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Review Article

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ABSTRACT

Copper oxide films have direct band gap of about 1.2 to 2.6eV. They could be used in many applications including solar cell, sensor and optoelectronic industry. The aim of this work is to investigate the properties of copper oxide thin films under various deposition methods. The obtained results based on the structure, optical, morphology and electrical properties are discussed. The overall results found that different researchers have reported different properties of copper oxide based on experimental conditions.

INTRODUCTION

In recent years, chalcogenide thin films and metal oxide thin films (Table 1) have received much attention. There are two major groups of copper oxide, namely cupric oxide (CuO) and cuprous oxide (Cu_2O). Cu_2O films have cubic structure [Buono-Core *et al*., 2007; Reddy *et al*., 2010] with a lattice parameter of 4.27 Åand direct band gap of 2.1 to 2.6 eV [Mugwang *et al*., 2013]. Meanwhile, CuO films are monoclinic crystal structure semiconductor with direct band gap of 1.2 to 2.1 eV. These films have good electrical and optical properties. Because of their specific unique properties, they have been used as solar cells, cathode in lithium primary cell, gas sensor, electro chromic devicesand electronic device fabrication.

In this work, the preparation of CuO and Cu_2O films by using various deposition techniques will be investigated and discussed. The resulting films are characterized in terms of optical, compositional, structural, morphological and electrical properties.

LITERATURE SURVEY

Cu_2O films are prepared by sol-gel spin coating method on indium tin oxide glass substrate using various additives such as ethylene glycol and polyethylene glycol as described by Halin *et al* (2014). It is evident from field emission scanning electron microscope (FESEM) analysis that film thickness and band gap were increased from 102 to 395 nm and 1.85 to 1.9 eV, respectively after adding polyethylene glycol. In another case, the addition of ethylene glycol with thickness of 59 nm, indicates that the films were irregular in shape. Also, these films display the lowest optical absorbance and the band gap value was found to be 1.75 eV.Lastly, they conclude that additives added lead to different optical properties and microstructures.

The influences of temperature of oxidation on the thermal vacuum evaporated copper films were investigated at four different temperatures of 150, 250, 350 and 450 °C for two hours each as reported by Kasim *et al* (2013). The films deposited at 150 °C indicate very low resistivity value of $1.92X10^{-6}$ ohm.cm. However, at the end of the oxidation treatment when the temperature varied from 250 - 450 °C, the resistivity changes to higher value in the range of 127 to 1076 ohm.cm. In terms of energy dispersive X-ray (EDX) analysis, the percentage of copper decreases and percentage of oxygen increases, under these deposition conditions.

Cu_2O films were prepared by electro deposition method onto substrates using aqueous solution of cupric acid, lactic acid and sodium hydroxide as suggested by Mahalingam *et al* (2006). X-ray diffraction (XRD) studies indicated that the formation of

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cubic structure with the preferential orientation (200). Furthermore, they point out that the crystal sizes were about 210 nmfor as-deposited films. Optical and electrical studies found that the band gap and electrical resistivity value were 1.98 eV and 10^6 ohm.cm, respectively. On the other hand, the electrodeposited Cu_2O thin films were prepared at bath temperatures of 30-90 °C and pH values of 5-11 as proposed by Mahalingam *et al* (2005). They observe that Cu_2O peaks could be confirmed at higher pH (pH 9, 11). However, metallic Cu peaks could be seen in the XRD patterns at the lower pH (less than pH 7). In terms of the effect of bath temperature, they can explain that the increase of grain size and the peak intensities due to the increased rate of deposition at higher temperatures.

Table 1 Examples of chalcogenide metal films and metal oxide films

Chalcogenide metal thin films	
Ni_4S_3	Anuar *et al* (2011d)
CuS	Anuar *et al* (2013)
In_2S_3	Mesa *et al* (2015)
CoS	Kamble *et al* (2015)
FeS	Muhammad *et al* (2015b)
	Anuar *et al* (2010b)
ZnS	Bacha *et al* (2016)
	Anuar *et al* (2011c)
	Muhammad *et al* (2015a)
SnSe	Anuar *et al* (2012)
PbS	Ho *et al* (2013a)
Cu_2S	Nourhene *et al* (2010)
ZnSe	Anuar *et al* (2011a)
	Agawane *et al* (2014)
CdSe	Deshpande *et al* (2013)
PbSe	Anuar *et al* (2011b)
As_2S_3	Mane *et al* (2004)
CdTe	Chauhan *et al* (2014)
SnS	Ho *et al* (2013b)
CdS	Barote *et al* (2011)
FeS_2	Anuar *et al* (2010a)
$Ni_3Pb_2S_2$	Ho (2015)
$CuInS_2$	Lugo *et al* (2014)
Cu_4SnS_4	Anuar *et al* (2009)
Metal oxide thin films	
Zinc oxide	Shaikh *et al* (2016)
	Ismail *et al* (2016)
	Zhao *et al* (2013)
Tin oxide	Shadia (2012)
	Khallaf *et al* (2012)
	Rifai *et al* (2011)
	Han *et al* (2006)
Nickel oxide	Osuwa and Onyejiuwa (2013)
	Reddy *et al* (2011)

Photoluminescence (PL) behavior of chemical bath deposited Cu_2O thin films were studied by Ahirrao *et al* (2011). The chemical bath contains sodium thiosulphate, copper sulphate and sodium hydroxide. The photoluminescence study indicated there are three peaks could be seen in spectra. The obtained results show that the peak at 627 nm (red emission) is more intense than the peaks at 503 and 540 nm (green emission). Solache-Carranco *et al* (2009) have synthesized Cu_2O films using the two step crystallization technique. In the first part, the copper plates are oxidized at 1020 °C. Then, the growth of large crystalline is promoted by annealing process for long times as indicated in the second part. The obtained films were analyzed using PL spectra. The results reflect that there are two strong emission peaks at 720 and 920 nm. Rachel *et al* (2012) have compared the characteristics of the Cu_2O films prepared using electro deposition method and electron beam evaporation method. A fluorescence spectrometer was used to record the photoluminescence spectra during experiment. It is observed that the evaporated films display two peaks at 480 nm and 520 nm. However, the spectra show only one peak for electrodeposited films. They explain that 480 nm is due to copper vacancies, meanwhile the peak at 520 nm can be attributed to band to band transition involving photon absorption.

The influence of sputtering power and pressure on the properties of Cu_2O films prepared using magnetron sputtering method was studied by Rastkar *et al* (2009). They found that the increase in pressure led in a higher growth rate than increasing sputtering power.In addition, they also mentioned that the increase in power formed films that were detrimental to the optical transmission properties. Some researchers (Zhu *et al*., 2009) have investigated sputtered thin films by varying oxygen partial pressure in their experiment. The synthesis of Cu_2O, CuO and Cu_4O_3 with different microstructures could be observed under these deposition conditions. However, only Cu_2O films could be seen at a constant oxygen partial pressure of 0.066 Pa. Further, they reveal that these films have a very high absorption in the visible region.

Morales *et al* (2005) have reported the preparation of CuO films using spray pyrolysis method. An aqueous solution of Cu $(CH_3COO)_2$ was pumped into the air stream by spray nozzle for a preset time of 30, 60 and 80 minutes. They found that increasing of deposition time led to a dense, compact homogeneous films and the formation of some cracks in parallel to the increase in the total amount of deposited. For instance, the film thickness and mass deposited was 660, 1100, 1250 nm and 0.36, 0.56, 0.73 $mgcm^{-2}$, for the films prepared for 30, 60 and 80 minutes, respectively. On the other hand, Varadharaja *et al* (2012) reported the influence of different concentrations of precursor on the sprayed CuO films. They observe that the formation of films as amorphous nature for the films prepared using 0.02 M to 0.06 M concentrations of precursor. The films prepared using higher concentrations of precursor such as 0.08 M and 0.1M were found to be polycrystalline in nature with a monoclinic structure. The scanning electron microscopy (SEM) results show that the grain size was increased as the concentration increases. In another case, the copper (II) chloride will be dissolved in deionized water to deposit CuO films onto glass substrate using spray pyrolysis method was constructed by Saravanakannan& Radhakrishnan(2014). They have reported that the band gap, resistivity and film thickness increase with increasing solution concentration of copper chloride from 0.1 M to 0.2 M.

The influence of annealing temperature on the CuO films prepared by successive immersion of glass substrates in solutions was investigated by Mohd *et al* (2011). The XRD data reveals that there are two phases (CuO and Cu_2O) coexist for the films deposited at 300 °C. However, there is only CuO peak could be observed for the films deposited at 400 °C. This data was supported by Fourier transform infrared spectroscopy (FTIR) results. The FTIR measurements proved that the conversion from copper (II) oxide into copper (I) oxide after annealing the films at 300 °C.

Reactive radio frequency magnetron sputtering method was employed to prepare CuO films as describe by Cho (2013). The films prepared at 25 °C showed a monoclinic structure and the crystallite size was about 50 nm. Lastly, they also point out that the optical transmittance of 63% in the wavelength range of 800 to 1100 nm for the annealed films at 300 °C.

CONCLUSIONS

Cu_2O films and CuO films were successfully deposited by using various deposition methods. The obtained films were characterized and analyzed using various tools such as XRD, SEM, FTIR, EDX and UV-Visible spectrophotometer.

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