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# Fabrication and Characterization of P-Type Co-Doped Tin Oxide Nano-Films

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**ABSTRACT**

Cadmium and Nitrogen co-doped in Tin Oxide thin films $Cd_xN_{0.1-x}$ : $SnO_2$ with different doped molar ratio (x = 0.01,0.03 and 0.05) have been fabricated by employing Ultrasonic Spray Pyrolysis (USP) technique at the grown thicknesses ( 106.74, 67.46 and 71.82) nm, respectively. The structural, optical, morphological, and electrical properties of the fabricated films have been investigated . X-ray diffraction studies revealed a polycrystalline phase, predominantly, of $Cd_xN_{0.1-x}$ : $SnO_2$ with (110) and (200) oriented films. The Hall effect measurement system depicted concentration a majority charges carriers (holes density ) and conductivity of the samples . The surface morphology have been observed of these films using Atomic Force Microscope (AFM) . This paper deals with structural , optical and electrical properties of the films grown at the temperature substrate 300 C.



## Introduction

Tin oxide is the first transparent conductor to have received significant commercialization . Among the different transparent conductive oxides $SnO_2$ films doped with Cadmium or Nitrogen seem to be the most appropriates for use in P-N junction solar cells, owing to its p-type $SnO_2$ thin films and high optical transmittance . $SnO_2$ is chemically inert, mechanically hard and can resist high temperature. Many excellent reviews of transparent conductive oxides are available.

Recently, p-type $SnO_2$ thin films by Indium co-doping with Gallium were successfully realized, but the hole mobility of the In–$SnO_2$ and Ga–$SnO_2$ was relatively low. One possible factor influencing the mobility is the lattice distortion caused by In or Ga dopant. Considering that co-doping method was reported to reduce strain effect and enhance mobility in other materials [1,2], Qinan Mao et al prepared p-type $SnO_2$ thin films by In–Ga co-doping method with high mobility [3].

In the present work , we propose using Cadmium–Nitrogen co-doping method to realize p-type $SnO_2$ thin films and studying structural, electrical and optical properties of thin films prepared.

## Characterization of film:

The thickness of film was measured by the Film Thickness Measurement with Reflection, (TF Probe 2.4, Developed by Angstrom Sun Technologies Inc.) and Atomic Force Microscopy (AFM) (AA3000 Scanning probe microscope, Angstron Advanced Inc.) . The transmittance of film coated was measured in the wavelength range of (190 - 1200) nm using a (SPECTRO UV/VIS Double Beam (UVD-3500) Labomed, Inc.). A blank sample of substrate was used as a reference in the measurement of optical transmittance and thickness. Composition and crystal structure studied by X- ray diffraction (XRD Shimadzu 6000, Cu-Kα) for USP coating . The surface morphology of sample was studied by AFM investigation .The electric properties of samples measured by Hall Effect Measurement System (HMS-3000,VER 3.5, Ecopia Inc ).

## Basic theory :

The optical properties of thin films in the present work were the variation of transmittance , reflective and optical energy gap with the doped molar ratio (x) . The optical band gap of the thin film have been investigated for the allowed direct transition in accordance with the theory of Bardeen et al from the equation (1)[ 4,5].

$$h\nu * \alpha = B * \left[h\nu - E_g\right]^{1/2} .. (1)$$

Where, h is the Planck constant, (α ) is the absorption coefficient , ν is the light frequency , Eg is the optical energy gap and B is empirical constant .

The electrical studies contained the variation of charges mobility, carrier concentration and conductivity measured at room temperature against the doped molar ratio (x). Film degeneracy is established by evaluating the Fermi energy by the expression [6].

$$E_F = \left(\frac{h^2}{8m^*}\right)\left(\frac{3n}{\pi}\right)^{\frac{2}{3}} \ldots . (2)$$

Where h is the Plank's constant, n is the concentration of free carriers and m* is the reduced effective mass. In all the calculations a mean value of $m^* = 0.3m_0$ [7] . where $m_0$ is the electron rest mass.

Another condition is that the mean free path (l) of the free carriers should be comparable to the size of the grains (D) in the films. For the degenerate samples (l) can be estimated with the expression[6,7,8] :

$$l = \left(\frac{h}{2e}\right)\left(\frac{3n}{\pi}\right)^{\frac{1}{3}} \mu \ldots . (3)$$

where μ is the measured mobility and e is the charge of electron. The grain size of the crystallite thin film from the XRD data was calculated using the Debye–Scherrer formula [9]:

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$$D = \frac{0.9 * \lambda}{\beta * \cos(\theta)} \ldots (4)$$

where D is the grain size of the crystallite, λ (1.54059 Å) is the wavelength of the X-rays used, β is the broadening of diffraction line measured at the half of its maximum intensity in radians and θ is the angle of diffraction .

**Experimental**

Nano thin films of $Cd_xN_{0.1-x}$ : $SnO_2$ , with different doped molar ratio (x = 0.01 , 0.03 and 0.05) , were fabricated applying aerosol assisted chemical vapor deposition (AACVD) technique by using ultrasonic frequency (1.5MHz) to spray pyrolysis of the precursor solution on per-heated glass substrates. The precursor solution prepared of mixture of 2.0308 g of $SnCl_2.2H_2O$ (purity-99.99%, Aldrich) salt and 5 ml of HCl is heated slightly. This mixture is diluted by adding 20 ml of methanol and the diluted solution is made up to 30 ml by adding triply distilled water.

**Table 1. Illustrates of Materials Weights versus doped molar ratio(x)**

| Molar ratio (x) | Materials Weights (g) | | |
|---|---|---|---|
| | $SnCl_2.2H_2O$ | $NH_4OH$ | $CdCl_2.H_2O$ |
| 0.01 | 2.0308 | 0.0315 | 0.0201 |
| 0.03 | 2.0308 | 0.0245 | 0.0603 |
| 0.05 | 2.0308 | 0.0175 | 0.1006 |

The Weight of (0.01) mole of $CdCl_2.H_2O$ equivalent to 0.0201g mixture with 5 ml of HCl and the diluted by adding methanol and the diluted solution is made up to 10 ml and mixture with $SnCl_2.2H_2O$ solution .The Weight of (0.09) mole of $NH_4OH$ equivalent to 10 ml of 0.09 M of $NH_4OH$ mixture with precursor solution and the total solution volume to become 50 ml, Table (1) illustrates Materials Weights of doped molar ratio of $Cd_xN_{0.1-x}$ : $SnO_2$ thin films . The resulting mixture was stirred at 40°C for 30 min using an ultrasonic agitator in order to obtain a clear solution which was used for synthesizing then $Cd_xN_{0.1-x}$ : $SnO_2$ thin films on glass slides . The latter slides (2.5cm x 7.5cm) were ultrasonically cleaned in ethanol and de-ionized water, and dried at 60°C .A glass slide was sprayed manually with the precursor synthesis solution at 300°C over a time period of 30 min utilizing the ultrasonic spray pyrolysis device by using ultrasonic frequency (1.5MHz). The preceding procedure was repeated with other glass slides over doped molar ratio concentration (x = 0.02 and 0.05) to obtain thin films of different doped concentration. The temperature of the substrate was monitored using an infrared temperature indicator technique.

**Results and discussion**

**Structural studies:**

The crystallographic structure of the films was characterized by X-ray diffraction and is presented in Fig (1). The XRD results indicate that the film $Cd_xN_{0.1-x}$ : $SnO_2$ deposited with (x = 0.01) was polycrystalline and retain the $SnO_2$ peaks of the film corresponding to (110), (200), and (211) reflections without any other phases appearing , the film deposited with (x = 0.03) was polycrystalline and retain the $SnO_2$ peaks of the film corresponding to (110) and (101) reflections without any other phases appearing but the film deposited with (x = 0.05) was polycrystalline with $SnO_2$ peaks of the film corresponding to (110) and (211) reflections without any other phases appearing as shown in Fig (1). The sizes of the crystallites $Cd_xN_{0.1-x}$ : $SnO_2$ with (110),(200) and (211) oriented films were estimated from the XRD results using Scherrer's formula in the equation (4) and inserted in table(2) .

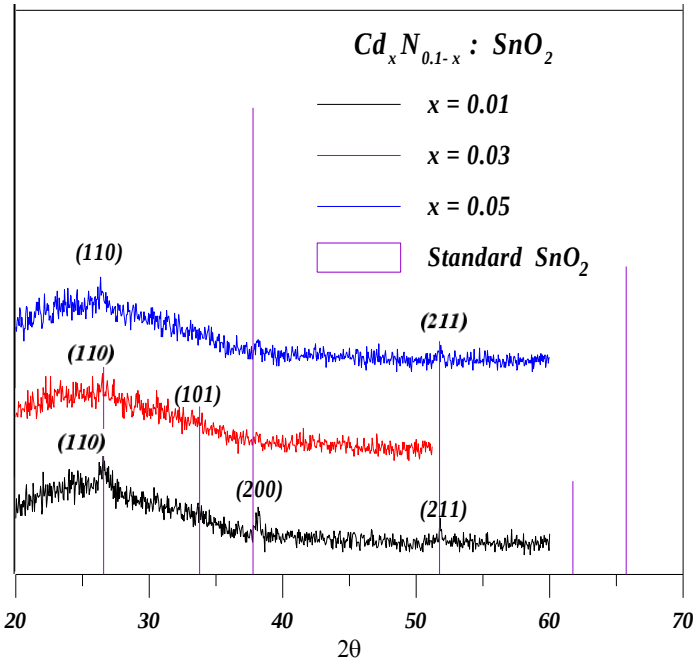


**Fig. (1) shows XRD of $Cd_xN_{0.1-x}$ : $SnO_2$ films**

**Table 2. Illustrates of the grain size of the crystallites (nm) versus doped molar ratio(x)**

| Doped molar ratio (x) | grain size of the crystallite (nm) | | |
|---|---|---|---|
| | (110) | (200) | (211) |
| 0.01 | 10.58 | 13.22 | 13.22 |
| 0.03 | 26.45 | | |
| 0.05 | 10.58 | | 17.63 |

**Optical and surface morphology studies:**

Fig (2) depicts the UV–Vis transmittance spectra of $Cd_xN_{0.1-x}$ : $SnO_2$ thin films doped with different concentration (x = 0.01,0.03 and 0.05). Clearly, a good agreement in the transmittance spectra with different doped ratio (x) is obtained. The average transmittance in the visible range is about 78%. The $(\alpha h\upsilon)^2$ vs. E plots for the films $Cd_xN_{0.1-x}$ : $SnO_2$ are shown in the inset of Fig (3), The optical band-gap of the films deduced by extrapolating the linear portion to the energy axis (E) are evaluated 4.006, 3.94 and 3.97 eV of $Cd_xN_{0.1-x}$ : $SnO_2$ films deposited with different doped concentrations (x = 0.01,0.03 and 0.05) , respectively. The wide optical band gaps of the films are obtained so that a good transmittance obtained in the visible range have been achieved. Fig (4) shows an AFM image for surface morphology of the sample prepared with doped concentration (x = 0.01). The surface roughness average is within 5.85 nm and Root Mean Square of surface roughness is 7.69 nm. This result indicates that the sample layer forms homogeneously. The thickness measurements in the image AFM confirm the thickness results using the Film Thickness Measurement with Reflection (TF Probe 2.4, Developed by Angstrom Sun Technologies Inc) . Fig (5) shows that Reflection and thickness measurements were measured by the Film Thickness Measurement with Reflection. The Samples deposited with doped concentration (x = 0.01,0.03 and 0.05) have been grown with thicknesses (106.74, 67.46 and 71.82) nm, respectively . Clearly , the reflections in the visible range of the samples observed with increased when the doped ratio (x) increased too .

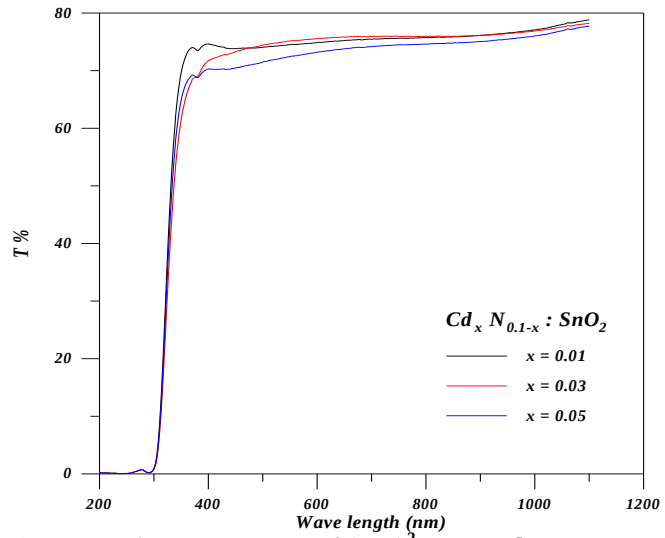


**Fig 2. Inset illustrates plots of $(\alpha h\upsilon)^2$ versus photon energy (E) to the $Cd_xN_{0.1-x}$ : $SnO_2$ samples.**

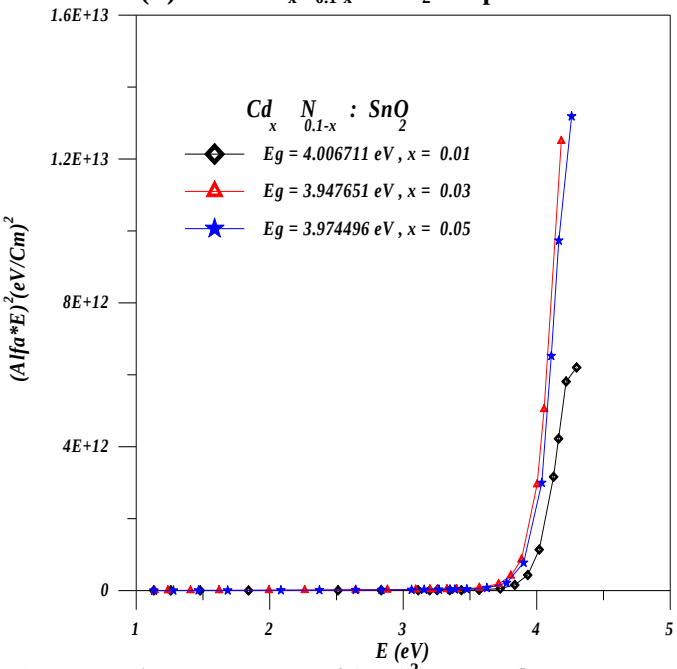


**Fig 3. Inset illustrates plots of $(\alpha h\upsilon)^2$ versus photon energy (E) to the $Cd_xN_{0.1-x}$ : $SnO_2$ samples**

**Electrical studies:**

The electric properties of samples such as conductivities (σ), carriers concentrations (n), Hall coefficients (H) and Charges mobility (μ) were measured by Hall effect measurement system (HMS-3000, Ecopia Inc) . The experiment conditions were electric current ranges (I = 1nA-1mA) and magnetic field (B=0.55T) . Hall effect data of the sample deposition with doped ratio (x=0.01) was depicted in the fig (6) . The data of average Hall coefficient of each sample were inserted in table (3), We observed the Hall coefficients have positive data that refer to the majority charges which participating of electric conductivity were positive hole charges . Hall coefficients were observed to decrease when doped molar ratio decreased too. The variation of carriers balk concentration ($n_h$) , Hall mobility (μ) and conductivity (σ) measured at room temperature against the doping concentration (x) were shown in the Fig (7). The observed variations of the Hall mobility and the mean free path initially increased with increased concentration doped (x) and then decreases , as shown in table (3). The conductivity and carriers bulk concentration were increased with increasing concentration doped (x) , as shown in fig (7) and table (3). The evaluated ( $E_F \approx 0.03$ eV) values of N-Type fluorine and antimony doped $SnO_2$ thin films were very high compared to (kT=0.025eV) level at room temperature , so that $E_f$ level was near to the conductive band [8] . In the present work , The evaluated $E_F$ values of P-Type Cadmium and Nitrogen doped $SnO_2$ thin films , calculated with equation (2) , were very low compared to (kT) level at room temperature , as shown in table (3) , so that $E_f$ level was near to the valance band. These (l) values calculated with equation (3) were considerable shorter than crystallite dimensions grain size calculated using X-ray data , in table (2) . Based on the above discussion it is concluded that grain boundary scattering was not the dominant mechanism.

**Table 3. Illustrates of the electric properties versus doped molar ratio(x)**

| Electrical properties | Doped molar ratio (x) | | |
|---|---|---|---|
| | 0.01 | 0.03 | 0.05 |
| H *$10^6$ ($m^2$/C) | 7.911 | 2.056 | 0.6848 |
| n *$10^{11}$(holes/$cm^3$) | 7.89 | 30.36 | 91.16 |
| μ ($cm^2$ $V^{-1}1$ $s^{-1}$) | 153 | 8462 | 3477 |
| l ($A^0$) | 0.28 | 24.9 | 14.79 |
| σ (1/Ω cm) | 1.94e-5 | 4.11e-3 | 5.078e-3 |
| $E_f$ (eV) | 1.029E-6 | 2.527E-6 | 5.2612E-6 |

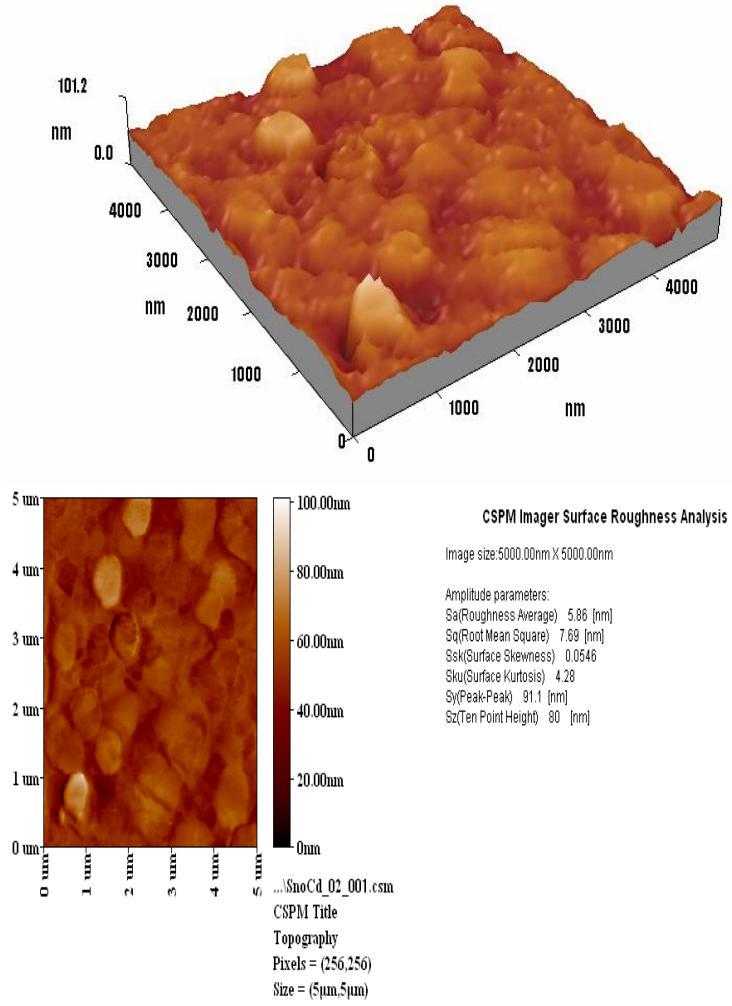


**Fig 4. AFM image of the film deposited with doped ratio (x =0.01)**

**Conclusions:**

The structural ,optical and electrical properties of aerosol assisted chemical vapor deposited $Cd_xN_{0.1-x}$ : $SnO_2$ thin films at different doped molar ratio were studied. The structural study indicated that the best crystallinity oriented with the face (110) . It revealed that the grain size of the films increases with the

doped molar ratio (x=0.03). The AFM image shows that the film is uniform and compact. The study of Optical properties such as transmittance, reflection and the optical band gap reveals that $Cd_xN_{0.1-x}$ : $SnO_2$ thin films have allowed direct transitions and wide optical band gap . The optical band gap energy of the films varies from 3.97 eV to 4 eV with different doped molar ratio. The study of electric properties such as bulk concentration of charges , charges mobility and conductivity reveals that the majority charge carriers of $Cd_xN_{0.1-x}$ : $SnO_2$ thin films were holes. Holes mobility of thin film deposited with doped molar ratio (x = 0.03) was highest than other. Conductivity of the samples is increased when doped molar ratio is increased too.

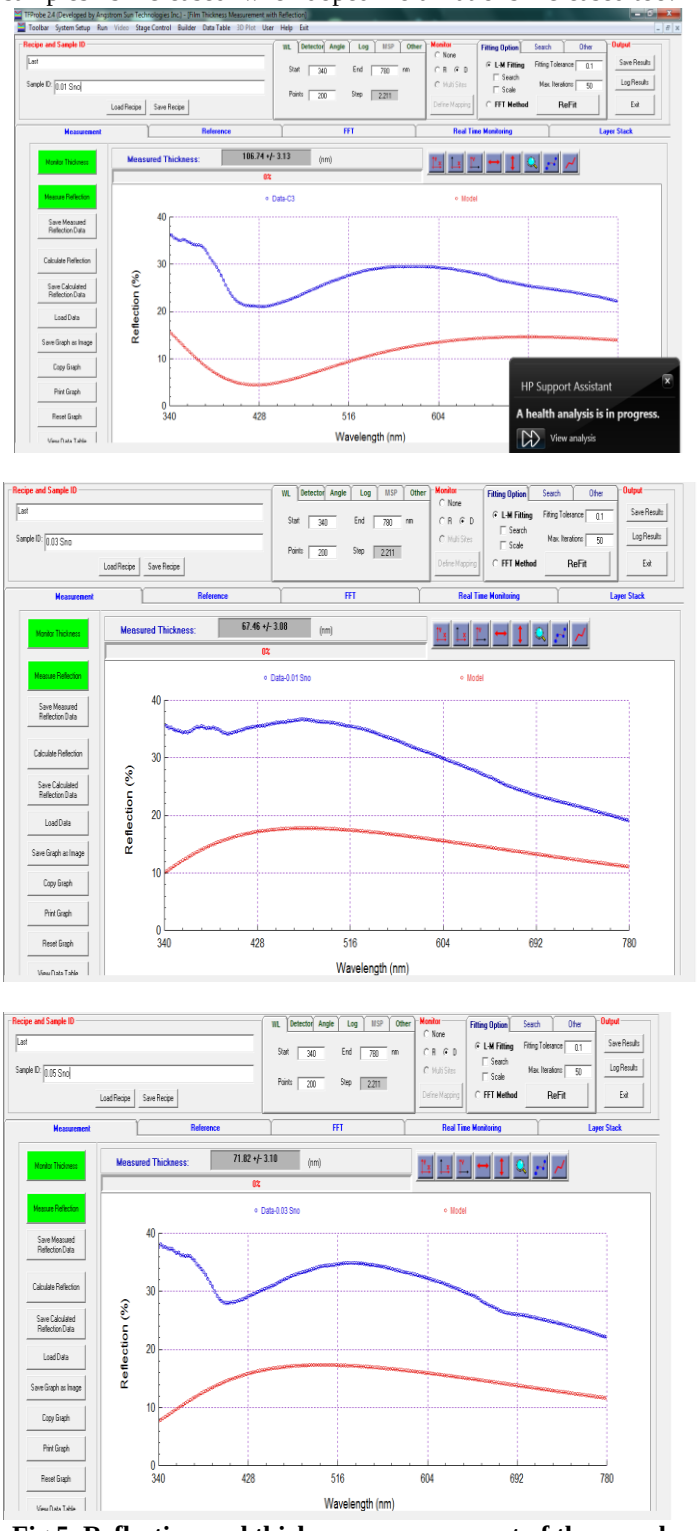


**Fig 5. Reflection and thickness measurement of the samples deposited with doped ratio (x =0.01,0.03 and 0.05) .**

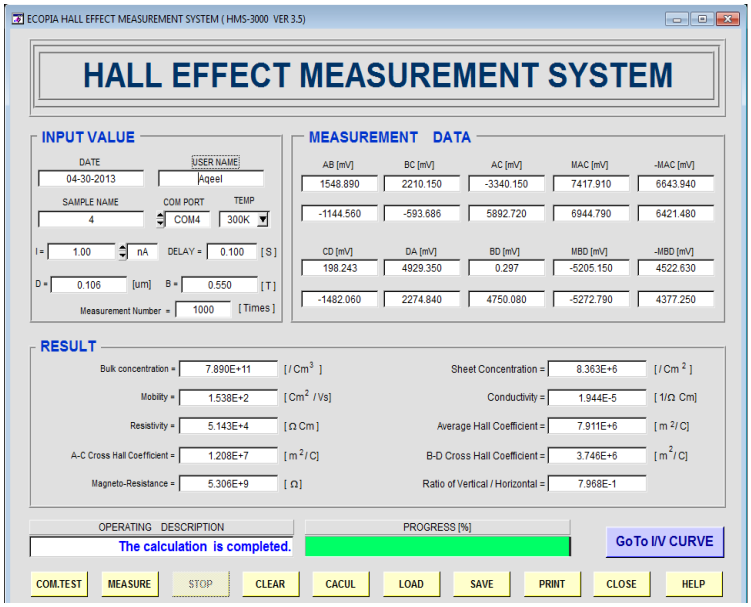


**Fig 6. Hall effect measurement of the film deposited with doped ratio (x =0.01) .**

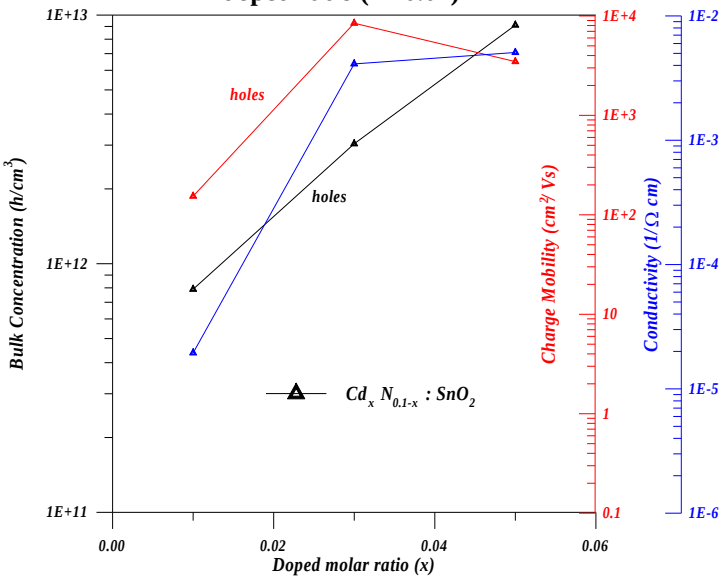


**Fig 7. Inset illustrates plots electric properties versus doped ratio (x) to the $Cd_xN_{0.1-x}$ : $SnO_2$ samples**

## References

1. J. G. Lu, Y. Z. Zhang, Z. Z. Ye, L. P. Zhu, L. Wang, B. H.Zhao, and Q. L. Liang, Appl. Phys. Lett. 88, 222114 (2006).
2. H. B. Yuen, S. R. Bank, M. A. Wistey, J. S. Harris, Jr., M.-J. Seong, S. Yoon, R. Kudrawiec, and J. Misiewicz, J. Appl. Phys. 97, 113510 (2005).
3. Qinan Mao , Zhenguo Ji and Lina Zhao," Mobility enhancement of p-type SnO2 by In–Ga co-doping", Phys. Status Solidi B 247, No. 2, 299–302 (2010)/ DOI 10.1002 /pssb. 200945545.
4. Bardeen J , Blatt F.J, Hall L.H. , Proceedings of the photoconductivity Conference, Atlantic city, Wiley, New York, (1956) 146.
5. K.Vijayakumar and L.Amalraj," Spray pyrolysised tin disulphide thin films at different precursor concentration ratios", Elixir Thin Film Tech. 53 (2012) 11900-11904,www.elixirpublishers.com
6. S. Noguchi, H. Sakata, J. Phys. D: Appl. Phys. 13 (1980) 1129.
7. H. Haitjema, J.J.Ph. Elich, Sol. Energy Mater. 16 (1987) 79.

8. B. Thangaraju ," Structural and electrical studies on highly conducting spray deposited fluorine and antimony doped SnO2 thin films from SnCl2 precursor" , Thin Solid Films 402 (2002) 71–78 .

9. A.V. Moholkar , S.M. Pawar , K.Y. Rajpure , Saleh N. Almari , P.S. Patil , C.H. Bhosale," Solvent-dependent growth of sprayed FTO thin films with mat-like morphology", Solar Energy Materials & Solar Cells 92 (2008) 1439–1444.