Comparison of some physical properties for SnO_2, SnO_2: F and SnO_2: Sb films deposited on glass substrates

DEMET TATAR*, GÜVEN TURGUT, ERDAL SÖNMEZ, BAHATTİN DÜZGÜN
K. K. Education Faculty, Department of Physics, Ataturk University, Erzurum 25240, Turkey

Thin films of undoped, 20 wt. % flourine-doped and 2 wt. % antimony-doped tin oxide on glass substrates at 410 (±5) ^oC were deposited by spray pyrolysis technique. The effect of 20 wt. % fluorine(F) and 2 wt. % antimony(Sb) doping on the structural, electrical and optical properties of tin oxide thin films were investigated. X-ray diffraction (XRD) analysis showed that undoped and Sb-doped films were prefentially oriented along the (110) direction, which changed to (200) direction for F-doped film. The films were found to be of cassiterite type with a tetragonal rutile structure, F and Sb doping increased the crystallinity. Atomic force microscopy (AFM) analysis showed that (RMS) roughness of 22.52 nm for undoped film has been slightly reduced to 15.52 nm and 15.56 nm for F and Sb doping fims, respectively and the surfaces of all the films to be made of nanocrystalline particles. The electrical properties of the films were measured employing the van der Pauw configuration. The electrical studies revealed that the films to be n-type electrical conductivitiy, 20 wt. % F and 2 wt. % Sb doping increased electrical conductivity of the films. From the optical studies, it was found that the transmittance of undoped film increased from 52.46 % to a maximum 77.39 % and 69.56 % for 20 wt. % F-doped and 2 wt. % Sb-doped film, respectively.

(Received October 5, 2010; accepted September 18, 2013)

Keywords: Spray Pyrolysis, Transparent oxide, Conducting oxide, Thin film, Optoelectronics

1. Introduction

An important application of thin film technology has been the development of transparent and conducting oxide (TCO) coatings [1]. Transparent conducting oxides (TCO) such as tin oxide SnO_2 (TO), ZnO, In_2O_3, tin doped indium oxide, In_2O_3:Sn (ITO), fluorine doped tin oxide, SnO_2:F (FTO), antimony doped tin oxide, SnO_2:Sb (ATO), aluminum doped zinc oxide, ZnO:Al (AZO) and gallium doped zinc oxide, ZnO:Ga (GZO) are particularly attractive [2]. Among TCOs, tin oxide (TO) is a good insulator in stoichiometric form, but non-stoichiometry, in particular oxygen deficiency makes it a conductor [3, 4]. Also, TO is a wide band gap n-type semiconductor (Eg=3.6 eV) [5]. Tin oxide (SnO_2) is widely used in solar cells, display devices, hybrid microelectronics and many other opto-electronic devices [6], stable resistors, touch-sensitive switches digital displays [7], electro-chromic displays, gas sensors [8] and architectural windows [9] etc. due to theirs low electrical resistivity, high optical transmittance in the visible region, high infrared reflectivity, chemically inert and mechanically hard [10]. Further, TO thin films are stable up to high temperatures, have excellent resistance to strong acids and they have very good adhesion to many substares [11-13].

Many researchers focused on doping TO, because electrical, structural and optical properties of TO can be improved by doping many dopants such as Sb and F [2, 4, 6,7,8,11,14-28]. In earlier works, undoped or doped tin oxide thin films were prepared by variety of methods such as chemical vapor deposition(CVD) [11], sputtering [25], sol-gel process [21,26,28], spray pyrolysis [7,8,10,14,15,18,29-31], hydrothermal method [32] and pulsed laser deposition [33] and some physical properties of the films prepared were investigated. Among these techniques, the spray pyrolysis technique is an attractive method to obtain thin films because of its simple and inexpensive experimental arrangement [14], ease of adding doping materials, reproducibility, high growth rate and mass production capability for uniform large area coatings [29]. In this study, we prepared TO, FTO and ATO thin films by spray pyrolysis and we investigated effect of 20 wt. % F and 2 wt. % Sb doping on the structural, electrical and optical properties of tin oxide thin films.

2. Experimental

5g stannous chloride ($SnCl_2.2H_2O$ with 98% purity, Merck) was dissolved in 3 ml of hydrochloric acid (HCl) by heating for 10 minute. This mixture subsequently diluted with methanol served as starting solution. The addition of HCl was required in order to break down the polymer molecules that were formed when diluting with methanol [9,30]. For fluorine doping, ammonium fluoride (NH_4F with 98%, Sigma-Aldrich) dissolved in doubly distilled water was added with the starting solution whereas for antimony doping, antimony trichloride ($SbCl_3$) dissolved in isopropyl alcohol was added. The weight percentage of [F]/[Sn] and [Sb]/ [Sn] ratios in the spray solution were 20 and 2, respectively. In each case, the amount of spray solutions prepared was 25 ml. All the spray solutions were magnetically stirred for 1h and finally these solutions were filtered by syringe filter with 0.2 μm

pore size before spraying on substrate. The well-cleaned microscopic glasses with 1cm x1 cm x 1mm dimesions were used as subtstates.

Undoped (SnO_2), 20 wt. % fluorine-doped (SnO_2:F) and 2 wt. % antimony-doped (SnO_2: Sb) tin oxide thin films reported in the present study were prepared by using a homemade spray pyrolysis apparatus. The schematic diagram of the experimental set-up is seen in Fig. 1.

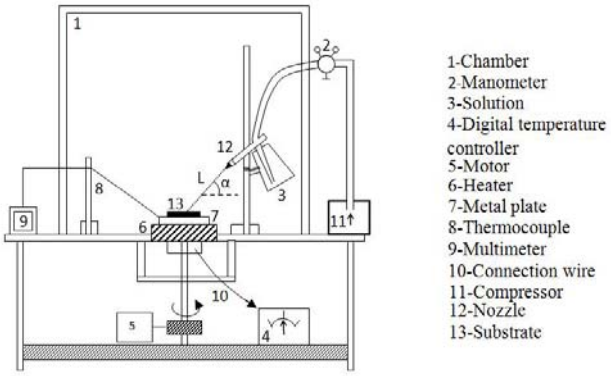


Fig. 1. Illustration of home-made ultrasonic spray pyrolysis deposition apparatus.

The spraying parameters; L distance which is between the spray nozzle and the substrate is 30 cm, the spray angle(α) is 45^o and the substrate temperature is 410 ($\pm$5) ^{o}C. The substrate temperature was maintained using a k-type thermocouple based digital temperature controller. Each spraying period was maintained about 10 s. To avoid thermal shock of the substrate due to excessive cooling, a few minutes of waiting time has to be allowed between successive spraying [34] and the optimized value of this spray waiting time was 1 minutes. The duration of the film deposition was about 35 min for each film. Uniform coating was achieved by rotating the substrate with a speed of 20 rpm/min in its plane. The flow rate of solution is 2 ml/min. After film deposition, coated substrates were allowed to naturally cool down to room temperature and the colour of the films was observed that varied from milky white for undoped SnO_2 to grayish white for 20 wt. % F-doped SnO_2 and light blue for 2 wt. % Sb doped SnO_2.

The structural characterization of the films was carried out by X-ray diffraction (XRD) measurements using a Rigaku D/Max-IIIC diffractometer with CuKα radiation (λ=1.5418 Å), at 30 kV, 10 mA. Surface morphology was examined by atomic force microscopy (AFM), which was produced by Nanomagnetics-Instrument. The electrical measurements were carried out by Hall measurements in Van der Pauw configuration. Optical transmittance measurements of the TO, FTO and ATO films were measured using UV-Vis spectrophotometer (Perkin Elmer, Lambda 35).

3. Results and discussion

3.1. Structural properties

The thickness of the deposited films was measured by using conventional mass method [34],

$$t = \frac{m}{A\rho} \quad (1)$$

where t is the thickness of film deposited, m is the mass of the film deposited on the area A and ρ is the bulk density of the material. The thickness of all the films were measured about 600 nm.

The crystal structure of the undoped, fluorine-doped and antimony-doped tin oxide thin films was determined by X-ray diffraction technique. The XRD patterns of the films were shown Fig. 2.

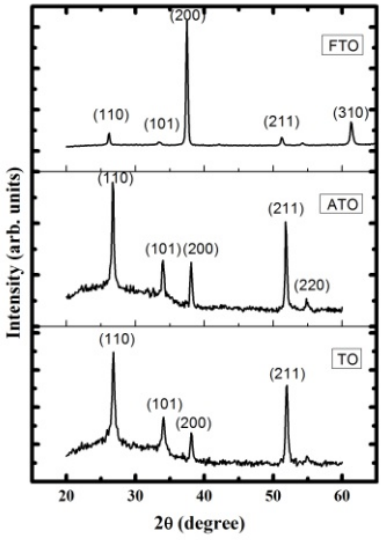


Fig. 2. XRD patterns of undoped, fluorine doped and antimony doped SnO_2 thin films.

XRD images showed that the films were polycrystalline. Whereas the fluorine doped tin oxide thin film was prefentially oriented along (200) direction, undoped and antimony doped tin oxide thin films were prefentially oriented along (110). Other orientations observed for TO and ATO films were (101), (200) and (211), whereas for FTO, other planes were (110), (101) and (211). From XRD data, the peak intensities of TO thin films increased with 20 wt. % F and 2 wt. % Sb doping, thus the crystallinity of TO thin film increased with F and Sb doping. In the study made by Moholkar et al. [2], they found that (200) prefential orientation 20 wt. % F doping and 20 wt. % F doping increased crystallinity of SnO_2 thin film. Ravichandran and Philominathan [16] reported that ATO films show a prefential growth along the (110) direction. Also, the increasing crystallinity of SnO_2 with Sb doping was observed by Elangovan et al. [30].

The observed ‘d’ values which ‘d’ is the interplaner distance were presented in Table 1 and these values were compared with the standard ones from the JPCDS 21-1252 data files. The matching of the observed and standard ‘d’

values confirms that the deposited films are of SnO_2 with tetragonal structure.

Table 1 Standard and observed'd' values

(hkl)	Standard d(Å)	Observed d(Å)		
		TO	FTO	ATO
110	3.351	3.324	3.348	3.336
101	2.644	2.627	2.642	2.634
200	2.369	2.360	2.366	2.360
211	1.765	1.717	1.763	1.764

The lattice constants 'a' and 'c', for tetragonal phase structure was determined by relation[**8**]

$$\frac{1}{d^2} = \left(\frac{h^2+k^2}{a^2}\right) + \left(\frac{l^2}{c^2}\right) \quad (2)$$

where 'd' is the interplaner distance and (hkl) miller indicies, respectively.

The calculated and standard lattice constants were given in Table 2. The calculated 'a' and 'c' values agree with JPCDS card no: 21-1252. As seen from Table 2, F and Sb doping not affected much lattice constans of SnO_2.

The avarage grain size was calculated using Scherrer Formula [12],

$$D = \frac{K\lambda}{\beta cos\ \theta} \quad (3)$$

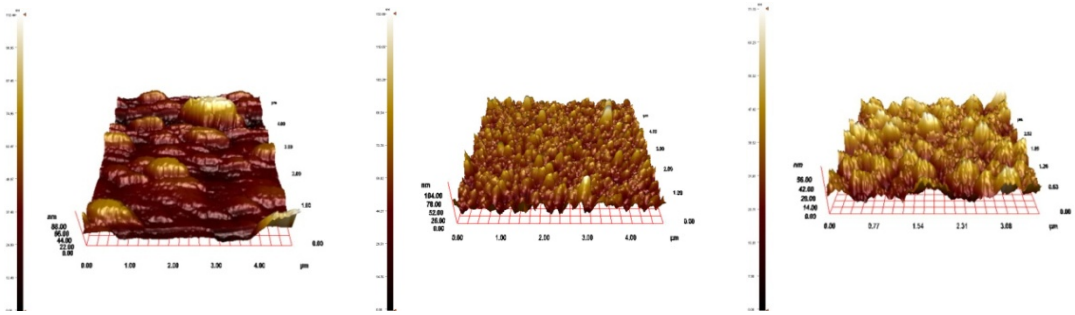
where D is mean grain size of nanoparticles, K=0.9, β is the full width at half of the peak maximum (FWHM) in radians and 'θ' is Bragg's angle.

The dislocation density(δ) was estimated using the equation, $\delta = 1/D^2$ (lines /m^2) **[6]**. The dislocation density(δ), defined as the length of dislocation lines per unit volume, and since δ is the measure of the amount of the defects in a crystal, the small vaue of δ obtained for FTO and ATO films confirmed that the crystallinity of SnO_2 improved by F and Sb doping. The calculated structural parameters were presented in Table 2.

Table 2 Structural parameters of SnO_2, SnO_2: F and SnO_2: Sb

Sample	Lattice constants(Å)		D(nm)	δ (x 10^{14} lines/ m^2)
	a	c		
SnO_2	4.701	3.167	24.18	17.1
SnO_2:F(20wt %)	4.742	3.194	37.31	7.18
SnO_2:Sb(2wt %)	4.718	3.249	36.32	7.58

Surface morphology of the films was examined by atomic force microscopy (AFM). Atomic force microscopy (AFM) images were obtained at 10 µm x10 µm planar in tapping mode, in 512x512 rezolusion and with 3 µm/s of scanning speed. Fig. 3 represented 3D surface morphologies of undoped, F-doped and Sb-doped SnO_2 films.



(a) (b) (c)

Fig. 3. AFM images of samples, a) SnO_2(TO), b) SnO_2:F (FTO), c)SnO_2:Sb(ATO).

Root mean square (RMS) roughness of the films was extracted from the AFM data. AFM studies showed that (RMS) roughness of 22.52 nm for undoped films has been slightly reduced to 15.52 nm and 15.56 nm for F and Sb doping fims, respectively. This behavior could be attributed to that 20 wt. % F and 2 wt. % Sb doping improved the crystallinity and surface morphology of SnO_2 film. This result is consistent with the XRD observations.

3.2. Electrical and optical properties

The Hall measurements show that the conductivity of the films is of n-type. The electrical resistivity of undoped film drastically falls from 12.15 × 10^{-4} Ω cm to 0.69x10^{-4} Ω cm and 2.7 × 10^{-4} Ω cm for F and Sb doped films. Similarly, the sheet resistance values for undoped, F and Sb doped films are 20.25 Ω cm^{-2}, 1.15 Ω cm^{-2} and 4.49 Ω cm^{-2}, respectively. These results indicate that a

relatively good SnO_2 thin films can be grown on a glass substrate at 410 ˚C by using spray pyrolysis method and the resistivity, conductivity and Hall mobility of the thin films are strongly dependent on the doping. The carrier concentration (n), Hall mobility (μ), resistivity (ρ) and sheet resistance (Rs) values were given in Table 3.

Table 3 Electrical and optical properties of SnO_2, 20 wt. %F and 2wt. % Sb doped tin oxide

Sample	Rs (Ω cm^{-2})	ρ (x 10^{-4} Ω cm)	n (x 10^{20}cm^{-3})	μ (cm^2 / V s)	T(%) at 800 nm	ϕ (Ω/cm^2)$^{-1}$
SnO_2	20.25	12.15	0.316	16.27	52.46	7.8x10^{-5}
SnO_2:F	1.15	0.69	14.70	61.59	77.39	6.7x10^{-2}
SnO_2:Sb	4.49	2.7	1.62	142.5	69.56	5.9x10^{-3}

The carrier concentration was found to increase considerably as expected due to Sb and F doping, which causes a decrease in sheet resistance and resistivity. A similar tendency for decreasing Rs and ρ with 20 wt. % F, 2 wt. % Sb was found by Elangovan et al. [14,10] and Mohalkar et al.[2]. According to our knowledges, the min. sheet resistance and resistivity (R_{sh}=1.15 Ω cm^{-2} , ρ = 0.69x 10^{-4} Ω cm) achieved in the present study was found to be very low among the earlier reported values for FTO films prepared from $SnCl_2.2H_2O$ precursor.

When flourine is incorporated in tin oxide films, each F^- anion substitutes an O^{2-} anion in the lattice and the substituted O^{2-} anion introduces more free electrons. Therefore the sheet resistance of the films decreases. But beyond a particular level of F content (solubility limit of F in the tin oxide lattice), the R_{sh} increases. This is because, the excess F atoms do not act as proper substitutional impurities, but behave as interstitial impurty ions and thereby raising the disorderlinessin the lattice. [2,15,6,18,35]. Because of the decreasing R_{sh} and ρ with 20 wt. % F doping, we can say that F^- anion substitutes an O^{2-} anion in the lattice and the substituted O^{2-} anion introduces more free electrons. Similarly in antimony doped tin oxide, Sb is in two different oxidation states namely, Sb^{5+} and Sb^{3+} [15,18]. When SnO_2 is doped with Sb some of the Sn^{4+} ions in the lattice are replaced by Sb^{5+} ions. This substitution results in the incorporation of free electrons in the lattice (n-type doping). Hence the sheet resistance (Rs) decreases with the increase in Sb doping ratio. But, this decrease in resistance stops at a particular doping level, beyond which, the resistance begins to increase [9,10,18,30]. The reason for this is that, when the doping level increases, a part of the Sb^{5+} ions reduces to the Sb^{3+} state, resulting in the formation of acceptor sites (p-type doping) and consequent loss of charge carries [6,23,24]. The lowest sheet resistance and resistivity in some studies [3,9,18,30] were obtained at 2 wt % Sb doping level and for this level was seen n- type doping. Hence, in present study, some of the Sn^{4+} ions in the lattice were replaced by Sb^{5+} ions and this substitution resulted in the incorporation of free electrons in the lattice. Therefore the sheet resistance of the films decreases. But beyond a particular doping level (both F and Sb), the R_{sh} increases. Hence, in this work, both of these dopants are simultaneously employed in order to achieve better conductivity.

The optical properties of the films were investigated using the transmission spectra (Fig. 4) observed in the wavelength range of 300-800 nm.

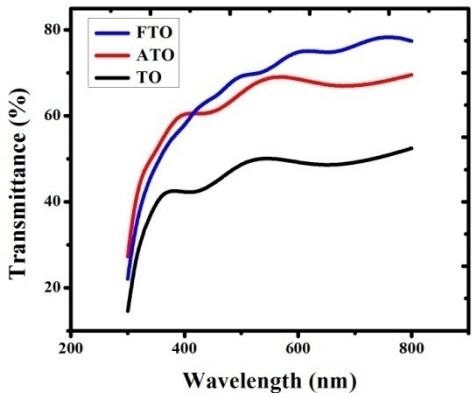


Fig. 4. Comparison of transmittance spectra of undoped, fluorine doped and antimony doped SnO_2 films

It was observed that visible transmittance would increase with flourine or antimony doping of tin oxide. The maximum transmittance observed for the TO, FTO and ATO thin films was 52.46%, 77.39% and 69.56%, respectively at the wavelength 800nm. Highest transmittance was obtained in FTO films, whereas a lower transmittance was observed in TO films. For undoped TO films, the transmittance at above 400nm range is found to decrease considerably. This important variation could be due to the optical scattering by doping of TO films in this work. The figure clearly shows the increase in transmittance due to doping at visible range of wavelength. Subramanian [36] observed a reduction in the transmittance of flourine doping. However, we and several workers have observed an increase in the transmittance of doping tin oxide films. This may be due to the precursor solution and doping concentration which, we have used [14,18,35]. Similarly, for the pure and antimony doped tin oxide films, Elangovan and Ramamurthi [9,18] found that the transmittance value of 42.24 % for the pure tin oxide films increased to 54.48 % on the addition of 0.5 wt. % of antimony. But, they found that the transmittance decreased for above 0.5 wt. % antimony concentration. However, in the present study, we have observed an increase in the

transmittance of 2 wt. % of antimony concentration. This may be due to the colour of our 2 wt. % Sb doped film is light blue whereas the colour of their film (2 wt. % Sb doped) is blakish blue.

For the solar cell and other opto-electronic applications, the figure of merit (ϕ) of the films plays an important role. It was calculated by using the Haacke formula **[8]**,

$$\phi = \frac{T^{10}}{R_S} \quad (4)$$

where T is the transmittance and R_s the sheet resistance. The calculated figure of merit values were showed in Table 3 and from Table 3, it can be seen that Sb and F doping increased figure of merit. Hence, for comparison purpose between optical and electrical properties the figure of merit serves useful function.

4. Conclusion

Polycrystalline thin films of SnO_2 with 20wt.% flourine and 2wt.% antimony doping concentrations were prepared using by spray pyrolysis from $SnCl_2.2H_2O$ precursor solution using a homemade spray pyrolysis apparatus.

Structural, electrical and optical properties of the films have been analysed for three cases: SnO_2, SnO_2:F and SnO_2:Sb. From the structural investigations made by using XRD, undoped and Sb doped films showed prefential growth along (110), which changed to (200) orientation for F doped film. The lattice parameters were not affected by the doping. The avarage grain sizes are approximately between 24.18-37.31 nm. AFM study showed that the roughness of the film is depent on the antimony and fluorine doping. In the films doped with 20 wt. % F and 2 wt. % Sb, Hall mobility and carrier concentrations was found to be higher than undoped film. The sheet resistance values are 1.15 and 4.49 Ωcm^{-2} for the SnO_2:F and SnO_2:Sb films, respectively. The films were found to be n-type semiconductors. All the films are degenarete with carrier concentrations in the range of 10^{20}. The resistivities of the samples are of the order of 10^{-4}. The min. sheet resistance and resistivity achieved in the present study was found to be very low among the earlier reported values for FTO films prepared from $SnCl_2.2H_2O$ precursor.

The film of low resistivity and high transmittance can be used as window layer in solar cell, in different opto-electronic devices such as flat plate collectors, photo-thermal convercion and as a working electrote in electro-depositon processes. Among these films prepared, FTO thin film has the best properties of structural, electrical and optical. Also, it was identified that properties of the films prepared agree with studies in the litherature.

References

[1] C.C. Lin, M.C. Chiang, Y.W. Chen, Thin Solid Films **518**, 1241 (2009).

[2] A.V. Moholkar, S.M. Pawar, K.Y. Rajpure, C.H. Bhosale , J.H. Kim , Applied Surface Science **255**, 9358 (2009)

[3] M. Batzill, U. Diebold, Progress in Surface Science. **79**, 47 (2005)

[4] A.V. Moholkara, S.M. Pawara, K.Y. Rajpurea, P. S. Patilb, C. H. Bhosalea, Journal of Physics and Chemistry of Solids. 68, 1981-1988 (2007)

[5] D. Jadsadapattarakul, C. Euvananont, C. Thanachayanont, J. Nukeaw, T. Sooknoi, Ceramics International. **34**, 1051 (2008)

[6] K. Ravichandran, G. Muruganantham, B.Sakthivel, Physica B. **404**, 4299 (2009)

[7] G. Jain, R. Kumar, Optical Materials. **26**, 27 (2004)

[8] R.R. Kasar, N.G. Deshpande, Y.G. Gudage, J.C. Vyas, Ramphal Sharma, Physica B. **403**, 3724-3729 (2008)

[9] E. Elangovan, K. Ramamurthi, Cryst. Res. Technol. **38**, 779 (2003)

[10] E. Elangovan, S.A. Shivashankar, K. Ramamurthi, Journal of Crystal Growth. **276**, 215-221 (2005)

[11] K.S. Kim, S.Y. Yoon, W.J. Lee, K.H. Kim, Surface and Coating Technology. **138**, 229-236 (2001)

[12] S. Chacko, N.S. Philip, K.G. Gophandran, P. Koshy, V.K. Vaidyan, Applied Surface Chemistry. **254**, 2179 (2008)

[13] E. Elangovan, M.P. Singh, K. Ramamurthi, Materials Science and Engineering B. **113**, 143 (2004)

[14] E. Elangovan, M. P. Singh, M. S. Dharmaprakash, K. Ramamurthi, J. Optoelectron. Adv. Mater. **6**, 197 (2004)

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

[16] S.Y. Lee, B.O. Park, Thin Solid Films. **510**, 154 (2006)

[17] K. Ravichandran, P. Philominathan, Materials Letters. **62**, 2980 (2008)

[18] E. Elangovan, K. Ramamurthi, Applied Surface Science. **249**, 183 (2005)

[19] D. Zaouka, R. al Asmarb, J. Podleckid, Y. Zaatarb, A. Khouryc, A. Foucaran, Microelectronics Journal. **38**, 884 (2007)

[20] A.A. Yadav, E.U. Masumdar, A.V. Moholkar, M. Neumann-Spallart, K.Y. Rajpure, C.H. Bhosale, Journal of Alloys and Compounds. **488**, 350 (2009)

[21] L. K. Dua, A. De1, S. Chakraborty, P. K. Biswas, Materials charecterization. **59**, 578 (2009)

[22] T.Krishnakumar, R. Jayaprakash, N. Pinna, A.R. Phani, M.Passacantando, S.Santucci, Journal of Physics and Chemistry of Solids. **70**, 993 (2009)

[23] K. Ravichandran, G. Muruganantham, B. Sakthivel, P. Philominathan, Journal of Ovonic Research. **5**, 63 (2009)

[24] E. Elangovan, K. Ramamurthi, J. Optoelectron. Adv. Mater. **5**, 415 (2003)

[25] J. Ma, X. Hao, H. Ma, X. Xu, Y. Yang, S. Huang, D. Zhang, C. Cheng, Solid State Communications. **121**, 345 (2002)

[26] D. Zhang, Z. Deng, J. Zhang, L. Chen, Materials Chemistry and Physics. **98**, 353 (2006)
[27] T.R. Giraldi, M.T. Escote, M.I. B. Bernardi, V. Bouquet, E.R. Leite, E. Longo, J. A. Varela, Journal of Electroceramics. **13**, 159 (2004)
[28] D. Zhang, L. Tao, Z. Deng, J. Zhang, L. Chen, Materials Chemistry and Physics **100**, 275 (2006)
[29] T. Serin, N. Serin, S. Karadeniz, H. Sarı, N. Tugluoglu, O. Pakma, Journal of Non-Crystalline Solids. **352**, 209 (2006)
[30] E. Elangovan, K. Ramesh, K. Ramamurthi, Solid State Communications. **130**, 523 (2004)
[31] K. Murakami, K. Nakajima, S. Kaneko, Thin Solid Films. **515**, 8632 (2007)
[32] J.Zhang, L. Gao, Materials Chemistry and Physics. **87**, 10 (2004)
[33] H. Kim, A. Pique, Applied Physics letters. **84**, 218 (2004)
[34] B. Thangaraju, P. Kaliannan, Semicond. Sci. Technol. **15**, 542 (2000)
[35] C. Agashe, J. Hüpkes, G. Schöpe, M. Berginski, Solar Energy Materials & Solar Cells **93**, 1256 (2009)
[36] N.S. Subramanian, B. Santhi, S. Sundareswaran and K.S. Venkatakrishnan, Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry. **36**, 131 (2006)

*Corresponding author: demettatar@atauni.edu.tr