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STUDY OF STRUCTURAL AND OPTICAL PROPERTIES $ZN_{1-X}CR_XO$ (X= 0.00 & 0.02) THIN FILMS DEPOSITED BY SPRAY PYROLYSIS ROUTE

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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 calls [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 spry pyrolysis route. For the deposition of $Zn_{1-x}Cr_xO$ (x= 0.00 & 0.02) films, zinc acetate dehydrate ($Zn(CH_3COO)_2.2H_2O$) and chromium nitrate nanohydrate ($Cr(NO_3)_3.9H_2O$) 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 pis) 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-Kα 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 spry 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.

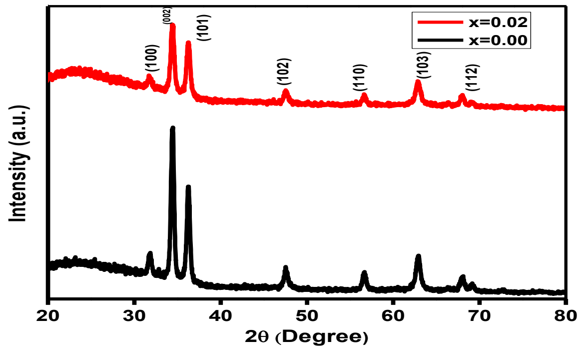

Figure 1 X-ray diffraction pattern of $Zn_{1-x}Cr_xO$ (x= 0.00 & 0.02) thin films.

The crystallite size (D) of $Zn_{1-x}Cr_xO$ (x= 0.00 & 0.02) films was calculated by using Scherrer formula,

$$D = \frac{0.9\lambda}{\beta Cos\theta} \qquad (1)$$

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,

$$\varepsilon = \frac{\beta cos\theta}{4} \qquad (2)$$

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

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,

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

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 $Zn_{1-x}Cr_xO$ (x= 0.00 & 0.02)

ZnO Sample	$D\times10^9$	$\delta\times10^{14}$ lines/m²	$\varepsilon\times10^{-3}$	Lattice Parameter (Å)	
	m			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 $Zn_{1-x}Cr_xO$ (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.

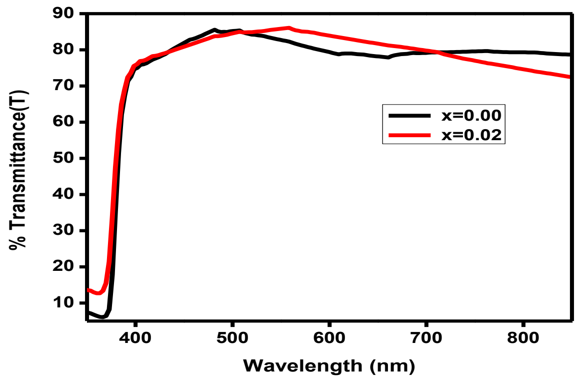

Figure 2: Transmissions spectra of $Zn_{1-x}Cr_xO$ (x= 0.00 & 0.02) thin films.

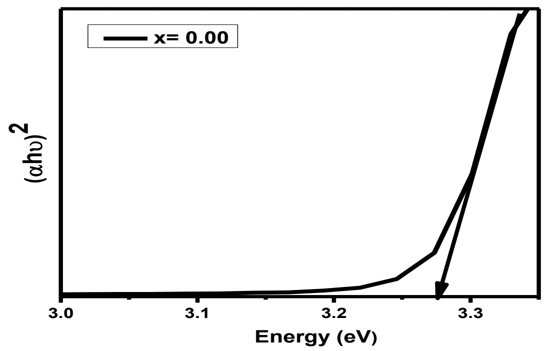

Figure 3a: Optical band gap of $Zn_{1-x}Cr_xO$ (x= 0.00) thin films.

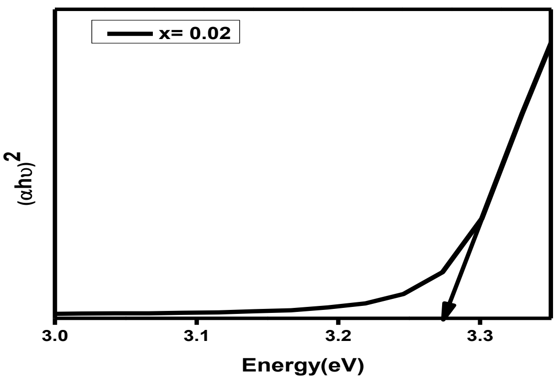

Figure 3b: Optical band gap of $Zn_{1-x}Cr_xO$ (x= 0.02) thin films.

To investigate optical band gap of $Zn_{1-x}Cr_xO$ films from the absorption spectra we plot a graph of $(\alpha h\nu)^2$ versus photon energy (hν) for all the films. The band gap of the films is calculated by the relation,

$$\alpha h\nu = A\,(h\nu - E_g)^2 \quad (5)$$

Where hν is the photon energy, A is a constant and E_g is the band gap. The linear intercept of this plot on the energy axis at α=0 gives the energy band gap of the films. The band gap of $\mathbf{Zn_{1-x}Cr_xO}$ film for x=0.00 is found to be 3.27eV and decreased to 3.25 for x=0.02 as shown in figure 3a and 3b. This result is matched with previous result reported on Cr doped ZnO films. The decrease in optical band gap may be attributed to the defects induced by Cr in ZnO lattices which introduced new states near to the conduction band [16]. Refractive index play an important role in semiconducting material in order to determining the optical and electrical properties of crystals and useful for the application of optoelectronic devices, in heterostructure laser and in solar cell. A correlation between refractive index and energy band gap has extensive aspect on the band structure of semiconductor. The calculated value of refractive index of $Zn_{1-x}Cr_xO$ films for x=0.00 and x=0.02 was found to be 1.9865 and 1.9884 respectively.

CONCLUSION

We successfully prepared $Zn_{1-x}Cr_xO$ (x= 0.00 & 0.02) thin films by simple chemical spry pyrolysis method. Nearly stoichiometric films with much better structural and optical properties were obtained. X-ray diffraction patterns reveal that all films have polycrystalline in nature with hexagonal crystal structure. Average crystallite size decreased from 32nm to 22nm for Cr doped ZnO thin films. Optical absorbance investigation shows that optical band gap energy was decreased from 3.27eV to3.25eV.

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