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Ti doped In_2O_3 Thin Films suited for TCO by a Cost effective Perfume Atomizer Technique

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Abstract: Pure and titanium doped indium oxide (TIO) thin films were prepared by a low cost and simplified spray pyrolysis method employing a perfume atomizer. The XRD analysis showed that these films have cubic structure of polycrystalline In_2O_3 phase.A high mobility (69 cm^2/Vs), lower resistivity ($1.12 \times 10^{-4}\Omega$cm), high figure of merit ($2.02\times10^{-3}\Omega^{-1}$) and carrier concentration ($1.519\times10^{20}cm^{-3}$)with high optical transmittance (85%) were achieved for the TIO films prepared at the doping level of 2 at. %. From the photoluminescence studies, we showed that the intensity of emissions of these films has been significantly vary with the effect of doping level and also shown the subsequent morphological changes due to variation in Ti concentrations.
Keywords– X-ray diffraction; TCO; Solar cells; Photoluminescence.

Introduction and Experimental

In recent times, the usage of transparent conducting oxides (TCO) has become vital and wide due to their immediate applicability in various areas such as flat panel displays, photovoltaic cells, touchscreens and in high speed operational electronic devices.More recently, titanium doped indium oxide thin films have attracted considerable attention due to theirenhanced mobility and transparent conducting properties [1-2]. According to the literature survey, as there is no report of titanium doped indium oxide thin films prepared by a simplified spray pyrolysis technique which employs a perfume atomizer, considering the features of perfume atomizer method [3], we wish to report the transparent conducting properties of titanium doped indium oxide thin films.To start with, $InCl_3$ (Alfa acer 995) and $TiCl_4$ have been considered as sources of indium oxide and titanium. An appropriate amount of $InCl_3$(0.08 M) and $TiCl_4$ (2 at. %, 4 at.% and 6 at.%) were dissolved separately by suitable solvent after that both solutions were mixed together and stirred for an hour at atmospheric conditions. The final transparent solution was used to deposit TIO films (Ti doped indium oxide) on glass substrates at 400° C. The structural, optical, electrical, photoluminescence and morphological studies were carried out by X-ray diffractometer, UV-Vis-NIR spectrometer, Hall effect apparatus, spectrofluorometer and Atomic force microscope respectively.

Results and Discussion

XRD patterns were carried out for 0 at.%, 2 at.%, 4 at.% and 6 at. % respectively and depicted in Fig. 1(a). The XRD studies revealed the formation of cubic structure of In_2O_3 phase (JCPDS No. 00-006-0416).Pure indium oxide film has preferential orientation growth along (2 1 1) direction and orientation growth was changed to (2 2 2) direction for titanium doped indium oxide thin films observed from the XRD pattern. The crystalline size was estimated from data obtained from XRD analysis and found that the crystalline size is a function of dopant concentration as summarized in Table. 1.

Table. 1. Summary of grain size, electrical parameters and estimated optical parameters.

Ti concentration (at. %)	**Grain size (nm)**	**Resistivity (ρ (Ω cm))**	**Mobility (μ (cm^2/Vs))**	**Carrier concentration (n (cm^{-3}))**	**Figure of merit (×10^{-3} $Ω^{-1}$)**	**Band gap (*eV*)**
0	18	3.121×10^{-2}	46.1	1.012×10^{18}	1.56×10^{-3}	3
2	20	1.12×10^{-4}	69.83	1.519×10^{20}	2.02×10^{-3}	3.3
3	31	2.5×10^{-4}	52.8	1.619×10^{20}	1.22×10^{-3}	3.5
4	32	2.9×10^{-4}	49.19	1.765×10^{20}	7.1×10^{-4}	3.8

The microstructure of the surface was obtained from AFM studies as shown in Fig. 2 (a=0at.%, b=2at.%, c=4at.% and d=6at.%), the AFM images show the smaller grains with uniform and continuous distribution without any voids were found for the film prepared at 2 at.%, further, for increase in doping concentration the grain size became significantly large as evident in Fig. 3 and the high surface roughness was obtained for higher doping level (2 at. %=17.35, 4 at. % = 26.54,6 at. % = 35.97 and 0 at. % = 20.15). The electrical studies at room temperature were obtained from the Hall measurement with vander Pauw configuration[1].A lowest value of resistivity (1.12×10^{-4}Ωcm) was found for the film prepared at 2 at.% compared with other films as shown in Table. 1.A high mobility (69 cm^2/Vs) was achieved at dopant concentration of 2 at. %, which may be due to the reason that probably the Ti ions would have replaced the In ions and thus by liberating more carriers[1]. Enhanced electrical properties were achieved while employing this cheap fabrication (Perfume atomizer method) method which may be treated as an attempt for obtaining improvised results than earlier reports [1-2]. A maximum visible transmittance of 84%found in the wavelength range of 600 nm then it extended to 85% in near infrared region (NIR) for the film prepared at 2 at. % as depicted in Fig. 1(b).A low optical transmission at higher doping levels (4 at.% and 6 at.%) may be attributed to the scattering of photons, which is due to increase in surface roughness of these films (evident from AFM mages Fig. 2(a), (c)& (d)). The optical band gap values estimated from the plot of $(\alpha h\upsilon)^2$*Vs* the photon energy *($h\upsilon$)* are tabulated in Table. 1, the band gap increases from 3 *eV* – 3.8 *eV*, which attributed to Burstein-Moss (B-M) effect (Shifting in band gap). Theoretical band gap of 3.5 *eV* is needed for TCO application and the prepared samples have achieved the above basic requirement. For solar cell application of these films, the figure of merit (φ) play a significant role, which is estimated from the following relation $\frac{T_a^{10}}{R_s}$, and the calculated values of figure of merit listed in Table. 1. The highest value of figure of merit $2.028 \times 10^{-3}Ω^{-1}$ was obtained for 2 at. % of Ti doped indium oxide thin film. The room temperature photoluminescence (PL) studies were characterized for pure and Ti doped In_2O_3 thin films with the excitation wavelength of 350 nm as shown in Fig. 1(c). Pure indium oxide film has two distinct peaks located at UV region (398 nm) and green wavelength region (528 nm). In case of Ti doped In_2O_3 films, five distinct emission peaks were found and they corresponding to UV region (355 nm), blue region (411 nm, 452 nm, 467 nm) and green wavelength region (550 nm). The emission at blue region can be attributed to imperfections and defects due to oxygen vacancies. The near band edge emission (emission at UV region) was due to the recombination of free exciton through an exciton-exciton collision process. The green emission peaks was commonly referred to the deep level or trap state emissions due to oxygen vacancies similar result was found from earlier report for In_2O_3 nanoparticles [4].

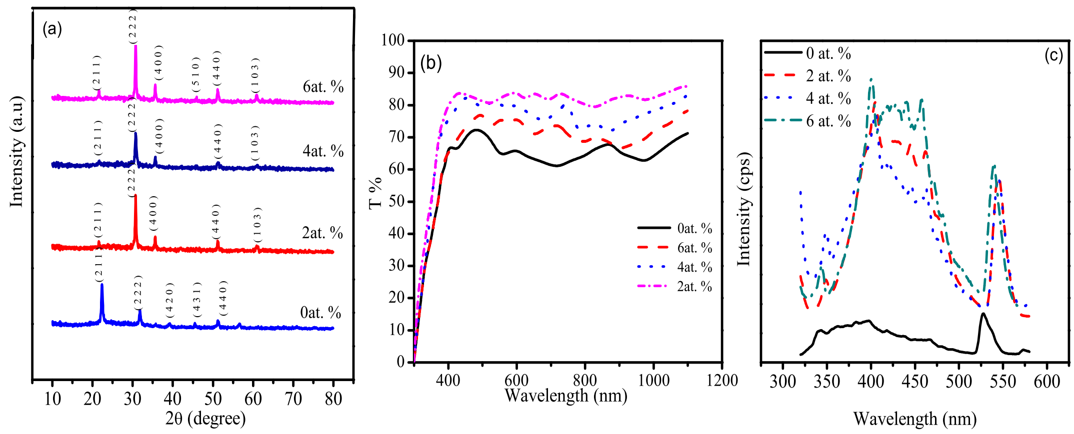

Fig. 1.(a) XRD pattern (b) Transmission spectra and (c) PL spectra of pure and Ti doped In_2O_3 films

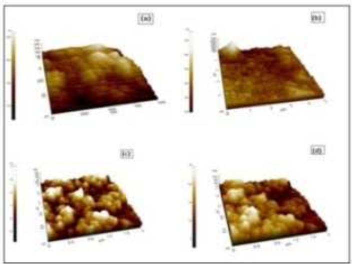

Fig. 2. AFM images of pure and Ti doped In2O3 films.

In the present study, a simplified spray pyrolysis technique was employed to fabricate pure and Ti doped indium oxide films with different dopant concentration. The enhanced crystallinity was confirmed by XRD analysis. An interesting outcome this investigation is that we could achieve 85% transmittance in NIR region with low resistivity and high mobility even from low concentration (at 2 at.%) employing this simple fabrication technique; to get appreciable enhancement of solar efficiency in NIR region.Thehighly intense green emission due to photoluminescence as an indicator suited for applications in electro-optical device as a green light source.

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