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Effect of deposition temperature on the physical properties of RF magnetron sputtered Ag–Cu–O films with various Cu to Ag ratios

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Thin films of Ag–Cu–O were deposited on glass substrates held at various temperatures in the 303–523 K range by RF magnetron sputtering of $Ag_{90}Cu_{10}$, $Ag_{80}Cu_{20}$ and $Ag_{70}Cu_{30}$, and elemental copper and silver targets in an oxygen partial pressure of 2×10^{-2} Pa and sputtering pressure of 4 Pa. The deposited films were characterised by energy dispersive X-ray analysis, X-ray diffraction (XRD), atomic force microscopy, UV–Vis–NIR spectroscopy and employing four-point probe method. The atomic ratio of Cu/Ag in the films formed at 303 K was in correlation with the composition of the starting sputter targets. The increase in substrate temperature induced the decomposition of the Ag–Cu–O films into a mixture of metallic silver and copper oxide. The electrical resistivities of silver oxide and copper oxide films formed at 303 K were $3 \times 10^{-3}\,\Omega$ cm and 29 Ω cm, respectively. The electrical resistivity of the films formed with $Ag_{70}Cu_{30}$ target at 303 K was 8.2 Ω cm and it decreased to 2.4 Ω cm with increase in substrate temperature to 523 K due to structural changes in the films. The optical band gap of the Ag–Cu–O films formed at 303 K increased from 1.60 to 1.95 eV with the increase of copper to silver atomic ratio from 0.10 to 0.30 in the films. The optical band gap of the films formed with $Ag_{70}Cu_{30}$ target increased from 1.95 to 2.15 eV with the increase in substrate temperature from 303 to 523 K, respectively.

1 Introduction The silver–copper–oxygen (Ag–Cu–O) system consists of various binary compounds Cu_2O, Cu_4O_3, CuO, Ag_2O and AgO and ternary compounds $Ag_2Cu_2O_4$ and $Ag_2Cu_2O_3$. Synthesis of ternary compound $Ag_2Cu_2O_3$ in 1999 marked the birth of a new family of oxides containing silver and copper [1]. The $Ag_2Cu_2O_4$ phase was synthesised by electrochemical oxidation of suspension of the precursor $Ag_2Cu_2O_3$ [2] and room temperature ozone oxidation [3]. Curda et al. [4] achieved $AgCuO_2$ samples by precipitation from the aqueous solutions of silver nitride and copper nitride and determined their structure. Tejada-Rosales et al. [5] investigated on the electrical and magnetic properties of $Ag_2Cu_2O_3$. Nolan and Elliott were calculated the band structures of Cu_2O and Ag doped Cu_2O [6]. Adelsberger et al. [7] calculated the crystal structure of $Ag_2Cu_2O_3$. May and Vaughey [8] used $Ag_2Cu_2O_3$ as cathode in primary lithium batteries and achieved an average discharge voltage of 2.0 V though a low value compared to vanadium based silver oxide of $Ag_2V_4O_{11}$.

It has been established recently that the sputtering process in the presence of oxygen can be efficiently used to synthesise the new silver–copper oxides. Furthermore, this process allows the preparation of films with different Ag/Cu atomic ratio [9]. The effect of oxygen partial pressure [10–12], current applied to the sputter target [13] and annealing temperature [14] on the structural, electrical and optical properties of the silver–copper oxide films formed by reactive magnetron sputtering were studied. The excess of silver atoms in the deposited films compared to copper induced the synthesis of biphased coatings of metallic silver and silver–copper oxide films [13]. The silver nanoparticles embedded in oxide matrix find applications in transparent conducting coatings [15], gas sensors [16], photocatalic [17] and antibacterial coatings [18].

In the present investigation, an attempt is made in the deposition of Ag–Cu–O films by RF reactive magnetron sputtering technique from the mosaic targets of $Ag_{90}Cu_{10}$, $Ag_{80}Cu_{20}$, $Ag_{70}Cu_{30}$, and elemental copper and silver targets for the formation of standard copper oxide and silver oxide films. The influence of Cu/Ag ratio on the structure, electrical and optical properties was studied on the films deposited at room temperature (303 K) using different composition of targets. The effect of substrate temperature on the physical properties was also studied on the films formed by sputtering target of $Ag_{70}Cu_{30}$ at various substrate temperatures in the 303–523 K range.

2 Experimental details Thin films of Ag–Cu–O were deposited on glass substrates (1 mm thick microscope slides from Blue Star) by RF sputtering of metallic $Ag_{90}Cu_{10}$ (*i.e.* Cu/Ag atomic ratio of 0.10), $Ag_{80}Cu_{20}$ and $Ag_{70}Cu_{30}$, and elemental copper and silver targets (50 mm diameter and 3 mm thick) at an oxygen partial pressure of 2×10^{-2} Pa and a total sputtering pressure of 4 Pa. The sputter chamber was evacuated to the base pressure of 5×10^{-4} Pa using diffusion–rotary pump combination. The required quantities of oxygen and argon gases were admitted in to the sputter chamber through fine controlled needle valves followed by the Tylan mass flow controller. Before deposition of each film, the target was presputtered in pure argon gas for 15 min to remove the surface oxide layer if any formed on the sputter target. The sputter target was powered with Advanced Energy 500 W RF power generator. The target to substrate distance was maintained at 65 mm. The power fed to the sputter target was fixed to 65 W. The duration of the deposition runs was 20 min. In order to study the effect of the target composition on the structural, electrical and optical properties, the films were deposited at room temperature (303 K). The effect of substrate temperature on the physical properties was studied on the films formed at different substrate temperatures in the 303–523 K range from the sputter target of $Ag_{70}Cu_{30}$.

The thickness of the films deposited was in the range 200–250 nm using multiple beam interference method. The composition of the deposited films was estimated by using X-ray energy dispersive spectroscopic analysis (EDS) attached to the scanning electron microscope (Philips XL.30S field effect gun). The accelerating voltage fixed to the electron was 25 kV for the chemical composition estimation. The crystallographic structure of the films was determined with grazing angle X-ray diffraction (XRD) taken on a Bruker D8 Advance Diffractometer at the grazing angle of 4° using monochromatic Cu $K\alpha_1$ radiation. The surface morphology of the films was analysed by employing atomic force microscope (AFM). The electrical resistivity of the films (size of 15 mm × 12 mm) was measured at room temperature using four-point probe (Jandel multiposition wafer probe) technique with tungsten carbide electrode spacing of 1 mm and a diameter of 0.4 mm. No electrode was deposited on the surface of the film before electrical resistivity measurements. There was no transient current–voltage behaviour which indicated that the electrical contacts were of Ohmic with the deposited films. The correction factor used for determination of the electrical resistivity was 4.52 [19]. The optical transmittance of the films was recorded using Perkin-Elmer double beam spectrophotometer in the 300–2500 nm wavelength range.

3 Results and discussion Since the Ag–Cu–O film composition was determined using EDS analyses, the estimation of the oxygen concentration is not accurate hence the copper to silver atomic ratio was calculated. The films deposited with the $Ag_{90}Cu_{10}$ target exhibited a Cu/Ag atomic ratio of 0.103 ± 0.010. The films formed using $Ag_{80}Cu_{20}$ target showed the ratio of 0.205 while those prepared with $Ag_{70}Cu_{30}$ target was 0.302. The chemical composition of the films analysed with energy dispersive spectroscopy was correlated with the composition of the sputter target used for the deposition of the films. From here onwards we presented the films formed with $Ag_{90}Cu_{10}$ target as Cu/Ag = 0.10, the $Ag_{80}Cu_{20}$ target as Cu/Ag = 0.20 and the $Ag_{70}Cu_{30}$ target as Cu/Ag = 0.30.

The X-ray diffractograms of various Ag–Cu–O films deposited at room temperature are presented in Fig. 1. The diffractograms of silver oxide and copper oxide standards are also presented. 'Pure' silver oxide film is poorly crystallised. A diffraction peak with low intensity is detected close to 39°. This position may correspond to the (−202) planes of the AgO or Ag_2O_2 phase that crystallises in a monoclinic structure. Addition of copper leads to an improvement of the film crystallisation. Furthermore, diffraction peaks with low intensity are also evidenced. Three structural hypotheses may be considered to index the X-ray diffractogram:

(i) The first one is related to the formation of a $Ag_2Cu_2O_3$ phase. Indeed, the main diffraction peak may correspond to the (202) planes of this ternary oxide. However, the Cu/Ag atomic ratio measured by EDS (0.10) is too low to consider the formation of a pure $Ag_2Cu_2O_3$ film. Since

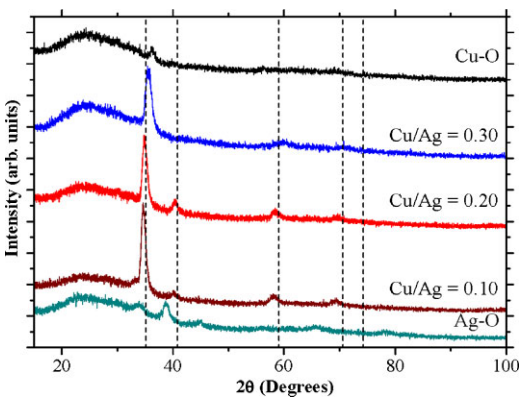

Figure 1 (online colour at: www.pss-a.com) XRD profiles of Ag–Cu–O films formed at 303 K (room temperature). The vertical dashed lines are related to the theoretical position of a hypothetic fcc silver–copper oxide phase with a lattice constant of 0.442 nm.

the silver +II valence state is not stable, a silver over-stoichiometric phase cannot be further considered. To explain the formation of a $Ag_2Cu_2O_3$ phase into a film exhibiting a Cu/Ag atomic ratio of 0.10 needs to consider the formation of a biphased film: $Ag_2Cu_2O_3$ + a silver oxide.

(ii) The second hypothesis is related to the partial substitution of Ag(+I) ions in the Ag_2O_2 phase by Cu(+I) ones, inducing a progressive shift of the diffraction peaks towards higher angle values.

(iii) Finally, the third hypothesis is to consider the formation of an fcc phase with a lattice constant close to 0.442 nm. However such a phase was never reported in the literature.

The increase in the Cu/Ag atomic ratio comes with a shift of the diffraction peak position towards higher angle values that could be in agreement with the second and the third previous hypothesis. The XRD analysis of the pure copper oxide film shows that the single metal oxide film is poorly crystallised, confirming that the addition of copper into silver-based oxide film improves the film crystallinity.

Figure 2 presents the effect of the deposition temperature on the X-ray diffractogram of films deposited using the $Ag_{70}Cu_{30}$ target. Films deposited at RT, 348 and 423 K exhibit nearly the same diffractogram that could match with the silver–copper oxide solid solution with the fcc phase. On the other hand, at 523 K, the diffraction peaks may be assigned to metallic silver, indicating a decomposition of the silver oxide-based phase. This result is in agreement with the low thermal stability of silver oxide phase [20].

The mean crystallite size of the films was determined from the full-width at half maximum (FWHM) of the diffraction peak using the Debye–Scherrer's relation neglecting the peak broadening due to the internal stresses present in the films. The crystallite size of the silver oxide films formed at 303 K is about 5 nm. The films formed with

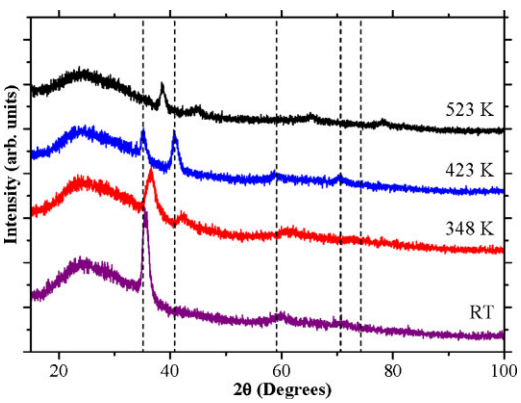

Figure 2 (online colour at: www.pss-a.com) XRD profiles of Ag–Cu–O films formed at various substrate temperatures with sputter target of $Ag_{70}Cu_{30}$. The vertical dashed lines are related to the theoretical position of a hypothetic fcc silver–copper-oxide phase with a lattice constant of 0.442 nm.

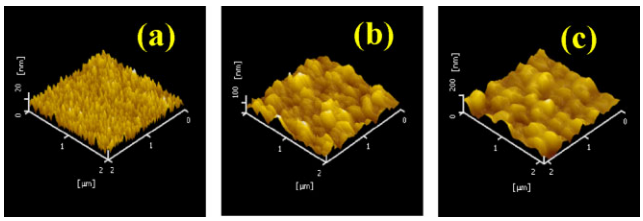

Figure 3 (online colour at: www.pss-a.com) AFM of the Ag–Cu–O films formed with Cu/Ag = 0.30 at different substrate temperatures: (a) 303, (b) 423 and (c) 523 K.

copper to silver ratio of 0.10 show larger crystallilte size of 20 nm. The crystallite size of the films decreases to about 12 nm with the increase of copper to silver ratio to 0.30. The pure copper oxide films show the crystallites with size of about 2 to 3 nm. The crystallite size of copper oxide films was lower than the value of 10 nm achieved in RF magnetron sputtered films formed from the sputter target of 200 mm diameter where the power density applied to the target was 1.9 W cm^{-2} [21]. In the present case the films were deposited with high sputter power density of 3.3 W cm^{-2} which leads to the high sputtering yield hence of lower size of crystallites.

The surface morphology of the films was analysed with the AFM. Figure 3 shows the (AFM) images of the Ag–Cu–O films formed at different substrate temperatures using sputter target of $Ag_{70}Cu_{30}$. The films exhibited different morphology of surface grains depending on the substrate temperature. Surface of the films formed at 303 K was rough with fine grains. Increase in substrate temperature leads to the enhancement in the size of the grains as shown in the figures. Since XRD show no grain size increase as a function of the deposition temperature, the grains evidenced by AFM should be polycrystalline.

The electrical resistivity was measured on the Ag–Cu–O films formed at different compositions and at different substrate temperatures. The electrical resistivity of pure silver oxide films formed at 303 K was 3×10^{-3} Ω cm. Barik et al. [22] obtained the resistivity of 2.3×10^{-4} Ω cm that is one order lower than the present ones. It is in good agreement with the values achieved by Rivers et al. [23] in electron beam evaporated films in the presence of reactive ECR oxygen plasma. The incorporation of copper in the silver-based oxide films (sputtered from $Ag_{90}Cu_{10}$ target) increases the resistivity of the films to 0.6 Ω cm. Further increase in the copper content (sputtered from $Ag_{80}Cu_{20}$ target) leads to higher electrical resistivity (2.3 Ω cm). When the Cu/Ag atomic ratio in the film is 0.30 a higher resistivity of 8.2 Ω cm is observed. The electrical resistivity of the films sputtered from $Ag_{70}Cu_{30}$ target decreased from 8.2 to 2.1 Ω cm with the increase in substrate temperature from 303 to 523 K, respectively. The high value of the electrical resistivity of the films deposited at 523 K suggests that another phase than silver (evidenced by XRD) is present in the film as an amorphous phase. Then, the film deposited at 523 K should be biphased: metallic silver and an oxide phase. Furthermore, electrical resistivity measurements indicate

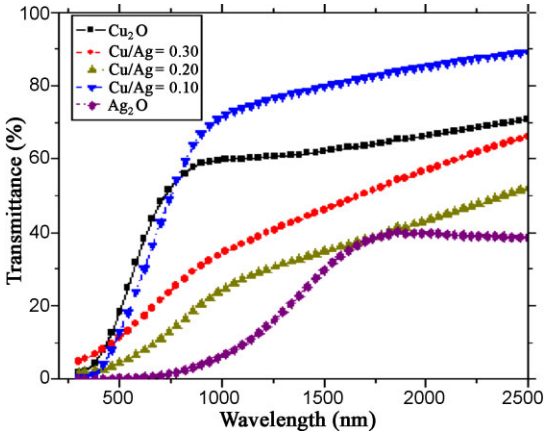

Figure 4 (online colour at: www.pss-a.com) Optical transmittance spectra of Ag–Cu–O films formed at room temperature with different compositions.

that the silver grains do not percolate in the oxide matrix. Pure copper oxide films exhibited the electrical resistivity of 29 Ω cm. Sivasankar Reddy et al. [24] achieved the electrical resistivity of 95 Ω cm in DC magnetron sputtered films where the sputter power applied to the target was lower value of 1.15 W cm^{-2} when compared to the present RF magnetron sputtered films in which the applied RF power to the sputter target was 3.2 W cm^{-2}. Lu et al. [25] noticed low electrical resistivity of 1.8 Ω cm in DC magnetron sputtered films.

Figure 4 shows the wavelength dependence of optical transmittance of Ag–Cu–O films formed at 303 K with different compositions. The optical transmittance of pure silver oxide films was high (70%) at wavelengths higher than 800 nm. Ag–Cu–O films formed with $Ag_{90}Cu_{10}$ target exhibit low transmittance and the optical absorption edge is shifted to higher wavelength values. Further increase in the copper content in the films leads to the increase of the transmittance and the absorption edge is progressively shifted to the lower wavelength side. The pure copper oxide

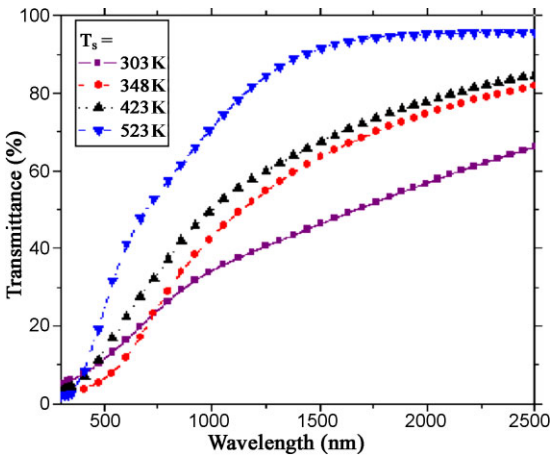

Figure 5 (online colour at: www.pss-a.com) Optical transmittance spectra of Ag–Cu–O films formed with $Ag_{70}Cu_{30}$ target at different substrate temperatures.

films exhibit a transmittance of about 70% of the pure silver oxide films at higher wavelength region. The substrate temperature strongly influences the optical spectra of the films. Figure 5 shows the optical transmittance spectra of the films formed with $Ag_{70}Cu_{30}$ target at different substrate temperatures in the 303–523 K range. The transmittance of the films increased with the increase in substrate temperature. The optical absorption coefficient (α) was calculated from the optical transmittance (T) and reflectance (R) data using the relation

$$T = (1 - R)^2 \exp(-\alpha t), \tag{1}$$

where t is the film thickness.

The optical band gap (E_g) of the films was evaluated from the Tauc's plots of $(\alpha h\nu)^2$ *versus* photon energy ($h\nu$) for the direct transitions between top of the valence band and bottom of the conduction band using the relation

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

where A is the optical absorption edge width parameter since the thin films of Ag_2O [23] and Cu_2O [24] were showed the direct optical band gap. Extrapolation of the linear portion of the plots of $(\alpha h\nu)^2$ *versus* the photon energy to $\alpha = 0$ resulted the optical band gap. The optical band gap of the pure silver oxide films was 2.05 eV. The films formed with $Ag_{90}Cu_{10}$ target showed a low optical band gap of 1.60 eV. Further increase of copper content induces an increase in the optical band gap of the films. The films formed with high content of copper that is from $Ag_{70}Cu_{30}$ target exhibited the optical band gap of 1.95 eV. The pure copper oxide films contained the optical band gap of 2.25 eV. In the literature, Lu et al. [25] and Sivasankar Reddy et al. [26] achieved the optical band gap values of 2.01 and 2.05 eV in DC magnetron sputtered films, Nair et al. [27] obtained 2.11 eV in dip coated films while 2.45 eV was measured in RF magnetron sputtered copper oxide films [28]. The difference in the band gap values was mainly due to the difference in the deposition method employed and the process parameters maintained during deposition of the films. To the best of our knowledge there are no reports on the optical band gap values of the Ag–Cu–O films formed with low copper concentrations, *i.e.* Cu/Ag < 0.40. The optical band gap of the films was highly influenced by the substrate temperature. The band gap of the films formed with $Ag_{70}Cu_{30}$ target increased from 1.95 to 2.15 eV with the increase in substrate temperature from 303 to 523 K respectively. Though the films formed at substrate temperature of 523 K may contained metallic silver and the silver oxide based phase, a single absorption edge observed correspond to the optical band gap of 2.15 eV related to the silver oxide based phase films.

4 Conclusions Ag–Cu–O films were deposited on glass substrates by RF magnetron reactive sputtering of mosaic silver–copper targets. In this paper, we presented the effect of the target composition and the deposition

temperature on the structure, the optical and the electrical properties of the films. Compared to previous studies related to Ag–Cu–O films, our work was focused on films with high silver content.

Three hypotheses were suggested to describe the film structure ($Ag_2Cu_2O_3$ containing films, solid solution of silver-based oxide and a fcc silver–copper oxide). At a given Cu/Ag atomic ratio, the increase in the deposition temperature induced the formation of biphased films: Ag + copper oxide-based phase.

Incorporation of copper into silver-based oxide films formed at room temperature showed an increase in the electrical resistivity from 0.6 to 8.2 Ω cm with the increase of Cu/Ag ratio from 0.10 to 0.30. The electrical resistivity of the films with Cu/Ag ratio of 0.30 decreased from 8.2 to 2.1 Ω cm with the increase of substrate temperature from 303 to 523 K.

Further a strong shift of the absorption edge was noticed by addition of copper in the silver-based oxide films. The optical band gap of the films formed at room temperature shifted from 1.65 to 1.95 eV with the increase of Cu/Ag ratio from 0.10 to 0.30. The films formed with Cu/Ag ratio of 0.30 the optical band gap shifted from 1.95 to 2.15 eV with the increase in substrate temperature from 303 to 523 K, respectively.

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