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OPTICAL PROPERTIES OF MODIFIED- SILAR GROWN COPPER OXIDE NANOCRYSTALLINE THIN FILMS

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ABSTRACT

Pristine thin films of copper oxide have been prepared to glass substrates by a simple technique, namely, SILAR method with slight modification which employs successive dipping in 1M NaOH, kept at 70 degrees copper complex solution at room temperature successively for 20 s, followed by rinsing in triple distilled water for 10 seconds. The structure of the films were studied using XRD and the films are found to be polycrystalline with mixed phases before annealing and tend to become monoclinic after having annealed. The morphology details of thin films were characterized using scanning electron microscopy and the morphology is formed by needle like grains. The optical properties of the films were studied using ultra violet- visible measurements within the energy ranges 1.45 to 2.3 eV. The band gap, was estimated using Tauc's method. The annealed sample exhibited a band gap of 1.7 eV. The films are suitable for optical applications.

INTRODUCTION

There is a growing interest in the development of transition metal oxides and their electrical properties, as observed in the literature of recent years (Thirukonda Anandamoorthy Vijayan *et al*., 2008; Vijayan *et al*., 2008; Muru *et al*., 2010; Muruganatham *et al*., 2012; Ravikumar *et al*., 2012). Copper oxide is a P-type transition semiconductor metal oxide semiconductor which has attracted wide interest due to its attractive structure comprising monoclinic unit cell and square – planar co-ordinates (Ito *et al*., 1998; Asbrink *et al*., 1970), which is similar to that in high Tc superconductors. Further, copper oxide is attractive due to its excellent properties like selective solar absorbency and low thermal emittance (Banerjee and Chattopadhyy, 2005). Owing to its prospective applications the thin films of Copper oxide derives continuous attractions.

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Polycrystalline thin and thick films of copper oxide have been prepared by various techniques such as chemical vapour deposition (Muruganatham *et al*., 2012), ionized cluster beam deposition (Sun and Kwok, 1999), DC reactive magnetron sputtering (Subramanyam *et al*., 2000), pulsed laser deposition (Kim *et al*., 1999), chemical bath deposition (Ezema, 2003; Tanusevski *et al*., 2003; Eze and Okeke, 1997; Nair and Nair, 1991; Ndukwe, 1998) and others. Many of these methods are expensive and require a high vacuum environment (Pushparajan *et al*., 1994). The chemical bath technique and its modifications like, dip technique, Successive Ionic Layer by Adsorption and Reaction (SILAR) with and without modifications have frequently been used for the deposition of metal oxide thin films (Chandramohan *et al*., 2012; Valanarasu *et al*., 2013; Rathinam Chandramohan *et al*., 2013). The technique has also been used widely to deposit many materials of commercial interest (Tanusevski *et al*., 2003; Nair *et al*., 1991). In normal SILAR method the anionic and cationic precursor solutions are taken separately. However, in modified

SILAR the precursor solutions are taken together in a same beaker. In the modified SILAR the number of beakers required for one cycle may be modified. In this modified SILAR method employed in this study three separate beakers were used containing NaOH in one beaker which may be heated to desired temperature. The anionic and cationic precursors were taken together in the second beaker and the third beaker contained triple distilled water at a desired temperature. Modifications in number of beakers, temperature of bath, etc make the successive ionic layer by adsorption reaction suitable for varieties of systems. The films are made by dipping successively in 1M NaOH kept at 70 degrees Celsius for 20 seconds, a solution comprising anionic and cationic precursor of suitable concentration for 20 seconds and triple distilled water at room temperature for 10 seconds respectively. The deposition cycles were repeated for different timings. A typical deposition cycles of 5 to 30 immersion cycles were performed. This (m-SILAR) offers many advantages like lower preparation costs, the rapidity of growth, and convenience for extending to large area deposition and also offers a wide flexibility on the choice of chemicals, etc. The quality of the films is in comparison with physical methods. The deposition conditions play a major role in the physical properties of copper oxide films prepared. Present paper reports on the preparation, structure, microstructure and optical properties of copper oxide nano films grown on a glass substrate, using a modified SILAR technique.

Experimental Procedure

To prepare the copper oxide thin films on to glass substrates modified chemical bath deposition called m-SILAR method was used. The chemicals used for the preparation were copper sulfate pentahydrate ($CuSO_4.5H_2O$), Sodium thiosulfate ($Na_2S_2O_3.5H_2O$) and sodium hydroxide (NaOH) from products of merck. A 1M NaOH solution was prepared in a glass beaker and heated to 70°C. The copper thiosulfate complex solution was prepared by adding approximately 25 ml of 0.1 M sodium thiosulfate to 25 ml of 0.1 M copper sulfate pentahydrate solution until a colorless solution results. Formation of colorless solution could be represented by,

$$2Cu^{2+} + 4S_2O^{3-}{}_2 \longleftrightarrow 2[Cu(S_2O_3)]^- + [S_4O_6]^{2-}$$

As a first step, the substrates were immersed in a hot NaOH solution holding the slide vertically using sample holder. In order to obtain uniform thin films, a time period of 20's of immersion was chosen in first two dippings. As a result, OH^- from NaOH solution adhered to the surface of substrate. Second immersion of the substrate was performed in the copper ion complex solution and the immersion period was 20's. In the solution of thiosulfate cuprate(I), the Cu(I) ions formed by the dissociation equilibrium,

$$[Cu(S_2O_3)]^- \longleftrightarrow Cu^+ + S_2O_3{}^{2-},$$

adhere to the substrate and react with $(OH)^-$ ions present on the surface to form Cu_2O by the reaction

$$2Cu^+ + 2OH^- \longrightarrow Cu_2O + H_2O$$

This completes one cycle of the ion layer adsorption and reaction process gives successive cycles leading to thin film deposition. It was observed that after 2 to 3 immersion cycles a, very thin, nearly transparent film appeared with a silvery in reflection. The deposition can be terminated after undergoing desired number of deposition cycles. The thin films were characterized subsequently. The crystal structure of CuO was determined using a Philips X'PETR-PRO diffractometer employing Cu Kα radiation (λ = 1.54060 Å) operated at 40 kV and 30 mA in the wide angle region from 10° to 70°. The surface morphology of the samples was studied using a scanning electron microscope (Model XL30; M/s FEi, The Netherlands). The UV-Visible optical absorption and transmittance spectra of CuO have been carried out with a view to explore their optical properties. The spectral absorption spectra were recorded using UV visible spectrophotometer (Model: Lambda 35, Make – Perkin Elmer) in the wavelength ranges from 400 to 900 nm.

RESULTS AND DISCUSSION

X-ray Diffraction Studies

The X-ray diffraction analysis was used as the major tool for identification of phases of the as-prepared copper oxide thin films. TheX-ray diffract meter of the copper oxide thin films annealed in air at 450 °C along with that of the as-prepared sample were shown in Fig(1). Well defined peaks for as-prepared samples at 2 theta value 36.31 degrees corresponded to reflections from (111). They originated from the presence of crystallographic phase of Cu_2O (Cubic, JCPDS: 35-1091) . Moreover, it is observed that the as-deposited samples of Cu_2O are observed to be unstable and that may be fully converted to CuO when heat treated. For the annealed film (at 450 °C) the peaks were observed at two theta values at 38.93 and 53.7 degrees corresponding to reflections from (200) plane. They were also arising from the mixed phases of CuO (Monoclinic, JCPDS: 89-5899). The conversion of Cu_2O into CuO might have resulted from the diffusion of oxygen in to the films during air annealing. The mechanism may be visualized as follows: Cu_2O starts reacting with O and forms the CuO phase by the following reaction: $2Cu_2O + O_2 \rightarrow 4CuO$. It gives a predominant monoclinic structure. The lattice parameters are estimated as a = 4.689 Å, b = 3.420 Å, c = 5.130 Å. The temperature dependence of five lattice parameters for nanocrystals of monoclinic CuO relative to the values at 280 K (a = 4.6896(3) Å, b = 3.4305(3) Å, c = 5.1448(6) Å, β = 99.352(4)° and V = 81.67 Å^3) (Ezema, 2003). The values in parentheses represent the error bars for each value. The inset shows how the volume of the unit cell for nanocrystals of CuO increases as it is cooled at low temperatures, whereas it remains approximately constant for micrometre-sized particles of CuO. The solid line depicts a negative volume expansion coefficient of -1.1×10^{-4} K^{-1}. It has also been reported that the value of the lattice constant 'a' does not change significantly with temperature at low temperature for nanocrystals (~4 nm) or micrometre-sized particles of NiO. At higher temperatures, the positive thermal expansion seen in the nanocrystals is similar to that observed for the bulk material (Zheng *et al*., 2008). Temperature dependence of three lattice constants for nanocrystals and micrometre-sized particles of MnF_2 for the micrometre-sized particles have indicated a small increase in the values. NTE can be seen in the nanocrystals below the magnetic ordering temperature of 67 K. There are fewer NTE data points for MnF_2 than for CuO

because MnF has a much lower magnetic ordering temperature. The composition CuO is maintained even upon annealing at 450 °C. The sample annealed at 450 °C resulted in an increase in average crystallite size (1 to 5µm). The increase in crystallite size can be attributed to the change in crystallographic phase from Cu_2O to CuO [Table 1]. The grain size of crystallites was calculated using a well-known Debye-Scherrer's formula:

$$D = 0.9\lambda / \beta \cos\theta$$

Where D is the grain size of crystallite, λ is the wavelength of X-ray used (λ = 1.54060 Å), β the broading of diffraction line measured at half its maximum intensity in radians and θ the angle of diffraction. The grain size values of the crystalline CuO thin films are 30.96 nm and 71.49 nm and the dislocation density of $24.767X10^{14}$ line/m^2 and $3.2926X10^{14}$ lines/m^2 for as-deposited and annealed film respectively. It can be seen that the grain size increases with the annealing of the films as expected as grains tend to agglomerate upon receiving energy. This relatively small crystallite size in nanometer was due to the low growth rate of copper oxide film.

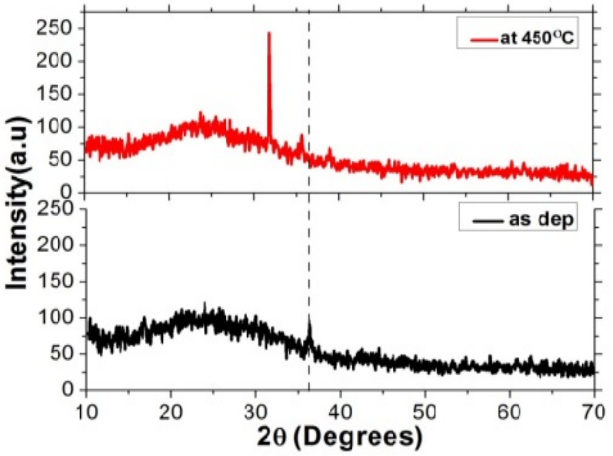

Fig. 1. XRD of Copper oxide thin films for as-pre and 450°C

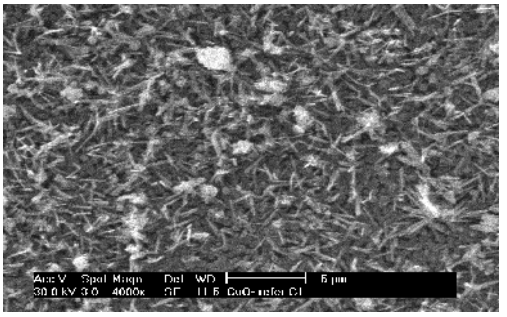

Fig .2(a). SEM images of as prepared Cu_2O Thin Film

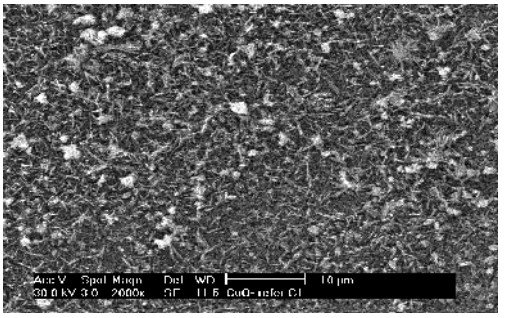

Fig .2(b). SEM images of as prepared CuO Thin Film

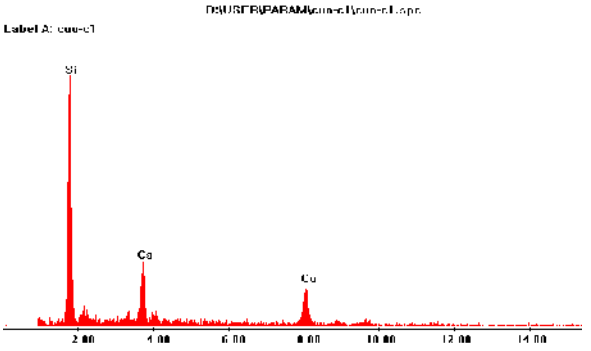

Fig .2 (c). EDAX images of as prepared CuO Thin Film

Table 1. Estimated structural and optical band gap of as deposited and annealed Copper oxide thin films

Information of samples		XRD Analysis			JCPDS Values	Energy band gap E_g(eV)	Grain size (nm)	Urbach Energy (meV)
S.No	T °C	Phase	hkl	Peak position2Θ(°)				
1	As-Pre	Cu_2O	111	38.912	35-1091	1.4 and 2.3	30.96	533
2	450°C	CuO	200	38.93	80-1917	1.7	71.49	470

Morphology and Composition

The surface morphology was studied by scanning electron microscopy (SEM) using a model XL30 (M/s FEi, The Netherlands). The respective secondary electron micrographs were obtained on the films grown by optimized conditions, which are shown in the figure (2) (a and b). It is observed that the substrate is filled with needle type grains of various lengths ranging between 20 nm to 500 nm. At some region agglomeration of these grains into popcorn like structure typical of chalcogenides is observed whose diameter is about 1 µm. The discontinuities in the grains are also observed without a well defined grain boundary. EDX studies showed presence of a trace Calcium in the films that may be due to the sample handling in figure (2(c)). No other impurities are detected. The Si peak owes its origin to the substrate.

Optical properties

Figure (3) shows the typical optical absorption spectra obtained for the copper oxide thin films under as deposited and annealed conditions. Usually when there is a small variation in thickness of the films oscillations may be present in the transmittance or absorption patterns. It does not show any oscillation and hence testify that the film surface is smooth with wavelength longer than 600 nm. The presence of powdery deposit found on inspection on the as deposited films would have caused some scattering losses from the film surface. The absorption is observed to decrease with wavelength. The linear relation is obtained by plotting the usual Tauc's plot of $(\alpha h\nu)^2$ against hν and is given in the insert to Fig (3). Also for the as deposited film the Tauc's plot exhibit two linear regions. One region lies in the low energy (1.45 eV for indirect band gap), and the other

in the high energy (2.3 eV for direct band gap) range. The insert to figure(3) also shows that the direct optical energy band gap of the CuO films is observed to be decreased from 2.3 eV, for as-deposited film, to 1.7 eV, due to annealing at 450° C. The decrease in Eg is an agreement with observed increase in the amorphous film for annealed (Tariq J.ALWAN and Mushtak A. JABBAR, 2010). This may be associated to the crysallographic changes as observed in structural studies. The density of the localized states in the band can be evaluated from the Urbach energy (ΔE). The Urbach energy can be calculated from the equation

$\alpha = \alpha_0 \exp(h\nu/\Delta E)$

by plotting ln(α) as a function of hν as shown in figure(4) for CuO films (Tariq J.ALWAN and Mushtak A. JABBAR, 2010). The reciprocal slope of the linear parts gives the values of ΔE for CuO films for as-deposited and annealed temperature and is shown in figure(4). It is observed that the ΔE increased with annealing. This may be associated with the shift in the on set of absorption attributed to the modification of band gap. Figure(5) shows the Fourier Transformation Infrared spectrum of copper oxide thin films for as- deposited and annealed at 450º C. Both films are exhibited between 411 cm^{-1} to 549 cm^{-1}. All the peaks are revealed the stretching vibrations of Cu-O bond in the cubic and monoclinic crystal structure of Cu-O (Mageshwari and Sathyamoorthy, 2013).

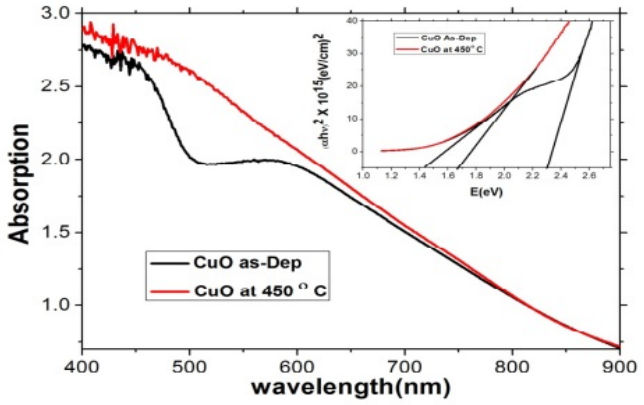

Fig. 3. Typical optical absorption spectra for as deposited and annealed Copper oxide thin film (Insert) Tauc's plot of as deposited and annealed copper oxide thin films

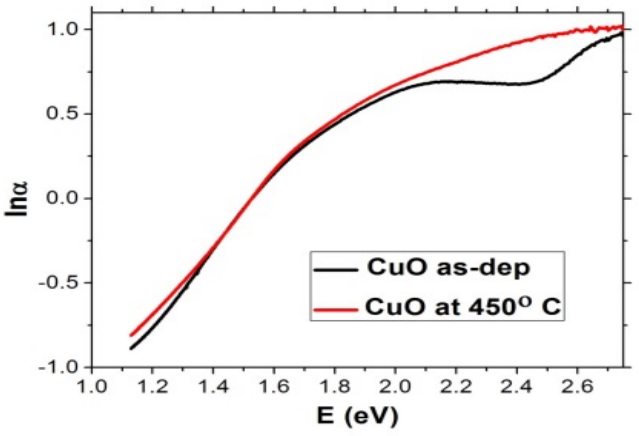

Fig. 4. Ln alpha Vs Energy graph for the estimation of Urbach energy of Copper oxide thin film

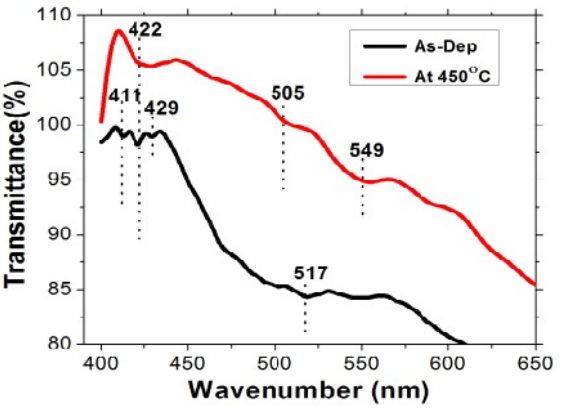

Fig. 5. FTIR spectrum of Copper Oxide thin films for as and annealed

Conclusion

Synthesis of copper oxide thin films through a modified SILAR technique by successive immersion of a glass substrate in solution of NaOH at 70°C and a copper complex at room temperature was successfully demonstrated. The thin film thus grown was systematically characterized for their structure, morphology and optical properties. The band gap of the film is found 1.7 eV after annealing which matches well with that observed in literature for nanocrystalline CuO. FTIR reveals the confirm of the stretching vibrations of Cu-O peaks nearly the wavenumber between 411 cm^{-1} to 549 cm^{-1}. The films were characterized for morphology and composition. The SEM studies revealed the needle type grains getting agglomerated.

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