Effect of substrate temperature on the optoelectronic properties of DC magnetron sputtered copper oxide films

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Abstract

Copper oxide thin films are deposited on quartz substrates by DC magnetron sputtering and the effect of deposition temperature on their optoelectronic properties is examined in detail. Scanning Electron Microscopy (SEM), X-ray diffraction (XRD) analysis, Raman spectroscopy, UV-Vis spectroscopy, and four-probe sheet resistance measurements are used to characterize the surface morphology, structural, optical, and electrical properties respectively. Deposition is carried out at room temperature and between 200 and 300 °C. XRD analysis indicates that the oxide formed is primarily Cu_2O and the absorption spectra show the films have a critical absorption edge at around 300 nm. The sheet resistance gradually decreases with increase in deposition temperature thereby increasing the conductivity of these thin films. Also observed is the increase in band gap from 2.20 eV for room temperature deposition to 2.35 eV at 300 °C. The optical band gap and the variation of sheet resistance with temperature shows that the microstructure plays a vital role in their behavior. These transformation characteristics are of huge technological importance having variety of applications including transparent solar cell fabrication.

Keywords: Copper oxide; Reactive sputtering; Optoelectronic properties; Substrate temperature

1 Introduction

Copper oxide is a *p*-type nontoxic metal oxide semiconductor, possessing a wide range of applications in gas sensors, as hole transport layers in solar cells, and also in electrochromic devices [1, 2]. There are normally two oxides of copper: cuprous or copper (I) oxide (Cu_2O), with a direct band gap slightly above 2.0 eV and cupric or copper (II) oxide (CuO) having an indirect band gap between 1.3-2 eV [3–6]. A metastable, intermediate copper oxide compound between the above mentioned two phases, Cu_4O_3 , having catalytic properties has also been reported [7,8]. Cu_2O crystallizes in a cubic structure with the lattice parameter a = 0.427 nm, CuO and Cu₄O₃ have monoclinic and tetragonal structures respectively. Cu_2O is the more stable oxide at low temperature while CuO is stable at high temperature [9]. Due to its tunable band gap, the copper (I) oxide acts as a good absorber in polycrystalline hetero junction solar cells, e.g., ZnO/Cu_2O , In_2O_3/Cu_2O , ITO/Cu_2O and $ZnIn_2O_4/Cu_2O$ [1, 10, 11]. The *p*-type semiconducting behavior of Cu_2O arises due to its non-stoichiometry [12]. The high optical absorption coefficient in the visible range and electrical properties make the material highly useful for optoelectronic applications, such as a channel material for p-type oxide thin film transistors [13,14]. Generally, the oxide properties depend on the growth method employed, deposition conditions, and post-annealing processes (if any) [15]. To date, the oxides of copper have been prepared using several deposition techniques that include thermal evaporation, sol-gel method, chemical vapor deposition, and magnetron sputtering [9, 16–19]. Among the various techniques, DC magnetron sputtering is a versatile method to prepare copper oxide films, as the sputtering of the metallic target in the presence of various reactive gas environments provides large area deposition, with good uniformity and adhesion between the substrate and thin films and good repeatability. Although several studies are reported in the literature [13, 20, 21] on the oxides of copper, this work is an attempt to prepare copper oxide films from metallic copper by DC reactive magnetron sputtering in the presence of a mixture of argon and oxygen gases. The effect of deposition temperature on the structure, optical, and electrical properties of the deposited films, are extensively studied. The stabilization of the copper (I) oxide phase and the change in its properties with substrate temperature will be useful in device fabrication applications.

2 Experimental Section

Copper oxide thin films of approximately 70 nm were grown on quartz substrates using DC magnetron reactive sputtering using a pure Cu target. The substrates (with dimensions $2 \times 2 \text{ cm}^2$) were cleaned ultrasonically in acetone/ethanol/deionized water for 15 min each (in this order) and then dried in air before loading in the sputtering chamber. The background pressure of the sputtering chamber was set at 5×10^{-6} mbar, and the working pressure was recorded at 1.2×10^{-3} mbar. Argon gas of purity 99.999% was used as the sputtering gas filling the chamber along with oxygen gas of purity 99.999% as the reactive gas. The substrate temperature was stabilized for 5 min prior before process. DC power of 90 W was used and deposition was done for 15 min keeping both the Ar and O₂ flow rate constant at 20 standard cubic centimeters per minute (sccm). Deposition was done at room temperature and at higher temperatures, namely 200, 250, and 300 °C.

Structural characterization was carried out using RIGAKU Miniflex 600 Benchtop 6th Generation X-ray diffractometer with Cu-K α radiation of wavelength 0.154 nm in grazing angle. The surface morphology was imaged using scanning electron microscopy (SEM) (FEI Inspect F). The transmittance of the films was recorded using an UV-Vis spectrophotometer (Jasco V-570). The electrical properties of films were measured using a four-point probe instrument (Jandel RM3000). Raman spectroscopy was done using the Alpha300 R advanced Raman imaging system.

3 Results and discussions

3.1 Structural properties

XRD was used to understand the evolution of the phases as a function of the deposition temperature. Figure 1 shows the XRD patterns of the films deposited at room temperature and higher substrate temperatures. From the XRD pattern, it is clear that the copper oxide film deposited at room temperature exhibits a mixed character with phases such as Cu₂O (ICDD number: 00-005-0667), CuO (ICDD number: 01-074-1021), and the metastable state Cu₄O₃ (ICDD number: 01-083-1665). No Cu peaks were observed in the XRD plot indicating that oxide formation is complete under these conditions. From the plot, well defined reflection peaks were observed at 2θ values of 29.4 (Cu₂O (110)), 35.9 (CuO (-111)), 39.2 (CuO (200)), 42.9 (Cu₂O (200)), 47.2 (Cu₄O₃(301)) and 48.3 (Cu₄O₃(204)) respectively. A preferred orientation of (110) is also observed for the Cu₂O phase. From this, it is evident that these films are polycrystalline in nature and the different phases formed correspond to the limited diffusivity and the formation of metastable phases under low temperature deposition. As the substrate temperature is increased, the intensity of the other phases except the Cu₂O phase starts decreasing, confirming the transformation into a single phase. However, for the substrate temperature of 300 °C, appearance of a weak peak or the peak splitting indicates a transformation to a lower symmetry phase. The appearance of sharp and strong peaks revealed overall good crystallinity of copper oxide thin films.

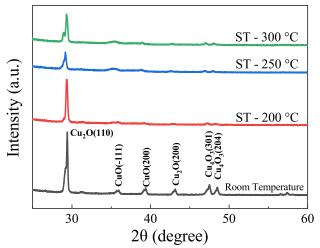


Figure 1. The XRD patterns of copper oxides films deposited at different substrate temperatures (referred as ST), ranging from room temperature to 300 °C. The predominant phase is Cu₂O.

The data from the XRD plots are extracted and presented in table 1, which consolidates the structural properties of the deposited films. The average grain size and the lattice strain are also estimated [22, 23]. Using the prominent diffraction peak, corresponding to the (110) plane of Cu_2O , in each of the XRD patterns, the average grain size was estimated using the Debye-Scherrer formula given below.

$$D_{av} = \frac{K\lambda}{\beta_{hkl}cos\theta} \tag{1}$$

where K is taken as 0.9, λ is the X-ray wavelength, θ is the diffraction angle, and β_{hkl} the full width at half maximum (FWHM) of the corresponding diffraction peak (in radians). The lattice strain developed in the film is estimated by Willamson-Smallman (W-S) formula as given below

$$\epsilon = \frac{\beta_{hkl}}{4tan\theta} \tag{2}$$

Table 1. The structural properties of the copper oxide thin films deposited at different temperatures. The grain size and lattice strains are estimated using the Debye-Scherrer and Williamson-Smallman formula.

Substrate Temperature (°C)	FWHM (β_{hkl})	Grain size (nm)	Lattice strain $(\times 10^{-3})$
Room Temperature	0.098 ± 0.009	87.6 ± 7.6	1.6
200	0.098 ± 0.005	71.5 ± 3.4	2.0
250	0.157 ± 0.010	87.5 ± 7.7	1.6
300	0.079 ± 0.007	108.6 ± 11.3	1.3

It is clear from Table 1 that the grain size is small at lower deposition temperatures, as the deposited atoms instead of diffusing and integrating to the neighboring grains and raising their size condense and remain stuck to their regions forming new nuclei and clusters. As the deposition temperature increases, the grain size increases with a size of approximately 108.64 nm at 300 °C. This may be attributed to the increased mobility of the arriving atoms. Corresponding to the increased deposition temperature there is also a slight decrease in the lattice strain. The cause of internal strain might be due to the difference between thermal expansion coefficients of copper and the quartz substrate that is developed because of the displacements of atoms with respect to their reference lattice positions. Increased mobility with deposition temperature and a corresponding increase in average size decreases this lattice strain.

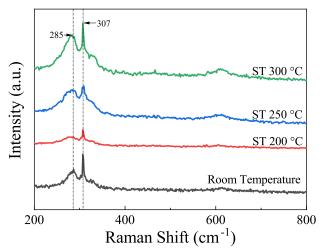


Figure 2. Raman spectra of copper oxide films deposited at different substrate temperatures. The predominant peaks can be indexed to Cu_2O and CuO.

Figure 2 plot the Raman spectra recorded for the copper oxide films deposited at different substrate temperatures. The Raman spectra show the characteristic phonon frequency of crystalline Cu_2O . It can be seen from the figures that there are two Raman peaks at 285 and 307 cm⁻¹. It is well established that the Raman spectra of Cu_2O has a peak at (308 cm⁻¹) [24]. Another weak peak observed near 285 cm⁻¹ is close to the peak normally attributed to the CuO phase [25, 26]. With increase in deposition temperature, the spectra show an increase in this CuO peak compared to Cu_2O , which is indicative of a phase conversion with annealing. Although in the XRD patterns, CuO phase is almost absent (see figure 1), one can conclude from the Raman data that while the predominant phase formed is of the Cu_2O phase there is also some small amount of the CuO. Given that Raman spectroscopy is more surface sensitive than XRD [27] it is possible that this phase is located closer to the film surface.

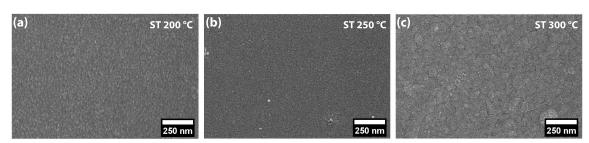


Figure 3. Scanning Electron Micrographs of the oxide films deposited at different substrate temperatures. The grain size increases with deposition temperature.

3.2 SEM Analysis

Figure 3 shows the SEM images of the samples deposited at different substrate temperatures. It can be observed from the SEM images that the morphology of the films are significantly influenced by the change in deposition temperature during sputtering. The copper oxide film prepared at the substrate temperature of 200 °C exhibits spherical uniformly distributed grains. A similar behaviour is also observed at 250 °C. Also the grains are distributed uniformly with no porosity or agglomeration. For the film grown at 300 °C, the grain size has increased due to increased coalescence at higher deposition temperature [28]. The results are also consistent with the crystallite size measurements from XRD (table 1), which shows that there is nearly a 25% increase in crystallite size going from 250 to 300 °C.

3.3 Optical Analysis

Optical transmittance spectra were recorded to study the bandgap variation of the copper oxide thin films and the plots are summarized in Figure 4. From the absorption spectra, it is clear that the thin films have a critical absorption edge around 300 nm. The optical bandgap can be determined by applying the Tauc model (the plots between $(\alpha h \nu)^2$ versus $h\nu$) [9,29–31] for the films and are illustrated in the inset. The analysis indicates that the optical gap value increases with deposition temperature with values of 2.02, 2.09, 2.21, and 2.35 eV for room temperature, 200, 250, and 300 °C deposition respectively. The reason could be the partial filling of the conduction band, which results in blocking of the lowest states causing a widening of the optical band gap (blue shift) known as the Burstein-Moss shift i.e., shifting of the unoccupied states towards higher energies in the allowed bands.

3.4 Electrical Properties

The electrical properties were studied using the standard four-probe method. The sheet resistance as a function of different substrate temperatures are compiled in Table 2. The conductivity(σ) of the samples were calculated using the following formula

$$\rho = R_s \times t \tag{3}$$

$$\sigma = \frac{1}{\rho} \tag{4}$$

where R_s is the sheet resistance and t is the thickness of the copper oxide film.

The as-deposited film shows a comparatively lower resistance than the substrate treated film, which may be due to the presence defects and multiple phases of the oxide. The conductivity of the film deposited at the substrate temperature of 200 °C is the lowest, while conductivity values are higher for the films grown at 250 and 300 °C. The increase in conductivity might be caused by an increase in the free path of the carrier concentration (higher mobility) or an increase in carrier

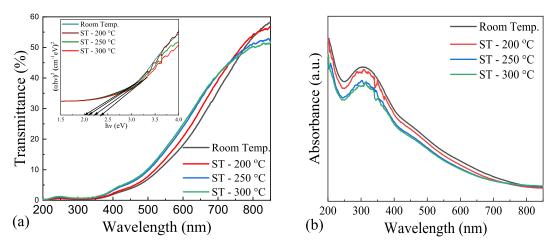


Figure 4. (a) Transmittance spectra (with Tauc plot as inset) and (b) absorbance spectra, for the copper oxides films deposited at different substrate temperatures.

 Table 2. The variations in the electrical properties of the copper oxides films deposited at different substrate temperatures

Substrate Temperature (°C)	Sheet Resistance (M Ω /sq.)	Conductivity (Sm^{-1})	Band Gap (eV)
Room Temperature	0.02	646.6	2.02
200	0.19	78.6	2.13
250	0.07	212.0	2.21
300	0.02	711.0	2.35

concentration [12, 18]. The increase in the conductivity can also be correlated with the growth in the grain size with increasing substrate temperature.

4 Conclusions

Thin films of copper oxide have been deposited successfully onto quartz substrates at room temperature, 200, 250, and 300 °C respectively. XRD analysis revealed that the prepared films at room temperature were polycrystalline in nature with Cu_2O as the dominant phase with the preferred orientation along the (110) plane. Structural parameters such as grain size and lattice strain were estimated and found to be strongly dependent on the substrate temperature. Transmittance measurements were used to measure the optical gap which was found to increase with deposition temperature. This highly stable Cu_2O thin film can be a promising material for Cu_2O based solar cells, anti-reflection coatings due to their increased bandgap and excellent electrical properties. Hence these parameters provide a promising way to control the properties of copper oxide film for desired device applications. Future work will focus on using these films for electrochromic studies.

Author Contributions

All authors contributed to the conception and design. The experiments were performed the experiments and characterized by Aarju Mathew Koshy. Dr. A. Sudha helped in analysis of the results and writing the manuscript drafts. The overall work and manuscript preparation was carried out under the supervision of Dr. Satyesh Kumar Yadav and Dr. Parasuraman Swaminathan.

Conflicts of interest

There are no conflicts to declare.

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