Research Article

Process-Parameter-Dependent Structural, Electrical, and Optical Properties of Reactive Magnetron Sputtered Ag-Cu-O Films

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Silver-copper-oxide thin films were formed by RF magnetron sputtering technique using Ag80Cu20 target at various oxygen partial pressures in the range 5 \times 10^{-3}–8 \times 10^{-2} Pa and substrate temperatures in the range 303–523 K. The effect of oxygen partial pressure and substrate temperature on the structure and surface morphology and electrical and optical properties of the films were studied. The Ag-Cu-O films formed at room temperature (303 K) and at low oxygen partial pressure of 5 \times 10^{-3} Pa were mixed phase of Ag2Cu2O3 and Ag, while those deposited at 2 \times 10^{-2} Pa were composed of Ag2Cu2O4 and Ag2Cu2O3 phases. The crystallinity of the films formed at oxygen partial pressure of 2 \times 10^{-2} Pa increased with the increase of substrate temperature from 303 to 423 K. Further increase of substrate temperature to 523 K, the films were decomposed into Ag2O and Ag phases. The electrical resistivity of the films decreased from 0.8 \Omega cm with the increase of substrate temperature from 303 to 473 K due to improvement in the crystallinity of the phase. The optical band gap of the Ag-Cu-O films increased from 1.47 to 1.83 eV with the increase of substrate temperature from 303 to 473 K.

1. Introduction

Silver-copper-oxygen (Ag-Cu-O) system consists of ternary compounds of Ag2Cu2O3, Ag2Cu2O4, and AgCuO2. May and Vaughey [1] used Ag2Cu2O3 as cathode in primary lithium batteries and achieved an average discharge voltage of 2.0 V. AgCuO2 and Ag2Cu2O3 emerged as new type of solar energy semiconductors with high absorption coefficient of 3 \times 10^5 cm^{-1}[2]. The silver nanoparticles embedded in oxide matrix find applications in transparent conducting coatings, photocatalytic and antibacterial coatings [3–5]. Gómez-Romero et al. [6] first synthesized the ternary compound of Ag2Cu2O3. Muñoz-Rojas et al. [7] produced Ag2Cu2O3 at room temperature by solid-state transformation of Ag2Cu4O3 using ozone oxidation. Curda et al. [8] synthesized microcrystalline AgCuO2 by low temperature route. Majumdar et al. [9] prepared silver-copper-oxide composite powders (60–95% of Ag) by spray pyrolysis. Pierson et al. [3] deposited Ag-Cu-O thin films for the first time with various Cu/Ag ratios by reactive magnetron sputtering of mosaic targets and cosputtering of Cu and Ag targets. Petitjean et al. [10, 11] reported the effect of annealing temperature on the decomposition- and structure-related properties of reactively sputtered Ag2Cu2O3 films deposited with Ag50Cu50 and with Ag50Cu40 sputter targets. Uthanna et al. [12] reported the influence of deposition temperature on the structural and optical properties of Ag2Cu2O3 films formed by RF magnetron sputtering. Tseng et al. [13] deposited Ag-doped Cu2O films (0–50 at. % of Ag) by cosputtering of silver and copper targets and showed that Ag-Cu-O (4 at. % of Ag) is the mixed phase of Ag2O-CuO which is most sensitive to light irradiation and useful for optoelectronic related applications.

The reactive magnetron sputtering process is widely employed for the growth of various metal oxide thin films by sputtering of metallic target in a mixture of argon and oxygen gases or pure oxygen gas. Addition of a second metal either by cosputtering of two metal targets or by composite target allows the formation of defined ternary compound films [14, 15] or nanostructure coatings where
the constituting phases are immiscible [16, 17]. The physical properties of the magnetron sputtered films mainly depend on the deposition parameters such as oxygen partial pressure, substrate temperature, and substrate bias voltage apart from the sputter power and sputter pressure.

In this investigation, thin films of Ag-Cu-O were deposited on glass substrates by RF magnetron sputtering of Ag$_{50}$Cu$_{50}$ target at various oxygen partial pressures and substrate temperatures. The effect of oxygen partial pressure and substrate temperature on the chemical binding configuration, crystallographic structure, surface morphology, electrical and optical properties of the deposited films was systematically studied.

2. Experimentation

Thin films of Ag-Cu-O deposited on glass substrates using RF magnetron sputtering technique. The sputter system is capable of producing base pressure of $5 \times 10^{-4}$ Pa using diffusion pump and rotary pump combination. Pure Ag$_{50}$Cu$_{50}$ target of 50 mm diameter and 3 mm thick was used for sputter deposition of the films. Pure argon was used as sputter gas and oxygen as reactive gas. Two Tylan mass flow controllers were used to control the flow rates of argon and oxygen gases individually. The power given to sputter target was 65 W by using Advanced Energy RF power generator. The Ag-Cu-O films were deposited at various oxygen partial pressures ($p_{O_2}$) in the range $5 \times 10^{-3}$–$8 \times 10^{-2}$ Pa and at different substrate temperatures ($T_s$) in the range 303–523 K. The deposited films were characterized for chemical composition, chemical binding configuration, crystallographic structure, surface morphology, electrical and optical properties. The chemical composition of the deposition films was determined by using X-ray energy dispersive spectroscopic analyser (EDS) attached to the scanning electron microscope (Philips XL 308 field effect gun). The chemical binding configuration of the films was analyzed with Fourier transform infrared spectrophotometer ( Nicolet model 5700 FTIR) in the wavenumber range 400–3800 cm$^{-1}$. The crystallographic structure of the films was determined using X-ray diffraction (XRD) taken on a Bruker D8 Advance diffractometer at the glancing angle of 4$^\circ$ using monochromatic Cu K$_{\alpha 1}$ radiation. The surface morphology of the films was analysed by using atomic force microscope (AFM). The electrical resistivity of the films was measured at room temperature using four probe method (Jandel multiposition wafer probe). The optical transmittance of the films was recorded using Perkin-Elmer (UV-Vis-NIR) double-beam spectrophotometer in the wavelength range 300–2500 nm.

3. Results and Discussion

Thickness of the deposited films was measured using Veeco Dektak (model 150) depth profilometer, and it was in the range 210–250 nm. The deposition rate of the films formed at oxygen partial pressures up to $8 \times 10^{-3}$ Pa was about 10.5 nm/min. The deposition rate gradually decreased to 5.5 nm/min with the increase of oxygen partial pressure to $5 \times 10^{-2}$ Pa, and at higher oxygen partial pressures, it remains almost constant. The high deposition rate at low oxygen partial pressures was due to the high sputtering yield of metallic silver-copper and insufficient oxygen available in the sputter chamber to react and form silver-copper oxide. The decrease in the deposition rate with increase of oxygen partial pressure was due to the decrease of sputter yield in the presence of reactive gas of oxygen and formation of Ag-Cu-O films. For moderate to highly reactive chemical system, the reactive sputtering process comes with the abrupt decrease in the films deposition rate when the process turned into so-called reactive sputter mode [18]. Such a decrease in the deposition rate with the increase of oxygen partial pressure also reported in the deposition of DC reactive magnetron sputtered silver oxide films formed with silver target [19], cuprous oxide films with copper target [20], and Ag-Cu-O films with Ag$_{50}$Cu$_{50}$ target [21].

A representative energy dispersive spectroscopic spectrum of Ag-Cu-O film formed at an oxygen partial pressure of $2 \times 10^{-2}$ Pa is shown in Figure 1. The atomic ratio of copper to silver determined from EDS spectrum was nearly a constant value of 0.208 $\pm$ 0.010. The oxygen content in the films was correlated with the oxygen partial pressure prevailing in the sputter chamber. At low oxygen partial pressure of $5 \times 10^{-3}$ Pa, the oxygen content in the films was 38.6 at. %. The films formed at oxygen partial pressure of $2 \times 10^{-2}$ Pa was 49.4 at. %, and it remained almost constant at higher oxygen partial pressures.

The X-ray diffraction profiles of the films deposited at different oxygen partial pressures are shown in Figure 2. The films formed at low oxygen partial pressure of $5 \times 10^{-3}$ Pa showed weak diffraction peak at $2\theta = 34.8^\circ$ correspond to the (202) reflection of Ag$_2$Cu$_3$O$_7$ [22] and the peak observed at 38.8$^\circ$ correspond to the (111) reflection of metallic Ag [23]. It indicated that the microcrystals were embedded in the amorphous matrix. It revealed that the films formed at low oxygen partial pressure of $5 \times 10^{-3}$ Pa showed Ag$_2$Cu$_3$O$_7$ along with unoxidized metallic silver. The presence of mixed

![Figure 1: EDS spectrum of Ag-Cu-O film formed at an oxygen partial pressure of $2 \times 10^{-2}$ Pa.](image-url)
The films formed at 303 K were polycrystalline in nature with the presence of (202) and (008) reflections of Ag$_2$Cu$_2$O$_3$ formed at different substrate temperatures. X-ray diffraction profiles of the films formed at oxygen partial pressure of $2 \times 10^{-2}$ Pa showed a mixed phase of Ag$_2$Cu$_2$O$_3$ and Ag$_2$Cu$_2$O$_4$. With further increase of oxygen partial pressure to $5 \times 10^{-2}$ Pa, the intensity of the (202) reflection of Ag$_2$Cu$_2$O$_3$ was diminished. From these studies, it revealed that the films formed at oxygen partial pressure of $2 \times 10^{-2}$ Pa showed mixed phase of Ag$_2$Cu$_2$O$_3$ and Ag$_2$Cu$_2$O$_4$.

In order to study the influence of physical properties of the films with the effect of substrate temperature, the films were deposited at constant oxygen partial pressure of $2 \times 10^{-2}$ Pa at different substrate temperatures in the range 303–523 K. X-ray diffraction profiles of the films formed at different substrate temperatures are shown in Figure 3. The films formed at 303 K were polycrystalline in nature with the presence of (202) and (008) reflections of Ag$_2$Cu$_2$O$_3$ and (111) and (−312) reflections of Ag$_2$Cu$_2$O$_4$ [24]. It indicated that the films formed at oxygen partial pressure of $2 \times 10^{-2}$ Pa showed a mixed phase of Ag$_2$Cu$_2$O$_3$ and Ag$_2$Cu$_2$O$_4$. With further increase of oxygen partial pressure to $5 \times 10^{-2}$ Pa, the intensity of the (111) reflection of Ag$_2$Cu$_2$O$_4$ was enhanced while the intensity of the (202) reflection of Ag$_2$Cu$_2$O$_3$ was diminished. From these studies, it revealed that the films formed at oxygen partial pressure of $2 \times 10^{-2}$ Pa showed mixed phase of Ag$_2$Cu$_2$O$_3$ and Ag$_2$Cu$_2$O$_4$.

The crystallite size of the films formed at 303 K was 15 nm. The crystallite size (L) of the films was evaluated from the full width at half maximum intensity of X-ray diffraction peaks using the Debye-Scherrer’s relation

$$L = \frac{k\lambda}{B\cos \theta},$$

where $k$ is a constant with a value of 0.89 for the target and $B$ the full width at half maximum intensity of diffraction peak. The crystallite size of the films formed at 303 K was 15 nm. The crystallite size of the films increased to 32 nm with the increase of substrate temperature to 473 K. The films formed at high substrate temperature of 523 K, and the crystallite size decreased to 15 nm due to the presence of mixed phase of Ag and Ag$_2$O.

The Fourier transform infrared transmittance spectra (FTIR) of the films formed at different substrate temperature are shown in Figure 4. The FTIR spectra of the films formed at substrate temperature of 303 K showed an absorption peak at 303 K and a peak at 473 K. The peak at 303 K is due to the presence of Ag$_2$O, and the peak at 473 K is due to the presence of Ag
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Figure 2: X-ray diffraction profiles of Ag-Cu-O films formed at different oxygen partial pressures: (a) $5 \times 10^{-3}$ Pa, (b) $2 \times 10^{-2}$ Pa, and (c) $5 \times 10^{-2}$ Pa.

Figure 3: X-ray diffraction profiles of Ag-Cu-O films formed at different substrate temperatures.

Figure 4: Fourier transform infrared absorption spectra of Ag-Cu-O films formed at different substrate temperatures.
Figure 5: Continued.
band at about 518 cm\(^{-1}\). When the substrate temperature increased to 473 K the absorption band shifted to 511 cm\(^{-1}\) with the presence of another weak broadband around 795 cm\(^{-1}\). The intense band at about 520 cm\(^{-1}\) is the characteristic of Ag linearly coordinated with oxygen [26]. The weak band at about 795 cm\(^{-1}\) was related to cuprous oxide with combination modes of optically active phonons [27]. The films deposited at substrate temperature of 523 K showed an absorption band at 493 cm\(^{-1}\). The band located at 493 cm\(^{-1}\) was related to the infrared-active Ag-O mode for the Ag\(_2\)O. Therefore, the films formed at 303 K were of Ag-Cu-O phase while those deposited at higher substrate temperature of 523 K were of mixed phase of Ag\(_2\)O and Ag.

The surface morphology of the deposited films was analysed with atomic force microscopy. Figure 5 shows the atomic force three-dimensional and two-dimensional micrographs of the films formed at different substrate temperatures. The films exhibited different morphology of surface grains depending on the substrate temperature. The grain size of the films increased with the increase of substrate temperature as shown in Figure 6. The grain size of the films formed at 303 K was 85 nm. The grain size of the films increased to 310 nm with the increase of substrate temperature to 473 K due to improvement in the crystallinity of the films. It is also seen that the shape of the grains was almost spherical. It indicated that the increase of substrate temperature modified the surface morphology of the grown films. With further increase of substrate temperature to 523 K, the films showed larger grain size of 345 nm with irregular shape. This may be due to the coexistence of silver oxide and silver phases. The films formed at 303 K were of smooth surface with root mean square surface roughness of 3.7 nm. The root mean square surface roughness of films increased to 52.4 nm with the increase of substrate temperature to 523 K.

The electrical resistivity of the films was highly influenced by the substrate temperature. Figure 7 shows the dependence of electrical resistivity of the films on the substrate temperature. The electrical resistivity of the films formed at 303 K was 2.3 \(\Omega\)cm. As the substrate temperature increased to 473 K, the electrical resistivity of the films decreased to 0.8 \(\Omega\)cm due to improvement in the crystallinity of the films. The low electrical resistivity of 3.6 \(\times\) \(10^{-3}\) \(\Omega\)cm was exhibited in the case of the films formed at high substrate temperature.
of 523 K due to the existence of mixed phase of Ag$_2$O and Ag as shown in X-ray diffraction. The low value of electrical resistivity obtained at 523 K was controlled by the metallic silver grains since Ag$_2$O were of high electrical resistivity [28]. Majumder et al. [9] reported the sheet resistance of $3.5 \times 10^{-3}$ Ω/□ in 80 at. % Ag-doped Ag-Cu-O composite powders prepared by spray pyrolysis. A decrease of electrical resistivity also observed in sputtered Ag$_2$Cu$_2$O$_3$ films formed with Ag$_{50}$Cu$_{50}$ target and annealed at temperatures in the range 423–523 K due to the decomposition of metallic Ag and CuO [10].

The optical transmittance of the films critically depends on the substrate temperature of the deposited films. Figure 8 shows the variation of optical transmittance with the wavelength of films formed at different substrate temperatures. The optical transmittance (at wavelength of 1000 nm) of the films formed at 303 K was low value of 24%. The optical transmittance of the films increased to 36% with the increase of substrate temperature to 473 K. With further increase of substrate temperature to 523 K, the high optical transmittance value of 62% was achieved. The optical absorption edge of the films shifted towards lower wavelength side with the increase of substrate temperature. The optical absorption coefficient ($\alpha$) was calculated from the optical transmittance ($T$) data using the relation

$$\alpha = \left( \frac{1}{t} \right) \ln T,$$

where $t$ is the film thickness. The optical band gap ($E_g$) of the films was determined from the plot of ($\alpha h\nu$)$^2$ versus photon energy ($h\nu$) using Tauc’s relation

$$($$\alpha h\nu$$)$^2 = A(h\nu - E_g)^{1/2},$

where $A$ is the absorption edge width parameter. Extrapolation of the linear portion of the plots of ($\alpha h\nu$)$^2$ versus photon energy of the Ag-Cu-O films to $\alpha = 0$ yields the optical band gap of the deposited films. Figure 9 shows the plots of ($\alpha h\nu$)$^2$ versus photon energy of Ag-Cu-O films formed at different substrate temperatures. The optical band gap of the films increased from 1.47 to 1.83 eV with the increase of substrate temperature from 303 to 473 K. Recently, Singh developed theory on the optical absorption in low-dimensional systems such as quantum dots, nano wires, and wave guides [29–31]. The increase of optical band gap with the increase of substrate temperature is due to the improvement in the crystallinity of the films. Such increase in the optical band gap with increase of substrate temperate was also reported in DC magnetron sputtered CuAlO$_2$ films [32, 33].

The films deposited at higher substrate temperature of 523 K showed a band gap of 2.20 eV. The high band gap value
observed at higher substrate temperature of 523 K was due to presence of Ag₂O. The optical band gap of pure Ag₂O films reported values was 2.23 eV in RF magnetron sputtered [28] and 2.32 eV in DC magnetron sputtered [34].

4. Conclusions

Thin films of Ag-Cu-O films were formed on glass substrates by reactive RF magnetron sputtering of Ag₈₀Cu₂₀ target at different oxygen partial pressures in the range 5 × 10⁻³–8 × 10⁻² Pa and substrate temperatures in the range 303–523 K. The influence of oxygen partial pressure and substrate temperature on the crystallographic structure and surface morphology, chemical binding configuration, electrical and optical properties of the films was studied. The content of oxygen in the films was correlated with the oxygen partial pressure maintained in the sputter chamber during the growth of the films. X-ray diffraction studies on the films deposited at room temperature (303 K) and at low oxygen partial pressure of 5 × 10⁻³ Pa was mixed phase of Ag₂Cu₂O₃ and Ag. The films grown at oxygen partial pressure of 2 × 10⁻² Pa showed the mixed phase of Ag₂Cu₂O₃ and Ag₂Cu₂O₄ phases. The crystallinity of the films formed at a constant oxygen partial pressure of 2 × 10⁻² Pa increased with the increase of substrate temperature from 303 to 473 K. The films formed at higher substrate temperature of 523 K were decomposed into Ag₂O and Ag. The grain size of the films increased from 85 to 345 nm with the increase of substrate temperature from 303 to 523 K. The electrical resistivity of the Ag-Cu-O films formed at oxygen partial pressure of 2 × 10⁻² Pa decreased from 2.3 to 0.8 Ωcm with increase of substrate temperature from 303 to 473 K, respectively, due to improvement in the crystallinity of the films. The low electrical resistivity of 3.6 × 10⁻² Ωcm was observed in the films formed at high substrate temperature of 523 K due to presence of Ag₂O and Ag, which was mainly controlled by the metallic silver grains. The optical band gap of the Ag-Cu-O films increased from 1.47 to 1.83 eV with the increase of substrate temperature from 303 to 473 K. The films formed at higher substrate temperature of 523 K exhibited the optical band gap value of 2.20 eV related to Ag₂O phase.

References


