EFFECT OF ANNEALING TEMPERATURE ON ELECTRICAL AND DIELECTRIC PROPERTIES OF CO-DOPED SNO_2

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ABSTRACT

Annealing temperature plays a crucial role in the surface morphology and properties of Co doped SnO_2 . In this paper, we present a systematic investigation of the effect of annealing temperature on the electrical and dielectric properties of Co doped SnO_2 . $Sn_{1-x}Co_xO_2$ samples have been chemically synthesized with low Co concentration (≤ 1%). The X-ray diffraction (XRD), and scanning electron microscopy (SEM), are used to characterize these samples. The XRD pattern shows the tetragonal rutile structure. The annealing temperature is found to play crucial role in tuning the structural, electrical and dielectric properties of the Co doped SnO_2. The electrical behaviour of the prepared samples has been studied by measuring the *I-V* characteristics at different annealing temperature. The dielectric properties of these samples have been studied at frequency range of 1KHz – 10 MHz for different annealing temperatures. The dielectric behaviour shows that the value of dielectric constant (ε_r) decreases rapidly in the lower frequency region, whereas it depicts a slight dispersion in the middle and higher frequency range. The *ac* conductivity shows a linear dependence with frequency

Keywords:- Co-doped SnO_2, Diluted Magnetic Semiconductor, Sol-Gel method, Dielectric properties, *ac* conductivity.

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Introduction

Diluted magnetic semiconductors (DMSs) have attracted broad interest in interdisciplinary material science and future spintronics due to their technological applications in the field of optoelectronics, magnetoelectronics and microwave devices (Batzil and Diebold, 2005: Coey et al., 2004: Punnoose et al., 2004: Ogale et al., 2003). The main challenge in the practical applications of the DMS materials is the attainment of ferromagnetism. In search of materials with high Curie temperatures along with precise controllable spin properties wide band gap oxide based DMSs doped with transition metal ions (Co, Mn, Ni, Fe, Cr etc.) have attracted considerable attention. Various transition metal doped systems such as Ge, GaAs, TiO2, SnO2 & ZnO have been reported to show strong ferromagnetism and excellent electrical and optical properties (Deng et al., 2008).

Tin Oxide (SnO_2) presents special properties such as transparency, remarkable chemical and thermal stabilities, high transparency in the visible spectral range and low electrical resistivity (Hu et al., 1999: Satyaseelan et al., 2010: Bahrami et al., 2008: Godinho et al., 2009: Nomura et al., 2011: Zhou et al., 2012: Li et al., 2010: Wu et al., 2012: Okabayashi et al., 2012) with direct applications for photodetectors, solar cells, semi-conducting gas sensors, liquid crystal displays and transparent conducting electrodes. The co-existence of tin interstitials and oxygen vacancies in SnO_2 gives unique combination of transport and optical properties (Batzil and Diebold, 2005). Doping the SnO_2 with metals and metal oxides without altering the optical transparency is the primary means of controlling electrical conductivity which makes it an important component for optoelectronic applications. Hence doping strategy is an effective route to optimize the electrical transport properties. The valence of the doping ion determines the corresponding transport behaviour to great extent. The 3d-transition metal ions as dopants with open d-shell electronic configurations have unique physical properties that make them attractive for alternating the magnetic and other physical properties of their host semiconductors (Kimura et al., 2002). Several studies on the effect of the Fe substitution in SnO_2 (Coey et al., 2005: Tschope, 2001) have shown that by doping, the electrical conductivity increases and keeps the optical transparency in visible region. The conduction mechanism in SnO_2 has been thoroughly studied by Ogawa et al., 1982 using Hall measurements. Studies have shown that doping enhances the dielectric response and ac conductivity of metal oxide semiconductor (Kaur et al., 2012).

In this work, we have chemically synthesized undoped and Co –doped SnO_2 powders with low Co concentration (≤ 1%) and studied the effect of annealing temperature on electric and dielectric properties of Co –doped SnO_2 samples. A systematic investigation of dielectric properties of these samples sintered at different annealing temperatures has been done to understand its origin in accordance with appropriate growth conditions.

Experimental Method:-

Undoped and Co –doped SnO_2 powders were synthesized by reacting appropriate amounts of $SnCl_2.2H_2O$ and $CoCl_2.6H_2O$ in proportion 50:1, dissolved in 100ml of deoxygenated distilled water. The salts were then precipitated at 80°C using 50 ml of NH_4OH and kept at this temperature for several hours. The precipitate was then filtered, thoroughly washed and dried in air for several hours. The dried precipitates were then prepared by annealing for 2 hrs at different temperatures between 350°C to 650°C to obtain the final Co –doped SnO_2 powder. Characterization of the samples by x-ray diffraction (XRD) and SEM showed the formation of $Sn_{1-x}Co_xO_2$, when prepared by annealing the precipitates in the 350°C to 650°C range. The crystalline quality and the grain size of the samples were evaluated using XRD measurements.

Results and Discussion:-

Structural Investigations: Fig.1 shows the room temperature X-ray diffraction spectra for SnO_2:Co (≤ 1%) prepared at 350°C to 650°C for 2 hrs. The XRD patterns of $Sn_{1-x}Co_xO2$ samples have tetragonal rutile structure and comparable with the standard data**.** No additional phases such as the SnO_2 orthorhombic phase, metallic Co or other SnO or CoO based phases are observed. With increase in annealing temperature the cassiterite SnO_2 phase decreases while the relative concentration of the orthorohombic phase gradually increased. The average crystallite size (D) has been determined using the diffraction peaks (110) and (101) using Scherer's formula

$$D = \frac{k\lambda}{\beta\cos\theta} \qquad (1)$$

where K is a constant whose value is taken as 0.89, λ is the wavelength of CuK radiation and β is the corrected full width at half maximum (fwhm) of the diffraction peak.

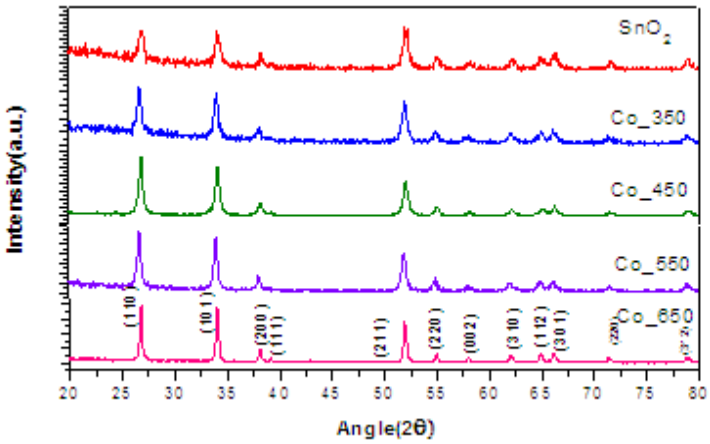

Fig:1 XRD patterns of Co doped SnO_2 (x=0.005) annealed between 350°C to 650°C and pristine SnO_2 annealed at 450°C

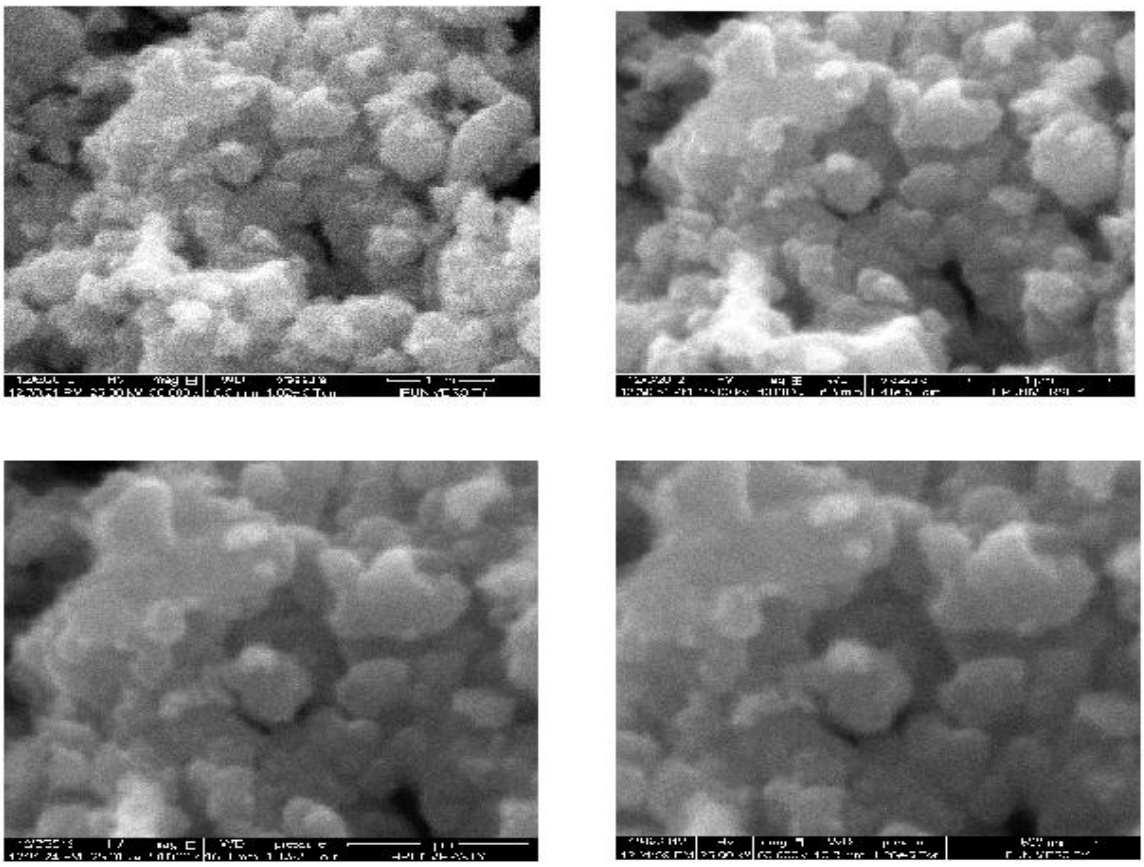

Fig.2 SEM morphology images for nanocrystalline Co doped SnO_2 powders annealed at (a) 350^oC (b) 450 ^oC (c) 550 ^oC , and (d) 650 ^oC

Scanning Electron Microscopy (SEM) investigations :- Fig. 2 illustrates the surface morphology of nanocrystalline Co doped SnO_2 powders prepared by annealing at 350^oC , 450 ^oC , 550 ^oC , and 650 ^oC. It can be seen from the morphological images that the particles are found to aggregate with increasing annealing temperature and may be attributed to a lesser number of nucleation centres leading to surface redistribution of grains. With increasing annealing temperature, number of surface defects during annealing process also increases which may be attributed to the diffusion of randomly distributed Co ions toward the surface with increasing grain growth. A similar surface diffusion of dopants with increasing annealing temperature was reported earlier. Average particle sizes are in the range 25-53nm and are in agreement with those obtained from the XRD data.

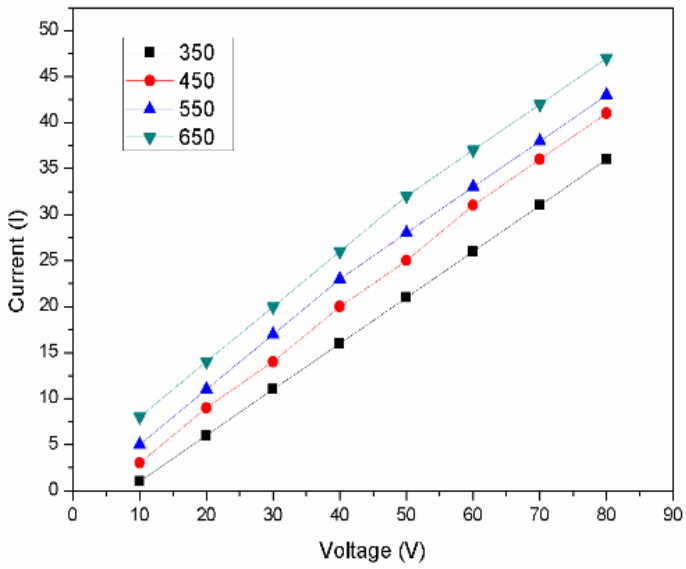

Fig. 3 *I-V* parameters of Co-doped SnO_2 at different annealing temperatures.

Electrical Measurements:- Fig. 3 shows the *I-V* characteristics of Co doped SnO_2 measured at four different annealing temperatures 350^oC to 650^oC range. The voltage is varied between 10 to 80 V in a step wise manner and current is measured at varying annealing temperature. *I-V* characteristics show almost linear relationship and it is noticed that the value of current increases

with every applied voltage and also with increase in annealing temperature. Increase in the value of current with increase in annealing temperature is due to the thermal expansion and rapid increase in ion mobility.

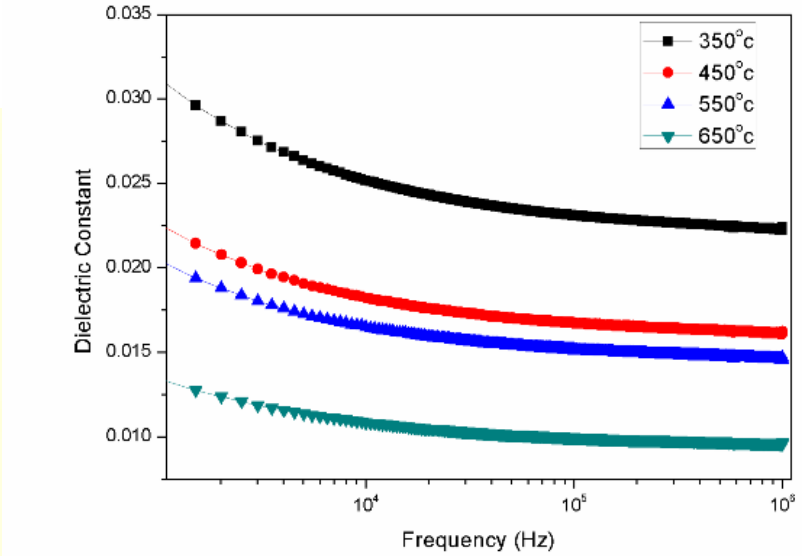

Fig. 4 Variation of dielectric constant with frequency

Dielectric Measurements:- Dielectric response of the Co- doped SnO_2 samples have been studied in the frequency range of 1 KHz- 10 MHz at different annealing temperatures from 350°C to 650°C in Fig 4. The dielectric constant (ε_r) is calculated by using the relation

$$\varepsilon_r = c_p d/\varepsilon_o A \,, \qquad (2)$$

where d is the thickness of the sample, $\varepsilon_o = 8.854*10^{-12}$ F/m (permittivity of free space), A is the effective area (m^2). The dielectric permittivity (ε_r) decreases with increasing frequency. In lower frequency range (1-10 KHz), the decrease of ε_r value is more pronounced than at higher frequencies and at a frequency of 10 KHz it reaches a constant value. The rapid decrease in ε_r in lower frequency range (upto 10 KHz) is because of space charge contribution i.e. by electron hopping between heterogeneities. However in mid to high frequency range (10 KHz-10MHz) the dispersion less dielectric response is observed due to the resonance effect (Indulal et al., 2010: Verma et al., 2010). The observed dielectric behaviour is frequency dependent which can be explained on the basis of Maxwell-Wagner Model (Wagner, 1973). According to this model, a

dielectric medium is assumed to be made of well conducting grains which are separated by poorly conducting (or resistive) grain boundaries. Under the application of external electric field, the charge carriers can easily migrate into the grains but are accumulated on the grain boundaries. This process can produce large polarization and high dielectric constant. The small conductivity of grain boundaries contributes to the high value of dielectric constant at low frequency. The higher value of dielectric constant can also be explained on the basis of interfacial / space charge polarization due to inhomogeneous dielectric structure. The inhomogeneity present in the system may be due to porosity or grain structure. The polarization decreases with increase in frequency and then reaches a constant value which is due to the fact that beyond a certain frequency of external field the hopping between different metal ions ($Sn^{4+,}$ $Co^{2+)}$ cannot follow the alternating field.

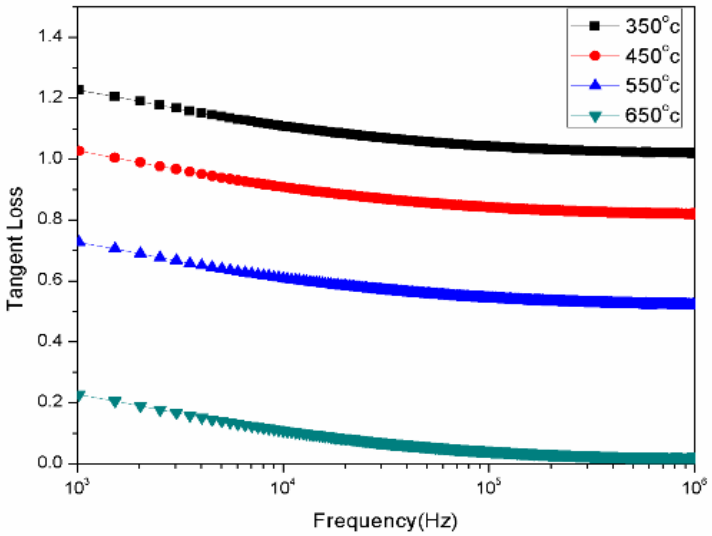

Fig. 5 Variation of Tangent Loss with frequency

Tangent loss or loss factor (tanδ) represents the energy dissipation in the dielectric system. At low frequency dielectric loss is very high and difficult to control. Fig. 5 shows that the dielectric loss factor decreases with increase in frequency range upto 10 KHz and it reaches a constant value at the frequency above 10KHz . According to Koop's model (Koops, 1951), the decrease of the tanδ is explained by the fact that at lower frequency where the resistivity is high and the grain boundary effect is dominant, more energy is required for the exchange of electrons

between the metal ions and dopant ions located at grain boundaries i.e. energy loss tanδ is high whereas at high frequencies, the resistivity is comparatively lower and grains themselves play a dominant role, thus very small amount of energy is required for hopping of electrons between the ions located in a grain and therefore tanδ is also small. The maximum value of the tangent losses is observed when hopping frequency corresponds to the frequency of the external field.

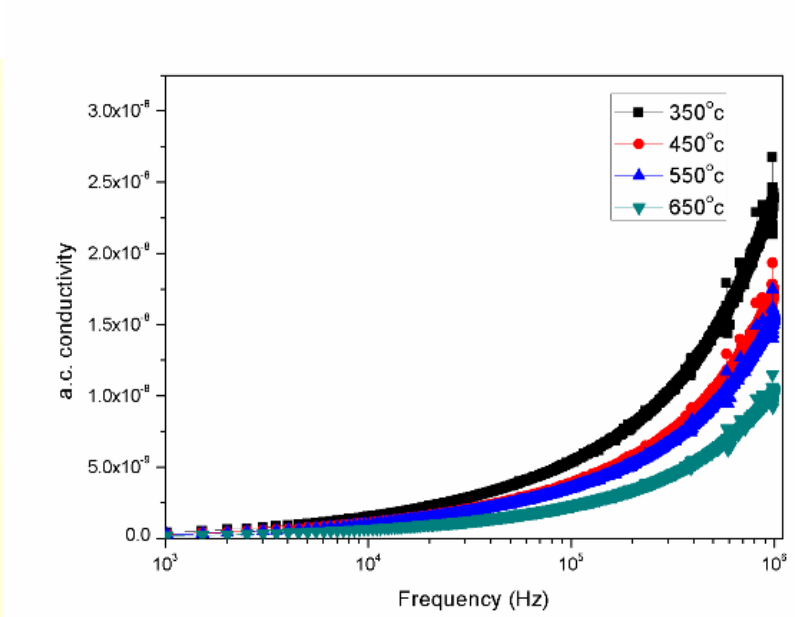

Fig. 6 Variation of ac conductivity with frequency

***ac* Conductivity Measurements:-**

The ac conductivity of the material is measured using a simple relation:

$\sigma_{AC} = \omega \tan\delta\varepsilon_o \varepsilon_r$ where $\omega = 2\pi f$ (3)

Fig. 6 represents the variation of *ac* conductivity (σ_{AC}) with varying frequency for different annealing temperature. It is observed that the dielectric constant decreases with increasing frequency and accordingly σ_{AC} increases with increasing frequency because the mobility increases between the grains. This pattern shows that it must be related to the bound carriers trapped in the sample or due to gradual decrease in series resistance with increasing frequency. Frequency dependence of the *ac* conductivity reassembles that of hopping type conduction. Hopping of charge carriers among the trap levels situated in the band gap of the material may

give rise to frequency dependent *ac* conductivity. Two other possible explanations may be attributed to the increase in conductivity: one is the electric energy associated with high *ac* frequency which can effectively encourage the electric charge to jump between the nano -size particles. The second possible explanation could be attributed to the enhanced dielectric relaxation of the polarization of SnO_2 in a high frequency region (Tataroglu et al., 2005: Daniel, 1967: Chen et al., 1999).

Conclusions:- In the present investigations, Co doped SnO_2 (x=0.005) powder samples have been synthesized successfully by co-precipitation technique to study their structural, electrical and dielectric properties with varying annealing temperatures. It has been concluded that the structural properties are affected by the local disorder and grain structure. From the morphological images it is seen that the particles aggregate more with increasing annealing temperature and may be attributed to a lesser number of nucleation centres leading to surface redistribution of grains. In lower frequency range (1-10 KHz), the decrease of ε_r value is more pronounced than at higher frequencies and at a frequency of 10 KHz it reaches a constant value. The dielectric constant (ε_r) decreases rapidly in lower frequency range (upto 10 KHz) because of space charge contribution i.e. by electron hopping between heterogeneities. The observed dielectric behaviour is frequency dependent which has been explained on the basis of Maxwell-Wagner Model. The dielectric loss factor (tanδ) decreases in the frequency range upto 10 KHz and it reaches a constant value at the frequency above 10KHz . The decrease in tanδ has been explained by Koop's model. The frequency dependent ac conductivity (σ_{AC}) shows higher resistivity in the lower frequency range and ac conductivity increases with increasing frequency which explains the dispersion in dielectric behaviour by hopping type conduction.

References:-

[1] Bahrami B, Khodadadi A, Kazemeini M & Mortazavi Y *Sensors Actuators* B **133**, (2008) pp-352.

[2] Batzil M & Diebold U, *Prog. Surf sci*., 79 (2005) pp-47.

[3] Chen B, Sha J, Ye X S, Jiao Z G & Zhang L D, *Sci China*, 42 (1999) pp-510.

[4] Coey J M D, Douvalis A P, Fitzgerald C B & Venkatesan M, *Appl. Phys. Lett.* 84, (2004) pp-1332.

[5] Coey J M, Venkatesan M & Fitgerald C D, *Nature Mater*., 4 (2005) pp-173.

[6] Daniel V V, *Dielectric Relaxation, Academic press, London*, 1967.

[7] Deng J X, Tian Y F, Yan S S, Cao Q, Liu G L, Chen Y X, Mei L M, Ji G & Zhang Z, *J Appl. Phys.* 104, (2008) pp-013905.

[8] Godinho K G, Walsh A & Watson G W *J. Phys. Chem.* C **113, (**2009) pp-439.

[9] Hu J T, Ouyang M, Yang P D & Lieber C M, *Nature* 58 (1999) pp-399.

[10] Indulal C R, Sanjeev Kumar G, Vaidyan A V & Raveendran R , *Indian J Pure Appl. Phys.*, 48 (2010) pp-893.

[11] Kaur J, Gupta V, Kotnala R K, Verma K C, *Indian J Pure Appl. Phys*, 50(2012) pp-57.

[12] Kimura H, Fukumura T, Kawasaki M, Inaba K, Hasegawa T & Koinuma H, *Appl. Phy. Lett.*, 80 (2002) pp-94.

[13] Koops C G, *Phys. Rev.*, 83 (1951) pp-121.

[14] Li T, Yi J et al. *J. Mater. Chem.* 20 (2010) pp-5756.

[15]Nomura K, Okabayashi J, Okamura K & Yamada Y *J. Appl. Phys.* 110 (2011) pp-083901.

[16] Ogale S B et al. (15 auths): *Phys. Rev. Lett.* 91, (2003) pp-077205.

[17] Ogawa H, Nishikawa M & Abe A, *J Appl. Phys.* , 53 (1982) pp-4448.

[18]Okabayashi J, Kono S, Yamada Y & Nomuro K *J. Appl. Phy.* 112 (2012) pp-073917.

[19] Punnoose A, Hays J, Shutthanandan V & Gopal V, *Appl.Phys. Lett.* 85, (2004) pp-1559.

[20] Sathyaseelan B, Senthilnathan K, Alagesan T, Jayavel R, Sivakumar K, *Mater Chem Phys.*, 124 (2010) pp-1046.

[21] Tataroglu A, Altindal S & BulBul M M, *Microelectron Eng.*, 81 (2005) pp-140.

[22] Tschope A, Sommer E & Birringer R, *Solid State Ionics*, 139 (2001) pp-255.

[23] Verma K C, Ram M, Kotnala R K, Bhatt SS & Negi N S, *Indian J Pure Appl. Phys.*, 48 (2010) pp-593.

[24] Wagner K W, *Am. J Phys.*, 40 (1973) 317.

[25]Wu P, Zhou B & Zhow W *Appl. Phy. Lett.* 100 (2012) pp-182405.

[26] Zhou B, Wu P, Zhou W et al. *Appl. Phy. Lett.* 101 (2012) pp-182404.