Proceedings of the E-MRS Fall Meeting, Symposium H: Warsaw, Poland, September 19–23, 2011

Substrate Temperature Influenced Structural and Electrical Behaviour of RF Magnetron Sputtered $Ag_2Cu_2O_3$ Films

A. Sreedhar[a], M. Hari Prasad Reddy[a], S. Uthanna[a], R. Martins[b], E. Elangovan[b,*] and J.F. Pierson[c]

[a]Department of Physics, Sri Venkateswara University, Tirupati — 517 502, India

[b]CENIMAT/I3N, Departamento de Ciencia dos Materiais, Faculdade de Ciencias e Tecnologia, FCT Universidade Nova de Lisboa and CEMOP-UNINOVA, 2829-516 Caparica, Portugal

[c]Institut Jean Lamour (UMR CNRS 7198), Department CP2S, Ecole des Mines, Nancy Université 54042 Nancy cedex, France

$Ag_2Cu_2O_3$ films were deposited on glass and silicon substrates by RF magnetron sputtering of metallic equimolar ($Ag_{50}Cu_{50}$) alloy target in Ar–O_2 mixture at different substrate temperature (T_s) ranging between 303 and 523 K. The effect of T_s on the core level binding energies, structural and electrical properties of the films was systematically studied. The films deposited at room temperature were amorphous. The films deposited at 373 K were polycrystalline and the crystallinity was increased when the T_s was increased to 423 K. The films deposited at 423 K and subsequently annealed at 498 K exhibits single phase $Ag_2Cu_2O_3$. In the case of films deposited at higher T_s of 523 K, Ag_2O was decomposed into Ag. The electrical resistivity of the films deposited at 303 K was 1.2×10^{-5} Ω cm, whereas the films formed at 423 K and subsequently annealed at 498 K showed electrical resistivity of 2.2×10^{-3} Ω cm due to improvement in the crystallinity of single phase $Ag_2Cu_2O_3$.

PACS: 71.20.−b, 71.15.Mb, 78.20.Ci, 74.25.Gz

1. Introduction

Silver and copper are found together in alloys and some ternary phases of chalcogenides and tellurides. Gomez-Romero et al. [1] first synthesized silver–copper mixed oxide: $Ag_2Cu_2O_3$. It is isostructural with paramelaconite structure (Cu_4O_3 or $Cu_2^+Cu_2^{2+}O_3$) with silver cations located at the Cu^+ positions. Munoz-Rojas et al. [2] have oxidized the $Ag_2Cu_2O_3$ at room temperature, both electrochemically and by ozone oxidation to achieve the $Ag_2Cu_2O_4$ (or $AgCuO_2$). It crystallizes with crednerite structure ($Cu^+Mn^{3+}O_2$) with Ag cations located at the Cu^+ positions and Cu cations at the Mn^{3+} sites [3]. $Ag_2Cu_2O_3$ finds application as cathode in primary batteries and achieves an average discharge voltage of 2.0 V [4]. Feng et al. [5] have performed theoretical studies on the electrical and optical properties of AgCuO and $Ag_2Cu_2O_3$. Pierson et al. [6] have deposited Ag–Cu–O films with different compositions by co-sputtering the composite targets of silver and copper. Petitjean et al. have reported the influence of annealing temperature on the structure of $Ag_2Cu_2O_3$ films formed with $Ag_{50}Cu_{50}$ target [7], and the effect of oxygen partial pressure on various properties of Ag–Cu–O films deposited utilizing $Ag_{60}Cu_{40}$ target [8]. Uthanna et al. [9] have reported the effect of deposition temperature on the structural, electrical and optical properties of Ag–Cu–O films RF magnetron sputtered using the $Ag_{70}Cu_{30}$ target. Narayana Reddy et al. [10] have studied the effect of oxygen partial pressure and substrate temperature (T_s) on the structural, electrical and optical properties of Ag–Cu–O films deposited using $Ag_{80}Cu_{20}$ target. In this investigation, thin films of $Ag_2Cu_2O_3$ were deposited by RF magnetron sputtering of $Ag_{50}Cu_{50}$ target at different T_s and studied the effect of T_s on the core level binding energies, crystal structure, surface morphology and electrical properties.

2. Experimental details

$Ag_2Cu_2O_3$ films were deposited on glass and p-type (111) silicon substrates by RF reactive magnetron sputtering of equimolar silver–copper ($Ag_{50}Cu_{50}$) target of 50 mm diameter at various T_s in the range of 303–523 K, at oxygen partial pressure of 2×10^{-2} Pa and sputtering pressure of 4 Pa. The power applied to the sputter target was 65 W by using Advanced Energy RF power generator. Thickness of the deposited films measured using Veeco Dektak (model 150) depth profilometer was ranging between 200 nm and 600 nm. The core level binding energies of the deposited films was analyzed with X-ray photoelectron spectroscopy (XPS). The crystallographic structure of the films was confirmed using a Bruker D8 advanced diffractometer at a fixed grazing angle of 4° using monochromatic Cu K_{α_1} radiation ($\lambda = 1.5406$ Å). The surface morphology of the films was analyzed using an atomic force microscopy (AFM). The electrical properties of the films were measured at room temperature

* corresponding author; e-mail: eevan2003@yahoo.co.in; elam@fct.unl.pt

using four probe techniques in van der Pauw configuration.

3. Result and discussion

Figure 1 shows a representative XPS survey scan spectrum of the $Ag_2Cu_2O_3$ film deposited on silicon substrate at 303 K and oxygen partial pressure of 2×10^{-2} Pa. The spectrum contained the characteristic core level binding energy peaks of silver, copper and oxygen. The core level binding energy peaks observed at about 368 and 374 eV were related to the Ag $3d_{5/2}$ and Ag $3d_{3/2}$ due to the spin–orbit splitting of the energy levels. The peak observed at about 530 eV was related to core level binding energy of O 1*s*. The peaks observed at around 934 and 954 eV were the characteristic core level binding energies of Cu $2p_{3/2}$ and Cu $2p_{1/2}$, respectively [11]. The chemical composition of the films was determined from the core level binding energy peak areas and sensitive factors of the constituent elements. The chemical composition of the films was maintained as very close to $Ag_2Cu_2O_3$.

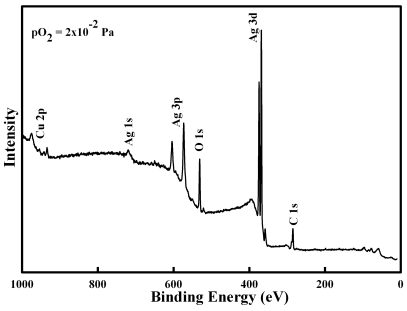

Fig. 1. XPS survey scan of $Ag_2Cu_2O_3$ film deposited at 303 K.

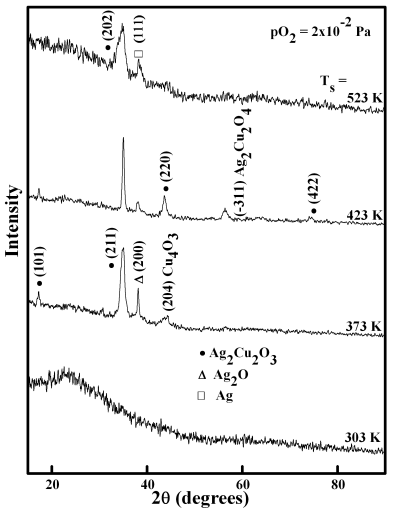

Fig. 2. X-ray diffraction patterns of $Ag_2Cu_2O_3$ films formed at different substrate temperatures.

Figure 2 shows the X-ray diffraction patterns of Ag–Cu–O films deposited on glass substrates kept at different T_s. The films deposited at 303 K were amorphous. The films deposited at 373 K showed diffraction peaks at diffraction angles ($2\theta°$) of 17.28, 35.07, 38.16, and 44.28°. The broadening of the obtained diffraction peaks indicates the growth of nanocrystalline films. The peaks observed at 17.28° and 35.07° are related to the diffractions from (101) and (211) planes of $Ag_2Cu_2O_3$ [12]. The peak observed at 38.16° is related to the diffraction from (200) plane of Ag_2O [13], whereas the peak observed at 44.28° belongs to the Cu_4O_3 phase [14]. It is understood that the films deposited at 373 K have mixed phase of $Ag_2Cu_2O_3$, Ag_2O and Cu_4O_3. Further increase in T_s to 423 K has decreased the intensity of Ag_2O peak while the Cu_4O_3 phase disappeared. An additional peak observed at 56.37° was related to the diffraction from $(\bar{3}11)$ plane of $Ag_2Cu_2O_4$ [15] and the peaks observed at 43.62° and 74.04° correspond to the diffractions from (220) and (422) planes of $Ag_2Cu_2O_3$. The intensity of (101) and (211) diffraction peaks of $Ag_2Cu_2O_3$ was also enhanced due to the improvement in crystallinity of the films. The XRD analysis revealed that the films deposited at 423 K belong to single phase $Ag_2Cu_2O_3$ with a fraction of $Ag_2Cu_2O_4$ phase. Further increase in T_s to 523 K has resulted in the formation of films showing a weak diffraction from (211) plane of $Ag_2Cu_2O_3$ and a diffraction from (111) plane of silver due to the temperature induced growth. The films deposited at 423 K were also subjected to open air annealing at 498 K for 3 h. The films annealed at 498 K showed the diffractions from (101), (211), (220) and (422) planes corresponding to the single-phase $Ag_2Cu_2O_3$ films as shown in Fig. 3. The intensity of the diffraction peaks has been enhanced in annealed films, which is presumably due to the improvement in the crystallinity. The crystallite size of the films calculated from the full width at half maximum of (211) reflection is increased from 12 to 20 nm for the increase in T_s from 373 to 423 K. The crystallite size of the films formed at high T_s of 523 K was relatively smaller (7 nm), which is probably due to the decomposition of the films into the metallic silver. The films deposited at 423 K and annealed at 498 K exhibited the large crystallite size of 24 nm that is attributed to the improvement in the crystallinity.

The surface microstructures obtained from AFM analysis indicates that grain size of the films is increased from 42 to 110 nm for the increase in T_s from 303 to 423 K, which may be related with the improvement in crystallinity. It is understood that the increase in T_s modifies the surface microstructures of the deposited films. The films deposited at 303 K contained spherical shaped grains, while those deposited at elevated temperatures consisted of grains that are pyramidal in shape. The films grown at 303 K showed a smooth surface with root mean square roughness (R_{rms}) of $\approx$ 4.6 nm, which is increased to $\approx$ 20.0 nm for the increase in T_s to 473 K. The single phase $Ag_2Cu_2O_3$ films obtained from anneal-

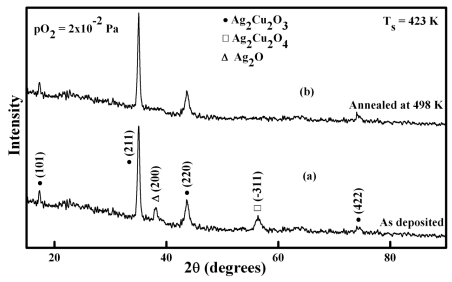

Fig. 3. X-ray diffraction patterns of $Ag_2Cu_2O_3$ films: (a) deposited at $T_s = 423$ K and (b) deposited at $T_s = 423$ K and post-annealed at 498 K.

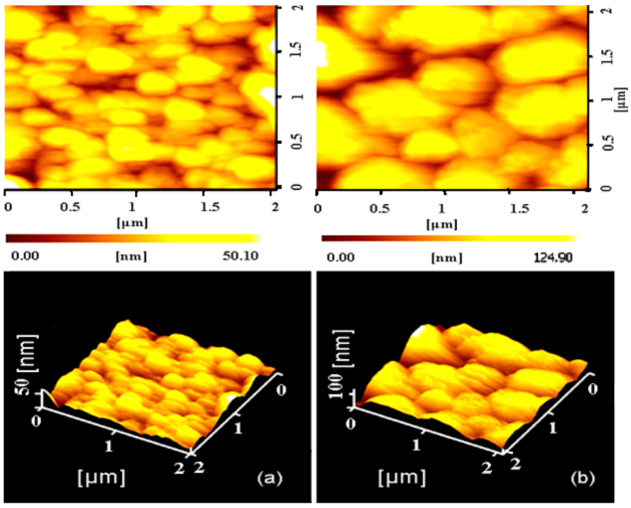

Fig. 4. Surface microstructures (scan area: 2 μm × 2μm) obtained through AFM analysis from $Ag_2Cu_2O_3$ films: (a) deposited at $T_s = 423$ K and (b) deposited at $T_s = 423$ K and post-annealed at 498 K.

ing at 498 K showed large size grains size of which are ranging about 280 nm, which has understandably increased the R_{rms} to ≈ 28 nm as shown in Fig. 4.

The electrical resistivity (ρ) of the films deposited on glass substrates meanly depends on the deposition temperature. The ρ of the films deposited at 303 K was very low, measuring about 1.2×10^{-5} Ω cm, whereas the ρ has been increased with the increase in T_s to reach a value of 9.5×10^{-3} Ω cm at 423 K. The observed low electrical resistivity at 303 K may be due to the presence of ternary phase along with elemental silver. The films deposited at high T_s of 523 K show ρ of 5×10^{-5} Ω cm, suggesting that ρ is controlled by the metallic silver grains present in the films [16]. The films deposited at 423 K and subsequently annealed at 498 K showed ρ of 2.2×10^{-3} Ω cm due to improvement in the growth of single-phase $Ag_2Cu_2O_3$. Petitjean et al. [8] achieved an electrical resistivity of 3×10^{-3} Ω cm from the pulsed DC magnetron sputtered films deposited at room temperature followed by air annealing at 473 K.

4. Conclusions

$Ag_2Cu_2O_3$ were deposited on glass and silicon substrates using RF reactive magnetron sputtering of metallic equimolar $Ag_{50}Cu_{50}$ alloy target at various substrate temperature (T_s) ranging between 303 K and 523 K, with an oxygen partial pressure of 2×10^{-2} Pa and a sputtering pressure of 4 Pa. The influence of T_s on the core level binding energies, crystallographic structure and electrical properties of the deposited films was studied. The films deposited at 303 K were amorphous. The films deposited at 423 K were of $Ag_2Cu_2O_3$ phase with a fraction of $Ag_2Cu_2O_4$. The films deposited at 423 K followed by an air annealing at 498 K were of single phase $Ag_2Cu_2O_3$. The crystallite size of the films is increased from 12 to 20 nm for the increase in T_s from 303 to 423 K, while those annealed at 498 K showed an enhancement in the crystallite size to 24 nm. The electrical resistivity of the films is decreased with the increase of T_s, which was controlled by the presence of silver and silver oxide phase in $Ag_2Cu_2O_3$. The electrical resistivity of the films annealed at 498 K was 2.2×10^{-3} Ω cm.

References

[1] P. Gomez-Romero, E.M. Tejada-Rosales, M. Rosa-Palacin, *Angew. Chem. Int. Ed.* **38**, 524 (1999).

[2] D. Munoz-Rojas, J. Fraxedas, P. Gomez-Romero, N. Casan-Pastor, *J. Solid State Chem.* **178**, 295 (2005).

[3] D. Munoz-Rojas, *Mater. Today* **14**, 119 (2011).

[4] C.D. May, J.T. Vaughey, *Electrochem. Commun.* **6**, 1075 (2004).

[5] J. Feng, B. Xiao, J.C. Chen, C.T. Zhou, Y.P. Du, R. Zhou, *Solid State Commun.* **149**, 1569 (2009).

[6] J.F. Pierson, D. Wiederkehr, J.M. Chappe, N. Martin, *Appl. Surf. Sci.* **253**, 484 (2006).

[7] C. Petitjean, D. Horwat, J.F. Pierson, *Appl. Surf. Sci.* **255**, 7700 (2009).

[8] C. Petitjean, D. Horwat, J.F. Pierson, *J. Phys. D, Appl. Phys.* **42**, 025304 (2009).

[9] S. Uthanna, M. Hari Prasad Reddy, P. Boulet, C. Petitjean, J.F. Pierson, *Phys. Status Solidi A* **207**, 1655 (2010).

[10] P. Narayana Reddy, A. Sreedhar, M. Hari Prasad Reddy, S. Uthanna, J.F. Pierson, *J. Nanotechnology*, 2011, article ID 986021, doi: 10.1155/2011/986021.

[11] D. Munoz Rojas, J. Oro, P. Gomez-Romero, J. Fraxedas, N. Casan-Pastor, *Electrochem. Commun.* **4**, 684 (2002).

[12] ICDD-International centre for diffraction data, ICCD card no. 01-073-6753.

[13] ICDD-International centre for diffraction data, ICCD card no. 00-41-1104.

[14] ICDD-International centre for diffraction data, ICCD card no. 01-071-6397.

[15] ICDD-International centre for diffraction data, ICCD card no. 01-070-9128.

[16] M.T.S. Nair, L. Guerrero, O.L. Arenas, P.K. Nair, *Appl. Surf. Sci.* **150**, 143 (1999).