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Effect of Annealing on Structural and Optical Properties of Cu Doped In_2O_3 Thin Films

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Cu-doped In_2O_3 thin films were prepared using flash evaporation method at different Cu-doping levels. The effect of annealing was studied on the structure, morphology and optical properties of the thin films. The films exhibited cubic structure and optical transmittance of the films increasing with annealing temperature. The highest optical transmittance of 78 % was observed with band gap of 4.09 eV.

Keywords: Indium oxide, Flash evaporation, Transparent conducting oxide.

PACS numbers: 68.55.Jk, 73.61. – r, 78.55. – m

1. INTRODUCTION

It is well known that transparent conducting oxides (TCOs) found various optoelectronic applications [1]. In order to achieve high optical transmittance at high conductivity, continuous efforts are made such as introducing the foreign elements into the host matrix [2-4], creating the oxygen deficiency [5], or method of preparation such as dc reactive magnetron sputtering [6], chemical spray pyrolysis [7], pulsed laser deposition[8], high density plasma evaporation [9], etc. In order to enhance the efficiency of solar cells, tremendous efforts were made to allow much radiation for the cell. It can be done by using TCO as a top electrode which can allow the most of the radiation and observe conductance (window layer). In order to achieve that, solar cells with heterojunction structures are used. Wide band gap TCO materials such as CdO, ZnO, SnO_2 and In_2O_3 can fulfill this requirement [10, 11]

Currently In_2O_3 is attracting much interst as it is the best TCO among the other TCOs. In_2O_3 is a wide band gap semiconductor with cubic bixbyite structure. In_2O_3 is widely used in optoelectronic and spintronic applications. In addition to this its cubic structure will allow to use low cost substrates such as MgO, which has interesting applications. In order to enhance the band gap, various doping elements such as Li, Cr, Ni [12-14] were doped into the host material and their physical properties were extensively studied. Hence here the attempt is made to dope the impurity copper (Cu) to study the change in structural, optical properties of In_2O_3 by doping using the flash evaporation method.

2. EXPERIMENTAL PROCEDURE

2.1 Preparation of Cu Doped In_2O_3 Thin Films

Cu-doped In_2O_3 thin films were prepared by flash evaporation method using 12 in. vacuum coating unit (Model: 12A4D). Pure In_2O_3 (99.999 %, Sigma Aldrich) and Cu_2O (99.99 %, Sigma Aldrich) powders were taken as the source materials and mixed thoroughly by mechanical method at 1-5 at. % of doping levels of Cu. The powder was added in the chute which is coupled with vibrating motor. The substrate temperature of 373 K was maintained and the films were coated on a corning 7059 of glass substrates. After that one set of films had been annealed in air at 523 K for 2 hrs and the other set of films had been annealed in the air ambience at 623 K for 2 hrs.

2.2 Characterization of Cu Doped In_2O_3 Thin Films

The structural characteristics were done using powder X-ray diffractometer (D8 Advance, BRUKER), surface and chemical analyses were done using SE and EDS (Oxford make Inca Penta FETX3 EDS attachment in Carl Zeiss EVO MA 15 SEM instrument), the optical transmittance, absorbance were studied using UV-Vis-NIR spectrophotometer (JASCO-V-670).

3. RESULTS AND DISCUSSION

Fig. 1(a), (b) and (c) show the X-ray diffraction patterns of Cu doped In_2O_3 thin films deposited at 373 K, annealed at 523 K and 623 K with different Cu doping levels (1, 3, and 5 at. %). In Fig. 1(a) X-ray diffraction patterns of Cu doped In_2O_3 films at copper doping levels of 1, 3 and 5 at. % were shown in order to present clearly the changes in the diffraction peaks. Polycrystalline nature was observed in the films deposited at 373 K. The diffraction peaks (101), (002) and (202) reflect the presence of unreacted indium (In) in the films. It indicates that the substrate temperature of 373 K was not sufficient for the complete oxidation of indium (In) into In_2O_3. It may be due to insufficient thermal energy for the films to be oxidized. In Fig. 1(a) the intensity of the peak (101) is higher at lower Cu doping levels (3 at. %) and thereafter it decreases at higher Cu doping levels (5 at. %). And the (002) orientation with low intensity was also observed at lower doping levels but it completely disappeared at higher doping levels (5 at. %). The shift in diffraction angle (2θ) towards lower values was observed when the doping levels were increased from 1-5 at. %. It clearly reflects that the substitution of doping occurs in the matrix In_2O_3. The grain size was calculated using Debye-Scherrer's relation and it found that they are in the range of 22 nm to 50 nm. The summary of copper

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doping levels, diffraction angle (2θ), full width at half maxima (FWHM), inter planar distance observed (d_{obs}), calculated (d_{cal}), orientations and grain size were given in Table 1.

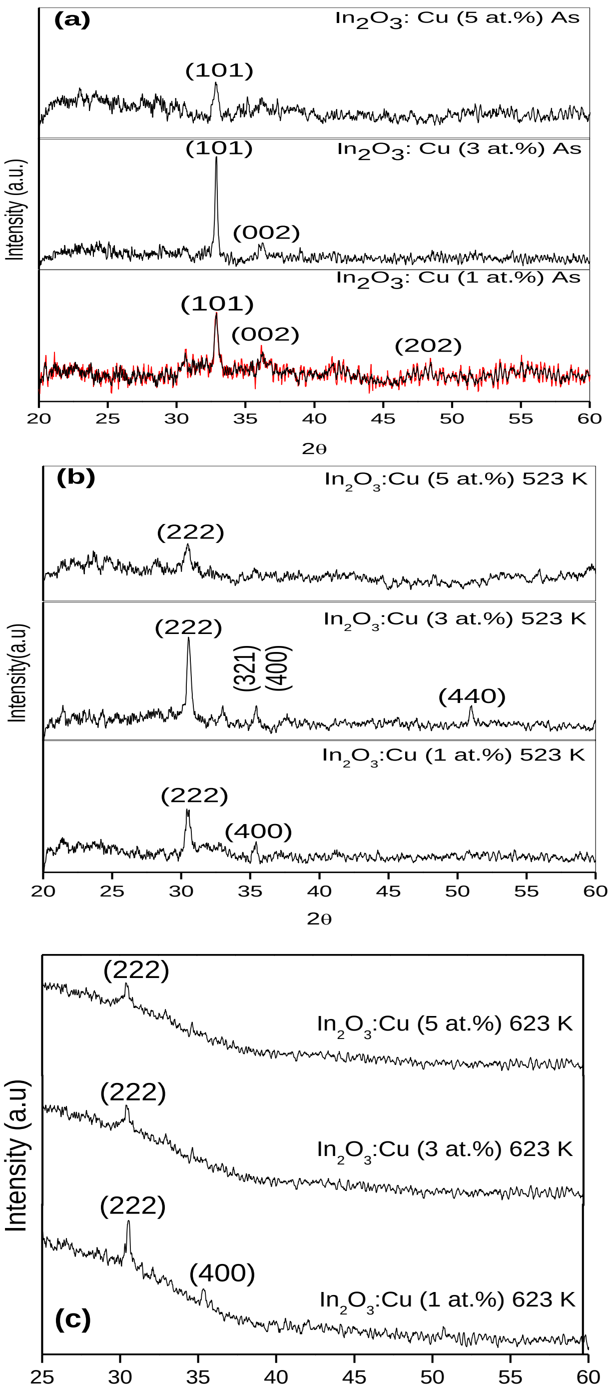

Fig. 1 – X-ray diffraction patterns of the Cu doped In_2O_3 films (a) deposited at 373 K (b) annealed at 523 K and (c) annealed at 623 K

Fig. 1(b) shows XRD patters of the 1, 3 and 5 at. % of Cu-doped In_2O_3 thin films annealed at 523 K. In order to avoid excess of indium in the films deposited at 373 K, the films were annealed to 523 K for 2 hrs in air ambience. The diffraction pattern shows a clear change in the structure of the films from tetragonal indium to cubic indium oxide. The orientation

Table 1 – The summary of copper doping levels, diffraction angle (2θ), full width at half maxima (FWHM), inter planar distance observed (d_{obs}), calculated (d_{cal}), orientations and grain size

Cu (at. %)	FWHM	2θ	d_{obs}, Å	d_{cal}, Å	*hkl*	β (nm)
1	0.217	32.96	2.714	2.718	101	39
		36.33	2.470	2.473	202	37
		48.37	1.880	1.882	202	126
3	0.129	32.88	2.721	2.724	101	67
		36.29	2.473	2.475	202	22
5	0.190	32.84	2.720	2.727	101	45

(222), (400), (321) and (440) reflect the cubic structure of indium oxide thin films [15]. No new orientations other than indium oxide were observed in the X-ray diffraction patterns. It indicates that the metal indium was not observed in the X-ray diffraction patterns. Moreover, crystallinity of the films was enhanced by increase in annealing temperature. The grain size of Cu doped In_2O_3 thin films was calculated from Debye-Scherrer relation [16] and it decreased from 38 nm to 18 nm for 1-5 at. % of Cu-doping levels. The shift in diffraction angle (2θ) towards higher angles was observed at lower doping levels. Similar results were also observed in Ga-doped CdO thin films [17]. But no significant change in diffraction angle (2θ) even at 5 at. % was observed in Mn-doped ZnO thin films [18]. The summary of copper doping levels, full width at half maxima (FWHM), inter planar distance calculated (dcal), grain size, lattice constant and strain were calculated and tabulated in Table 2.

Fig. 1(c) shows X-ray diffraction patterns of the Cu-doped In_2O_3 films deposited at different doping levels (1-5 at. %) which were post annealed at 623 K. It was done because the structural changes were observed from the deposited to the post annealed films and the orientations of the films also changed with the post annealing. Hence here 5 different doping levels (1-5 at. %) were considered and annealed at 623 K for 2 hrs. Further improvement in the crystalline nature of the films was observed. No significant change in either the orientation of the films or structure of the films was observed. The increase in the intensity of the films was observed and the orientation (222) remains constant even up to 5 at. % of Cu doping level. But the (400) orientation disappeared at higher doping levels. It clearly says that stable cubic structure was observed for the films annealed at 623 K. The grain size of the films decreased from 39 nm to 22 nm for the films at (1-5 at. %) of Cu doping levels. Further raise in annealing temperature was not done as high temperature is not favourable for flexible substrates like plastics or polymer. The mechanical strain was calculated for the films annealed at 523 K and 623 K for 2 hours using the relation $(\beta\cos\theta) / 15$ and it is given in Table 2 and Table 3.

Fig. 2 shows the EDAX spectrum of the Cu-doped In_2O_3 thin films at 3 at. % annealed at 623 K for elemental composition. The percentages of Cu, In and O were found to be as follows oxygen 60.08 %, copper 2.51 % and indium 37.41 %.

Fig. 3 shows the scanning electron microscope (SEM) images of the Cu-doped In_2O_3 films (3 at. %)

annealed at 523 K and 623 K for 2 hrs. Very small grains of spherical shape over entire substrate surface were observed and average grain size is about 30 nm which is close approximation to XRD data.

Table 2 – The summary of copper doping levels, full width at half maxima (FWHM), inter planar distance calculated (d_{cal}), orientations and grain size, lattice constant (Å) and strain developed of Cu doped In_2O_3 thin films

Cu. (at. %)	FWHM	$d_{cal,}$ (Å)	hkl	β (nm)	a (Å)	Strain
1	0.224	2.933	222	38	10.160	0.0144
		2.537	400	36	10.148	
3	0.249	2.925	222	34	10.132	0.0160
		2.932	222	22	10.156	
5	0.454	2.933	222	18	10.160	0.0292

Table 3 – The summary of copper doping levels, full width at half maxima (FWHM), inter planar distance calculated (d_{cal}), orientations and grain size, lattice constant (Å) and strain developed of Cu doped In_2O_3 thin films

Cu. (at. %)	FWHM	$d_{cal,}$ (Å)	hkl	β (nm)	a (Å)	Strain
1	0.220	2.929	222	39	10.146	0.0141
	0.248	2.540	400	36	10.160	0.0157
2	0.335	2.923	222	30	10.128	0.0215
	0.216	2.923	400	40	10.133	0.0137
3	0.282	2.927	222	25	10.141	0.0181
4	0.389	2.933	222	22	10.161	0.0523
5	0.250	2.937	222	34	10.174	0.0160

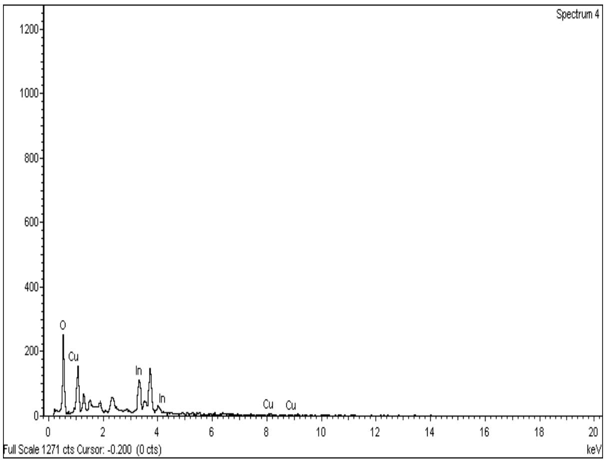

Fig. 2 – EDAX spectrum of Cu-doped In_2O_3 films (3 at. %) annealed at 523 K

Fig. 4 shows the optical transmittance spectra of the Cu-doped In_2O_3 thin films annealed at 623 K. The optical transmittance of the deposited films was poor. It was about 20 %. It may be due to reflectance as indium was not completely oxidized in the films. Similar results were also observed in X-ray diffraction patterns in which the films were indium rich. Hence low optical transmittance for the deposited films was observed. The optical transmittance of the films decreased with the increase in doping level. But for the films annealed at 623 K, the optical transmittance increased and became maximum of 78 % at 5 at. % of Cu doping level. Moreover, all the films exhibited high optical transmittance in IR region. The optical band gap of the

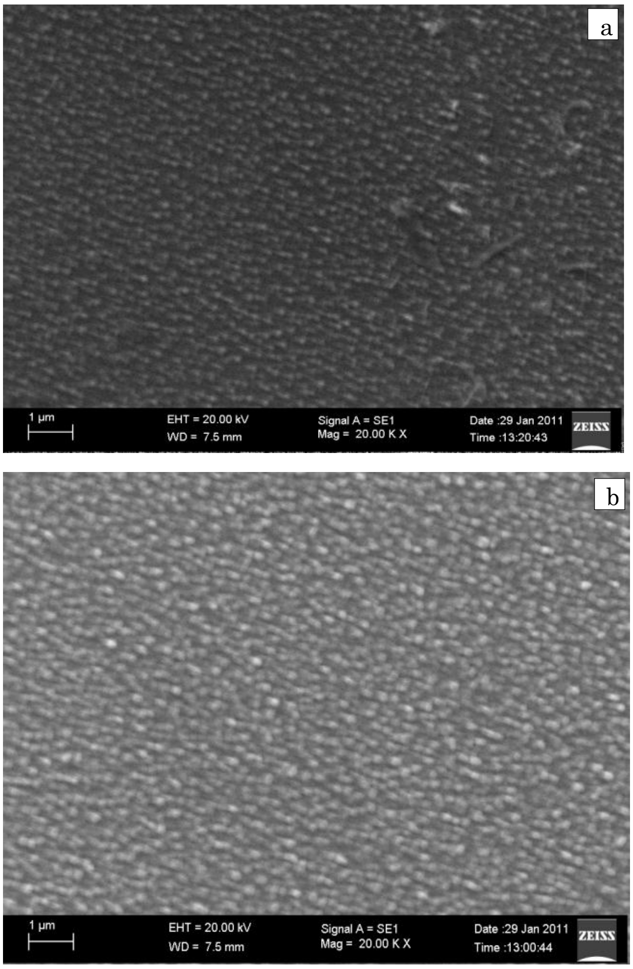

Fig. 3 – SEM images of Cu-doped In_2O_3 films (3 at. %) annealed at (a) 523 K and (b) at 623 K

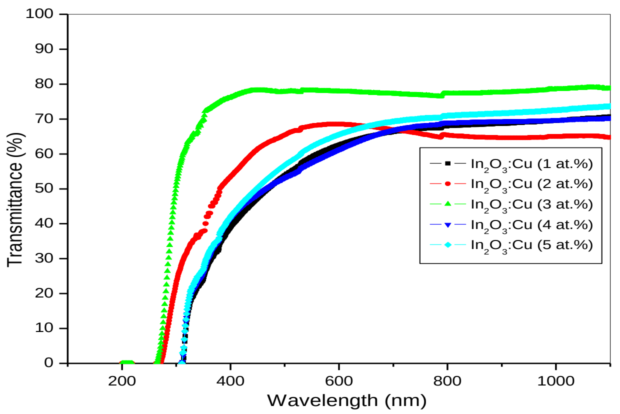

Fig. 4 – Optical transmittance spectra of Cu-doped In_2O_3 films annealed at 623 K for different Cu doping levels

films was determined using the relation [19]. The transmittance of the films increased to a large extent by post annealing treatment. The films annealed at 523 K exhibited an average optical transmittance of 65 % at 550 nm. Here indium rich films were oxidized and the transmittance of the films was increased. It may be due to increase in the grain size which can be confirmed from XRD. The improvement of the grain size can decrease the collisions. Hence the betterment of the optical transmittance was observed.

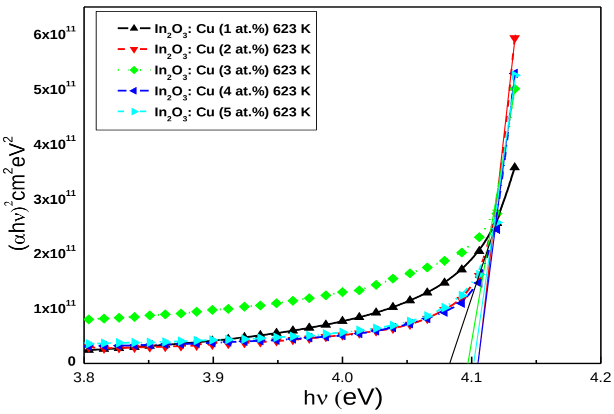

Fig. 5 – Plots of optical band gap of Cu-doped In_2O_3 films annealed at 623 K

The optical absorption coefficient was determined by using the relation

$$\alpha = -\ln(T) / t \qquad (1)$$

where, T is the transmittance and t is the thickness of the films. The absorption edge of the films shifted towards shorter wavelength with increasing doping concentration till Cu doping concentration of 3 at. % suggests widening of the energy band gap. The dependence of α with the photon energy (hυ) was found to obey the following relation

$$\alpha h\upsilon = A\,(h\upsilon - E_g)^{1/2} \qquad (2)$$

where, A is the constant and E_g is the optical band gap. The value of optical band gap E_g can be obtained by extrapolation of the linear region of the plots to zero absorption ($\alpha = 0$). Fig. 5 shows the variation of optical band gap of the films with different Cu-doping levels annealed at 623 K. The optical band gap of the films increased with the annealing temperature. The films which were annealed at 523 K exhibited almost the constant band gap of 3.25 eV. Whereas the films annealed at 623 K, the optical band gap of the films increased to a large extent. The optical band gap of the films increased from 4.08 eV to 4.10 eV. For the films annealed at 623 K the optical transmittance again decreased to lower values from 67 % to 78 %. The highest transmittance of 78% was observed for 3 at. % of Cu-doping level. The optical band gap was calculated for the films annealed at 523 K and at 623 K. It increased from 3.25 eV to 4.10 eV at 5 at. % of Cu-doping level.

4. SUMMARY AND CONCLUSIONS

Cu-doped In_2O_3 thin films were prepared at various doping levels ranging from 1-5 at. % of Cu. The deposited films exhibited poor optical transmittance with indium rich composition. The films annealed at 523 K exhibited lower optical transmittance of 65 % and band gap 3.25 eV. Whereas the films annealed at 623 K exhibited the highest optical transmittance of 78 % at 3 at. % of Cu with band gap of 4.09 eV.

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