Substrate Temperature Influenced Structural and Electrical Behaviour of RF Magnetron Sputtered Ag$_2$Cu$_2$O$_3$ Films

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Ag$_2$Cu$_2$O$_3$ 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$_2$Cu$_2$O$_3$. In the case of films deposited at higher T$_s$, of 523 K, Ag$_2$O was decomposed into Ag. The electrical resistivity of the films deposited at 303 K was $1.2 \times 10^{-5}$ $\Omega$ cm, whereas the films formed at 423 K and subsequently annealed at 498 K showed electrical resistivity of $2.2 \times 10^{-3}$ $\Omega$ cm due to improvement in the crystallinity of single phase Ag$_2$Cu$_2$O$_3$.

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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$_2$Cu$_2$O$_3$. It is isoelectronic with paramelaconite structure (Cu$_4$O$_4$ or Cu$_2^+$Cu$_2^{3+}$O$_3$) with silver cations located at the Cu$^+$ positions. Munez-Rejas et al. [2] have oxidized the Ag$_2$Cu$_2$O$_3$ at room temperature, both electrochemically and by ozone oxidation to achieve the Ag$_2$Cu$_2$O$_4$ (or Ag$_2$CuO$_2$). It crystallizes with croconite structure (Cu$^+$$^+$Mn$^{3+}$O$_3$) with Ag cations located at the Cu$^+$ positions and Cu cations at the Mn$^{3+}$ sites [3]. Ag$_2$Cu$_2$O$_3$ 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 structural and optical properties of AgCuO and Ag$_2$Cu$_2$O$_3$. 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$_2$Cu$_2$O$_3$ 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$_{50}$Cu$_{50}$ 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$_{50}$Cu$_{50}$ target. In this investigation, thin films of Ag$_2$Cu$_2$O$_3$ 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$_2$Cu$_2$O$_3$ 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 $\times$ 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$^\circ$ using monochromatic Cu $K_{\alpha1}$ 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.

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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$_2$Cu$_2$O$_3$ film deposited on a silicon substrate at 303 K and oxygen partial pressure of $2 \times 10^{-2}$ 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 1s. 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$_2$Cu$_2$O$_3$.

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$_2$Cu$_2$O$_3$ [12]. The peak observed at 38.16° is related to the diffraction from (200) plane of Ag$_2$O [13], whereas the peak observed at 44.28° belongs to the Cu$_4$O$_3$ phase [14]. It is understood that the films deposited at 373 K have mixed phase of Ag$_2$Cu$_2$O$_3$, Ag$_2$O and Cu$_4$O$_3$. Further increase in $T_s$ to 423 K has decreased the intensity of Ag$_2$O peak while the Cu$_4$O$_3$ phase disappeared. An additional peak observed at 56.37° was related to the diffraction from (311) plane of Ag$_2$Cu$_2$O$_3$ [15] and the peaks observed at 43.62° and 74.04° correspond to the diffractions from (220) and (422) planes of Ag$_2$Cu$_2$O$_3$. The intensity of (101) and (211) diffraction peaks of Ag$_2$Cu$_2$O$_3$ 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$_2$Cu$_2$O$_3$ with a fraction of Ag$_2$O in Cu$_4$O$_3$ 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$_2$Cu$_2$O$_3$ 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$_2$Cu$_2$O$_3$ 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 ≈ 4.6 nm, which is increased to ≈ 20.0 nm for the increase in $T_s$ to 473 K. The single phase Ag$_2$Cu$_2$O$_3$ films obtained from anneal-
4. Conclusions

Ag$_2$Cu$_2$O$_3$ 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 $2 \times 10^{-2}$ 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$_2$Cu$_2$O$_3$ phase with a fraction of Ag$_2$O$_4$. The films deposited at 423 K followed by an air annealing at 498 K were of single phase Ag$_2$Cu$_2$O$_3$. 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$_2$Cu$_2$O$_3$. The electrical resistivity of the films annealed at 498 K was $2.2 \times 10^{-3}$ Ω cm.

References

[12] ICDD-International centre for diffraction data, ICDD card no. 01-073-6733.
[14] ICDD-International centre for diffraction data, ICDD card no. 01-0716397.