IOSR Journal of Applied Physics (IOSR-JAP)
e-ISSN: 2278-4861.Volume 7, Issue 1 Ver. I (Jan.-Feb. 2015), PP 21-26
www.iosrjournals.org

Influence of Cr Doping On Structural, Morphological and Optical Properties of SnO_2 Thin Film Prepared By Spray Pyrolysis Technique

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Abstract: *Chromium doped nanostructured tin oxide (Cr:SnO_2) thin-films were prepared on glass substrates by the spray pyrolysis technique at constant substrate temperature of 450^oC. The chromium dopant concentrations were taken as 10% and 20%, respectively. Structural, morphological and optical properties of the as-deposited thin films were studied. X-ray diffraction (XRD) analysis reveals the polycrystalline nature of Cr:SnO_2 thin films with tetragonal phase. The films were highly oriented along (211), (002) and (400) planes. The increase in doping concentration impacts the interplaner spacing and crystallite size of the Cr:SnO_2 thin films. Scanning electron microscope (SEM) images support the XRD analysis of the thin films, while the optical absorbance study suggests blue-shift in the energy band gap with increase in the doping concentration.*

Keywords: *Cr: SnO_2 thin-film, nanocrystalline thin film, spray pyrolysis, X-ray diffraction, optical properties*.

I. Introduction

In recent trend of modern life and advance science, various semi-conducting material have been used for fabricating low cost gas sensor unit owing to their high sensitivity, fast response and short recovery time to sense the hazardous gases. Amongst them, metal oxides semiconductors like tin oxide (SnO_2) and zinc oxide (ZnO) have been widely used due to their wide energy band-gap, high transparency and low electron affinity. Although the as-deposited thin films of SnO_2 and ZnO have shown better gas sensing performance; but with further research it was found that the addition of an external dopant/impurity in the pure SnO_2 or ZnO, there is an increase in the gas response behavior with decrease in operating temperature. Hence, during the past few years, SnO_2 thin films with and without dopants have become an area of active investigation so as to control its sensitivity and improve the ease of fabrication [1, 2]. Significantly, an appropriate doping can influence the properties of SnO_2 thin-films. Commercial gas sensors are now well developed using SnO_2 containing a small amount of catalyst like Pt or Pd as sensing films deposited on ceramic heater substrates [3]. Several deposition techniques have been used to grow undoped and doped tin oxide thin and thick films, including sol–gel [4,5], screen-printing [6], thermal evaporation [7], spray pyrolysis [8], sputtering [9,10] and chemical vapor deposition (CVD) [11]. Among the various deposition techniques, spray pyrolysis is the most promising technique for the preparation of inexpensive Cr doped tin oxide (Cr:SnO_2) thin films. Therefore, considering all the aspects of past and present reported studies, the current work investigates the influence of Cr doping in SnO_2 thin films, which are prepared by spray pyrolysis technique. The structural, morphological and optical properties of the thin films are examined related to the increase in the chromium amount.

II. Experimental procedure

Cr:SnO_2 thin films were deposited onto the glass substrates by cost effective spray pyrolysis technique using stannic chloride ($SnCl_4$, $5H_2O$) and chromium dioxide (CrO_2) prepared in 10% and 20% in deionized water as stock solutions and methanol (i.e. aqueous and non-aqueous medium) as the initial ingredients. These solutions were prepared by adding appropriate amount by weights and methanol was used as solvent. To make the clear solution, 24 ml of 0.01M oxalic acid was added into the sprayed solution [12]. Ammonia is added to maintain pH of the solution. For each deposition, 10 ml from stock solution was mixed with 10 ml of methanol to make the final spraying solution of 20 ml, at a fixed carrier pressure of 1.35 kg/cm^2 with spray rate 4 ml/min onto the preheated constant temperature (450 ^oC) amorphous glass substrates. All the films were allowed to cool naturally to room temperature on hot plate after deposition.

The Cr:SnO_2 thin films prepared by spray pyrolysis technique were characterised for structural, morphology and optical properties. The structural characterization of deposited thin films was carried out by analyzing the X-ray diffraction patterns (XRD) obtained using a Philips X-ray diffractometer model PW- 1710 (λ = 1.5405 Å for CuKα radiation). The morphological and elemental analysis was obtained by scanning electron microscopy (SEM) by using JEOL system. The absorbance spectra were taken at room temperature and at normal incidence by UV–VIS spectrophotometer (Lambda 25) in the wavelength range 350–1000 nm.

III. Result and discussion

The XRD pattern of the Cr: SnO_2 thin films deposited at various doping concentration (%) is shown in Fig.1

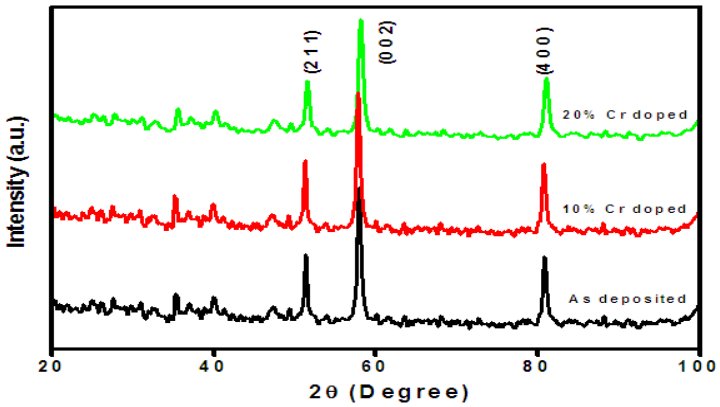

Fig. 1 XRD patterns of spray deposited Cr doped SnO_2 thin films at various concentrations

It shows that the material deposited is of polycrystalline in nature. The peaks show (2 1 1), (0 0 2) and (4 0 0) reflections of undoped SnO_2. Similar XRD patterns were obtained for all films with different Cr concentrations with a slight shift to the higher angles, which is more pronounced in case of the 20% doping [13-15]. A matching of the observed and the standard (h k l) planes confirms that the deposited films were of rutile tetragonal structure [16]. The formation of more crystallites with well-defined orientation along (0 0 2) plane was observed. Some other prominent peaks corresponding to (2 1 1) and (4 0 0) planes were also present in the XRD patterns. The comparative study of XRD pattern of pure and Cr:SnO_2 thin film, reveals that the peaks corresponding to (2 1 1), (0 0 2) and (4 0 0) orientations, shifted systematically towards the higher angles in case of Cr doped SnO_2. This may be due to the substitution of Cr in Sn site into the SnO_2 thin film and the interplaner spacing should exhibit a change with Cr concentration as is indeed observed and is shown in Fig. 2. This clearly indicates that Cr dissolves in SnO_2 [17]. The lattice constant 'a' and 'c' for tetragonal rutile structure are calculated and given in Table 1.

The lattice constant 'a' first decreased and then again increased; while lattice constant 'c' first increased and then decreased. It was observed that the lattice constant 'a' and 'c' calculated at 450 ^oC match well with the standard JCPDS data card [18]. The change in crystallite size is also associated with the concentration (%) of Cr in the solution as shown in Fig 3. The average crystallite size of Cr doped SnO_2 thin films were estimated for all the observed planes by using Scherrer's formula [19]. The variation in crystallite size with concentration (%) of Cr is also given in Table 1. The crystallite size 'D' decreases as concentration increases [20]. The dislocation density (ρ_o x 10^{15} lines/m^2) was determined using the relation [21] and is given in Table 1. It was observed that dislocation density increases in accordance with the concentration of Cr.

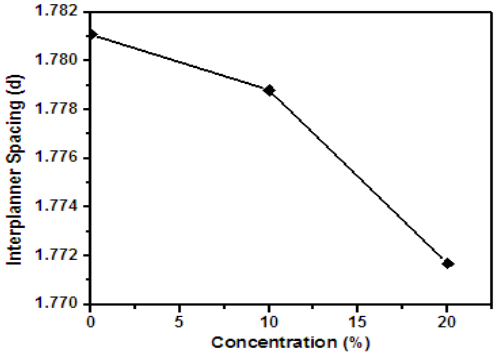

Fig. 2 Plot of Cr concentration (%) against interplaner distance

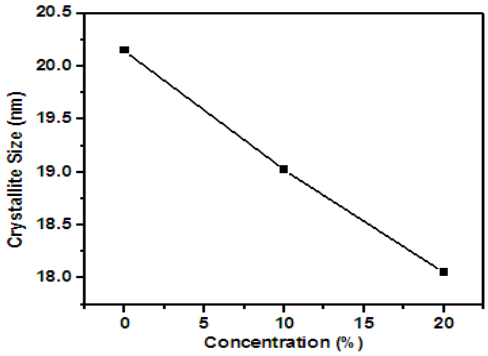

Fig. 3 Plot of crystallite size against Cr concentration (%).

Table 1 Structural parameters of Cr doped SnO_2 thin films

concentration wt%	d_{obs} (Å)	d_{std} (Å)	(hkl)	a (Å)	c (Å)	Average D (nm)	ρ_D x 10^{15} lines/m^2
0	1.7811	1.7641	211	4.8959	3.0371	20.15	2.46
	1.5933	1.5934	002				
	1.1890	1.1844	400				
10	1.7788	1.7647	211	4.7528	3.2162	19.02	2.76
	1.5914	1.5934	002				
	1.1881	1.1847	400				
20	1.7717	1.7647	211	4.7585	3.1985	18.05	3.06
	1.5860	1.5934	002				
	1.1853	1.1847	400				

Quantitative analysis of the film was carried out using the EDAX technique to study stoichiometry of the film. The elemental analysis was carried out only for Sn, Cr and O. Fig. 4a and 4b shows representative EDAX spectra of Cr (10 %) and (20%) doped SnO2 thin films, respectively. The detailed results of the EDAX analysis are tabulated in table 2.a and table 2.b, respectively. The observed atomic weight percentage was found to be almost equal i.e., initially as well as finally after the thin film formation. Also it confirms the presence of Cr doping in the SnO_2 matrix.

Table 2.a

Substrate	Name of element	Atomic %
Glass	O	66.31
	Sn	23.12
	Cr	10.57

Table 2.b

Substrate	Name of element	Atomic %
Glass	O	52.67
	Sn	27.21
	Cr	20.12

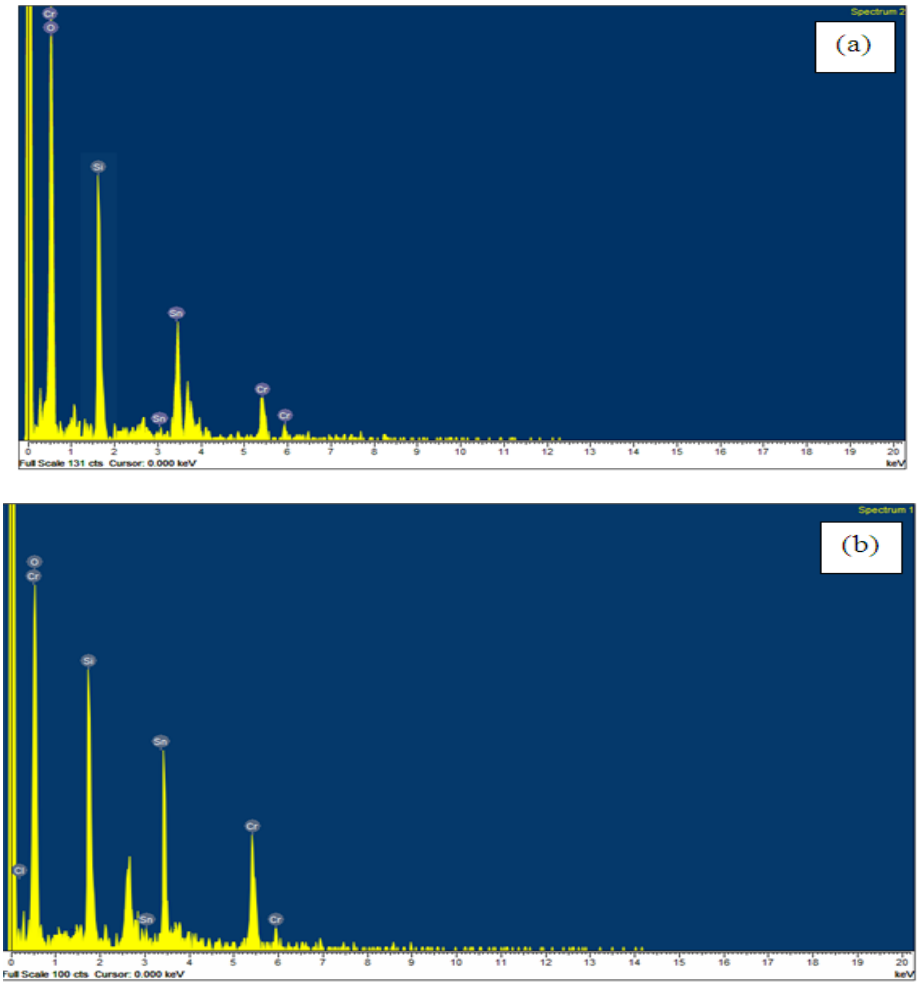

Figure 4a and 4b shows EDAX spectra of 10 % and 20% Cr doped SnO_2 thin films respectively, deposited on glass substrates

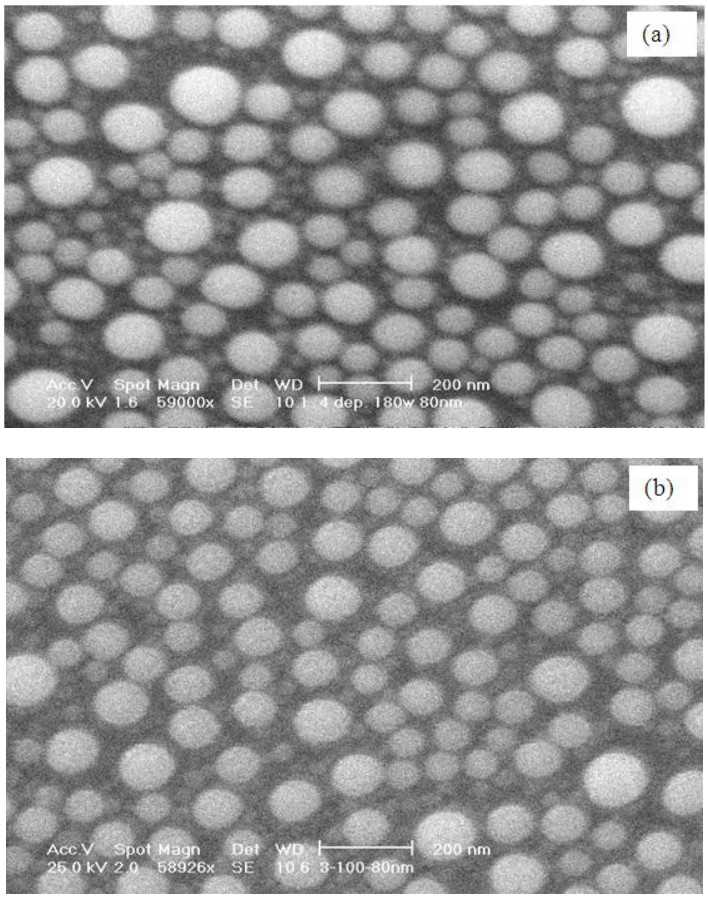

Fig. 5a and 5b shows SEM image of Cr (10 % and 20 %)) doped SnO_2 thin films deposited on glass substrates.

Fig. 5a and 5b shows the scanning electron microscope (SEM) images of the Cr doped SnO_2 films with 10% and 20% concentrations, respectively. The surface of the film is smooth, and the film displays a homogeneous crack-free appearance in all scanned areas of the sample. Spherical ball shaped grains of different sizes were seen in both the images. Also, it was found that on an average the calculated grain size was smaller in case of for 20% Cr:SnO_2 thin films as compared to 10% Cr:SnO_2 thin films. Thus it was clear that with more incorporation of Cr, the grain size of SnO_2 reduces suggesting that the dopant influences the grain growth of SnO_2 material. The reduction in particle size is quite gradual with dopant concentration which is in agreement with XRD results. The lower grain growth inhibition may be attributed to the increased nucleation sites that results from higher stacking fault energy due to Cr addition into the SnO_2 matrix.

The fundamental absorption corresponding to the optical transition of the electrons from the valence band to the conduction band can be used to determine the nature and values of the optical band gap E_g of the films. Depending on the characteristic property of the material, different theoretical equations were used to calculate the absorption coefficient (α) value as a function of photon energy (hν). The direct allowed optical band-gap of SnO_2 and Cr:SnO_2 thin films should be determined with the help of the equation given below

$$\alpha = \frac{A(h\nu - E_g)^{n/2}}{h\nu} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where 'α' is the absorption coefficient, 'K' is a constant and 'E_g' is the band-gap of the material. The exponent 'n' is equal to 1 or 4 for the direct or indirect transition, respectively. Many groups have used the above formula to calculate the band-gap of Cr doped SnO_2 films and reported that Cr doped SnO_2 is a direct band-gap material. The band-gap can be deduced from a plot of $(\alpha h\nu)^2$ versus photon energy (hν). Figure 6 shows the plot $(\alpha h\nu)^2$ versus photon energy (hν) for pure and Cr doped SnO_2 films. The linear fits for these plots are also shown in this figure. The E_g value for pure SnO_2 has been reported to be in the range 3.8–4.0 ± 0.2 eV, which depends on the preparation method and deposition conditions [22-25]. In our experiment, for pure SnO_2 films a band-gap of E_g = 3.18 eV (see inset of Fig. 6), has been obtained, which is in good agreement with the previously reported

values [26]. From figure 6, it is also clear that the band gap of the films increases upon increasing Cr concentration in the precursor solution. The absorption edge of Cr doped SnO_2 is largely blue-shifted from the absorption edge of pure SnO_2. Similar result was reported for the Eu^{3+}-doped SnO_2 thin film [27].

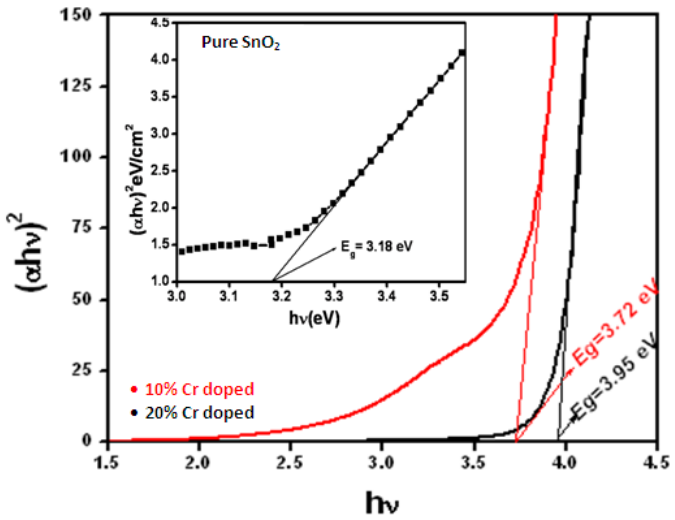

Fig. 6 Plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for Cr (10 % and 20 %) doped SnO_2 films deposited on glass substrates. Inset shows the plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for pure SnO_2 film.

IV. Conclusion

Finally, we can conclude that, the structural, morphology and optical properties confirms proper doping of Cr into the SnO_2 thin film deposited by cost effective technique i.e. spray pyrolysis. From this study it reveals that the properties of Cr:SnO_2 thin films have greatly improved with the increase in the doping percentage of Cr, which is rather very useful from application point-of-view.

Acknowledgements

One of the authors (RRK) is thankful to the Chairman and the Principal, G. T. Patil College, Nandurbar (M.S.) India, for motivating to carry out this research work. In addition, special thanks to Head, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad and Dr. D. M. Phase, Dr. N. P. Lalla and Vinay Ahire for providing characterization facilities with valuable suggestions.

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