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Indium doped silver oxide thin films prepared by reactive electron beam evaporation technique: electrical properties

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Abstract The indium doped silver oxide thin films have been prepared at 275 °C on soda lime glass and silicon substrates by reactive electron beam evaporation technique; the deposition rate has been varied (by varying the electron beam current) in the range 0.94–16.88 nm/s keeping the oxygen flow rate constant. These films are polycrystalline. The electrical resistivity for these films decreases with increasing deposition rate. The AIO films prepared with a deposition rate of 5.7 nm/s show near p-type conductivity. The work function has been measured on these films by contact potential method using Kelvin Probe. The surface morphology of the films has been evaluated using atomic force microscopy (AFM). The roles of indium doping and oxygen vacancies in the electrical properties of these films have been analyzed; the ionized impurity scattering is the dominant mechanism controlling the electrical conduction in these films.

Introduction

The silver oxide (AO) and indium oxide (IO) thin films have been studied by several investigators in view of the several applications of these thin films. The studies reveal that silver oxide exhibit p-type conduction under specific preparation conditions and indium oxide always is an n-type semiconductor. However, silver indium oxide (AIO) when formed into Delafossite crystal structure is predicted to show a p-type conduction. It has been indicated that to obtain a Delafossite structure in thin films and the window to obtain the p-type conduction in the transparent conducting oxides is extremely narrow [1]. Thus the p-type transparent conducting oxide (TCO) thin films is a topic of intense investigation by several groups to realize a transparent p–n junction [1–12]. A recent study carried out in our laboratory on the silver oxide thin films prepared by reactive electron beam evaporation [3] and DC magnetron sputtering techniques [4] has shown that (i) the rate of evaporation/deposition seems to be controlling the nature of conduction: p- or n-type in these films and (ii) the oxygen vacancies play a major role in the electrical conduction process. Silver doping in indium oxide (IO) thin films have interesting observations in the electrical properties, namely, type conversion (from n to p) with varying oxygen stoichiometry in the film [5]. The AIO thin films prepared by reactive electron beam evaporation technique have given very interesting results [6].

In the present investigation, we report the results of indium doping in the silver oxide thin films and the role of oxygen in these films prepared by reactive electron beam evaporation technique. The source material is a pellet prepared from thoroughly mixed powders (purity 99.99%) of Ag_2O/In_2O_3 = 80:20 mol%. During the ebeam evaporation, the oxides of silver and indium are dissociated; thus the evaporation rate determines the stoichiometry of the silver, indium and oxygen in the thin films. Thus the role of indium and oxygen in the silver oxide thin films may be analyzed. The physical properties of these AIO films depend upon the bonding among indium–silver and oxygen. P-type conduction is possible if the concentration of localized covalent bonds between silver and oxygen dominate over the oxygen ion vacancies available in the lattice;

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if the films posses Delafossite crystal structure, excess oxygen may give rise to the hole concentration [1].

Experimental methods

The indium doped silver oxide thin films are deposited at 275 (±3) °C by reactive electron beam evaporation technique on cleaned soda lime glass and silicon (100) oriented and single side polished, Float zone grown substrates in a commercially available evaporation unit (Hind Hivac, Model 12A4D). The silicon substrates are used for atomic force microscopy (AFM) measurements. The source material (placed in a graphite crucible) is a pellet prepared from thoroughly mixed powders (purity 99.99%) of Ag_2O/In_2O_3 = 80:20 mol%. The oxygen flow during the evaporation is kept constant at 0.54 sccm. The experimental details are given in our earlier paper [3].

The surface morphology of the samples has been evaluated by Atomic Force Microscopy (Digital Model DI 3000) in the tapping mode with a silicon tip. The compositional analysis of the films has been carried out by Energy Dispersive Analysis of X rays (EDAX). The crystalline nature of the films is observed by x-ray diffraction (Shimadzu, Model XD-D1) using Cu Kα radiation. The thickness of the films have been monitored at 170 nm by crystal thickness monitor and are also measured by Gaertner ellipsometer (Model 119 XUV) using He–Ne laser (632.8 nm). The electrical resistivity of the films is measured at room temperature (300 K) by the conventional van der Pauw method; the variation of electrical resistivity with temperature is measured by linear four probe method in the temperature range 25–300 K. The Hall effect measurements (with a maximum magnetic field of 0.75 T) have been carried out at room temperature (300 K) in an ''in house'' fabricated sample holder. The conductivity type of the film is determined by Hot probe technique [13]. The contact potential difference (cpd) between the films (as prepared) and the stainless steel reference electrode has been measured by an indigenously designed and fabricated Kelvin Probe set up [14]. The accuracy in the cpd measurement is 0.1 mV.

Results

In the present experiment, it is expected that the stoichiometry of the AIO film depends upon the electron beam filament current; with increasing filament current, the oxygen content in the film is expected to decrease (and indium content increases). The thickness of the films is 170 nm.

The X-ray diffraction pattern of the films (Fig. 1) show polycrystalline nature; the observed peaks (at 32.7°)

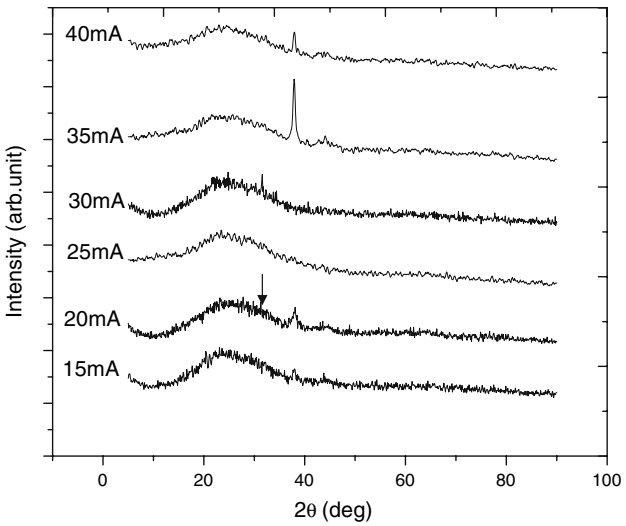

Fig. 1 X-ray diffraction for indium doped silver oxide thin films grown at different electron beam filament currents

correspond to Ag_2O (cubic) with preferred orientations of (111) planes for 15 and 20 mA filament currents. The films grown with 25 mA of filament current show amorphous nature. All the films except the one prepared with 25 mA filament current (5.7 nm/s deposition rate) are n-type (also confirmed by Hot probe technique); the carrier concentration (assuming that majority carriers are dominant in the conduction process), Hall mobility and the work function of these films measured at room temperature (300 K) are given in Table 1. The variation of resistivity of these films measured as a function of temperature (25–300 K); the data are fitted to a straight line and the slope and *y*-intercept are given in Tables 2 and 3 which show positive and negative slopes indicating that the films are metallic and semiconducting, respectively, dependant on the evaporation rate. The data are presented in Tables (instead of graphical presentation) mainly to show the subtle variations in the measured values.

The AFM pictures revealing the surface morphology of the thin films prepared (on silicon substrates) with different filament currents are given in Fig. 2. The average surface roughness parameter R_a is evaluated [15] and presented in Fig. 3.

Discussion

In the present experiment, the only process parameter varied is the electron beam filament current: 15–40 mA in steps of 5 mA (oxygen flow rate is kept constant at 0.54 sccm). The dissociation temperatures of the silver and indium oxides being different, the indium and silver concentration in the film are anticipated to vary with the

Table 1 Physical properties of indium doped silver oxide thin films grown with different filament currents (deposition rates)

Filament current (I_F)mA /deposition rate (nm/s)	Thick-ness (nm)	Film refractive index (632.8 nm) (n)	Hall Coeff (R_H) ~ 10^{-4} cm^3 $coul^{-1}$	Resistivity (Ohm cm) ~ 10^{-4}	Carrier conc. ~10^{22} cm^{-3}	Hall-mobility (μ_H) cm^2 v^{-1} s^{-1}	Work function (eV)	Degenerate temp T_D (10^3 K)	Mean free path ''l'' (nm)
15/0.94	169.6	1.216	–5.03	1.073	1.24	4.69	4.756	3.38	2.21
20/1.415	169.8	1.214	–2.60	0.481	2.40	5.40	4.739	5.26	3.17
25/5.70	171.2	1.218	–0.15	5.362	41.07	0.03	4.657	34.93	0.05
30/5.63	168.9	1.214	–3.45	0.790	1.81	4.37	4.765	4.35	2.33
35/16.88	168.8	1.211	–2.06	0.214	3.03	9.65	4.788	6.14	6.13
40/16.88	168.9	1.211	–3.68	0.385	1.70	9.55	4.777	4.18	5.00

Table 2 The variation of electrical resistivity of indium doped silver oxide thin films with temperature (25–300 K): the slope and y-intercept

Filament current (mA)/deposition rates (nm/s)	Slope = dρ/dT (10^{-8} Ohm cm/K)	ρ-intercept at 25 K (10^{-5} Ohm cm)	ρ-intercept at 300 K (10^{-5} Ohm cm)	
15/0.94	6.43	7.14	10.73	Positive
20/1.415	5.28	7.87	4.81	Negative
25/5.70	2.96	66.97	53.62	Negative
30/5.63	7.22	7.10	7.90	Positive
35/16.88	2.77	1.43	2.14	Positive
40/16.88	4.77	4.69	3.85	Negative

Table 3 The atomic concentration (as evaluated by EDAX) of silver, indium and oxygen in the AIO films grown at 275 °C substrate temperatures with different deposition rates (filament currents)

Substrate temperature (°C)	Filament current (mA)/deposition rate (nm/s)	EDAX results (at%)		
		Ag	In	O
275	10/0.05	46.10	12.34	41.56
	15/0.89	47.23	11.66	41.11
	20/2.67	55.12	6.93	37.95
	25/5.70	55.95	6.45	37.60
	30/5.33	56.59	6.04	37.36
	40/16.0	16.04	30.37	53.58

filament current. A closer look at the experiment suggests that with increasing filament currents, the dissociation of the oxides of silver and indium add to the volume of oxygen in the growth chamber. Thus, even though the oxygen flow is kept constant through mass flow controllers, the total oxygen in the chamber varies. The film formed on the substrate: indium doped silver oxide, depends upon the reactivity of indium and silver with oxygen at the substrate temperature: 275 °C. The EDAX data indicate the stoichiometry of the grown films.

All the films grown are polycrystalline (except the one grown with 25 mA of filament current which is amorphous). The X-ray diffraction data collected show the presence of Ag_2O (cubic) 32.8°, Ag_3O_4 (monoclinic): 33.4° and In_2O_3 (Rhombohedral): 30.9° for the filament currents of 15, 20, 35 and 40 mA. For filament current of 30 mA, the X-ray diffraction peaks do correspond to neither silver oxide nor indium oxide.

The AFM pictures (Fig. 2) of the indium doped silver oxide thin films indicate that the surface morphology depends upon the deposition rate. The scan area of observation is 1×1 μm^2. The clusters bonding the spherical grains in the films are seen; the size of the spherical grains gradually increases with filament current. Both average roughness (R_a) and root mean square (rms) roughness decrease with deposition rate (Fig. 3). With the increasing grain size and decreasing the surface roughness of the films, enhances the Hall mobility and the free carrier mean free path in the films contributing to the improved electrical properties (Table 1).

All the films (except the one prepared at 25 mA filament current) are n-type and are degenerate (Table 1) [16]; (for the calculation of degeneracy, the effective mass of the electrons is assumed to be $0.67m_e$ (m_e is free electron mass) in these films). The mean free path of the electrons (l) for these indium doped silver oxide films calculated from the carrier concentration and Hall mobility [17] range between 2.2 nm and 6.1 nm (Table 1) except for the amorphous films (25 mA filament current).

The AIO films prepared at 25 mA filament current show distinctive features in their properties (Table 1): namely, low (negative) Hall coefficient, low Hall mobility, very

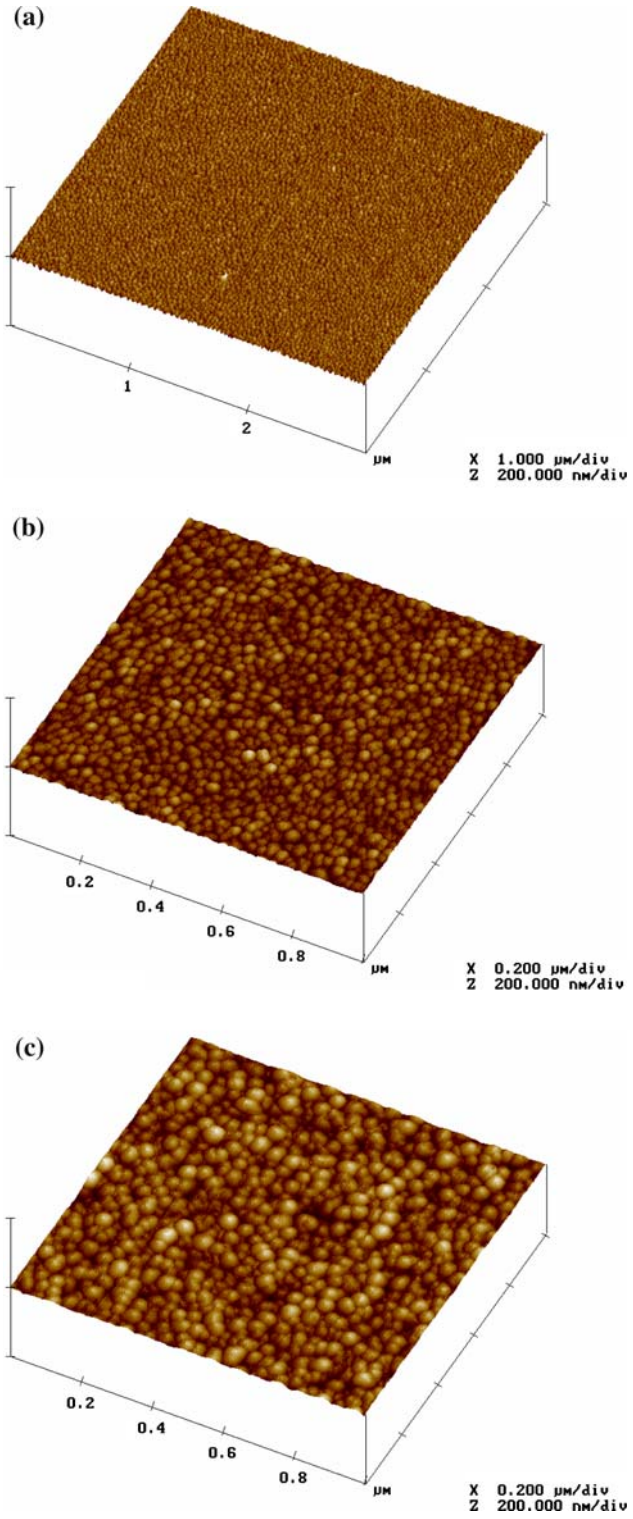

Fig. 2 AFM pictures for indium doped silver oxide thin films grown at different filament currents. (**a**) 15 mA, (**b**) 25 mA, (**c**) 40 mA

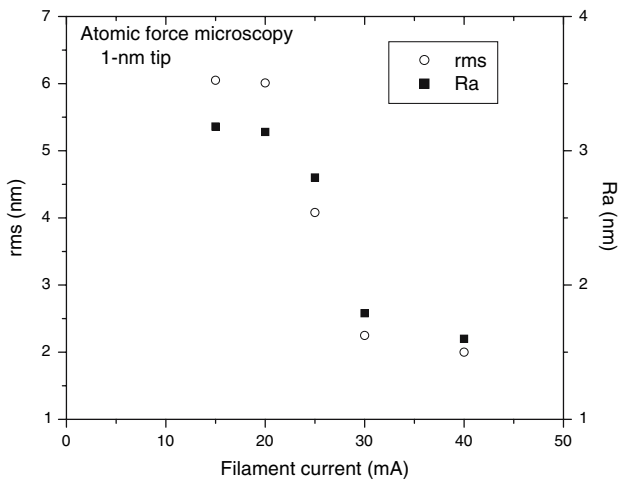

Fig. 3 The root mean square (rms) roughness and average roughness (R_a) versus filament current for indium doped silver oxide thin films as a function of filament current

high carrier concentration, positive Seebeck coefficient (by Hot probe technique) and very high cpd value (low work function). The interesting fact is that though the values measured/calculated: the carrier concentration (of 41.07×10^{22}/cc), Hall Mobility, Degenerate temperature and the mean free path are rather unrealistic; these results may be attributed to the bipolar conduction in the transport process where an extreme care and caution is to be exercised in evaluating the carrier concentration [4, 6]. All these features in conjunction with the arguments proposed in our earlier paper [4, 6], clearly indicate that the AIO films prepared at 5.7 nm/s are p-type (hole dominated). Where as the films deposited with an evaporation rate of 5.63 nm/s do not show any of the features: mainly the high carrier concentration and the lower work function substantiate the view that the window to prepare the p-type TCO thin films is extremely narrow [1]. The density of valence bonds (equivalently, the localization of the covalent bonds) is higher for the films deposited at 5.7 nm/s; more fundamental investigations are required for a detailed understanding.

It is well known that the electrical transport mechanism in metal oxides is controlled by the oxygen ion vacancies. The role of oxygen in the silver oxide thin films (including the partial ionic charge of silver) has been explained in our earlier paper [4]. In the present investigation, indium is doped into the silver oxide lattice. Ideally, for every oxygen vacancy, silver and indium contribute one and three conduction electrons, respectively. The chemical bond between silver–oxygen is ionic and indium–oxygen is partially covalent [3, 4, 18]. Thus, indium doping is expected to enhance the carrier concentration in the silver oxide thin films, contrary to the observation.

With the assumption that the thermal generation of free carriers is negligibly small in the temperature range studied (25–300 K); the variation of resistivity with temperature may be attributed to the mobility influenced by the

scattering mechanisms in the film. Three important scattering mechanisms operate in the films are due to the lattice, the grain boundaries and the ionized impurities. In the low temperature range (including the room temperature), the phonon scattering is very small. Following the analysis in our earlier paper [17], the grain boundary scattering is evaluated using Petriz type of relation:

$$\mu = \mu_0 T^{-1/2} \exp(-\Phi_B/KT) \quad (1)$$

where Φ_B is the activation energy which corresponds to grain boundary potential. The value of Φ_B is evaluated from the plot between Ln ($\mu T^{1/2}$) versus ($1/T$) is in the range 10–33 meV which is very small; also, the AFM measurements reveal that the grain size of the films increase with increasing ebeam current. Thus it may be inferred that the grain boundary scattering is not dominant in these films [17].

To calculate the ionized impurity scattering for these degenerate films (following Thomas Fermi approximation [16]), one requires the density of scattering centers (along with low frequency dielectric constant). It may be possible to infer qualitatively that the ionized impurity scattering is a dominant mechanism in these indium doped silver oxide thin films mainly because the silver–oxygen and indium–oxygen bonds are partially ionic.

It is expected that an effective enhancement of free carrier concentration (as measured by Hall effect) contributing to conductivity may elevate or lower the Fermi level; consequently, the work function of the material correspondingly changes. The variation of the Hall coefficient closely follows the variation in indium content in the film. It may be mentioned that evaluation of carrier concentration by Hall measurements having both electrons and holes, as in p-type transparent conducting oxide thin films, requires a careful reexamination [19].

Conclusion

The conclusions of the present investigation are (i) a p-type indium doped silver oxide thin films have been synthesized and (ii) the nature of conduction: n- or p-type, in the transparent conducting oxide thin films is shown to depend upon the rate of evaporation/sputtering as supported by the earlier work from our group [4].

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