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Electron Beam Evaporated Silver Doped Copper Oxide Thin Films

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ABSTRACT:
Thin films of pure and Ag doped Cu_2O have been deposited onto glass substrates by using electron beam evaporation. The as deposited films were characterized by X-ray diffraction, scanning electron microscopy andfour-probe technique. The intensity of peak decreased and peak width increased when Ag incorporated into Cu_2O. The obtained average crystallite size values are 6, 5 and 7nm for pure, Ag 4at.% and Ag 8at.% doped Cu_2O films. The Ag(4at.%) doped Cu_2O films shows dense structure. The electrical resistivity of Ag doped Cu_2O films are lower than the pure Cu_2O films.

KEYWORDS: Thin films; Copper oxide; Silver; Electron beam evaporation

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I. INTRODUCTION

Cuprous oxide (Cu_2O) is a p-type semiconductor and more suitable for photovoltaic devices, gas sensors, light emitting diodes, and rectifiers, because of its non-toxicity, high optical absorption coefficient, direct band gap of 2.1 eV and abundant raw material [1-4]. Cu_2O is most used absorber layer in thin film heterojunction solar cells due to its theoretical energy conversion efficiency of 20% [5]. However, the reduction of photocurrent was observed in Cu_2O due to its high resistivity [6]. According to the recent research reports the properties of semiconductor oxide films changed by doping of noble metal into the oxide matrix [7]. The small amount of silver added to the Cu_2O filmsmay significantlyreduce the resistivity at room temperature and it can also influence the band gap of Cu_2O [8,9].Various thin film deposition techniques such as magnetron sputtering [6,10], solution method [11], electro-deposition [12] have been attempted for the deposition of Ag-Cu_2O films and composites. To the best of our knowledge, no reports on the electron beam evaporated Ag doped Cu_2O films. Electron beam evaporation is an efficient technique for the thin film growth because of material loss is minimal, uniformity of the films over the substrate, useful for depositing alloy and compound materials, films having the stoichiometry close to the bulk. In the present work, pure and Ag doped Cu_2O films prepared at room temperature with different Ag amounts and study their properties.

II. EXPERIMENTAL

The pure(Cu_2O) and Ag doped Cu_2O (Ag-Cu_2O) thin films were prepared on the glass substrates using high purity Cu_2O and Ag-Cu_2O pellets by electron beam evaporation. The vacuum chamber was pumped with the combination of diffusion pump and rotary pump and is capable of creating an ultimate vacuum of $4x10^{-4}$Pa. The pressure was measured using combination of Pirani–Penning gauge. The pellets were prepared using high purity (99.99%) Cu_2O and Ag powders. The pellets were kept in a water-cooled copper crucible.The electron beam source and the substrate distance was60mm.The deposition parameters maintained during the preparation of Cu_2O films are given in Table 1.

Table.1. Deposition parameters of pure and Ag doped Cu_2O films during deposition

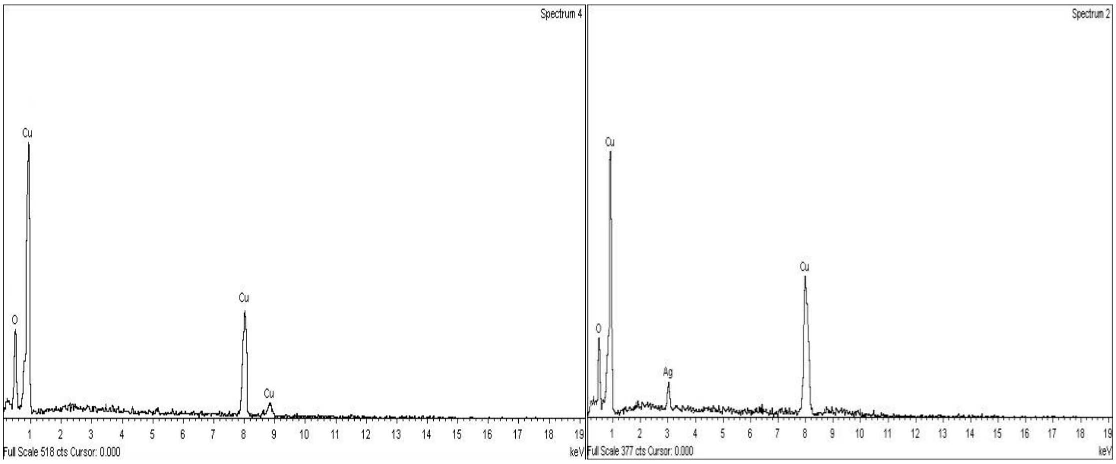
Deposition method : electron beam evaporation
Power source : e-beam power supply (3kW)
Pellet : Cu_2O and Ag-Cu_2O(10mm dia and 3mm thick)
Substrates : Glass
Target to substrate distance : 60mm
Ultimate pressure (P_U) : $4x10^{-4}$Pa
Evaporation pressure (P_W) : $3x10^{-2}$Pa
Substrate temperature (T_S) : 303K
Accelerating voltage : 4kV (films thickness ~187nm)
Filament current : 30mA
Deposition time : 8 to 11min

The chemical composition of the films was analyzed by Energy Dispersive Spectroscopy (EDS) attached with SEM of model Oxford instruments Inca Penta FET X3. The crystallographic structure of the films was analyzed by Seifert 3003TT X-ray diffractometer (XRD), using Cu Kα radiation (k = 0.1546 nm). The microstructure of the films was studied by scanning electron microscopy (SEM). The electrical properties of the films were measured by using standard four-probe method.

III. RESULTS AND DISCUSSION

3.1. Elemental composition and structural properties

Fig.1. shows the EDS spectra of pure and Ag(4at.%) doped Cu_2O films. EDS results confirmed that the films consist of copper, silver and oxygen only. The amounts of copper and oxygen were decreased after doping the Ag into Cu_2O. The obtained elemental composition results were listed in Table 2.



(a) (b)

Fig.1. EDS spectra (a) pure and (b) Ag(4at.%) doped Cu_2O films.

Table 2. Chemical composition of pure and Ag doped Cu_2O films.

Sample history	Element	Atomic percentage
Cu_2O	O	37.12
	Cu	62.88
Ag(4 at.%)-Cu_2O	O	36.81
	Cu	59.16
	Ag	4.03

Fig.2. shows the XRD patterns of pure and Ag dopedCu_2O films. The deposited films are exhibited the cubic structure of Cu_2O only and no peaks of Ag compounds or CuO are observed upto dopant concentration of 4at.%. This was may be due to the Ag or it oxide phase may form solid solution with copper oxide [6] or small content of Ag lies below the limit of XRD detection[13].However, the intensity of peak decreased and peak width increased in Ag doped Cu_2O films, this may be due to the segregation of Ag in the grain boundaries and/or formation of stresses induced by the difference in ion size between Cu and Ag. This indicates that adding of the Ag inhibits the growth of the crystallintiy of the Cu_2O. On further increasing the Ag concentration to 8at.%, the peak position shifted towards lower angle side, peak intensity increased slightly and Ag_2O phase was observed along with Cu_2O.

The average crystalline size of Ag doped Cu_2O films was calculated by using Scherrer's equation [14]. The crystalline size of the films was not changed greatly after doping the Ag in to the Cu_2O. The obtained values are 6, 5 and 7nm for pure, Ag 4at.% and Ag 8at.% doped Cu_2O films.

The lattice parameter (a) of the films was calculated using the relation

$$d = a / (h^2+k^2+l^2)^{1/2} \qquad \text{-----------(2)}$$

where h, k and l are the Miller indices. The interplaner spacing (d) was calculated from the X-ray diffraction data using the Bragg's relation. The obtained lattice parameter values are lower than the standard value (ICDD = 4.269Å**)**. The lattice parameter of the pure Cu_2O films is 4.147 Å and it slightly increases to 4.186 Å after dopoing the Ag(4 at.%) into the Cu_2O. The adding of the Ag into Cu_2O reduces the compressive stress in the films. Das et al.[15] observed that the peak position shifts toward lower angles and increasing the lattice spacing with increasing of Ag content in the CuO films.

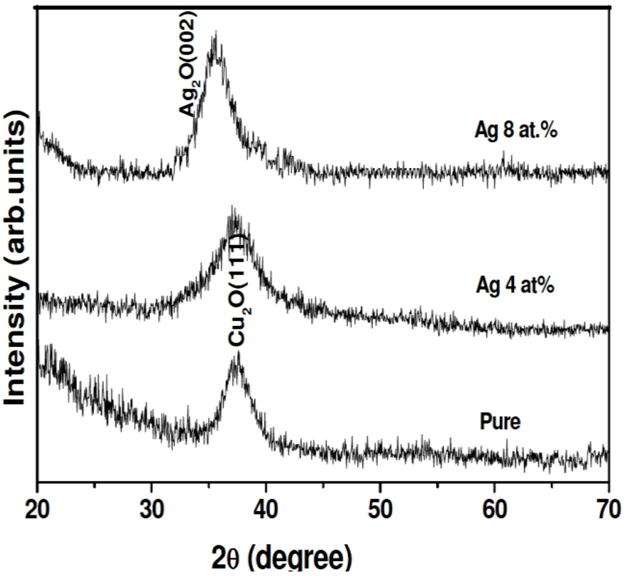
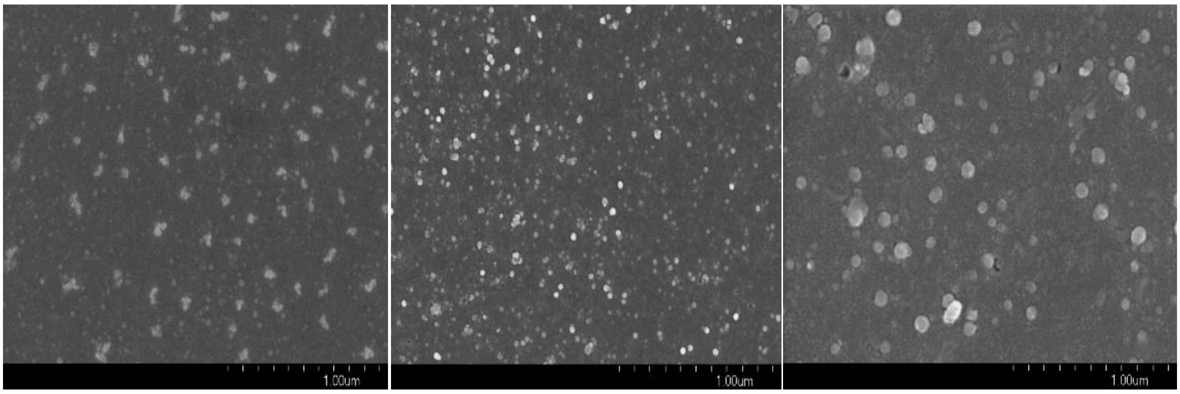


Fig.2. XRD patterns of pure and Ag doped Cu_2O films.

3.2. Microstructure

Fig.3. shows the SEM images of pure and Ag doped Cu_2O films. The difference in the surface morphology of the films was clearly appeared in the images. The uniformity of grains is better and dense structure in Ag(4at.%)-Cu_2O films compared to pure and Ag(8at.%)-Cu_2O films. The surface morphology was found to be improved in Ag doped Cu_2O films.



(a) (b) (c)

Fig.3. SEM images: (a) pure, (b) Ag(4at.%)-Cu_2O and (c) Ag(8at.%)-Cu_2O films.

3.4. Electrical properties

The electrical properties of the films are altered by adding the suitable dopants. The conductivity in the films is direct results of carrier concentration and mobility. The carrier concentration is strongly depending on the doping concentration, and carrier mobility is influenced by the lattice defect and grain boundary scattering [16]. The electrical properties of pure and Ag doped Cu_2O films are listed in Table 3. The electrical resistivity of Ag doped Cu_2O films are lower than the pure Cu_2O films. This was due to increasing the carrier concentration and additionally silver clusterization at the grain boundaries can also contribute for decreasing the films resistivity.The films show high resistivity at higher doping concentration was due to the formation of silver oxide along with Cu_2O and decreasing of the carrier concentration in the films.The similar behavior was observed in dc magnetron sputtered Au doped SnO_2 thin films by Reddy et al.[17].

Table 3. Electrical and optical properties of Cu_2O films at different Ag concentrations

Sample History	Resistivity (Ωcm)	Hall mobility (cm^2/V.sec)	Carrier concentration (cm^{-3})
Cu_2O	82	1.8	$4.2x10^{16}$
Ag(4at.%)-Cu_2O	5	4.7	$2.7x10^{17}$
Ag(8at.%)-Cu_2O	22	8.9	$3.2x10^{16}$

IV. CONCLUSIONS

Pure and Ag doped Cu_2O films were deposited on glass substrates by electron beam evaporation. The deposited films were exhibited the cubic structure of Cu_2O only and no peaks of Ag compounds or CuO are observed upto dopant concentration of 4at.%. The adding of the Ag into Cu_2O reduced the compressive stress in the films. The uniformity of grains was better and dense structure in Ag(4at.%) doped Cu_2O films compared to pure and Ag(8at.%) doped Cu_2O films.The low electrical resistivity was observed in Ag(4at.%) doped Cu_2O films.

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