.00		100.00	

Fig. 2: EDS analysis of the sample deposited with both copper cathode and anode at deposition potential -0.45V.



Element		(keV)	Mass%	Sigma	Atom%
O K		0.525	17.94	0.47	46.47
Cu L	*	0.930	82.06	1.13	53.53
Total			100.00		100.00

Fig. 3: EDS analysis of the samples that were deposited with both copper cathode and anode at deposition potential -0.50V.



Element		(keV)	Mass%	Sigma	Atom%	C
O K		0.525	17.95	0.48	46.49	
Cu L	*	0.930	82.05	1.15	53.51	
Total			100.00		100.00	

Fig. 4: EDS analysis of the samples that were deposited with both copper cathode and anode at deposition potential -0.55V.

B. Scanning electron microscope (SEM)

SEM was done to determine the surface morphology and grain size of the copper oxide. Fig. 5 shows the SEM surface morphology of copper substrate without copper oxide and copper oxide deposited using platinum anode. It was found that electrodeposition with Pt anode was non-crystalline, Fig. 5(b). Sphere shaped particles were present on the surface of the sample. These were mainly copper and also confirmed by EDS analysis, fig. 2. It was reported that at more negative potentials copper oxide transforms to copper [3]. For the platinum anode, the deposition potential may had become more negative, for which Cu^{2+}ion transformed to Cu and copper deposition was found instead of copper oxide [4].

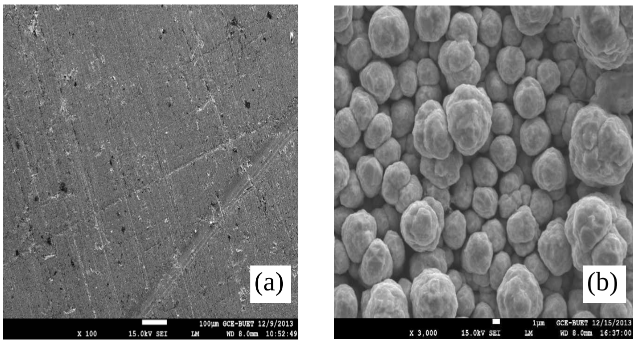


Fig. 5: SEM images of (a) bare copper substrate and (b) electrodeposition with Pt anode (-0.65V).

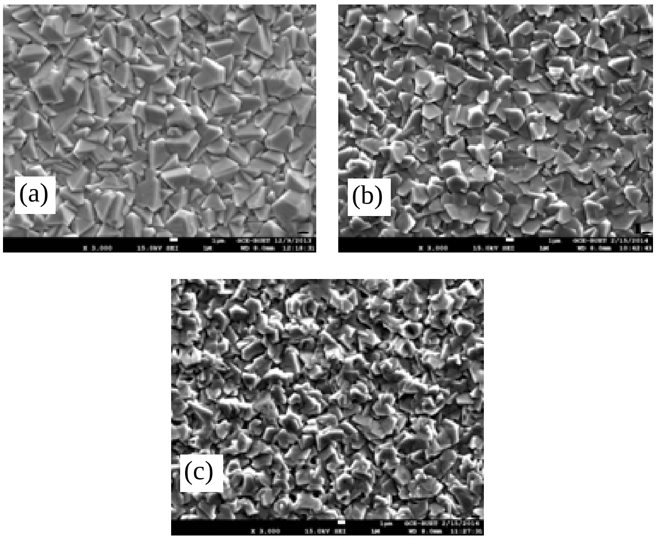


Fig. 6: SEM image of copper oxide electrodeposited at (a) -0.45V, (b) -0.50V and (c) -0.55V.

It was found that all the films consist of agglomerates of angular-shaped crystallites on copper substrate when deposited with copper cathode, Fig. 6. Because of the less negative potential copper oxide deposition occurs and it is also confirmed by EDS analysis, fig. 2, fig. 3 and fig. 4. Significant differences observed in these films. The grain sizes of copper oxides in the film decreases with the increase of negative potential. During the copper oxide deposition, frequencies of nucleation of copper oxide crystallites were likely to become higher when the applied potentials became more negative. This results in decrease of grain growth and smaller grain size. Although it is promising for the copper oxide film having large grains for photovoltaic applications because of its possible reduction of the recombination probability at grain boundaries [5].The compactness of the copper oxide film deposited at more negative potential -0.55V became better than the film with larger grain size prepared at more positive deposition potential.

C. *Effect of deposition parameters on current density and thickness of Copper oxide film*

The relation between film thickness and concentration of $CuSO_4{\cdot}5H_2O$ is shown in fig. 7(a). It can be said that, with the increase in concentration of $CuSO_4$. $5H_2O$ more copper ion in solution and hence the film thickness increased. It also affected the average current density which decreased with concentration, fig. 7(b). It may be due to the formation of a barrier to current flow more due to greater concentration. With the increase of operating voltage, the effect on thickness was almost same as that of the effect of concentration but current density change was random, fig. 8(a) and fig. 8(b). At the condition of -0.60V a major deviance was noticed compared to general trend for thickness and current density. It was observed that coating thickness increased with increasing deposition time, fig. 9(a). The increment was not linear and during experiment it was noticed that rate of increment decreased with increasing time. But average current density should decrease which was not obtained as required, fig. 9(b). No direct relationship was found between temperature and copper oxide film thickness, Fig. 10(a). The film thickness was minimum at 50 ^{o}C and increased suddenly at 60 ^{o}C, which was about 3.5 µm. In case of p^H it was observed that, at p^H 11.5 there was no copper oxide film and current density was also high compared to general values obtained in the other experiments, fig. 11(a) and fig. 11(b). At p^H 12.5, current density was in expected range but coating thickness was somewhat smaller. Actually at p^H 12.0 better results were obtained, as described in literature [1]. Because of this p^H 12.0 was used for all other operating conditions.

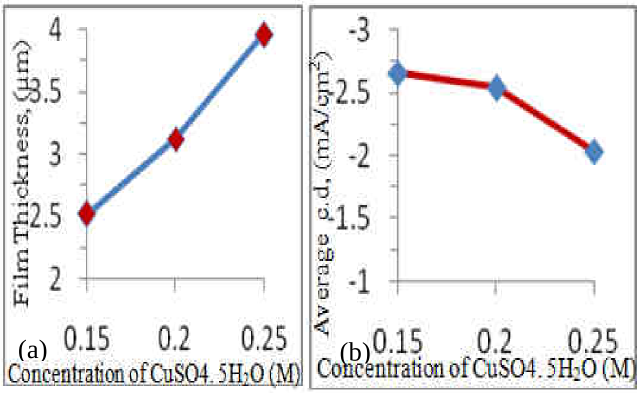


Fig. 7: Effect of concentration of $CuSO_4$. $5H_2O$ on (a) film thickness and (b) current density (c.d.).

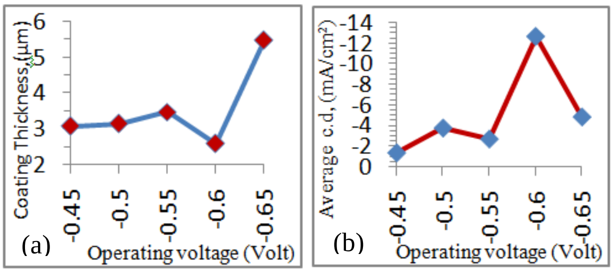


Fig. 8: Effect of operating voltage on (a) coating thickness and (b) current density (c.d.).

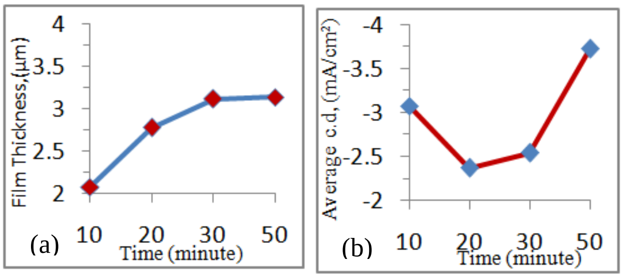


Fig. 9: Effect of operating time on (a) film thickness and (b) current density (c.d.).

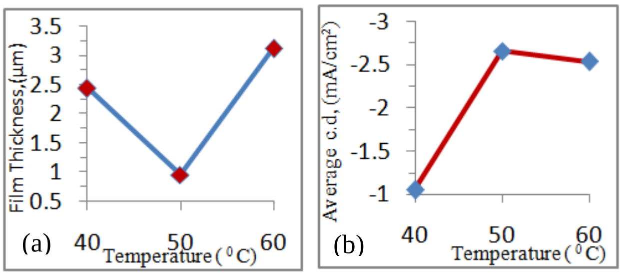


Fig. 10: Effect of operating temperature on (a) film thickness and (b) current density (c.d.).

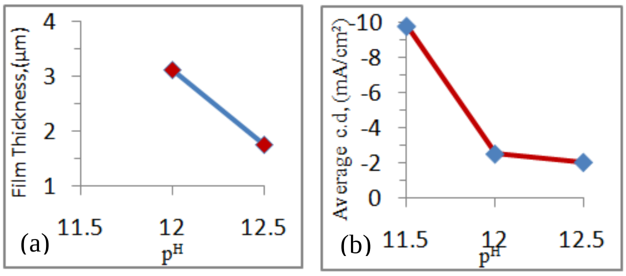


Fig. 11: Effect of solution p^H on (a) film thickness and (b) current density (c.d.).

D. *UV Spectrometer/Absorbance at fixed wavelength/ Recording absorption spectrum*

To observe the optical absorption profile of the electrodeposited copper oxides films, the optical absorbance was measured on the films**.** By this experiment the optical absorption spectrum of different samples that were deposited at different electrodeposition parameters was examined. Comparison between the samples absorption spectrum was also done.

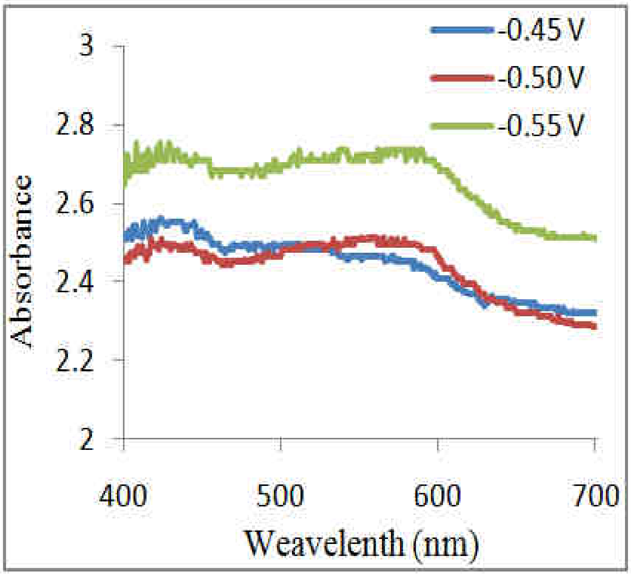


Fig. 12: Absorbance spectrum for deposition at different applied potentials vs. Ag/AgCl.

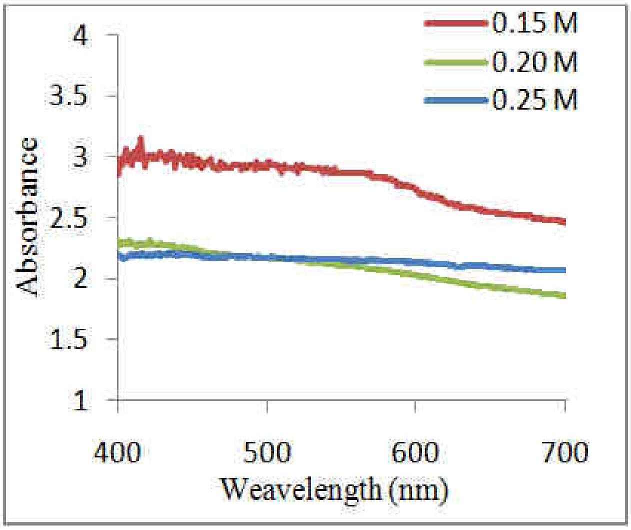


Fig. 13: Absorbance spectrum for deposition at different concentration of $CuSO_4.5H_2O$.

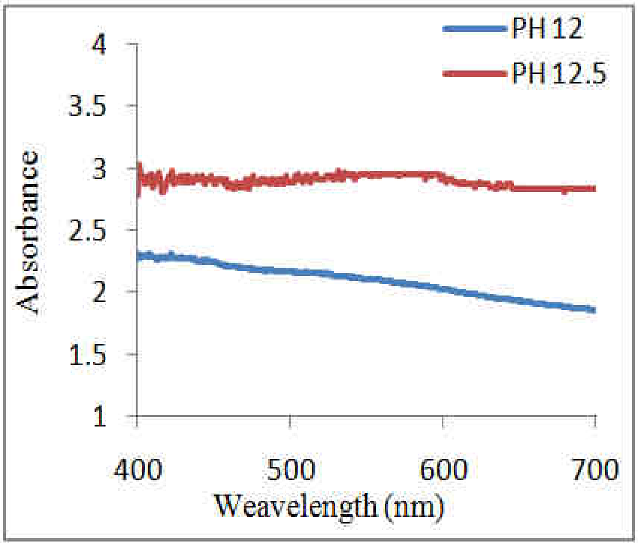


Fig. 14: Absorbance spectrum for deposition at different p^H.

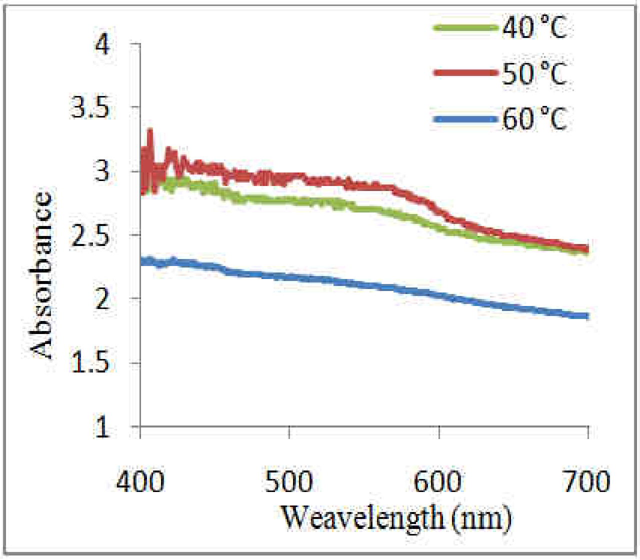


Fig. 15: Absorbance spectrum for deposition at different temperatures.

It can be observed that with the increase of deposition potential, optical absorbance increases; fig. 12. Copper oxide which was deposited at -0.55V showed the highest absorbance in wavelength range from 400 nm to 700 nm, while the oxide films which were deposited at -0.45V and -0.50 V showed almost same absorbance in the wavelength range mentioned before. The absorption spectrum of the copper oxide films which were deposited at different concentration of $CuSO_4$. $5H_2O$ is shown in fig. 13. It is observed that copper oxide deposited at lowest concentration of $CuSO_4$. $5H_2O$ shows very good absorbance in wavelength range of 400 nm to 700 nm. This copper oxide film showed higher absorbance than the copper oxides which were deposited at higher concentration of $CuSO_4$. $5H_2O$, 0.2M and 0.25M respectively. Copper oxide film that was deposited at p^H 12.5 showed good absorbance than copper oxide which was deposited at P^H 12, fig. 14. It was observed that with the increase of p^H optical absorbance of the copper oxide film increased. The absorption spectrum of the samples that were deposited at different temperatures is shown in fig. 15. Copper oxide film which was deposited at 60°C showed very poor absorbance than other two copper oxide films. The copper oxides which were deposited at 40°C and 50°C respectively demonstrated lower absorbance at higher wavelength but showed an onset of absorbance at about 600 nm. Absorbance of these two samples always remained very good in given wavelength range.

IV. CONCLUSION

The experimental results can be concluded as:

1. Copper oxides mainly cupric oxide, are prepared by electrochemical deposition process. The structural and optical properties of as-deposited copper oxides were evaluated.
2. Concentration of $CuSO_4$. $5H_2O$ and Operating Voltage both increases copper oxide film thickness.
3. Copper oxide film thickness increases with the increment of time but when deposition occurs for a long time film thickness increases very slowly.
4. Very good absorbance was found with film deposited at pH 12, applied potential -0.55V, temperature 60 °C and 15M concentration of $CuSO_4$. $5H_2O$.

V. ACKNOWLEDGMENT

We would like to express our deepest gratitude to Dr. Md. Moniruzzaman, professor, Department of Materials and Metallurgical Engineering, BUET for his valuable advice for copper oxide electrodeposition and Department of Glass and Ceramic Engineering, BUET to gave us the facilities for SEM and EDS analysis. The authors are also grateful to Centre for Advanced Research in Sciences (CARS), University of Dhaka for their UV-VIS absorption spectroscopy facilities. We are thankful to all of our respectful teachers and lab assistants of the Department of Materials and Metallurgical Engineering, BUET, Bangladesh.

REFERENCES

[1] Longcheng Wang. (2006). Preparation and characterization of properties of electrodeposited copper oxide films (doctoral dissertation, University of Texas at Arlingto).

[2] Rai B.P., (1988) Cu_2O Solar Cells Sol. Cells 25 p.265.

[3] Verka Georgieva, Atanas Tanusevski1 and Marina Georgieva. (2011). Low Cost Solar Cells Based on Cuprous Oxide. Solar Cells - Thin-Film Technologies, pp. 55-56.

[4] V. F. Drobny and D. L. Pulfrey. (1979). Thin Solid Films, 61, 89-98.

[5] Wilman Septina. (2010). Electrochemical Deposition of Cuprous Oxide Layers and Their Solar Cell Properties (Master Thesis, Osaka University).

[6] Galoppini, E., Rochford, J., Chen, H., Saraf, H., Lu, Y., Hagfeldt, A., & Boschloo G. (2006). Fast Electron Transport in Metal Organic Vapor Deposition Grown Dyesensitized ZnO Nanorod Solar Cells. The Journal of Physical Chemistry B 110, 16159-16161.

[7] Stareck, U.S. Patents 2, 081, 121 Decorating Metals, 1937.

[8] Jayanetti J.K.D., Dharmadasa I.M. (1996). Solar Energ.Mat.andSolar Cells 44 251-260.

[9] Mukhopadhyay A.K.,.Chakraborty A.K, Chattarjae A.P. and.Lahriri S.K. (1992). Thin Solid Films, 209, 92-96.

[10] Rakhshani A.E., JassarA.A.Aland, Varghese J. (1987) Electrodeposition and characterization of cuprous oxide Thin Solid Films, 148,pp.191-201.

[11] Rakhshani A.E., Makdisi Y. and Mathew X. (1996). Thin Solid Films, 288, 69-75.

[12] Abdu, Y.* and Musa, A.O. (2009). COPPER (I) OXIDE (Cu2O) BASED SOLAR CELLS - A REVIEW. Bayero Journal of Pure and Applied Sciences, 2(2): 8 – 12.

[13] Grondahl, L.O. (1933). Rev. Mod. Phys. 5: 141.

[14] Noguet, C. Tapiero, M. Schwab, C. Zielinger, J.P. Trivich, D. Komp, R.J. Wang, E.Y. and Wang, K. (1977). Cuprous Oxide as a Photovoltaic Converter. 1st European community Photovoltaic conference proc. P. 1170.

[15] Mittiga, A. Salza, E. Sarto, F. Tucci, M. and Vasanthi, R. (2006). Heterojunction Solar Cell with 2% Efficiency based on a Cu2O Substrate Applied physics letters, 88: 163 502-1 –163502-2.

[16] Economou, N.A. Toth, R.S. Komp R.J. and Trivich, D. (1982). Photovoltaic cells of electrodeposited cuprous oxide. 14th IEEE Photovoltaic Spec. Conf. Proc. New York: 1180-1185.