IOP Conf. Series: Materials Science and Engineering **438** (2018) 012002 doi:10.1088/1757-899X/438/1/012002

Electroless Deposition of p-type Cuprous Oxide Thin Film for Solar Application

Asif Mahmud, Shadman Sharar Mahmud and Md. Moniruzzaman

Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology, Dhaka 1000, Bangladesh

Abstract. Solar cells hold a promising prospect in the foreseeable future. Presently cuprous oxides (Cu_2O), due to their excellent photovoltaic properties, are being considered as p-type semiconductor materials for solar cell. This work aims at electroless deposition of p-type Cu_2O thin film on copper substrate and studying its various properties through characterizations. A bath containing varying amounts of $CuCl_2.2H_20$, $CoCl_2.6H_20$, $NaH_2PO_2.6H_20$ and KNaTar.$4H_2O$ (Potassium sodium tartrate tetrahydrate) was used for the process. NaOH pellets were used in order to get the desired pH level ranging from 11 to 14. The bath temperature was varied between 30°C to 70°C. The deposited films were characterized by Scanning Electron Microscope (SEM) equipped with Energy Dispersive Spectroscopy (EDS), X-ray diffractometer (XRD) and UV spectroscopy. It was observed that thin films were deposited at different conditions and uniform deposition of Cu_2O thin film was visible at pH 14. The coating thickness was found to be in the range of 0.48 to 4.6 μm. The bandgap for the deposited Cu_2O was found to be in the range of 1.3-1.4 eV. Some variation in results at different pH were observed and the reasons were identified.

1. Introduction

Cuprous oxide is a material that has been investigated for years with regard to solar cells due to its high theoretical efficiency and low potential cost [1-4]. It has direct bandgap of (E_g =1.85-2.2 eV) and a high absorption coefficient .It also absorbs visible wavelength upto 650nm. In addition, Cu_2O has several advantages such as non-toxicity and low cost, can be prepared with simple and cheap methods on large scale. Moreover, this material is known to have sufficient mobility and a relatively large minority carrier diffusion length. Its outstanding exciton properties including a large exciton binding energy (~140 meV) have been the target of much research efforts during the past decades [5]. Due to these specific features, fabrication of solar cells based on a Cu_2O photo absorber has been studied for a long time.

The goal of this work is to deposit cuprous oxide on copper plate by electroless technique as the absorber layer of a solar cell where copper plate acted as the back contact and to measure the bandgap of the deposited film. The structural and morphological properties of the as-deposited films were also evaluated.

2. Experimental

Electroless deposition technique was used to deposit cuprous oxide thin film on the copper substrate. The setup for this deposition consisted of hotplate, solution of Copper (II) chloride, Cobalt chloride, sodium hypophosphite and Sodium potassium tartrate as the electrolyte. The deposition parameters were chiefly bath composition and pH value. We prepared 24 samples altogether. The first set of samples were prepared keeping the bath composition fixed but changing the pH value. This helped us to find the best deposition

based on physical appearance. Further, samples were prepared by keeping the pH value fixed but with varied compositions. Finally, 7 samples were selected based on physical appearance of the deposition which were used for different characterizations. Table 1 denotes the first set of samples in which the bath composition was fixed but pH varied. Table 2 denotes the second set of samples in which the pH was fixed but bath composition varied.

Table 1. Different Experimental Conditions (pH altered)

Sample	pH	Bath Compositions	Time (mins)	Temperature (degree)
A	11	$CuCl_2.2H_2O$=0.024M $CoCl_26H_2O$=.0005M $NaH_2.PO_2.H_2O$=0.2M $KNaTar.4H_2O$=0.037M	60	60
B	12			
C	13			
D	14			

Table 2. Different Experimental Conditions (bath composition altered)

Sample	pH	Bath Compositions	Time (mins)	Temperature (degree)
D	14	$CuCl_2.2H_2O$=0.024M $CoCl_26H_2O$=.0005M $NaH_2.PO_2.H_2O$=0.2M $KNaTar.4H_2O$=0.037M	60	60
E		$CuCl_2.2H_2O$=0.036M $CoCl_26H_2O$=.00075M $NaH_2.PO_2.H_2O$=0.3M $KNaTar.4H_2O$=0.052M		
F		$CuCl_2.2H_2O$=0.038M $CoCl_26H_2O$=.0006M $NaH_2.PO_2.H_2O$=0.3M $KNaTar.4H_2O$=0.037M		
G		$CuCl_2.2H_2O$=0.04M $CoCl_26H_2O$=.0009M $NaH_2.PO_2.H_2O$=0.3M $KNaTar.4H_2O$=0.037M		

3. Result and discussion

We used SEM for the morphological study of the deposited thin film, XRD for the structural analysis, EDS for the compositional analysis and UV-VIS Spectroscopy for bandgap measurement.

3.1. SURFACE Morphology- SEM studies for deposited film

It is evident from Figure 1 that non uniform deposition was dispersed throughout the plate. The SEM image of sample C at pH 13 with concentration of copper being 0.024M showed minute granules with tiny porosity. The SEM image of sample D at pH 14 with the same conc. of copper revealed deposition dispersed throughout the plate. The SEM analysis of sample E at pH 14 with the concentration of copper being 0.038M showed comparatively thick deposition as well as granules dispersed with some porosity around. Even though the morphological study of all the samples gave an abstruse view of the images, keeping the solution at a pH of 14 will give a more uniform deposition.

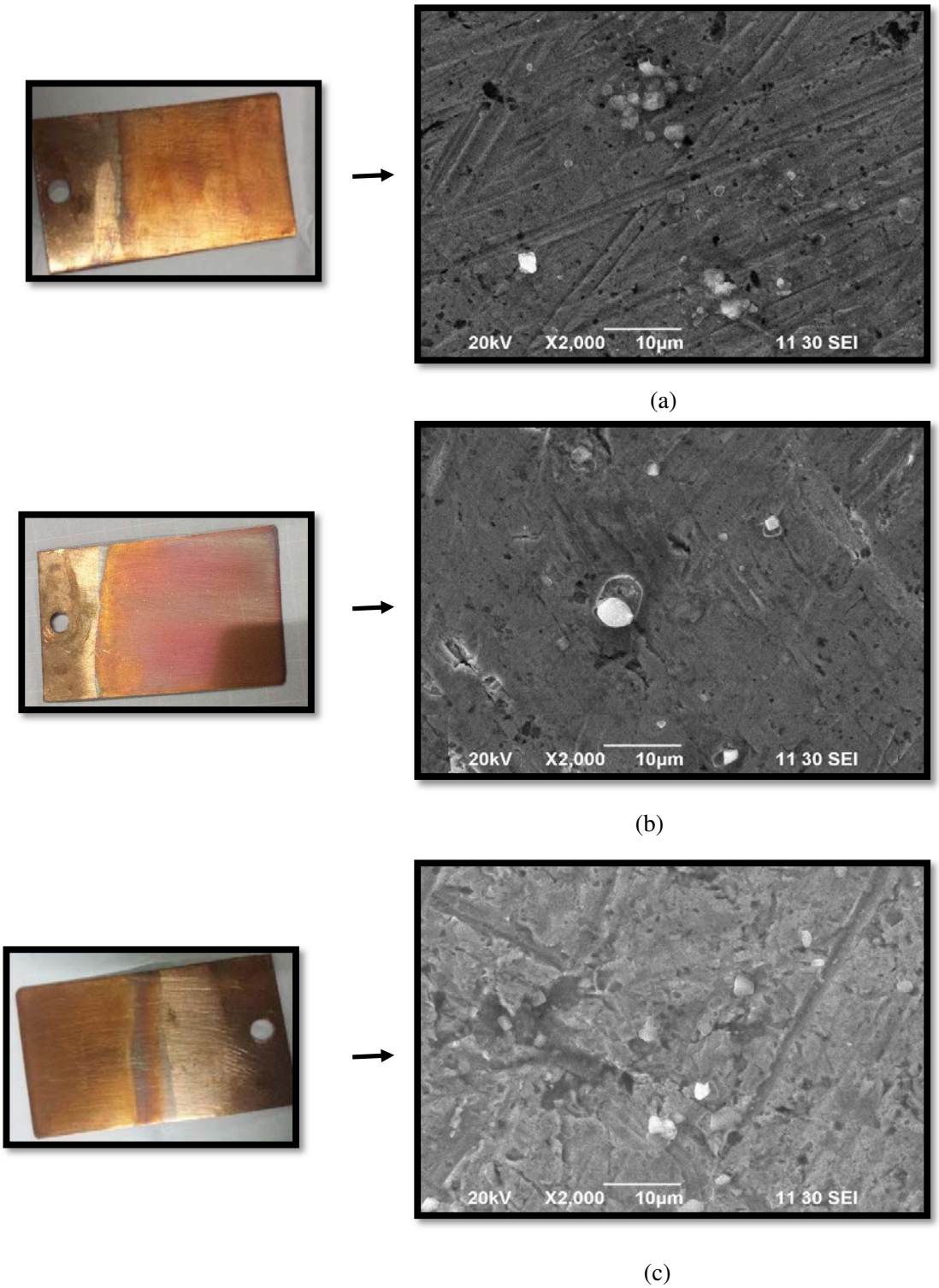


Figure 1: Deposited thin films and its corresponding SEM images (a) sample C (pH 13, conc. of Cu 0.024M) , (b) sample D ((pH 14, conc. of Cu 0.024M)
(c) Sample E (pH 14, conc. of Cu 0.036M)

3.2. Coating thickness calculation:

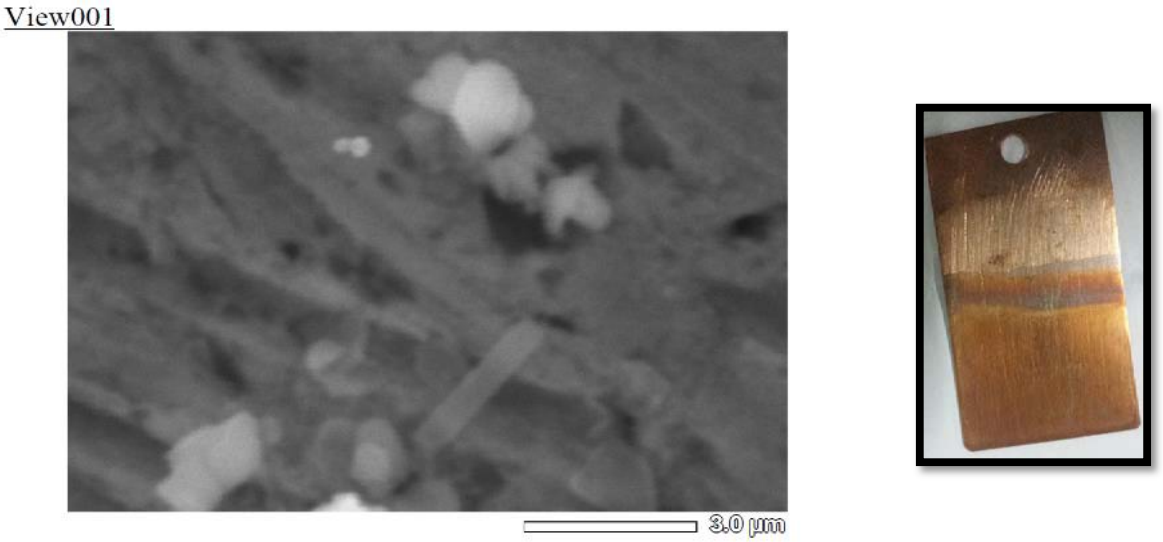
Table 3. Thickness of the deposited films

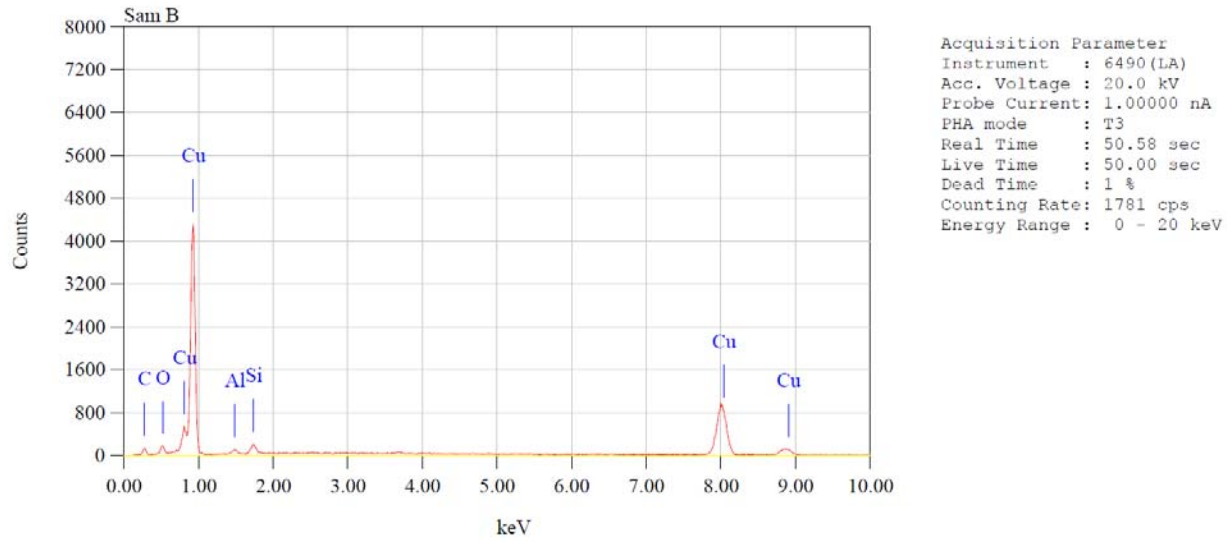
Sample	Coating thickness (µm)				Average thickness (µm)	Standard deviation
A	1.1	1.3	0.8	1.2	1.1	0.216025
B	3	3.3	2.1	2	2.6	0.648074
C	3.9	3.7	4.1	3.4	3.78	0.298608
D	0.79	0.39	0.24	0.5	0.48	0.232522
E	3.3	2.7	3.8	3	3.2	0.469042
F	1.9	1.5	2.6	2.8	2.2	0.60553
G	4	4.5	4.8	5.1	4.6	0.469042

Table 3 denotes the multiple readings of the coating thickness and average thickness of all the 7 samples chosen for our experiment. The thickness of the coating was calculated by coating thickness meter named as Fischer Dualscope. The thickness increased as solution gets more basic but dropped at maximum pH value while the concertation was kept fixed. When the pH was kept fixed thickness increased with increase in conc. of copper then dropped & then rose again.

3.3. EDS analysis- for deposited film

EDS analysis was performed for the analysis of mass percentage of copper and oxygen in the deposited films. To become cuprous oxide 11.18% oxygen and 88.82% copper by mass should be present whereas in cupric oxide 20.13% oxygen and 79.87% copper by mass should be present [6]. EDS was performed on sample (B) having pH 12 and concentration of copper being 0.024M. From Figure 2 we found that the mass % of copper was 91.23% and surprisingly the mass % of oxygen was close to 2%. Though the mass % of oxygen suggests that the deposition is not of cuprous oxide rather of copper alone and this deviation may be due to the non-uniform thin film deposition and presence of large percentage of copper is due to copper substrate itself.





Thin Film Standardless Standard Quantitative Analysis
Fitting Coefficient : 0.3803

Element		(keV)	Mass%	Counts	Error%	Atom%	Compound	Mass%	Cation	K
C K		0.277	3.70	539.04	0.04	15.61				0.7025
O K		0.525	1.89	721.32	0.10	5.96				0.2673
Al K		1.486	1.02	517.80	0.34	1.92				0.2022
Si K		1.739	2.15	1070.95	0.18	3.87				0.2052
Cu K	(Ref.)	8.040	91.23	9325.37	0.03	72.64				1.0000
Total			100.00			100.00				

Figure 2: EDS analysis of sample (B) with intensity peak

3.4. X-ray Diffraction (XRD) Analysis

XRD analysis was performed on sample F (0.038M, pH 14) and sample G (0.04M, pH14) to identify the phases present in the deposited films. In case of sample (F) the XRD spectra showed particularly two peaks- one at 43.158 ° (d spacing 2.09348 Å and relative intensity 100%) and the other at 50.272° (d spacing 1.8134 Å and relative intensity 73.42%) whereas in case of (G) two peaks were found at 43.325° (d spacing 2.08671 Å and relative intensity 100%) and 50.446° (d spacing 1.8134 Å and relative intensity 82.96%) respectively. According to JCPDS card no. 4-836 both of these peaks is the evidence of copper. The reason for obtaining sharp copper peaks and no cuprous oxide peaks as seen in Figure 3 may be due to the fact that the deposited films were very thin and X-ray penetration was large; hence, the larger copper peaks were those of the copper of the substrate.

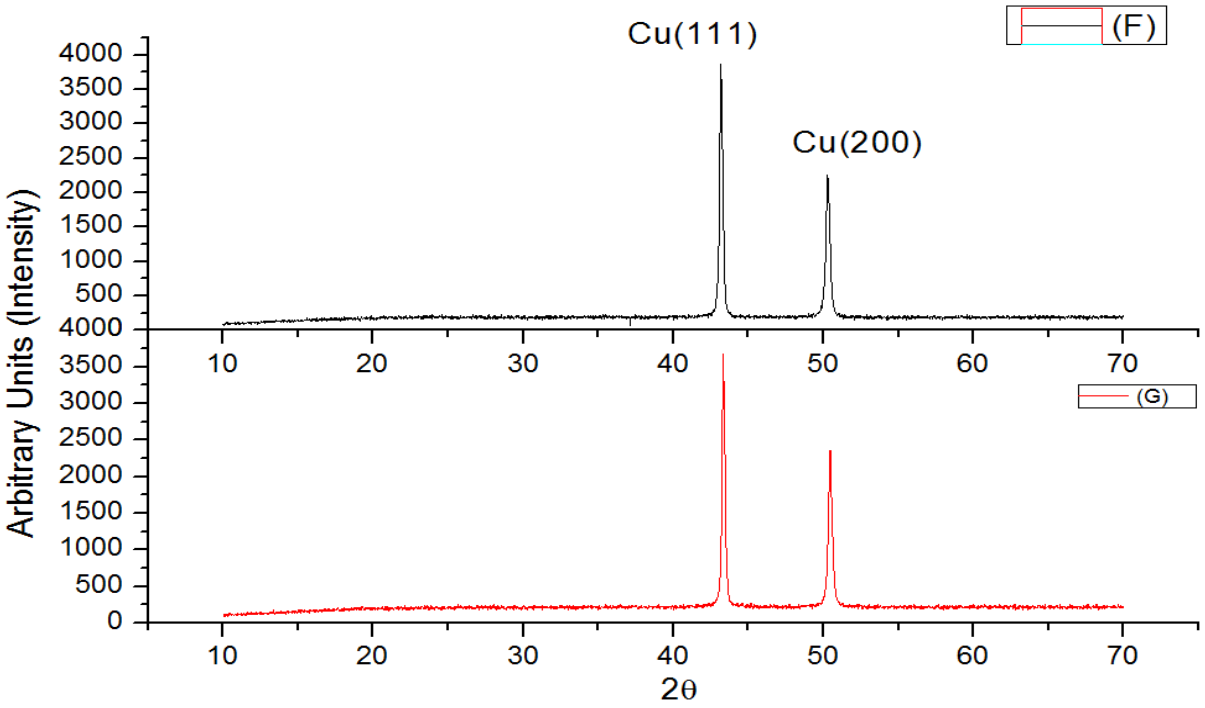


Figure 3: Overlay XRD spectra of sample (F) and (G)

3.5. UV-VIS SPECTROMETRY

To measure the optical absorption profile of the deposited films UV-Vis spectrometry was used. From Figure 4 for all the 7 samples it is observed that as the solution gets more basic (Table 1 and 2) absorption intensity gradually increased when the concentration was fixed. On the other hand, when pH was kept fixed at 14, on increase in concentration of copper absorption intensity increased but not significantly.

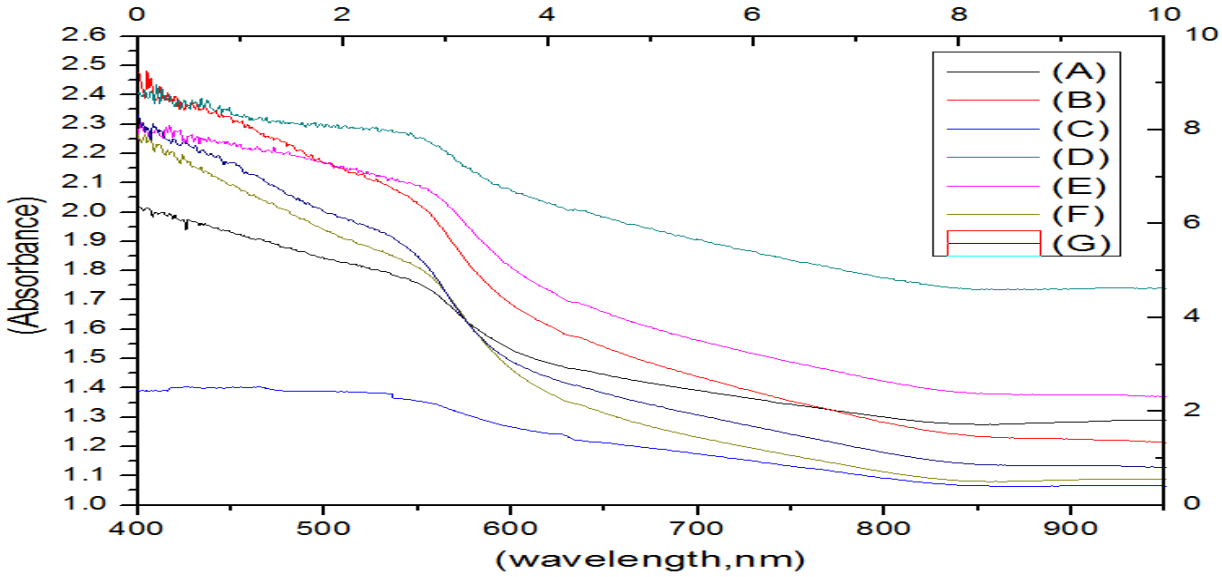


Figure 4: Overlay absorbance spectra of all the samples

3.6. BANDGAP MEASUREMENT

From the UV-Vis spectra, optical bandgap of the deposited films were calculated. Absorption coefficient α was calculated first and from this value $(\alpha h\nu)^2$ vs hν curve was plotted where hν is the photon energy. Cuprous oxide has a bandgap value of about 1.85-2.2 eV but the average bandgap value of the deposited films in this work was about 1.4 eV as seen in Figure 5 which is close to the bandgap value of metallic copper which might be due to the fact that lower film thickness may have caused greater penetration of the UV-Vis radiation and substrate spectrum may have overlapped with that of the film.

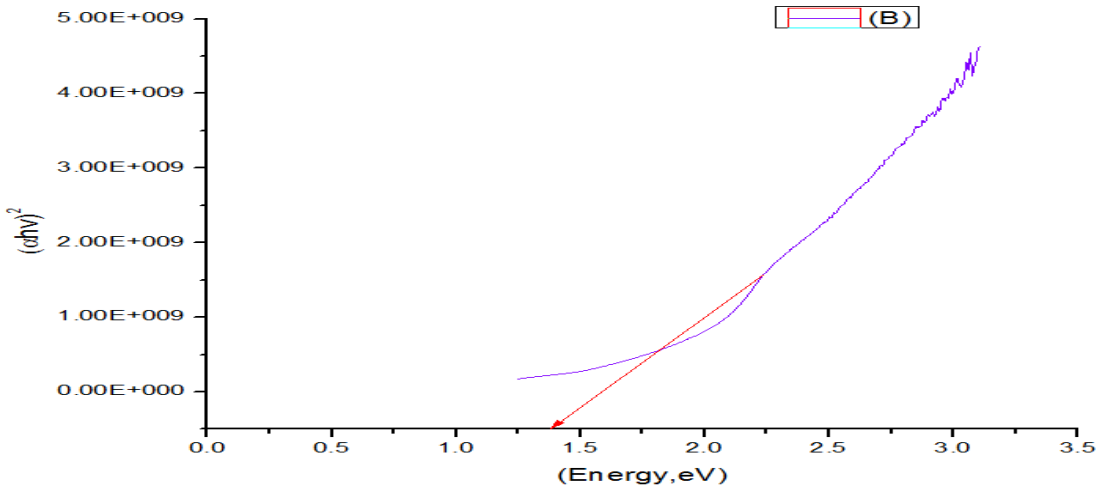


Figure 5: Bandgap measurement of sample (B).

4. Conclusion

The best parameters were pH 14 and concentrations of copper being 0.04M.The XRD pattern reveals the presence of Cu peak and EDS analysis confirms the presence of Copper and oxygen. The absorption intensity increased as the solution gets more basic and the bandgap value for the parameter (pH 14 and Conc. of Cu 0.04M) was about 1.4 eV. The thickness of the deposited film increased with increased pH value.

5. References

[1] Abdu, Y.* and Musa, *A.O,* "Copper(I) Oxide Cu_20 Based Solar Cells – A review*" Bayero Journal of Pure and Applied Sciences*, **2(2): 8 – 12**

[2] Charles Yianni Cummings," Electrodeposition and Characterization of Semiconductor Materials"

[3] Pim Reith & Gerben Hopman," Investigating electrodeposition to grow CZTS thin films for solar cell applications"

[4] Lytovchenko Oleksiyi, "Study of Thin Film Solar Cell based on Copper Oxide Substrate by DC Reactive Magnetron Sputtering" V. S. Arunach

[5] Abdelhamid El-Shaer , Abeer Ramadan Abdelwahed , AbdElraouf Tawfik , Mohsen Mossad , Dalal Hemada ," Effect of Deposition Parameters on Electrodeposited Cuprous Oxide Thin Films*," International Journal of Emerging Technology and Advanced Engineering*, Volume **4,** Issue **12.**

[6] Abu Sadat Md. Sayem Rahman, Md. Anisul Islam, Kazi Md. Shorowordi. Electrodeposition and Characterization of Copper Oxide Thin Films for Solar Cell Applications. *International Journal of Advanced Engineering and Nano Technology (IJAENT)*, ISSN: 2347-6389, Volume-**2** Issue-**2**, January 2015

[7] Charles B. Greenberg1 and J. Shannon Breininger, "Electroless Deposition of Cuprous Oxide." *J. Electrochem. Soc.* 1977 volume **124**, issue **11**, 1681-1685.
[8] Direct electroless deposition of cuprous oxide films. US 4315055 A. Feb 9, 1982.
[9] G Papadimitropoulos, N Vourdas, V Em Vamvakas and D Davazoglou. "Deposition and characterization of copper oxide thin films" © 2005 IOP Publishing Ltd *Journal of Physics: Conference Series*, Volume **10**, Volume **10.**
[10] R.Neskovska, M.Ristova, J.Velevska, M.Ristov "Electrochromism of the electroless deposited cuprous oxide films" Volume **515**, Issue **11**, 9 April 2007, Pages 4717-4721

Acknowledgements
The authors would like to thank Centre for Advanced Research in Sciences (CARS), DU for helping us in doing various characterizations. We also acknowledge partial financial support from Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology (BUET). We are also grateful to the laboratory assistants of MME department for their constant support.