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The Synthesis & Structural, optical and Electrical Characterizations of Variation Fluorine Doped tin Oxide Thin Films by Spray Deposition Techniques

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ABSTRACT

The Fluorine doped and undoped tin oxide thin films have been prepared by spray pyrolysis from $SnCl_2$ precursor at the substrate temperature of 600^0C. The Fluorine doped tin oxide thin films belong to special class oxides that combine high electrical conductivity with high optical transparency. Such transparent Conducting Oxide (TCO) thin films thus an important component for optoelectronic applications. Spray pyrolysis deposition is a simple and relatively low cost technique for thin film preparation. This work comparers the fluorine doped and undoped SnO2 thin films. The effect of fluorine doping on the structural, optical and electrical properties of thin films have been studies. The characterization of samples was carried out by X-ray diffraction, scanning electron microscopy, UV-VIS spectrophotometer and the four probe method. The as-prepared films are polycrystalline with a tetragonal crystal structure. The films have moderate optical transmission of the pure SnO_2 and fluorine doped SnO_2 deposited films is71.2% and 73.3%. The obtained results reveal that the properties of the films are greatly affected by doping levels. These films are useful as conducting layers in optoelectronics and photovoltaic devices.

Keywords: Pyrolysis; Tin oxide; X-Ray diffraction; Electrical properties and measurements.

I. INTRODUCTION

The FTO thin films have various applications. In recent best use of transparent conducting oxide thin films as conducting solar window materials in thin film solar cells [1–6], as heat reflectors for advanced glazing in solar application[7,8] and as gas sensors [9–13]. Tin oxide is the first transparent conductor which is significantly commercialized [14]. Among the different transparent conductive oxides, SnO_2 films doped with fluorine are most appropriate for use in solar cells, its low electrical resistivity and high optical transmittance. SnO_2 is chemically inert, mechanically hard and can resist high temperatures [5]. Doped or undoped SnO_2 can be synthesized by numerous techniques such as thermal evaporation, sputtering [13-17], painting [3, 17], chemical vapour deposition [18–20], sol–gel coating [17, 21], spray pyrolysis [3, 13] and hydrothermal method. In this various deposition techniques, the spray pyrolysis is the most essay method for the good thin films preparation of doped tin oxide because of its simple and inexpensive experimental arrangement. Simple spray pyrolysis technique is easy of add to various doping materials, reproducibility, high growth rate and mass production capability for uniform large area coatings.

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In this study, tin oxide and fluorine doped tin oxide (SnO_2) thin films were prepared by the spray pyrolysis technique at substrate temperature of 600^0C using precursor solution. This work is to study the relationship between the doping and undoing levels and some physical properties of SnO_2 & SnO_2: F thin films such as the structural, optical electrical and properties.

II. EXPERIMENTAL DETAILS

The fluorine-doped and undoped tin oxide thin films in the present study were prepared using a spray pyrolysis apparatus. The both Thin films was deposited on a micro slide glass substrate. Dehydrate stannous chloride ($Sncl_2$:$2H_2O$) was used for making the precursor 0.1.M solution. This precursor was dissolved in 4 mL concentrated hydrochloric acid (HCl) and then added with methanol served as the starting solution and ammonium Bifluoride (NH_4 HF_2) by ranging from 2 ml to 10 ml in step of 2 ml. Other preparative parameters like nozzle to substrate distance, air flow rate, and substrate temperature (600^0C) were kept constant as the optimized values. The samples were structural properties analyzed with X-rays diffractometr using a monochromatic radiation Cu-Kα, λ=1.5406 Å at 30 kV, 10 mA in the range of scanning angle 20° < 2θ < 79.99°. Surface morphological analysis of the films was carried out by Scanning electron microscope (SEM). Four probe set up was used for electrical measurements at room temperature. Optical transmittance spectra of the films were measured using a PC based, UV-VIS Systronics spectrophotometer in the range 200 nm to 999 nm of wavelength with air as reference.

III. RESULTS AND DISCUSSION

3.1 Structural characterization of tin oxide fluorine doped tin oxide thin films

Tin oxide thin films were prepared by chemical spray pyrolysis technique. The transparency of thin films so formed depends on parameters like substrate temperature and concentration of the precursor solution. Also other parameters such as spray duration, flow rate, pressure etc. also affects the features of the thin film. Transparency and thickness are two important features to be considered. Since the major application area is solar cells fabrication the thin films must possess high optical transparency and minimum thickness.

Samples of 0.1 M were prepared at 70˚C. The spray duration was set to 1 minute. For this temperature, the films formed were thick and not transparent, since the decomposition temperature of tin oxide is about 600˚C. Also the pressure was too high that the substrates were not remaining stationary above the hot plate. Another set of samples were prepared at a temperature of 600˚C and doped the fluorine concentration. The films formed for these conditions were better than the first set of samples. The prepared thin films are highly transparent and conductive films were study for Structural properties.

The high-angle region of XRD pattern of the as-synthesized thin film was used to determine the lattice parameters ‘a’ and ‘c’ of the tetragonal phase,

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

By using this equation, we calculated the values of lattice parameter which well matches with JCPDS (Card No. 72-1147) a = 4.737Ǻ and c = 3.185 Ǻ.

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Figure 1 shows the XRD patterns of the Tin oxide thin films at substrate temperature 600^0C. The tin oxide thin film possesses tetragonal rutile structured because its diffraction peaks are clearly observed at 2θ = 26.6°, 33.5°, 37.8° and 51.7°, which corresponding to (110), (101), (200) and (211) directions of the rutile structured SnO_2. The XRD pattern of suggests that average grain sizes of SnO_2 thin film synthesized at 600^0C are approximately obtained by using the Scherer formula:

$$D= \frac{0.9\lambda}{\beta \cos\theta}$$

Where D = Crystalline grain size,

k = Particle size dependent constant.

λ = is the wavelength for spectrometer radiation (1.54056nm for Cu Kα),

β = is the full width at half maximum,

θ = is the scanning angle.

The grain size was calculated to be approximately 9.358 nm

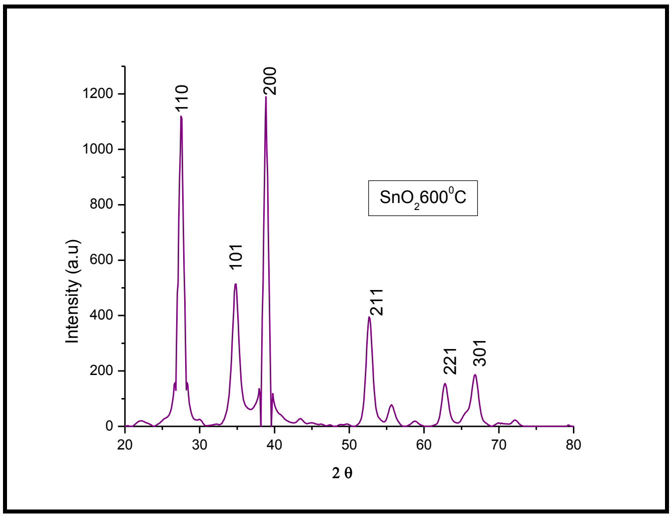

Fig. 1 XRD patterns of SnO_2 thin films.

Similarly, compare the XRD patterns of the Fluorine doped Tin oxide thin films (Fig 2.) at substrate temperature 600^0C for spray solution 10ml and fluorine doped by ranging from 2 ml to 10 ml in steps of 2 ml. Here SnO2: F thin films have tetragonal rutile structured because its diffraction peaks are clearly matches. The height of the peaks increase with increase in the fluorine concentration. A new direction of crystal growth appears corresponding to the reflection from the (1 1 0), (1 0 1) (2 0 0) and (2 1 1) planes at 2θ = 26.6°, 33.5°, 38° and 51.8°. The presence of other peaks such as (1 1 2), (2 2 0), (3 1 0) and (3 0 1) have also been detected but with substantially lower intensities at the higher doping concentration. Comparison of interplaner distance (d) values with JCPDS data show that phase present in the deposited films belongs to pure tetragonal structure.

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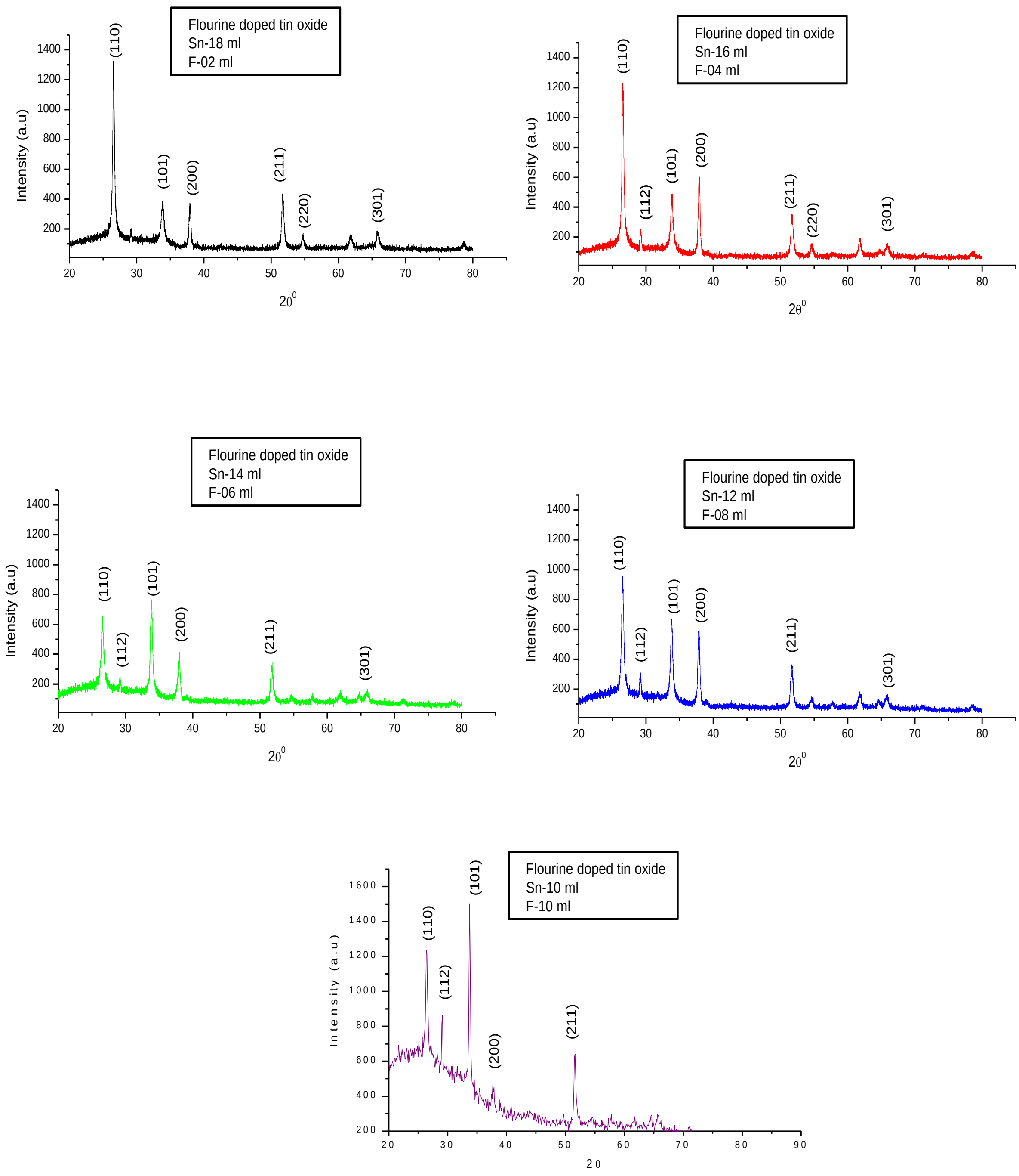

Fig. 2 XRD patterns of fluorine doped tin Oxide (SnO_2: F) thin films.

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3.2 Surface morphology of as-prepared films

Fig.3 shows a typical SEM micrograph of the tin oxide film deposited at 10 ml solution flow rate. The SEM microstructures reveal that, all the films have a homogeneous surface morphology with nanocrystalline grains, also all the films are without any cracks and holes. Patterns indicate that films are polycrystalline in nature. The EDAX spectra of the same film reveal the elemental analysis, which shows that Sn and O were found to be 89.55: 11.45 in percent.

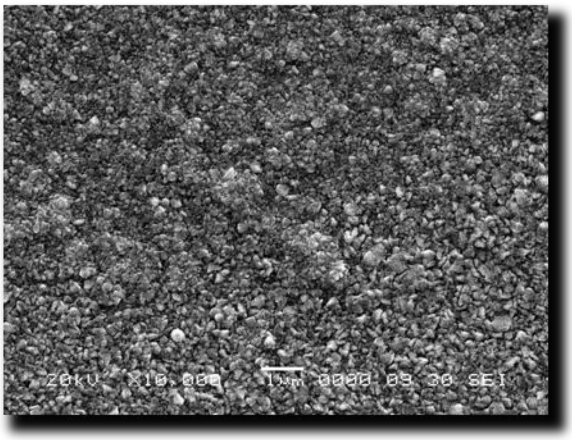

Fig 3. Typical SEM micrograph of SnO_2 thin films.

Fig.4 shows that SEM micrograph of the SnO_2: F thin film, fluorine doped by ranging from 2 ml to 08 ml in step of 2 ml. The SEM microstructures reveal that all the films have a homogeneous surface morphology with nanocrystalline grains, also all the films are without any cracks and holes. Patterns indicate that films are polycrystalline in nature and grain size ranges from 150 nm-250 nm.

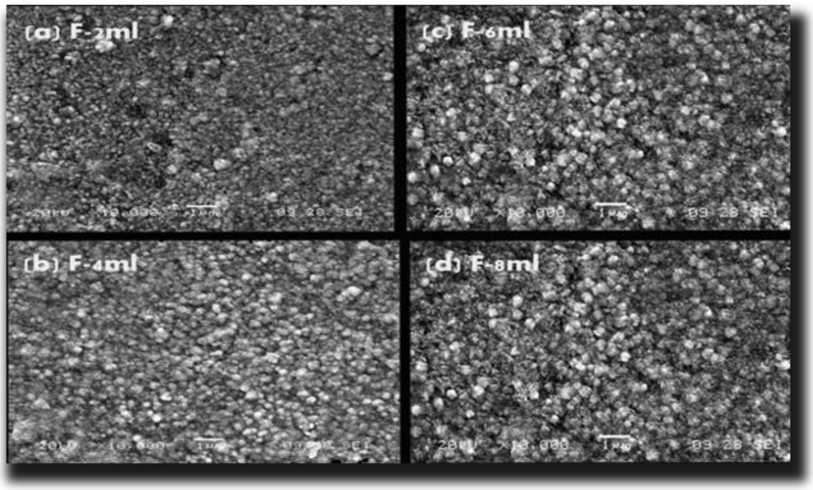

Fig.4: XRD Pattern for SnO_2: F thin film at (a) 2 ml (b) 4 ml(c) 6 ml and (d) 8 ml fluorine concentrations.

3.2 Optical properties

Fig.5 shows the variation of optical transmittance spectra in the range 200 nm - 999 nm for the SnO_2: F thin films. From the graph, the films deposited at the substrate temperatures 600^0C exhibits highest transmittance in the range of 744nm-760nm which maximum transmittance is 71.2% and 73.3%.

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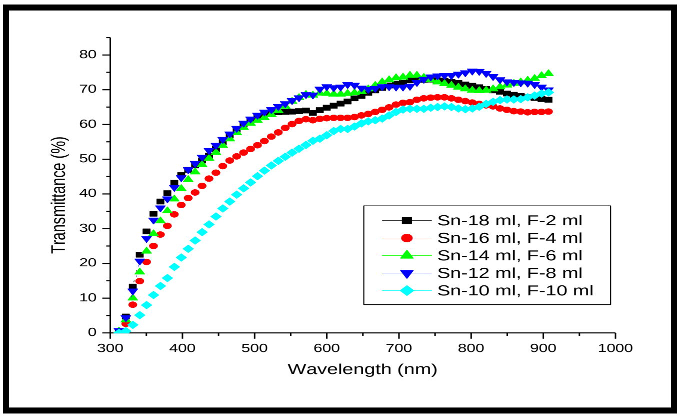
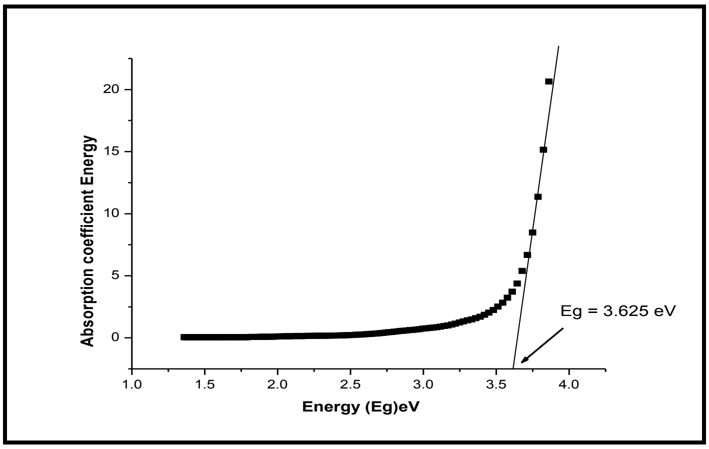


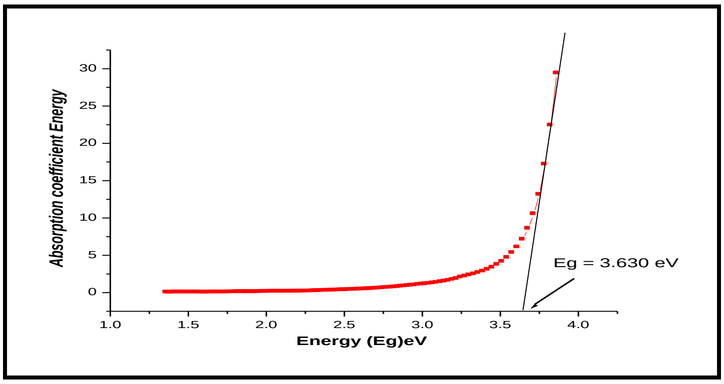
Fig5: Optical Transmittance against wavelength at different Fluorine concentration of the SnO_2 thin films.

Analysis on Optical Band-Absorption Coefficient:-

The analyzing the optical data with the expression for optical absorption coefficient 'α' and photon energy 'hυ' determine the optical band gap 'Eg'. Fig.6 (a & b) shows the plot of $(\alpha h\upsilon)^2$ vs 'hυ' .Extrapolation of the linear portion of the plots to energy axis yielded the direct band gap values of SnO_2: F & SnO_2 are 3.625eV & 3.60eV at 600^0C respectively.



(a)



(b)

Fig.6 (a & b) typical plot of absorbance coefficient Vs. Photon energy for SnO_2 : F & SnO_2 thin films.

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3.3 Electrical properties

Fig .8 shows the typical plot of voltage vs current for SnO_2: F thin film at room temperature. From the analysis of the I-V curves, it is observed shows the electrical I-V graph, it is observed that resistivity decrease with increase of fluorine rate, and more increases fluorine rate also increases resistivity. The calculated resistivity values are 0.0067, 0.0046, 0.0052, 0.016, 0.033 Ω-cm respectively. The deposited thin films with various fluorine % such as 10%, 20%, 30%, 40%, 50% respectively.

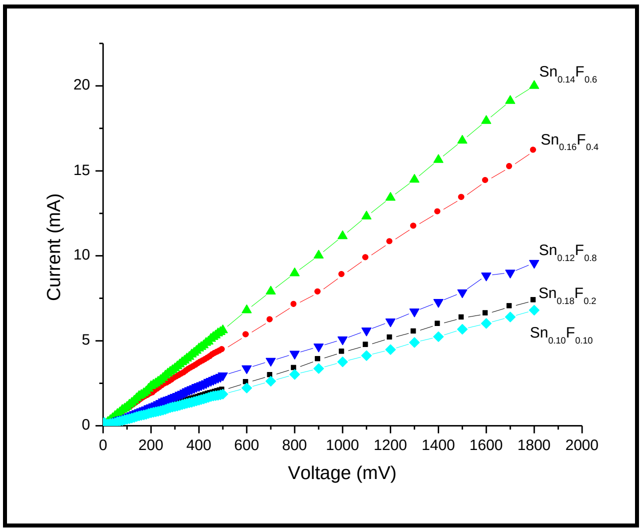

Fig.6 .28 I- V curve of SnO2: F thin films as a function of wavelength for different fluorine doping.

IV. CONCLUSIONS

In this work, SnO_2 and SnO_2: F thin films grown successfully by spray pyrolysis method. The structural investigation revealed that the both films are crystalline in nature with corresponding to (110), (101), (200) and (211) directions of the rutile structured as a preferred orientation with a tetragonal crystal structure. As deposited films was uniform and strongly adherent to substrate. The average transmittance of the deposited SnO_2 and SnO_2: F thin films were about 71.2 % and 73.3 % and optical band gap 3.625 eV & 3.630 eV respectively. The electrical studies conclude that resistivity decrease with increase in fluorine doping and there after it increases with increase in doping volume and values are 0.0067, 0.0046, 0.0052, 0.016, 0.033 Ω-cm respectively

REFERENCES:-

[1] D. Miao, Q. Zhaoa, S. Wua, Z. Wange, X. Zihanga and X. Zhaoa, *J. Non-Cryst. Solids* **356**, 2557 (2010).

[2] G. J. Exarhos and X. D. Zhou, *Thin Solid Films* **515**, 7025 (2007)

[3] A. A. Yadav, E. U. Masumdar, A. V. Moholkar, M Neumann-Spallart, K. Y. Rajpure and C. H. Bhosale, *J. Alloys and Compounds* **448**, 350 (2009)

[4] B. Thangaraju, *Thin Solid Films* **402**, 71 (2002)

IJARSE
ISSN (O) 2319 - 8354
ISSN (P) 2319 - 8346
[5] A. Goetzberger and C. Hebling, *Sol. Energy Mater. Sol. Cells* **62**, 1 (2000)

[6] G. Frank, E. Kaur and H. Kostlin, *Sol. Energy Mater.* **8**, 387 (1983)

[7] S. Chen, *Thin Solid Films* **77**, 127 (1981)

[8] W. Y. Chung, C. H. Shim, S. D. Choi and D. D. Lee, *Sens. Act.* **B20**, 139 (1994)

[9] J. R. Brown, P. W. Haycock, L. M .Smith, A. C. Jones and E. W. Williams, *Sens. Act.* **B63**, 109 (2000)

[10] P. Nelli, G. Faglia., G. Sberveglieri, E. Cerede, G. Gabetta, A. Dieguez and J. R. Morante, *Thin Solid Films* **371**, 249 (2000)

[11] I. Stambolova, K. Konstantinov and T. Tsacheva, *Mater. Chem. Phys.* **63**, 177 (2000)

[12] S. U. Lee, W. S. Choi and B. Hong, *Phys. Scr.* **T129**, 312 (2007)

[13] E. Elangovan, S. A. Shivashankar and K. Ramamurthi, *J. Crystal Growth* **276**, 215 (2005)

[14] P. S. Patil, *Mater. Chem. Phys.* **59**, 185 (1999)

[15] M. Ruske, G. Brauer and J. Szczrbowski, *Thin Solid Films* **351**, 146 (1999)

[16] Q. Zhao, S. Wu and D. Miao, *Ad.Mater.Res.* **150–151**, 1043 (2011)

[17] D. Belanger, J. P. Dotelet, B. A. Lombos and J. I. Dickson, *J. Electrochem. Soc.* **398**, 1321 (1985)

[18] A. C. Arias, L. S. Roman, T. Kugler, R. Toniola, M. S. Meruvia and I. A. Hummelgen, *Thin Solid Films* **371**, 201 (2000)

[19] P. S. Shewale, S. I. Patil and M. D. Uplane, *Semicond. Sci. Technol.* **25**, 115008 (2010)

[20] O. K. Varghese and .L K. Malhotra, *J. Appl. Phys.* **87**, 7457 (2000)

[21] M. K. Karanjai and D. D. Gupta, *J. Phys. D: Appl. Phys.* **21**, 356 (1988)