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STRUCTURAL AND MORPHOLOGICAL STUDIES ON CHROMIUM DOPED INDIUM OXIDE THIN FILMS PREPARED BY PULSED LASER DEPOSITION TECHNIQUE

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ABSTRACT

High purity Chromium oxide and Indium oxide powders are taken as starting materials to prepare Chromium doped Indium oxide powder by solid state reaction method to prepare robust targets for PLD. The prepared powders are cold pressed and made in to pellets of 1inch diameter and 2mm thickness. These pellets are sintered at 800^{o}C for 12hours. To prepare Chromium doped Indium oxide thin films, KrF laser has used with wavelength of 248nm, laser pulse time 10ns and with laser energy of 200mJ/pulse. For uniform target erosion and consumption a stepper motor was attached with 6rot/min. The films are deposited on ultrasonically cleaned quartz substrates maintained at a substrate temperature of 300^{o}C. The vacuum chamber evacuated by a turbo molecular pump to a base vacuum better than 10^{-6} Torr and oxygen partial pressure was maintained between 1mTorr to 0.01mTorr. The deposited films are characterized by using GIXRD, AFM, EDS and stylus profilometer. GIXRD suggests that the films deposited crystallizes in to a cubic structure with preferred (2 2 2) orientation. The surface roughness estimated from AFM for these films found to increase with decrease in oxygen partial pressure .At low oxygen partial pressure well oriented columns are seen.EDS analysis confirms the stoichiometry of Chromium doped Indium oxide thin films.

Keywords: *Thin film, GI XRD, AFM, EDS, pulsed laser deposition*

INTRODUCTION

Metal oxide thin films are of great interest because of the novelty of their fundamental properties and also due to their potential spintronic applications Wolf et al [1] and possibility of Curie temperature higher than 300K after the prediction by Diet et al [2] and the basis of future semiconductor spintronic technologies which promise integration of magnetic, semiconducting and optical properties and a combination of information processing and storage functionalities Teo et al [3].Semiconductor thin films have been attracting increasing attention because of their exceptional properties, which differ from those of their bulk counterparts, and their potential applications. Among them, Indium oxide (In_2O_3) has been investigated extensively for its semiconducting properties and intrinsic oxygen deficiencies whose conductivity can be effectively tuned by tuning the oxygen vacancies or by Sn doping He et al [4]. Compared with other transition metals Cr has large magnetic moment in the ionic state and unlike Co. Observation of ferromagnetism due to Cr clustering is ruled out since trace amount of Cr clusters are super paramagnetic, while bulk Cr is antiferromagnetic. Philip et al[5] has reported high temperature ferromagnetism in Cr doped In_2O_3 thin films grown by co-evaporation technique, and proposed that the magnetic behavior is only responsible by carrier-mediation.In_2O_3 thin films have been grown by number of different deposition techniques which include Direct current (DC) magnetron sputtering by Ivan Hotov *et al* [6], spray pyrolysis by Parthiban et al [7], sol-gel by Zhang *et al* [8], thermal evaporation by Pritty Rao *et al* [9] and electron beam evaporation by Shan *et al* [10]. Among them Pulsed Laser Deposition (PLD) is the most effective method for the formation of high-quality films. The adaptability of PLD lies in the fact that many experimental parameters such as laser fluence, pulse repetition rate and duration, preparation conditions include substrate temperature, target to substrate

distance, background gas and pressure can be altered and has a strong influence on the film properties. The present discussion is aim to understand influence of oxygen partial pressure on structural and morphological properties of Cr doped In_2O_3 Thin films.

Materials and methods:

In the deposition of Cr doped In_2O_3 thin films first priority goes to cleaning of the substrate. In order to achieve desirable film properties, cleaning of the substrate surface prior to film deposition is very much essential. For this the quartz substrates were cleaned by submerging them in double distilled water and chromic acid Y.Veeraswamy et al [11] and was then cleaned in a detergent solution with ultrasonicator for 15mts. After washing with double distilled water, they were rinsed with acetone and dried in an oven to get moisture free substrates. High purity chromium oxide (99.999%) and indium oxide (99.999%) powders(procured from Sigma Aldrich) are taken as starting materials to prepare 0.5at% Cr doped In_2O_3 powder by solid state reaction method to prepare robust targets for PLD. The well grounded mixture was heated in air at 800^{o}C for 10h and the prepared powder was cold pressed at 10ton load and made the pellets of 1inch diameter and 2mm thickness. These pellets are sintered at 800^{o}C for 12hours.Cr doped In_2O_3 thin films were grown on quartz substrates using PLD (Lambda physic complex 201 model) system consists of a turbo-molecular pump to control pressure inside the chamber. The turbo-molecular pump produces a vacuum of at least two orders of magnitude less than that of background gas to be used. KrF excimer laser with wavelength 248nm laser pulse time 10ns with laser energy of 200mJ/pulse for 15min deposition. The target to substrate distance was 5cm. For uniform target erosion and consumption a stepper motor was attached with 6rot/min. The films are deposited on ultrasonically cleaned quartz substrates maintained at a substrate temperature of 300^{o}C. The vacuum chamber was evacuated by a turbo molecular pump to a base vacuum better than 10^{-6} Torr and oxygen partial pressure was maintained between 1mTorr to 0.01mTorr. The films were characterized structurally using GIXRD (D8-Discover system of M/s Brucker) equipped with CuK_{α}.Surface micro structural characterization was investigated by AFM. Stylus profilometer (AMBIOS XP-1) used to measure the thickness of the films.

Table (1) Structural parameters of Cr doped In_2O_3 Thin films at oxygen partial Pressures.

Oxygen partial pressure (mTorr	FWHM	Crystallite size(nm)	Lattice Strain(10^{-3})	d-spacing (A^{o})	Dislocation density ($10^{-3}nm^{-2}$)	Thickness of the film(nm)
1	0.153	56	2.5	1.519	0.318	150
0.1	0.298	28	4.7	1.509	1.27	145
0.01	0.615	13	9.9	1.519	5.91	141

Table (2) AFM parameters of Cr doped In_2O_3 thin films at Oxygen partial pressures.

Oxygen partial pressures (mTorr)	RMS Roughness (R_q)(nm)	Mean Roughness (R_a)(nm)	Peak to peak (R_{pp})(nm)
1	110	87	812
0.1	180	149	981
0.01	214	189	953

Micro structural characterization

GIXRD (D8-Discover system of M/s Brucker) equipped with CuK_{α} was used to investigate the structural and crystallographic phases present in the thin films (λ= 0.15418 nm) under a voltage of 40 kV and a current of 30mA. The average size of Crystallites (D) of In_2O_3 films was estimated using Debye Sherrer formula by Beena, *et al* [12].

$$D = \frac{0.98\lambda}{\beta cos\theta} \quad \text{---------- (1)}$$

Where D=crystallite size, λ=wavelength of CuK_{α} radiation (0.15418nm), **β**=FWHM, θ=Bragg's diffraction angle.

The dislocation density (δ) is described as the length of dislocation lines per unit volume of the crystal. The dislocation density (δ) of the crystal gives information about the crystal structure. The dislocation density for preferential orientation can be calculated using the formula given below by Aydogu et al [13]

$$\delta = \frac{1}{D^2} \qquad \text{---------- (2)}$$

Where d is the crystallite size.

The surface morphology of the In_2O_3 thin films were analyzed by AFM (Park systems XE-70), with scanning area was 1µm x 1µm. The following three characteristic parameters for the analysis of the AFM measurements were used: (i) The Root Mean Square (RMS) Roughness (R_q), (ii) The Peak to Peak (R_{pp}) and (iii) The Mean Roughness (R_a), Veeraswamy et al [14]. The AFM measurements were performed in non contact mode. The elemental composition was recorded with Energy Dispersive X-ray Spectroscopy (EDS).

Results and discussion

Fig (1) shows the Cr doped In_2O_3 thin films grown at 1mTorr,0.1m Torr and 0.01mTorr of oxygen partial pressers on quartz substrates at substrate temperature of 300°C. The films are highly crystalline and in good agreement with the JCPDS file card no. 07-2195 for In_2O_3. All the films show peaks corresponding to In_2O_3 phase only, which suggests that Cr forms a solid solution with In_2O_3 in all our samples. It could be seen from Fig (1) that not all the peaks are present. This is due to the preferential orientation of the films in the (2 2 2) plane. Such type of preferential growth has been also observed for tungsten doped In_2O_3 films grown on quartz substrate by Gupta et al [15]. The observation of Fig (2) indicates that an obvious shift of the diffraction peaks with increasing oxygen partial pressure, which indicates an increase in the dislocation density shown in Table (1). At lower oxygen partial pressure (0.01mTorr) (222) peak got broadened, this can be attributed to the incorporation of smaller Cr ions into the Indium sites of the In_2O_3 lattice. Similar results are obtained for Ukah et al [16]. The dislocation density (δ) is described as the length of dislocation lines per unit volume of the crystal. The dislocation density is obtained from equation (2) for various crystallite sizes was tabulated in table (1). From the table (1), it confirms that with decrease of oxygen partial pressure the dislocation density was found to increase.

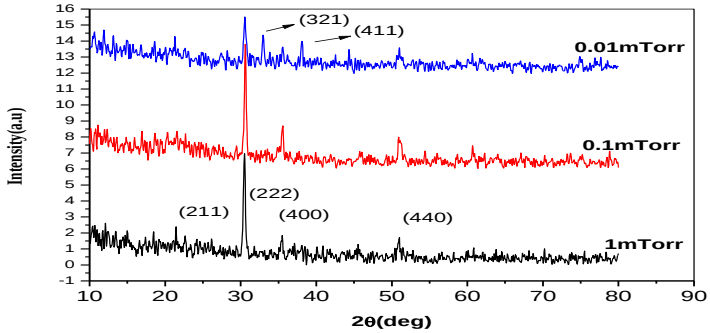


Fig (1) GIXRD of Cr doped In_2O_3 thin films deposited at different oxygen partial pressures.

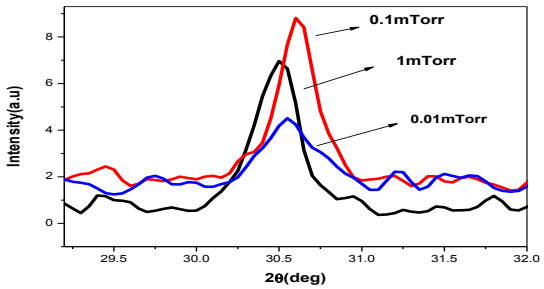
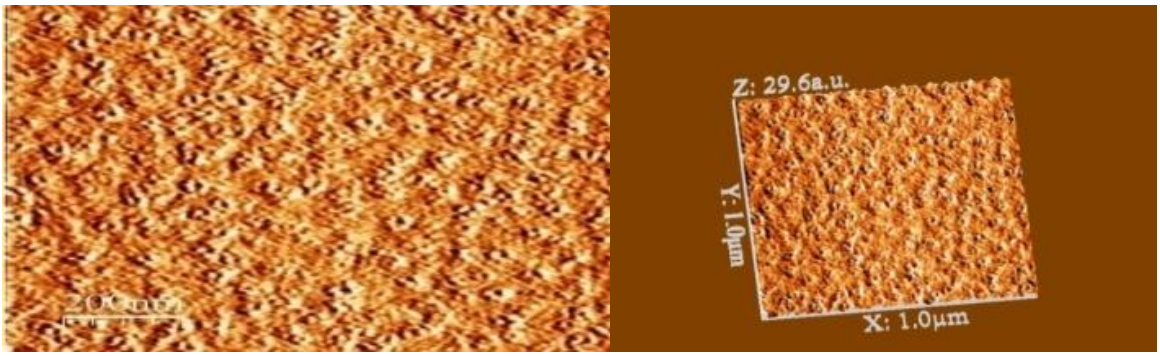
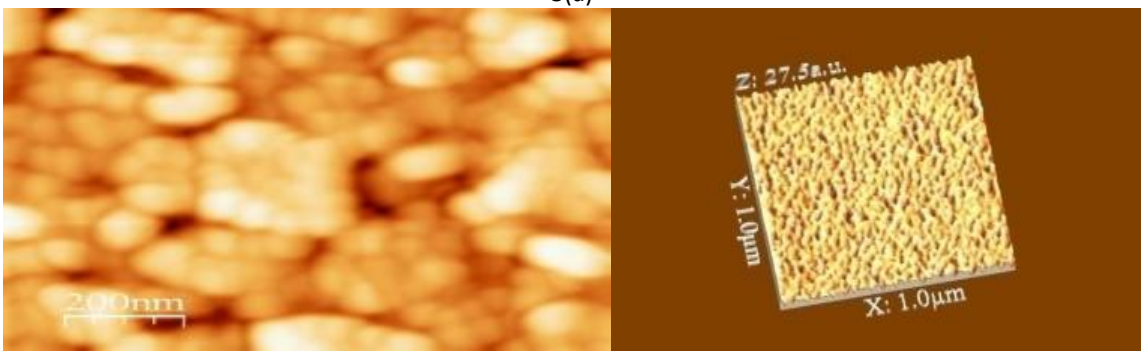


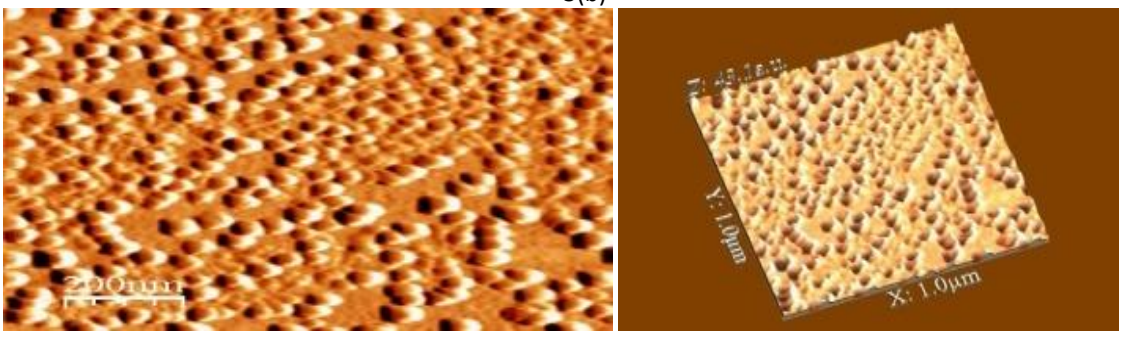
Fig (2) (222) orientation of Cr doped In_2O_3 thin films deposited at different oxygen partial pressures.



3(a)

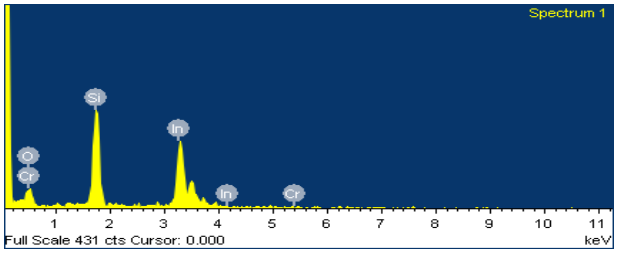


3(b)



3 (c)

Fig (3) (a, b, c) AFM 2D corresponding 3D micrographs of Cr doped In_2O_3 thin films for 1mTorr, 0.1mTorr and 0.01mTorr oxygen partial pressures.



Fig(4) EDS of Cr doped In_2O_3 thin films.

Fig (3) (a,b,c) shows the AFM micrographs of Cr doped In_2O_3 thin films on quartz substrates at different oxygen partial pressures (1mTorr,0.1mTorr and 0.01mTorr). The surface of the film found to be continuous without any pinholes for 1mTorr oxygen partial pressure. The film formed at 0.1mTorr oxygen partial pressure represents walnut like structures. At 0.01mTorr oxygen partial pressure, the micrograph changes to unique shape and size hillocks results into conical shape. These hillocks have comparatively flatter tops and their sides appear to be faceted. From table (2) RMS Roughness of Cr doped In_2O_3 thin films increases with decreasing oxygen partial pressure. The EDS analysis revealed that the nearly good stoichiometric films were formed as shown in Fig (4).

Conclusions

Nanostructured Cr doped In_2O_3 thin films were deposited on quartz substrates using pulsed laser deposition technique. The quantitative EDS study suggested that the amount of Cr dopant in the In_2O_3 films were quite close to that of target material. GIXRD of In_2O_3 thin films confirms the formation of cubic structure. The RMS roughness In_2O_3 thin films increases with decreasing oxygen partial pressure as confirmed from AFM.

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