

## STUDY OF STRUCTURAL AND OPTICAL PROPERTIES $Zn_{1-x}Cr_xO$ ( $x= 0.00$ & $0.02$ ) THIN FILMS DEPOSITED BY SPRAY PYROLYSIS ROUTE

S.S. SWAMI<sup>1</sup>, P.M. JHONDALE<sup>1</sup>, S.V. KUMBHAR<sup>1</sup>, L.H. KATHWATE<sup>1</sup>, P.M. KULAL<sup>2</sup>, V.D. MOTE<sup>1\*</sup>

<sup>1</sup>Thin Films and Materials Science Research Laboratory, Department of Physics, Dayanand Science College, Latur- 413 512, Maharashtra, India. <sup>2</sup>Department of Physics, Shivaji Mahavidyalaya, Renapur - 413 512, Maharashtra, India Email: vmote.physics@gmail.com

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### ABSTRACT

**Objective:** The High quality with low economical cost thin films has become a global need.  $Zn_{1-x}Cr_xO$  ( $x= 0.00$  &  $0.02$ ) thin film has been deposited on glass substrate by simple chemical spray pyrolysis route.

**Materials and Methods:** The structural and optical properties  $Zn_{1-x}Cr_xO$  ( $x= 0.00$  &  $0.02$ ) film were studied by using x-ray diffraction (XRD) pattern and UV-Visible spectra. The structural parameters such as lattice constant ( $a$  &  $c$ ), strain and dislocation density was also calculated by analyzing x-ray diffraction pattern

**Results:** The entire x-ray diffraction peaks confirm that the  $Zn_{1-x}Cr_xO$  films have polycrystalline nature with hexagonal (wurtzite) crystal structure. The mean crystalline size was determined by Debye-Scherrer formula. The crystallite size was found to be 32nm and 22nm for  $x=0.00$  and  $x=0.02$  respectively. The transmittance spectra reveal that all the films have high transmittance (higher than 80%) in the range of visible and near to the infrared wavelength region. There was decreasing band gap with Cr ( $x=0.02$ ) doping concentration.

**Conclusion:** Structural and optical properties reveal that films are of good quality that are suitable for several applications.

**Key Words:**  $Zn_{1-x}Cr_xO$  thin film, XRD pattern, UV-Visible spectra.

### INTRODUCTION

Zinc oxide (ZnO) is an interesting semiconducting material from II-VI group and having a wide band gap of 3.3eV, large exciton binding energy of 60meV, high thermal and mechanical stabilities, high electron mobility and non-toxicity [1]. Due to these unique properties, ZnO has a promising material for various applications such as solar cells [2], gas sensor [3,4], piezoelectric device [5,6], and photovoltaic application [7]. ZnO thin films have been deposited by a variety of deposition technique including sol gel [8], electron beam evaporation method [9], dip coating [10], chemical bath deposition (CBD) [11], spray pyrolysis [12], successive ionic layer adsorption and reaction (SILAR) [13], etc. Among all the deposition method we prefer spray pyrolysis method because it is a simple process, low cost production and it allows large area deposition. In order to improve the optical and magnetic properties of ZnO we doped it by transition metal. Also transition metal doped ZnO shows a good ferromagnetism at room temperature which is useful for the dilute magnetic semiconductors (DMSs). S. Yilmaz et. al. studied structural, optical and magnetic properties of Cr doped ZnO microrods prepared by spray pyrolysis method. It was also observed that Cr doped samples clearly showed ferromagnetic behavior; however, 2.5 at.% Cr doped ZnO showed remnant magnetization higher than that of 1.1 at.% and 4.6 at.% Cr doped samples, while 4.6 at.% Cr doped ZnO samples had a coercive field higher than the other doping [14].

In this work,  $Zn_{1-x}Cr_xO$  ( $x= 0.00$  &  $0.02$ ) films were deposited by spray pyrolysis method on to glass substrate at 400°C substrate temperature. The structural and optical properties  $Zn_{1-x}Cr_xO$  deposited thin films were characterized by x ray diffraction (XRD) and UV-Vis spectroscopy.

### EXPERIMENTAL

The  $Zn_{1-x}Cr_xO$  ( $x= 0.00$  &  $0.02$ ) films were deposited by using chemical spray pyrolysis route. For the deposition of  $Zn_{1-x}Cr_xO$  ( $x= 0.00$  &  $0.02$ ) films, zinc acetate dehydrate ( $Zn(CH_3COO)_2 \cdot 2H_2O$ ) and chromium nitrate nanohydrate ( $Cr(NO_3)_3 \cdot 9H_2O$ ) were used as a precursor. Both the chemical were analytical reagent grade (AR) with 99.99% purity and used further any purification. A 0.01M solution of zinc acetate was prepared by using double distilled water and

deposited on a glass substrate by chemical spray pyrolysis method. Cr doped ZnO films were deposited by using 2% wt. concentration of Cr. All deposited parameter such as substrate temperature (400°C), spray rate (3ml/min), pressure (40 psi) and distance between substrate to nozzle (21 cm) was maintained constant during the deposition.

The structural characterization of the spray deposited  $Zn_{1-x}Cr_xO$  ( $x= 0.00$  &  $0.02$ ) thin films was carried out by using a Philips x-ray diffractometer model PW-1710 (1.5406 Å for Cu-K $\alpha$  radiation). The transmission spectra have been recorded at room temperature and at normal incidence by Systronic make UV-VIS double beam spectrophotometer (2206) in the wavelength range 200 to 850 nm. In order to estimate the band gap of the  $Zn_{1-x}Cr_xO$  ( $x= 0.00$  &  $0.02$ ) thin films, optical absorption of the films deposited on quartz substrate have been studied at room temperature in the wavelength range of 200 to 850 nm.

### RESULT AND DISCUSSION

#### Structural study

Figure 1 shows x-ray diffraction (XRD) patterns of  $Zn_{1-x}Cr_xO$  ( $x= 0.00$  &  $0.02$ ) films deposited by chemical spray pyrolysis method on a glass substrate at 400°C temperature. All the diffraction peak confirm that  $Zn_{1-x}Cr_xO$  ( $x= 0.00$  &  $0.02$ ) film has polycrystalline in nature with hexagonal crystal structure. The XRD pattern of the sample are good consistence with the ICSD card no- 065119. It was observed that deposited sample exhibits peaks corresponding to (100), (002), (101) and (102) planes. Among these (002) peak shows heights intensity which indicates that deposited films have hexagonal crystal structure with preferred orientation along the c-axis. No extra peak corresponding to Cr doping was observed in XRD pattern which indicates the phase purity of deposited films.

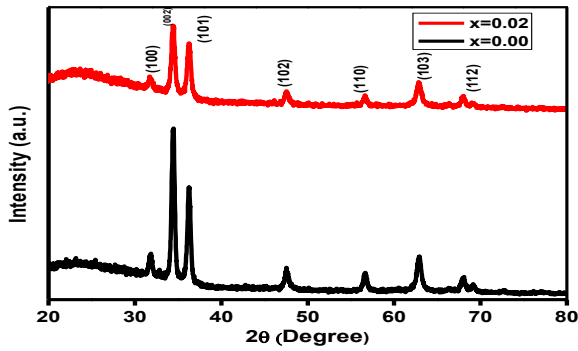


Figure 1 X-ray diffraction pattern of Zn<sub>1-x</sub>Cr<sub>x</sub>O (x= 0.00 & 0.02) thin films.

The crystallite size (D) of Zn<sub>1-x</sub>Cr<sub>x</sub>O (x= 0.00 & 0.02) films was calculated by using Scherrer formula,

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (1)$$

Where λ is the x-ray wavelength of Cu-Kα radiation, β is the full width half maximum of the peaks and θ is the diffraction angle.

The strain and dislocation density were calculated by using relation,

$$\epsilon = \frac{\beta \cos\theta}{4} \quad (2)$$

$$\delta = \frac{1}{D^2} \quad (3)$$

Table 1 show that both strain and dislocation density were increased for Cr doped ZnO films which is due to again difference in ionic radius of the Zn and Al.

The lattice constant 'a' & 'c' was estimated by the relation,

$$\frac{1}{d_{hkl}} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} \right) + \frac{l^2}{c^2} \quad (4)$$

Where 'd' is interplanar spacing and (h k l) are Miller indices. The estimated value of lattice constant 'a' and 'c' is found to be 3.2465 Å & 5.1989 Å for pure to 3.2526 Å & 5.2086 Å. The increase in the lattice parameter as Cr content indicates that sample was in a state of strain. It should be noted that the variation of lattice parameters does not coincide with that reported value. The reason for the change in this lattice parameter may be due to the concentration of foreign atoms and defects with respect to the substituted matrix ion ions. A. Nakrela et. al. was also observed that for lattice parameters of Al doped ZnO was increased due to saturation of substitutional sites take place [15].

Table 1 Average crystallite size, dislocation density, strain and lattice parameter of Zn<sub>1-x</sub>Cr<sub>x</sub>O (x= 0.00 & 0.02)

ZnO Sample	D×10 <sup>9</sup> m	δ×10 <sup>14</sup> lines/m <sup>2</sup>	ε ×10 <sup>-3</sup>	Lattice Parameter (Å)	
				a	c
x = 0.00	32	9.765	3.12	3.2465	5.1989
x = 0.02	22	20.66	4.39	3.2526	5.2086

**Optical study**

The optical transmittance spectra of Zn<sub>1-x</sub>Cr<sub>x</sub>O (x= 0.00 & 0.02) thin films at room temperature are shown in figure 2. The transmittance spectra reveal that all the films have high transmittance (higher than 80%) in the range of visible and near to the infrared wavelength region. It indicates that films have smoother surface morphology.

Also there is slight shifting of absorption edge towards the lower wavelength as Cr (x=0.02) doped with ZnO.

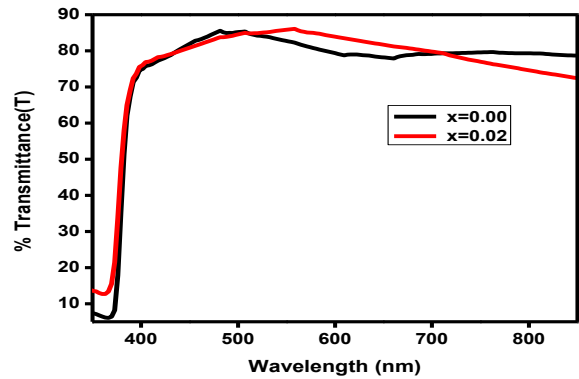


Figure 2: Transmissions spectra of Zn<sub>1-x</sub>Cr<sub>x</sub>O (x= 0.00 & 0.02) thin films.

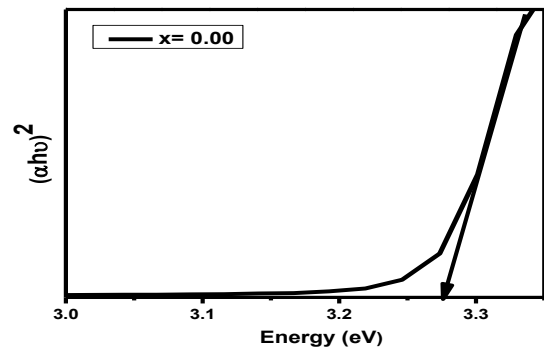


Figure 3a: Optical band gap of Zn<sub>1-x</sub>Cr<sub>x</sub>O (x= 0.00) thin films.

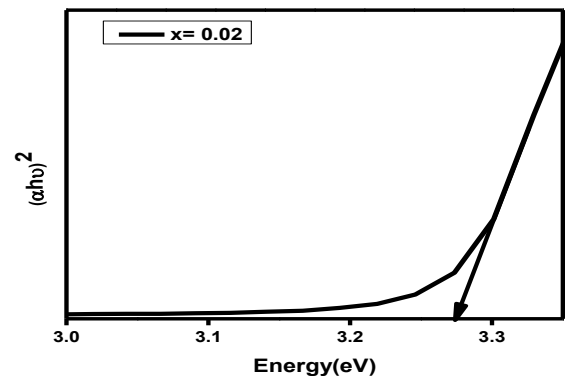


Figure 3b: Optical band gap of Zn<sub>1-x</sub>Cr<sub>x</sub>O (x= 0.02) thin films.

