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Technical Report

Characteristics of Electron Beam Evaporated and Electrodeposited Cu_2O thin films – Comparative study

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Cuprous oxide thin films (Cu_2O) are deposited by electron beam evaporation of Cu_2O powder and electrodeposition. As-deposited films are annealed at 150,250°C and the effect of annealing on structural and optical properties of the films are studied. The films are characterised by X-ray diffraction and UV-Vis. Spectroscopy. X-ray analysis revealed that the as-deposited films are amorphous while the annealed films are polycrystalline in nature. The grains had preferred orientation along (111) direction. Optical transitions involved are found to be direct and allowed and the calculated band gap value is in the range of 2.6-2.3 eV. A red shift in the optical band gap of the films is observed upon annealing. Though the prominent characteristics exhibited by Cu_2O thin films deposited by both the methods are similar there is marked difference in their characteristics in the application point of view.

Keywords: Cuprous oxide, Electron beam evaporation, Electrodeposition , X-ray diffraction, Band gap.

1. INTRODUCTION

Cu_2O is a versatile metal oxide which finds application in number of fields such as solar cells, photocatalysis, electrochromic devices and sensors [1-4]. Cuprous oxide (Cu_2O) is regarded as a promising material for solar energy application because of its suitable band gap and high absorption coefficient in the visible region. In addition with good optical and electrical properties the material has many advantages such as availability and abundance of the starting materials, non-toxic nature and low production cost [1,5]. Number of reports are available on the deposition and characteristics of the films deposited by various techniques such as electrodeposition [6], thermal evaporation [7], sol–gel [8],

solution growth [9], electron beam evaporation [10], pulsed laser deposition [11], chemical vapour deposition [12], and molecular beam epitaxy [13], magnetron sputtering [14–21]. In all deposition techniques, obtaining single phase material is challenging since the material easily gets converted to CuO. Deposition of Cu_2O film by evaporation of Cu_2O powder is a direct and simple way of deposition of Cu_2O thin film and the incorporation of impurities is reduced in this method when compared to chemical and electrochemical methods since it is carried out under vacuum. In the present work a novel attempt has been made to deposit Cu_2O thin films by electron beam evaporation of Cu_2O powder and by electrodeposition and to compare thecharacteristics of the films deposited by these two methods. Effect of post deposition annealing on the structural and optical properties of the films are also reported in this paper.

2. EXPERIMENTAL

Thin films of cuprous oxide (Cu2O) were deposited by electron beam evaporation technique using HINDHIVAC vacuum coating unit (model: 12A4D) equipped with electron beam power supply (model: EBG-PS-3K). Ultrasonically cleaned microscopic glass plates are used as the substrates. Source material was prepared by precipitation technique using copper nitrate, TEA and hydrazine where TEA and hydrazine served as complexing and reducing agents respectively. The reaction bath was kept still at room temperature for six hours and the material got precipitated at the bottom of the container. The precipitate is separated and washed with deionised water and acetone. The prepared power is made into a pellet and it is characterized by XRD for phase formation. After confirming the crystal phase of the material, the pellet is transferred into graphite crucible kept in water cooled copper hearth of the electron gun. The Cu2O pellet was heated by means of an electron beam collimated from the d.c. heated tungsten filament cathode. The surface of the Cu2O pellet was bombarded by 180° deflected electron beam with an accelerating voltage of 5 kV and a power density of about 1.5 kW/cm2. Prior to deposition vacuum of the order of 10-5 mbar was established in the deposition chamber. The substrate-target distance was 15 cm and films are deposited on the substrates kept at room temperature. Cuprous oxide thin films are potentiostatically electrodeposited on indium tin oxide coated glass substrates. A conventional three-electrode cell was used where the ITO coated glass, platinum and Ag/AgCl electrodes served as the working, counter and reference electrodes respectively. The film deposition conditions such as pH, deposition potential, bath temperature and electrolyte concentration are optimised. Deposition potential and solution PH are chosen as the variable deposition parameters and films are obtained by varying these two parameters and while the other parameters are maintained at optimum conditions. The films deposited at a pH of 11 are found be uniform and hence the films deposited under this pH are used for characterisation studies. The as-deposited films are annealed at 250°C for an hour.

Table 1. Film deposition conditions

Sl.No.	Concentration of Electrolyte (M)		PH of the bath	Deposition potential (V)	Thickness of the film (μm)
	Copper sulphate	Sodium Lactate			
1	0.001	3.0	9	0.4	2.15
2	0.001	3.0	11	0.4	4.61
3	0.001	3.0	13	0.4	3.65
4	0.001	3.0	11	0.3	3.69
5	0.001	3.0	11	0.5	4.58

As-deposited films are annealed in air at 150 and 250°C for an hour. Crystal structure of the Cu_2O thin films is studied by Panalytical (X-Pert Pro) X-ray diffractometer (XRD). Thickness of the deposited films is measured by stylus profilometer (Surftest-330) and the thickness of the films was found to be in the range of 0.5-1 μm. Surface morphology of the films is studied using scanning electron microscope (SEM JEOL JSM-7000F). UV-Vis-NIR double beam spectrophotometer (JASCO V-570) is used to record the optical transmittance spectra of the films. A fluorescence spectrometer is used to record the photoluminescence spectra of the films (VARIAN CARY ECLIPSE). The resistivity of the films is studied using a four probe apparatus (SES Instruments, Roorkee).

3. RESULTS AND DISCUSSION

The XRD patterns of the cuprous oxide thin films are shown in figure 1,2 . Electrodeposited cuprous oxide thin films are polycrystalline in nature which is evident from the appearance of well defined peaks in pattern.

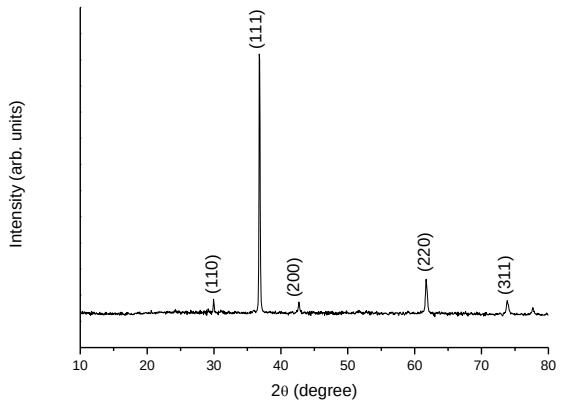


Figure 1. XRD pattern of electrodeposited Cu_2O thin film annealed at 250°C

The crystal planes are identified by comparing the peak positions with the standard data (JCPDS card no. 03-0898). Very broad peaks are obtained in the XRD pattern of electron beam evaporated Cu_2O thin films which indicate nanocrystalline nature of the films. The Cu_2O thin films deposited by both the deposition methods are of single phase and no secondary phase (CuO) was observed even after annealing the films at 250°C.

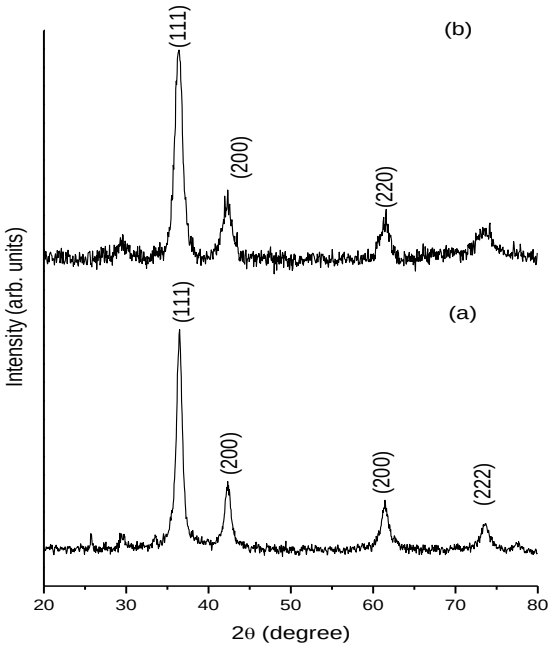


Figure 2. XRD pattern of a) Cu_2O powder b) Cu_2O thin film annealed at 250°C

Film Morphology

The surface morphology of the electrodeposited and electron beam evaporated films is analysed using scanning electron microscopy.

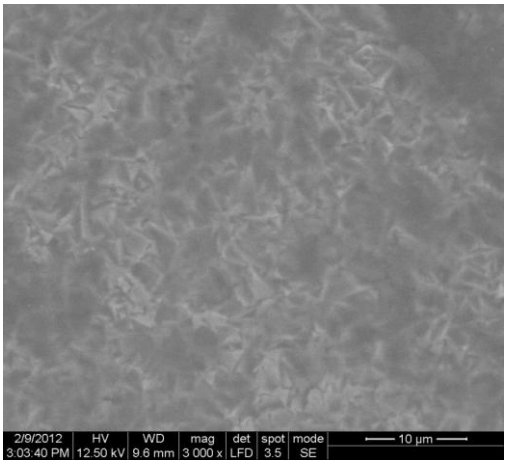


Figure 3. Scanning electron micrograph of electrodeposited Cu_2O thin film

The scanning electron micrograph of the films are shown in figures 3,4 . Electrodeposited film consisted of densely packed pyramid-like microstructures while electron beam evaporated films are highly porous and exhibited a net-like microstructure. SEM analysis also emphasises the observation that electrodeposited films had larger grains when compared to electron beam evaporated films. Moreover the electrodeposited films are densely packed which in turn will enhance the conductivity of the material. The electron beam evaporated films are highly porous there by suggesting the superiority of electrodeposited film over electron beam evaporated film for photovoltaic applications.

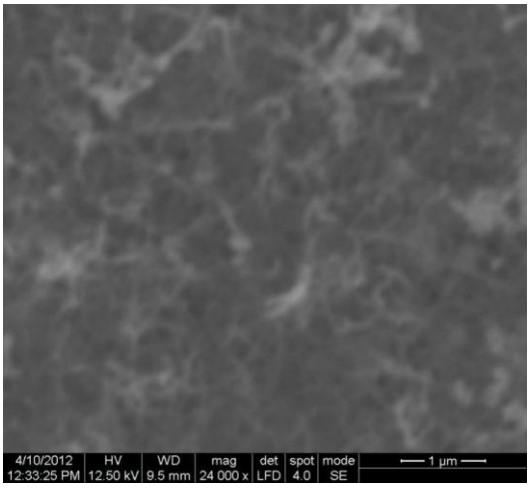


Figure 4. Scanning electron micrograph of electron beam evaporated Cu_2O thin film

Optical Properties of Cu_2O thin films

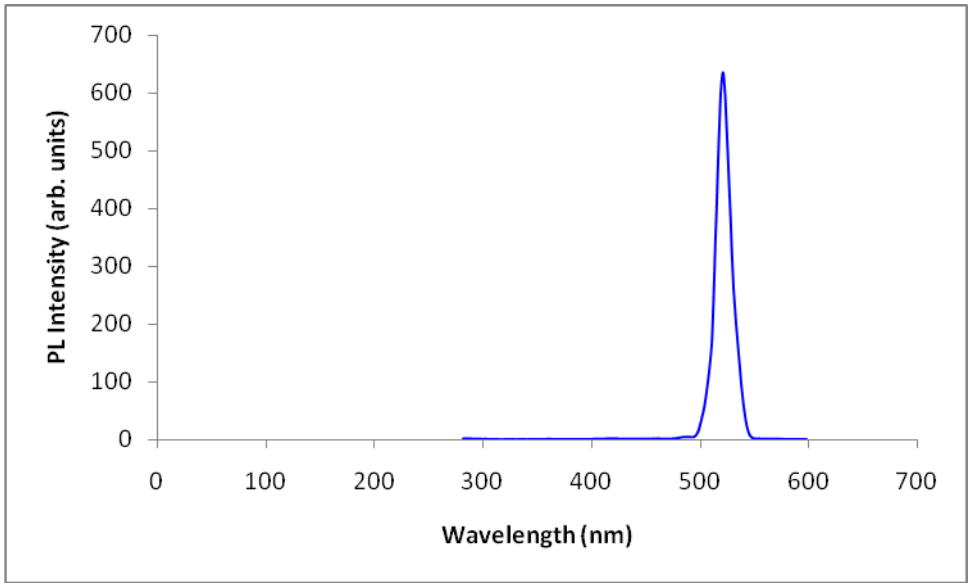


Figure 5. Photoluminescence spectra of electrodeposited Cu_2O thin film

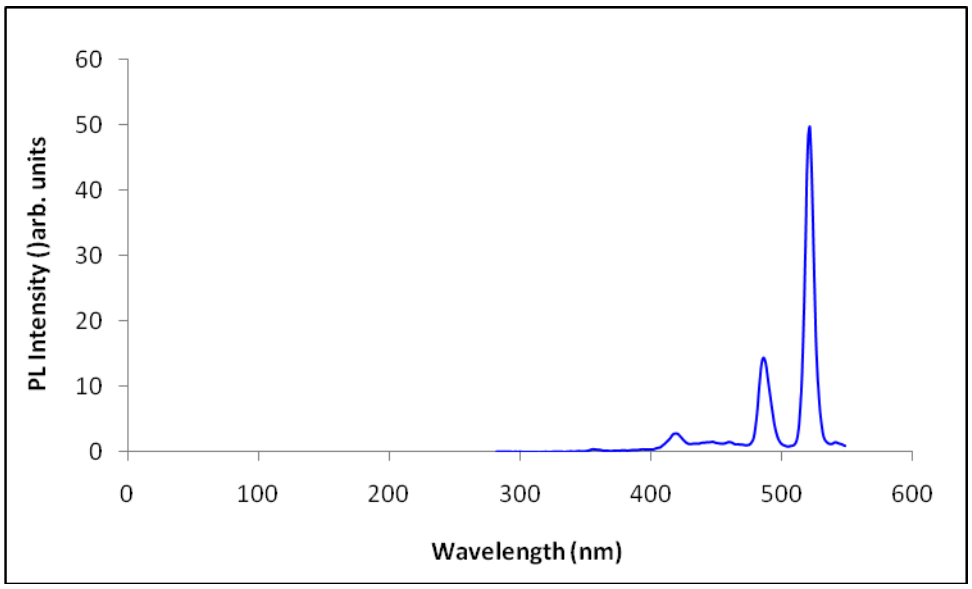
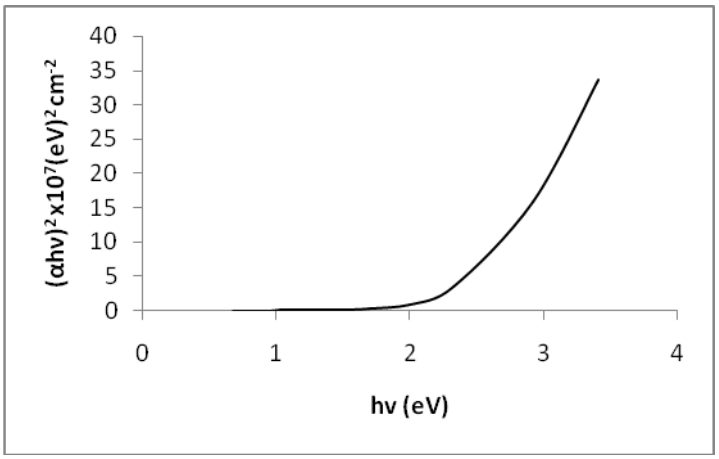
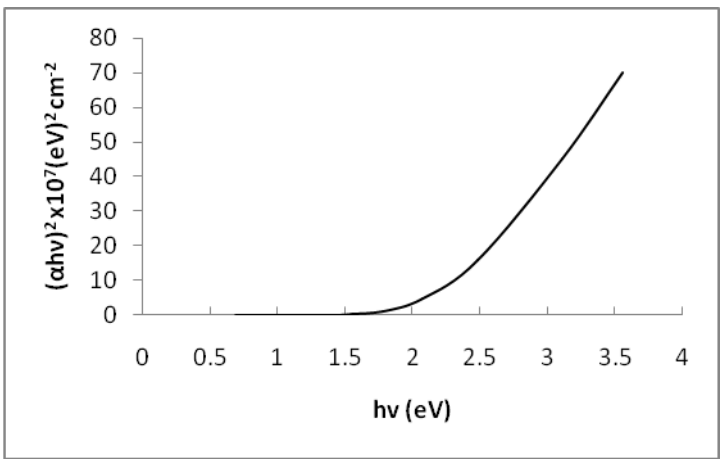


Figure 6. Photoluminescence spectra of electron beam evaporated Cu_2O thin film



A



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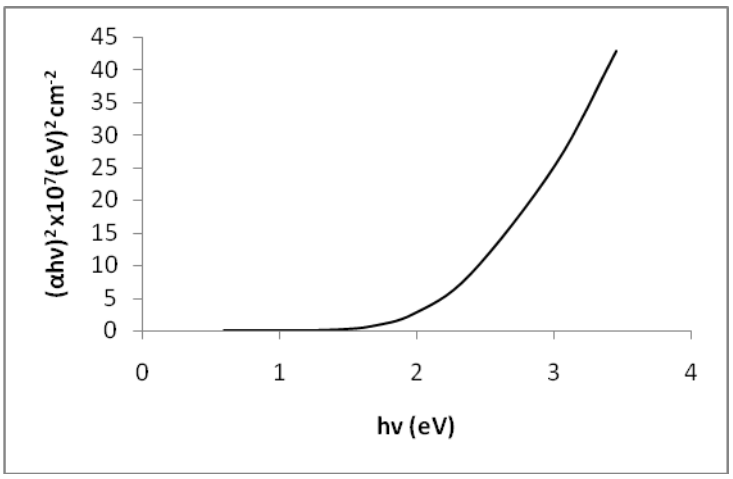

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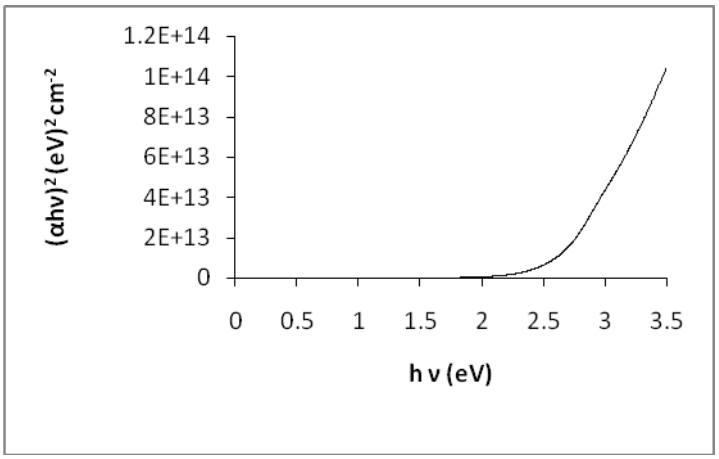
Figure 7. $(\alpha h\nu)^2$ vs. hν plots of electrodeposited Cu_2O thin films deposited at different deposition potentials a) 0.3V b) 0.4V c) 0.5 V



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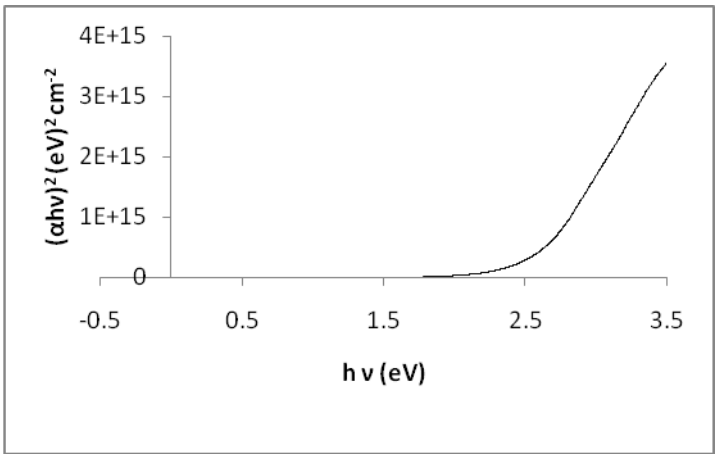

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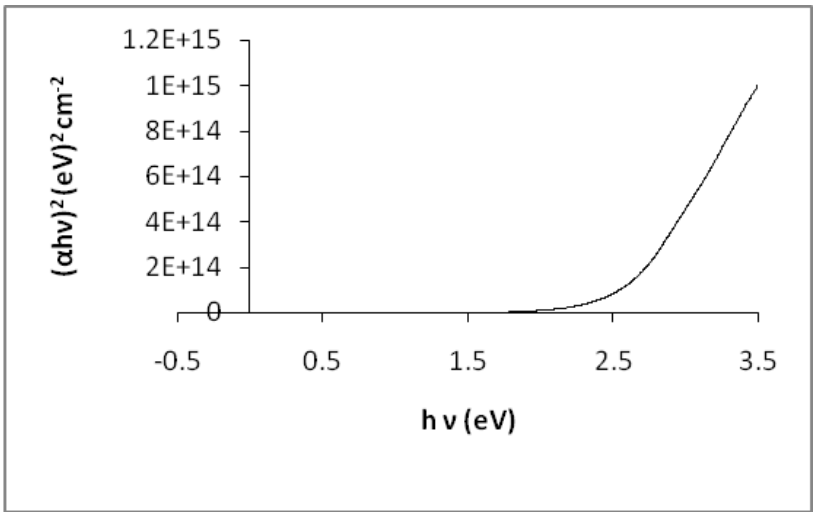

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Figure 8. $(\alpha h\nu)^2$ vs. hν plots of electron beam evaporated Cu_2O thin films of different thicknesses a)410 nm b)660 nm c) 880 nm

Table 2. Band gap of electrodeposited Cu_2O thin films

S.No.	Deposition Potential (V)	Band gap (eV)
1	0.3	2.4
2	0.4	2.2
3	0.5	2.1

Table 3. Band gap of electron beam evaporated Cu_2O thin films

S.No.	Thickness (nm)	Band gap (eV)
1	410	2.65
2	660	2.55
3	820	2.5

The films exhibit photoluminescence peaks at 480, 520 nm. The peak at 520 nm corresponds (figure 5, 6) to band to band transition involving photon absorption while the satellite peak occurring at 480 nm can be attributed to 'Cu' vacancies(figure 5). The linear nature of $(\alpha h\nu)^2$ vs. hν plots (at absorption edge) indicates that the optical transitions taking place in the material are direct and allowed (figure 7, 8). Optical band gap of the films are calculated by extrapolating the linear part of the curve to the energy axis. The calculated values of the band gaps(table-2 and 3) are well with the reported values [1, 18]

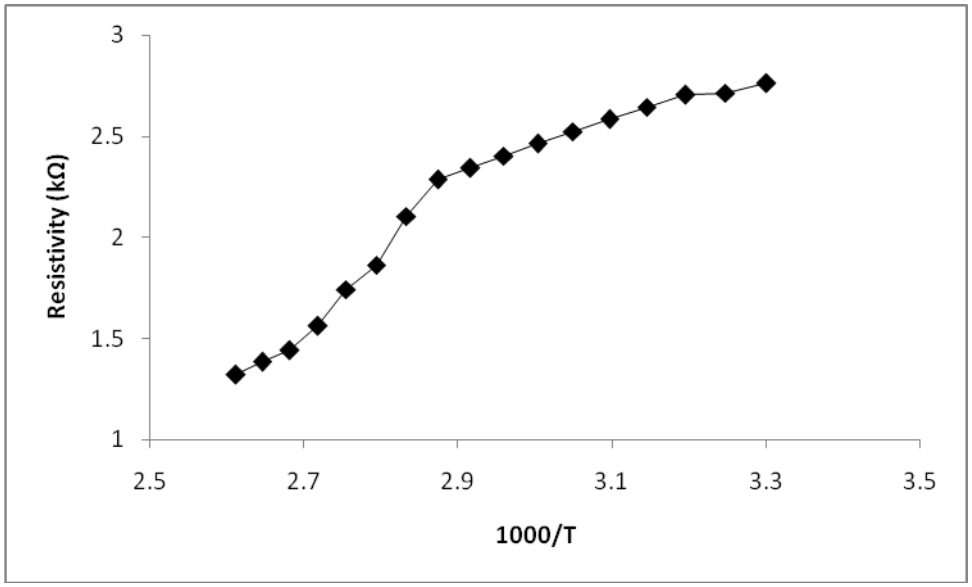

Figure 9. Variation of resistivity of electrodeposited Cu_2O thin film with temperature

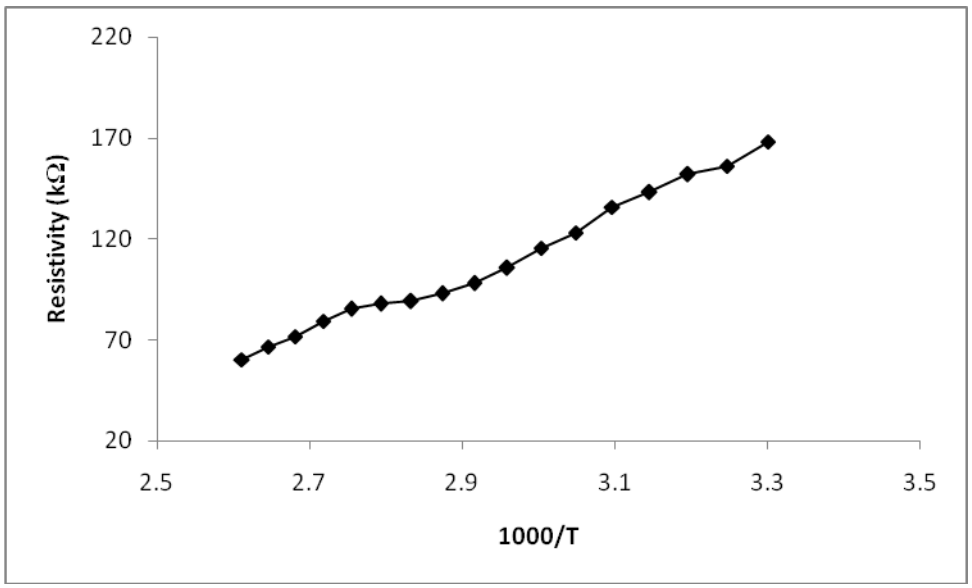

Figure 10. Variation of resistivity of electron beam evaporated Cu_2O thin film with temperature

Resistivity of Cu_2O thin films deposited by electrodeposition as well as electron beam evaporation decreases with increase in temperature there by suggesting the semiconducting nature of the films (figure 9,10). The resistivity of electrodeposited Cu_2O thin films is low (kΩ) when compared with electron beam evaporated Cu_2O thin films (MΩ). The electrical resistivity results agree well with the optical band gap values. Optical band gap and electrical resistivity are the most significant parameters defining the suitability of a material for photovoltaic application. Since the Cu_2O thin films deposited by electrodeposition exhibit lower band gap and lower resistivity when

compared to electron beam evaporated Cu_2O thin films, it may be concluded that the electrodeposited Cu_2O thin films are more suitable for photovoltaic application when compared to electron beam evaporated Cu_2O thin films.

4. CONCLUSIONS

Cuprous oxide (Cu_2O) – a material with potential for application in number of fields such as solar energy conversion, photocatalysis, sensors etc. has been prepared in thin film form using an electrochemical (electrodeposition) and a physical method (electron beam evaporation). A systematic study on the properties of cuprous oxide thin films deposited by electrochemical and physical method revealed the suitability of cuprous oxide thin films in two different applications. The electrodeposited cuprous oxide thin films had microcrystalline structure with a preferred orientation along (111) direction. The film was densely packed with cone- like microstructures. They have also exhibited good electrical conductivity and low optical band gap. In contrast, electron beam evaporated films were nanocrystalline in nature. These films had a highly porous net-like structure. The films are highly resistive when compared to electrodeposited films and also exhibited a larger band gap. These results reveal that he electrodeposited and electron beam evaporated cuprous oxide thin films are suitable for the preparation of photovoltaic cells and gas sensors respectively.

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