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Substrate temperature influenced structural and optical properties of RF magnetron sputtered pure andcopper doped silver oxide thin films

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Abstract: Pure and copper doped silver oxide films were deposited on glass and silicon substrates held at temperatures in the range 303 – 473 K and at oxygen partial pressure of $2x10^{-2}$ Pa by reactive RF magnetron sputtering technique. Effect of substrate temperature on the physical properties that is chemical binding configuration, structure and surface morphology and optical absorption of the films was systematically studied. Pure silver oxide (Ag_2O)films formed at 303 K wereofnanocrystallinewithgrain size of 75 nm and optical band gap of 2.15 eV. Copper doped silver oxide (Cu-Ag-O) films contained the content of Cu= 4.9 at. %. These films formed at 303 K were of mixed phase with the (202) reflection of $Ag_2Cu_2O_3$ with weak reflections of(-202), (224) and (-204) related to AgO, Cu_4O_3 and AgO respectively. As the substrate temperature increased to 473 K the films contained AgO along with weak reflection of $Ag_2Cu_2O_3$. The grain size of the Cu-Ag-O films increased from 95to 225 nm with the increase of substrate temperature from 303 to 523 K. The optical band gap of Cu-Ag-O films increased from 1.60 to 1.95 eV with increase of substrate temperature.
Key words: Copper doped silver oxide films, Substrate temperature, Structure, Optical properties.

Introduction

Silver oxide films are attracted by researchers for their novel applications in high density optical storage devices, gas sensors, solar cells and antibacterial coatings[1]. Addition of copper to silver oxide leads to ternary phases of $Ag_2Cu_2O_3$ and $Ag_2Cu_2O_4$.Theelectrical conductivity enhanced in silver doped copper oxide films formed by co-sputtering is reported[2]. Recently, silver copper oxide films were formed by co-sputtering of silver and copper targets[3], sputtering of composite $Ag_{80}Cu_{20}$[4], $Ag_{70}Cu_{30}$[5], $Ag_{60}Cu_{40}$[6] and $Ag_{50}Cu_{50}$[7,8,9] targets and studied their composition, structureand optical properties. In the present investigation, nanocrystallinepure and copper doped silver oxide films were deposited on glass and silicon substrates by RF magnetron sputtering under different substrate temperatures. Influence of substrate temperature on the crystallographic structure, surface morphology, chemical bonding configuration and optical properties of the films was systematically studied.

Experimentation

Silveroxide (Ag_2O)and copper doped silver oxide (Cu-Ag-O) films were deposited on glass and silicon substrates by reactive RF magnetron sputtering technique using pure silver and mosaic Cu-Ag targets of 50 mm diameter respectively. Sputter chamber was pumped to an ultimate pressure of $2x10^{-4}$ Pa by using diffusion and rotary pump combination. Pure oxygen gas was introduced in to the sputter chamber to theoxygen partial pressure (pO_2) of $2x10^{-2}$ Pa followed by the addition of sputter gas of argon to achieve the sputter pressure of 4 Pa. The films were formed at different substrate temperatures (Ts) in the range 303 – 523 K. RF power fed to the sputter target for deposition of the films was 65 Watt. The deposited pure and copper doped silver oxide films were characterized by their chemical binding configuration, crystallographic structure, surface morphology and optical properties. Thickness of the deposited films determined with VeecoDektak (model 150) depth profilometer was in the range 90 - 250 nm. The core level binding energies of the films was analyzed with X-ray photoelectron spectroscope (Model PHI 300).X-ray diffraction (XRD) (Bruker D8) with $CuK\alpha_1$ radiation was used to analyze the crystallographic structure of the films. Surface morphology of the films was analyzed by atomic force microscope (Model SPA 400). Optical transmittance of the films formed on glass substrates was recorded using Perkin-Elmer UV-VIS-IR double beam spectrophotometer in the wavelength range 300–2000 nm.

Results and Discussion

Fig. 1 shows the EDAX spectra of Ag_2O and Cu-Ag-O films formed at 303 K. Chemical compositions of the deposited silver oxide and copper doped silver oxide films was determined from their respective peaks. Silver oxidefilmcontained the chemical composition of Ag = 66.9 at. % and O = 32.9 at. %. It indicated that the grown films were Ag_2O. Copper doped silver oxide films showed the content of Cu = 4.9 at. %, Ag = 47.5 at. % and O = 47.6 at. %. There was no much variation in the chemical composition of the films formed at different substrate temperatures. It indicates that copper substituted the silver in the Ag_2O films.

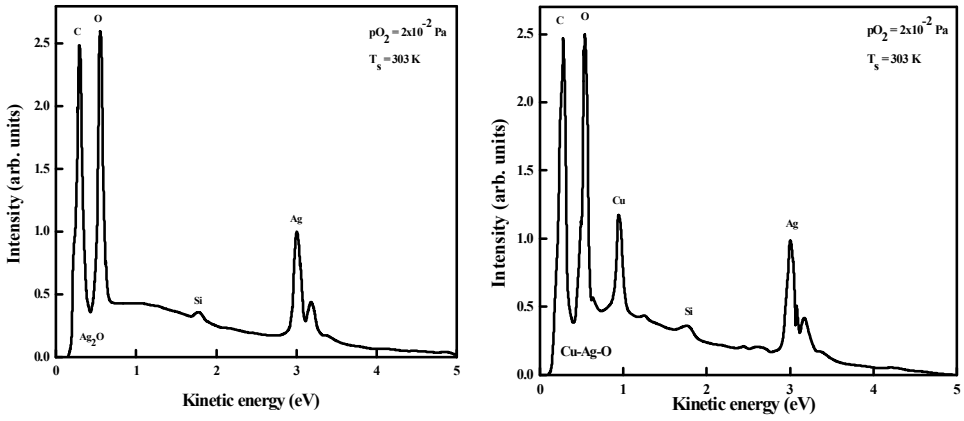

Fig. 1EDAX spectra of Ag_2O and Cu-Ag-O films

Core level binding energies of the films was studied with the X-ray photoelectron spectroscopy. Fig. 2 shows the representative X-ray photoelectron spectra of Ag_2O and Cu-Ag-O films formed at 303 K.Thespectra showed the characteristic core level binding energies of silver, copper and oxygen present in the films. XPS spectrum of pure silver oxide films contained thecore level binding energy of about 529 eVrelated to the oxygen O 1s. The peak seen at about 368 eV correspond to the silver Ag 3d and the peak at around 932 eV was related to the copper Cu 2p. Fig. 3(a) shows the XPS narrow scan spectra of the Ag_2O and Cu-Ag-O films in the binding energy range 364 – 377 eV.Ag_2O films spectra showed the characteristic core level binding energies of 367.6 eV and 374.2 eV related to the Ag $3d_{5/2}$ and$3d_{3/2}$respectively due to spin-orbit splitting[4]. The Cu-Ag-O films exhibited the core level binding energies of 368.2 and 373.6 eVrelated to Ag $3d_{5/2}$ and$3d_{3/2}$. Shift in the core level binding energies was due to the substitution of copper in silver oxide. It is also seen that the core level of oxygen O 1s was observedat 529.2 eV in Cu-Ag-O films (fig. 3.b). In the case of copper doped films the core level binding energy peaks observed at 932.7 eV and 947.8 eV were of copper Cu $2p_{3/2}$ and Cu $2p_{1/2}$ with separation in the binding energy of 15.1 eV. It is achieved Ag $3d_{5/2}$binding energy of 367.9 eV in $Ag_2Cu_2O_3$ and 366.5 eV in $Ag_2Cu_2O_4$[10].

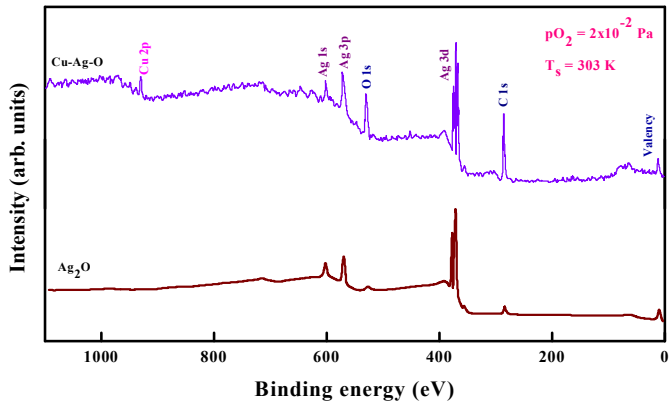

Fig. 2XPS spectra of Ag_2O and Cu-Ag-O films

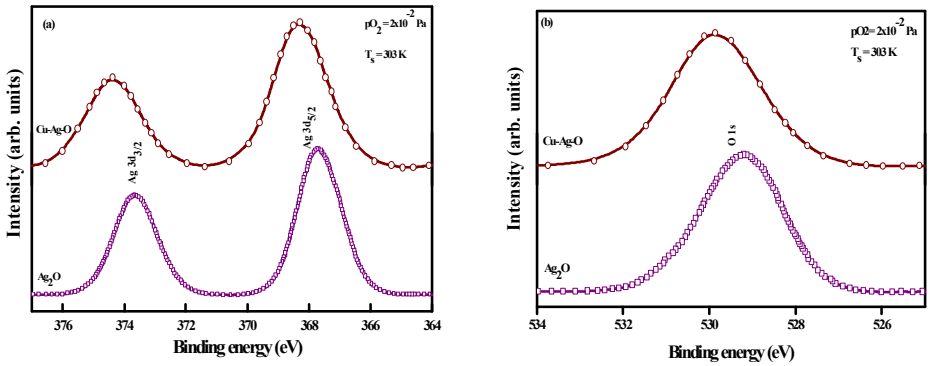

Fig. 3 XPS spectra of Ag_2O and Cu-Ag-Ofilms:(a) silver Ag 3d and (b) oxygen O 1s

Fig. 4(a)shows the X-ray diffraction profiles of Ag_2O films deposited on glass substrates held at temperatures in the range 303-473K. The Ag_2O films formed at 303K showed a strong peak at 2θ =32.7º of (111) Ag_2O (ICCD Card number: 00-41-1104) with cubic structure. As the substrate temperatureincreased to 423K the intensity of the (111) reflection of Ag_2O decreased, with the presence of reflections (111) and (200) of Ag (ICCD Card number: 00-004-0783). It revealed that the films formed at 423 K wereof mixed phase of Ag_2O and Ag. Athigher substrate temperature of 473 K, the (111) of Ag_2O disappeared and increase in the intensity (111) of Ag. It revealed that the films formed at 473Kwere transformed from Ag_2O phase to silver phase. Fig. 4(b) shows the X-ray diffraction profiles of Cu-Ag-O films formed at different substrate temperatures. The films deposited at 303 K showed strong reflection (202) of $Ag_2Cu_2O_3$ (ICCD Card number: 01-073-6753) along with weak reflections (-202) and (-204) of

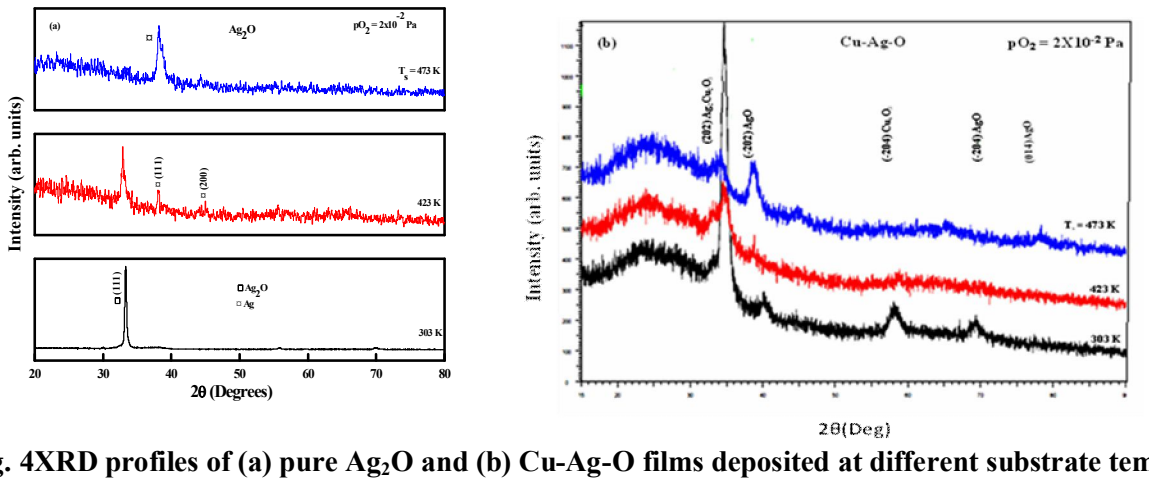

Fig. 4XRD profiles of (a) pure Ag_2O and (b) Cu-Ag-O films deposited at different substrate temperatures

AgO(ICCD Card number: 04-007-1369) and (-204) ofCu_4O_3 (ICCD Card number: 01-071-6397).As the substrate temperature increased 423 K, the full width at half maximum intensity of $Ag_2Cu_2O_3$ and (-202) reflection of AgO were decreased and (-204) of Cu_4O_3 phase disappeared. The broadening of the diffraction peaks indicated the growth of nanocrystalline films. At higher substrate temperature of 473 K the films showed the mixed phase of $Ag_2Cu_2O_3$ andAgO.Crystallite size of the films calculated from the X-raydiffraction peak using Debye - Scherrer'srelation decreased from 25 to 10 nm with increase of substrate temperature from 303 to 473 K respectively.

Surface morphology of the films was significantly influenced by the substrate temperature. Fig. 5 shows the three dimensional atomic force micrographs of theAg_2O and Cu-Ag-O films formed at different substrate temperatures. InAg_2O films, as the substrate temperature increased from 303 to 473 K the grain size increased from 75 to 195 nm respectively. Atomic force micrographs of Cu-Ag-O films formed at 303K showed spherical shape grains with size of 95 nm. When substrate temperature increased to 473K the size of the grains increased to 225 nm and also transformed from the spherical shape grains into pyramidal-like shape due to acquired thermal energy from the substrate.

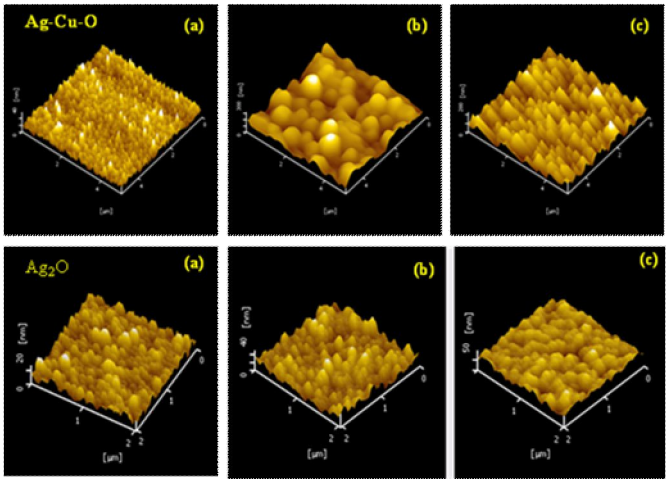

Fig. 5AFM Micrographs of Ag_2O and Cu-Ag- O films: (a) Ts =303 K, (b) 423 K and (c) 473K

Fig. 6 shows the optical transmittance spectra of Cu-Ag-O films formed at different substrate temperatures. The optical transmittance of the films formed at 303 K was low. As the substrate temperature increased the transmittance of the films increased. It is also noticed that the absorption edge of the films shifted towards lower wavelength side with increase of substrate temperature. The absorption coefficient (α) of the films was calculated from the optical transmittance (T) data using the relation

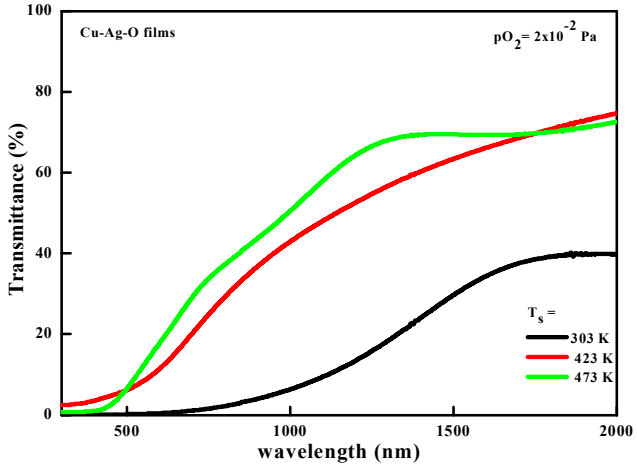

Fig. 6Transmittance spectra of Cu-Ag-O films formed at various substrate temperatures

$$\alpha = (1/t) \ln T \quad \text{----- (1)}$$

wheret is the film thickness. The optical band gap (E_g) of the films was estimated from the plots of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) using Tauc's relation[11]

$$(\alpha h\nu) = A (h\nu - E_g)^m \quad \text{----- (2)}$$

where exponent m = ½ for direct band gap assuming that direct transitions takes place in these films. Fig. 7shows the plots of $(\alpha h\upsilon)^2$ versus photon energy ($h\upsilon$) of Cu-Ag-O films formed at different substrate temperatures. Extrapolation of the linear portion of the plots of $(\alpha h\nu)^2$ versus photon energy to $\alpha = 0$ resulted the optical band gap of the films. Optical band gap of the films increased from 1.60 to 1.95 eV with increase of substrate temperature from 303to 473 K. It is to be noted that the optical band gap of pure Ag_2O films increased from 2.05 to 2.13 eV with increase of substrate temperature from 303 to 373 K due to enhanced crystallinity while those formed at 423 K exhibited 1.92 eV due to existence of mixed phase of silver oxide and silver[4]. It was reported that the optical band gap of $Ag_2Cu_2O_3$ films formed by RF magnetron sputtering with $Ag_{70}Cu_{30}O$ target, increased from 1.95 to 2.15 eV with increase of substrate temperature from 303 to 523 K while at 548 K decreased to 2.11 eV[5].An optical band gap of 2.24 eV in RF magnetron sputtered $Ag_2Cu_2O_3$ films formed at substrate temperature of 523 K is reported[8].

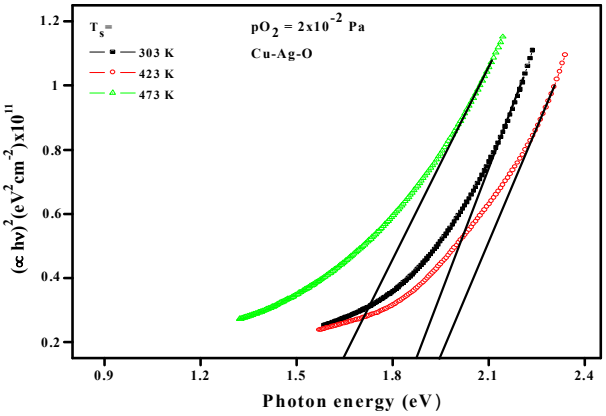

Fig 7$(\alpha h\nu)^2$ versus photon energy ($h\nu$) of Cu-Ag-O films

Conclusions

Thin films of pure and copper doped silver oxide were formed on glass and silicon substrates held at temperatures in the range 303 – 473 K by employing reactive RF magnetron sputtering technique. The deposited films were characterised for their chemical composition, structure and optical properties. The deposited films were nanocrystalline in nature. Silver oxide films formed at 303 K were of single phase Ag_2O while those deposited at 473 K were transformed in to metallic silver. The copper doped silver oxide (Cu-Ag-O) films formed at 303 K were of mixed phase AgO, Cu_4O_3 and $Ag_2Cu_2O_3$. As the substrate temperature increased to 473 K the films were of nanocrystalline with mixed phase of $Ag_2Cu_2O_3$ and AgO. XPS studies confirmed the characteristic core level binding energies of the constituent elements present in the films. Atomic force micrographs of the films revealed that the grain size was in the range 95 – 225 nm in the substrate temperature range of investigation. The optical band gap of the Cu-Ag-O films increased from 1.60 to 1.95 eV with increase of substrate temperature from 303 to 473 K respectively.

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