Research Journal of Applied Sciences, Engineering and Technology 14(11): 427-432, 2017
DOI:10.19026/rjaset.14.5143
ISSN: 2040-7459; e-ISSN: 2040-7467

Submitted: January 25, 2016 Accepted: April 22, 2016 Published: November 15, 2017

Research Article

Study of Structural and Optical Properties of Undoped and Cd Doped SnO₂ Thin Films Prepared by Sol-Gel Dip Coating Technique

[1, 2]M. Khechba, [1]A. Bouabellou, [3]F. Hanini and [1]S. Touati
[1]Department of Physics, University Frères Mentouri Constantine, Thin Films and Interfaces Laboratory, Route Ain El Bey, Constantine 25000,
[2]Department of Materials Sciences, Faculty of Nature and Life Sciences, University Larbi Tébessi Tébessa, Constantine Road, Tébessa 12002, Algeria
[3]Department of Materials Sciences, Applied and Theoretical Physics Laboratory, University Larbi Tébessi Tébessa, Constantine Road, Tébessa 12002, Algeria

Abstract: In this study, we report the study of the surface morphology, the structural and optical proprieties of transparent cadmium doped tin dioxide (Cd:SnO_2) thin films deposited on glass and Si(100) substrates by Sol Gel Dip Coating (SGDC) technique. The analysis was carried out using Grazing Incidence X-Ray Diffraction (GIXRD), Atomic Force Microscopy (AFM), UV-Vis spectrophotometry and Spectroscopic Ellipsometry (SE). The X-ray diffraction reveals that all films deposited on Si(100) substrate have tetragonal crystalline structure with preferential orientation along (310) plane, but an amorphous structure is obtained for all the films prepared on glass substrate. The surface roughness, observed by means of AFM varies from 19 to 4 nm. The optical measurements show that the deposited Cd:SnO_2 films have a high transparency (~86%) in the visible spectrum and a band gap energy decreasing from 3.60 eV to 3.31 eV with increasing Cd concentration. The obtained values of the refractive index of the films are ranging between 1.559 and 1.613.

Keywords: AFM, Cd: SnO_2, thin films, SE, Sol-gel, TCO, XRD, UV-vis

INTRODUCTION

Transparent Conducting Oxide (TCO) materials have a greater importance due to the large variety of their applications such as electrochromic devices (Kuo *et al.*, 2012), solar cells (Kim *et al.*, 2010), optoelectronics devices (Ramamoorthy *et al.*, 2006). Tin dioxide (SnO_2) is one of the most important (TCO) because of his numerous applications in modern technologies, such as flat panel displays, solar cells, light emitting diodes and gas sensors (Ginley and Bright, 2000; Young *et al.*, 2003; McDowell *et al.*, 2008; Thangaraju, 2002). Indeed, SnO_2 which is non toxic and abundant material in nature, is particularly characterized by a wide band gap (E_g = 3.6 eV), a high electrical conductivity, a high transmittance in the ultraviolet–visible region and a high infrared (IR) reflectance (Ginley and Bright, 2000; Minami, 2000). Additive elements such as Cu (Vasiliev *et al.*, 1998; Shuping *et al.*, 2008; Patil and Patil, 2006; Yamazoe *et al.*, 1996; Jin *et al.*, 2006), Pd (Shimizu *et al.*, 1998; Shen *et al.*, 2009; Manjula *et al.*, 2009; Pavelko *et al.*, 2009; Cioffi *et al.*, 2006), In Durrani *et al.* (2005) and Shukla *et al.* (2007) and rare earth elements (Samotaev *et al.*, 2007) are used to improve the sensor response, selectivity and also surface modification. Chemical vapor deposition, sol-gel, sputtering, spray pyrolysis, pulse laser deposition are the main deposition techniques used to synthesize SnO_2 films onto substrates (Fang and Chang, 2005; Bagheri-Mohagheghi and Shokooh-Saremi, 2004; Chen *et al.*, 2004; Chen *et al.*, 2003; Chen *et al.*, 2005; Chen *et al.*, 2006).

The aim of this study is to study the structural and optical properties of cadmium doped SnO_2 films deposited by SGDC technique onto silicon and glass substrates with different Cd doping concentrations. The effect of Cd doping on the physical properties of the fabricated SnO_2 thin films is elucidate.

MATERIALS AND METHODS

Undoped and Cd doped SnO_2 thin films were prepared by sol–gel dip-coating process using $SnCl_2$-$2H_2O$ and $CdCl_2$-$5H_2O$ as precursors. The starting sols of undoped and Cd doped SnO_2 with two different molar concentrations (6 and 10 at. % Cd) were prepared by a simple procedure. A mixture of $CdCl_2$-$5H_2O$ and

Corresponding Author: M. Khechba, Department of Physics, University Frères Mentouri Constantine, Thin Films and Interfaces Laboratory, Route Ain El Bey, Constantine 25000, Algeria

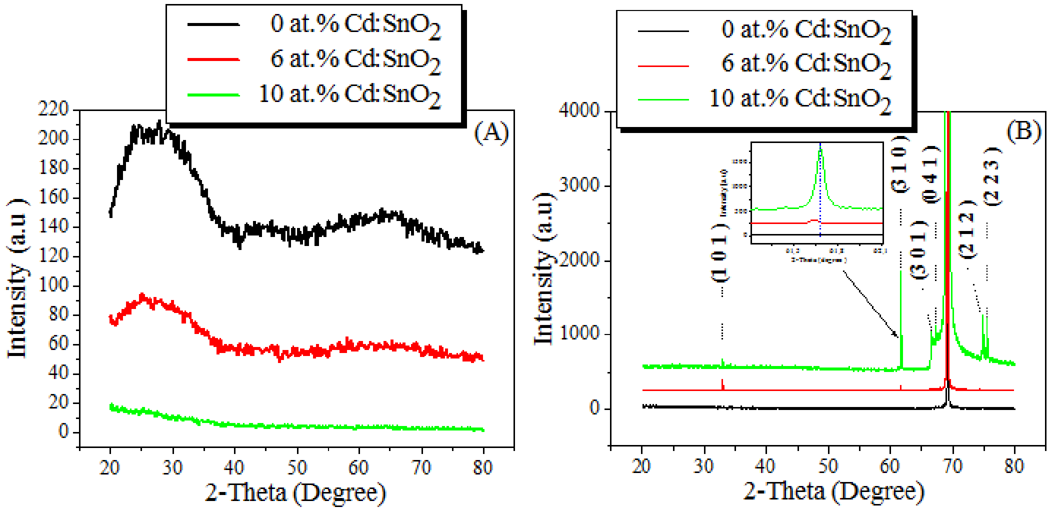

Fig. 1: Grazing incidence X-ray diffraction patterns of thin Cd: SnO_2 films deposited on glass (A) and Si (100) (B) substrates

$SnCl_2$-$2H_2O$ chemicals was dissolved in 20 ml of ethanol. After refluxing at 60°C during 2 hours under magnetic stirring, homogeneous mixtures of precursors were formed. Then, aging for two days at room temperature, the transparent sols were obtained. Subsequently, the sols were dip-coated on the glass and Si(100) cleaned substrates and then dried at 100°C for 15 min for the formation of the initial thin film. Different layers were obtained after repeating the operation several times. Finally, the samples were annealed in air at 550°C for 2 h.

The structural properties of the deposited films were studied by means of Grazing Incidence X-Ray Diffraction (GIXRD) using CuKα radiation (λ = 1.54056 Å) from Bruker-AXS.D8 diffractometer. The surface morphology was observed using a Pacific Nanotechnology atomic force microscope. The Spectroscopic Ellipsometry (SE) measurements were performed on a Horiba-Jobin-Yvon Ellipsometer UVISEL operating in the wavelength range 260-800 nm. The optical transmittance was recorded on a Shimadzu 3101 PC UV-visible spectrophotometer.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the undoped and Cd doped SnO_2 thin films deposited on glass and Si (100) substrates are shown in the Fig. 1A and 1B respectively.

As can be seen from the Fig. 1A, the X-ray diffraction spectra recorded in thin SnO_2 films deposited on a glass substrate do not contain any peaks, indicating that the films are amorphous. However, the X-ray analysis shows that SnO_2 films deposited on a monocrystalline silicon are polycrystalline with tetragonal structure (Fig. 1B). The most intense peak observed corresponds to the (310) line and weak additional (101), (301), (041), (212) and (223) lines are registered. It is easy to notice that the most important (310) line becomes more sharp and more intense with the increasing of Cd concentration from 6 to 10 at.%. It means that the high Cd doping leads to the formation of well-crystallized SnO_2 films. The peaks obtained experimentally are identified and compared with standard values of Joint Committee on the Powder Diffraction Spectra data (JCPDS No. 88-0287).

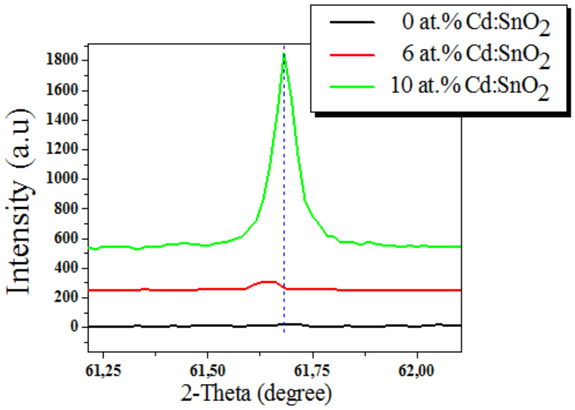

Fig. 2: X-ray diffraction (310) line of thin Cd:SnO_2 films deposited on Si

In Fig. 2, also the (310) peak position undergoes a shift which is due to mechanical strains created by the incorporation of a high Cd concentration in the SnO_2 lattice.

The optical transmittance spectra of pure and Cd doped SnO_2 thin films are recorded in the range 300–800 nm and plotted in the Fig. 3.

Figure 3 shows that the optical transmittance of all the studied samples is more than 80% in the spectral UV-Vis region and their absorption band is entirely in

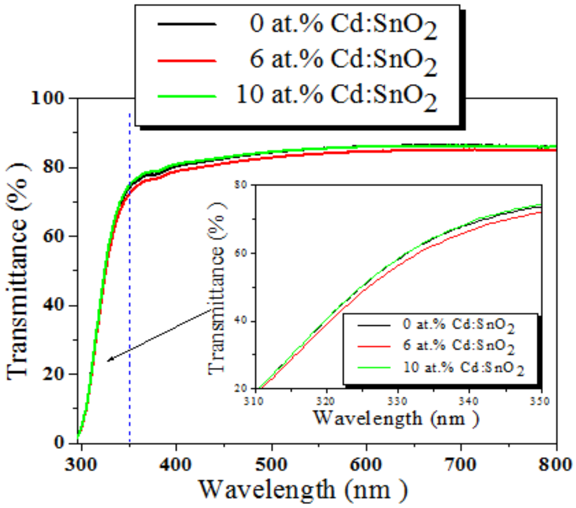

Fig. 3: Transmission spectra of undoped and Cd doped SnO_2 thin films deposited on glass

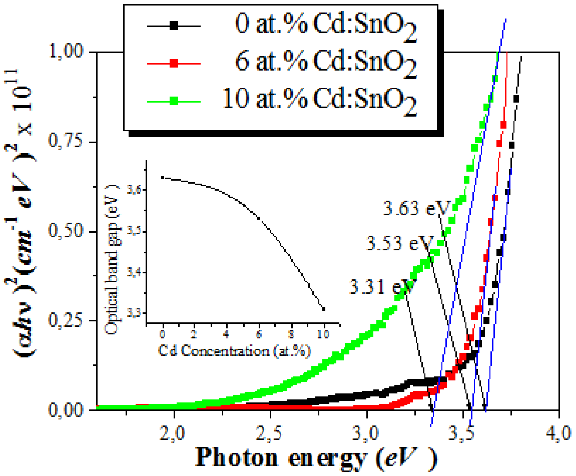

Fig. 4: Typical variation of $(\alpha h\nu)^2$ as a function of photon energy of undoped and Cd doped SnO_2 thin films deposited on glass

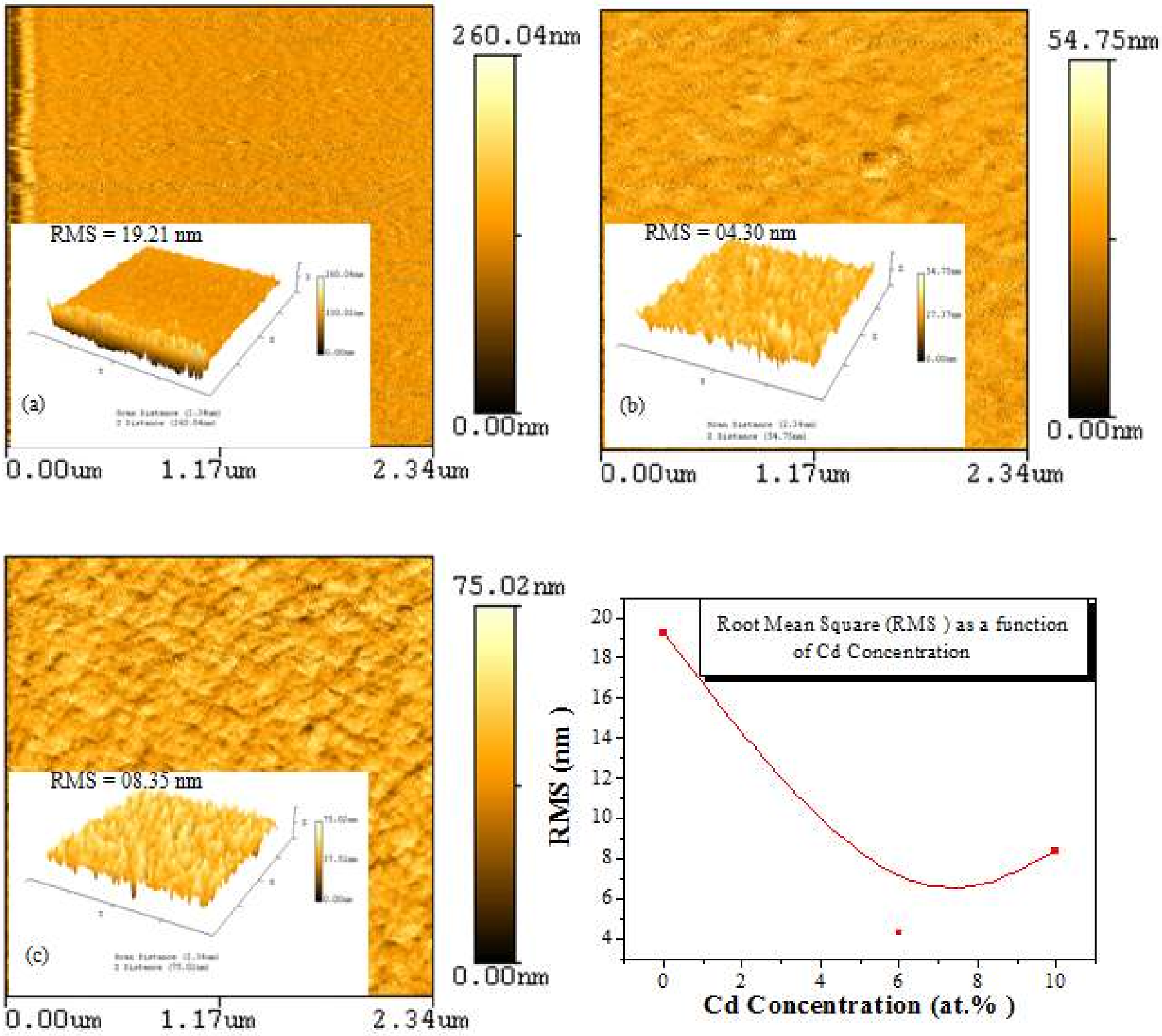

Fig. 5: AFM images of undoped and Cd doped SnO_2 thin films deposited on glass

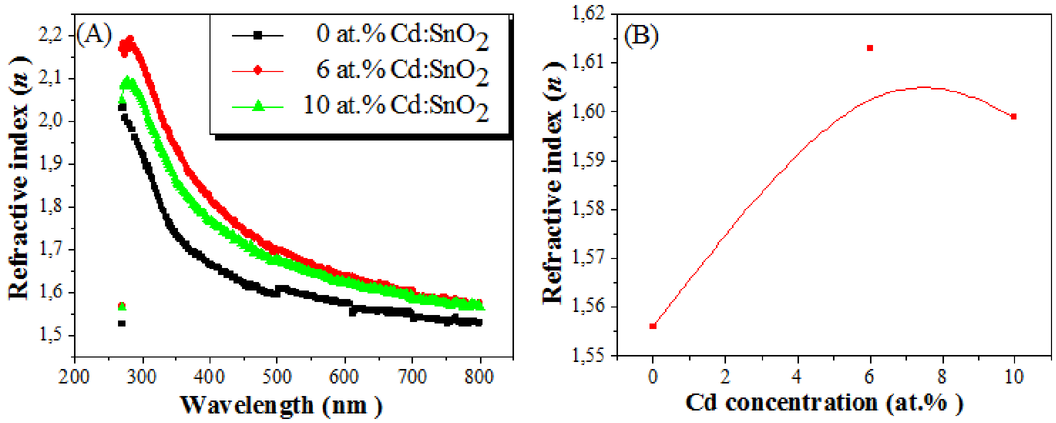

Fig. 6: (A) Dispersion of the refractive index for pure and Cd doped SnO_2 films, derived from SE measurements and (B) refractive index vs Cd concentration

the UV light region of 300-350 nm. The observed transmission values are compared with earlier reported values (Mariappan *et al*., 2013). A slight shift of the absorption edge toward higher wavelength region is found with increasing Cd concentration. The higher-energy electronic transitions from valence to conduction bands confirm the direct type semiconducting nature of the material (Pejova and Grozdanov, 2007). The E_g band gap of the deposited films is calculated by using the following Tauc formula (Tauc, 1974):

$$(\alpha hv) = A(hv - E_g)^m \qquad (1)$$

where,

v : The frequency
A : A constant
m : Assumes values 1/2, 2, 3/2 and 3 depending on the mode of interband transition, i.e., direct, allowed indirect, direct forbidden and indirect forbidden transition, respectively.

Typical plots of $(\alpha h\nu)^2$ versus $h\nu$ for pure and Cd doped SnO_2 films are shown in Fig. 4. The extrapolation of the linear portion of the $(\alpha h\nu)^2$ curves to the $h\nu$ energy axis gives the value of the energy gap for pure and Cd doped SnO_2 films. As can be seen, the optical band gap decreases from 3.60 eV for the undoped SnO_2 films to 3.31 eV for 10 at. % Cd doped SnO_2 films. The deduced 3.60 eV value is in agreement with the band gap energy of pure SnO_2 (Bhat *et al*., 2007). The reduction in the band gap energy may be due to the decrease of holes concentration with the increase of Cd doping (Mariappan *et al*., 2013).

Figure 5 shows AFM images of the undoped and Cd-doped SnO_2 thin films for different atomic Cd contents. By analyzing the AFM images, the roughness of the films is estimated through the root mean square (RMS) parameter. The Cd doping leads to a significant decrease in RMS values from 19.2 nm for SnO_2 to 4.3 nm for 6 at. % Cd:SnO_2. For the 10 at. % Cd:SnO_2 sample, the RMS is intermediate.

AFM images indicate the formation of polycrystalline thin films with uniform and smooth surface. Moreover, it is evident that lower surface roughness with more compact surface is achieved by addition of 6 Cd at.% doping. However, more compact surface significantly decreases the RMS factor of the films, which leads to TCO with higher transparency. It seems that the latter factor plays a key role in improving of properties of TCO films. As a result, the combination of more compact and homogenous surface with less RMS roughness provides new TCO with better properties compared to TCO films for devices applications.

The knowledge of optical constants of the thin films is very significant since they can determine the exact application of the films. Figure 6A shows the dispersion of the refractive index for pure and Cd doped SnO_2 thin films, derived from SE measurements.

It is clear from the Fig. 6A that the spectral behavior of refractive index for the pure and Cd doped films is almost similar and it is decreasing with wavelength. The refractive index is 1.559 for undoped SnO_2 films and this value increases to 1.600 and 1.613 for 10 at. % and 6at. % Cd doping respectively (Fig. 6B).

CONCLUSION

The cadmium doped tin oxide (Cd:SnO_2) thin films are deposited on glass and Si(100) substrates with different Cd concentrations. The XRD show an amorphous structure for the thin films deposited on glass substrate. However, the tetragonal crystalline structure with preferential orientation along (310) plane is revealed for the films elaborated on Si(100) substrate. The all obtained thin films are transparent with optical transmittance ~86%. From the optical studies it is observed that the band gap energy decreases from 3.60

eV to 3.31 eV with increase of Cd concentration. AFM images show that the surface roughness is reduced to lower values with addition of Cd. The measured refractive index reveals that the Cd:SnO_2 films grown by the sol-gel dip coating technique are suitable for interest applications such as optoelectronic devices.

REFERENCES

Bagheri-Mohagheghi, M.M. and M. Shokooh-Saremi, 2004. The influence of Al doping on the electrical, optical and structural properties of SnO_2 transparent conducting films deposited by the spray pyrolysis technique. J. Phys. D. Appl. Phys., 37(8): 1248-1253.

Bhat, J.S., K.I. Maddani, A.M. Karguppikar and S. Ganesh, 2007. Electron beam radiation effects on electrical and optical properties of pure and aluminum doped tin oxide films. Nucl. Instrum. Meth. Phys. Res. B., 258(2): 369-374.

Chen, Z.W., J.K.L. Lai, C.H. Shek and H. Chen, 2003. Synthesis and structural characterization of rutile SnO_2 nanocrystals. J. Mater. Res., 18(6): 1289-1292.

Chen, Z.W., J.K.L. Lai and C.H. Shek, 2004. Insights into microstructural evolution from nanocrystalline SnO_2 thin films prepared by pulsed laser deposition. Phys. Rev. B., 70: 165314.

Chen, Z.W., J.K.L. Lai, C.H. Shek and H.D. Chen, 2005. Nucleation and growth of SnO_2 nanocrystallites prepared by pulsed laser deposition. Appl. Phys. A., 81(5): 959-962.

Chen, Z.W., J.K.L. Lai and C.H. Shek, 2006. Mystery of porous SnO_2 thin film formation by pulsed delivery. Chem. Phys. Lett., 422(1-3): 1-5.

Cioffi, N., L. Traversa, N. Ditaranto, A.M. Taurino, M. Epifani, P. Siciliano, T. Bleve-Zacheo, L. Sabbatini, L. Torsi and P.G. Zambonin, 2006. Core-shell Pd nanoparticles embedded in SnO_X films. Synthesis, analytical characterisation and perspective application in chemiresistor-type sensing devices. Microelectr. J., 37(12): 1620-1628.

Durrani, S.M.A., E.E. Khawaja and M.F. Al-Kuhaili, 2005. CO-sensing properties of undoped and doped tin oxide thin films prepared by electron beam evaporation. Talanta, 65(5): 1162-1167.

Fang, T.H. and W.J. Chang, 2005. Nanomechanical characteristics of SnO_2:F thin films deposited by chemical vapor deposition. Appl. Surf. Sci., 252(5): 1863-1869.

Ginley, D.S. and C. Bright, 2000. Transparent conducting oxides. MRS. Bull., 25(8): 15-18.

Jin, C., T. Yamazaki, K. Ito, T. Kikuta and N. Nakatani, 2006. H_2S sensing property of porous SnO_2 sputtered films coated with various doping films. Vacuum, 80(7): 723-725.

Kim, T.Y., J.W. Lee, W.S. Park, S.K. Park, K.Y. Kim and I.B. Kang, 2010. Development of transparent conductive oxide for thin-film silicon solar cells. J. Korean Phys. Soc., 56(2): 571-575.

Kuo, C.G., C.Y. Chou, Y.C. Tung and J.H. Chen, 2012. Experimental study of the electrochromic properties of WO_3 thin films derived by electrochemical method. J. Mar. Sci. Technol., 20(4): 365-368.

Manjula, P., L. Satyanarayana, Y. Swarnalatha and S.V. Manorama, 2009. Raman and MASNMR studies to support the mechanism of low temperature hydrogen sensing by Pd doped mesoporous SnO_2. Sensor. Actuat. B-Chem., 138(1): 28-34.

Mariappan, R., V. Ponnuswamy, P. Suresh, R. Suresh, M. Ragavendar and C. Sankar, 2013. Deposition and characterization of pure and Cd doped SnO_2 thin films by the nebulizer spray pyrolysis (NSP) technique. Mat. Sci. Semicon. Proc., 16(3): 825-832.

McDowell, M.G., R.J. Sanderson and I.G. Hill, 2008. Combinatorial study of zinc tin oxide thin-film transistors. Appl. Phys. Lett., 92: 013502.

Minami, T., 2000. New n-type transparent conducting oxides. MRS. Bull., 25(8): 38-44.

Patil, L.A. and D.R. Patil, 2006. Heterocontact type CuO-modified SnO_2 sensor for the detection of a ppm level H_2S gas at room temperature. Sensor. Actuat. B-Chem., 120(1): 316-323.

Pavelko, R.G., A.A. Vasiliev, E. Llobet, X. Vilanova, N. Barrabés, F. Medina and V.G. Sevastyanov, 2009. Comparative study of nanocrystalline SnO_2 materials for gas sensor application: Thermal stability and catalytic activity. Sensor. Actuat. B-Chem., 137(2): 637-643.

Pejova, B. and I. Grozdanov, 2007. Chemical synthesis, structural and optical properties of quantum sized semiconducting tin(II) selenide in thin film form. Thin Solid Films, 515(13): 5203-5211.

Ramamoorthy, K., C. Sanjeeviraja, M. Jayachandran, K. Sankaranarayanan, P. Misra and L.M. Kukreja, 2006. Development of a novel high optical quality ZnO thin films by PLD for III–V opto-electronic devices. Cur. Appl. Phys., 6(1): 103-108.

Samotaev, N.N., A.A. Vasiliev, B.I. Podlepetsky, A.V. Sokolov and A.V. Pisliakov, 2007. The mechanism of the formation of selective response of semiconductor gas sensor in mixture of $CH_4/H_2/CO$ with air. Sensor. Actuat. B-Chem., 127(1): 242-247.

Shen, Y., T. Yamazaki, Z. Liu, D. Meng, T. Kikuta, N. Nakatani, M. Saito and M. Mori, 2009. Microstructure and H_2 gas sensing properties of undoped and Pd-doped SnO_2 nanowires. Sensor. Actuat. B-Chem., 135(2): 524-529.

Shimizu, Y., E. Kanazawa, Y. Takao and M. Egashira, 1998. Modification of H_2-sensitive breakdown voltages of SnO_2 varistors with noble metals. Sensor. Actuat. B-Chem., 52(1-2): 38-44.

Shukla, S., P. Zhang, H.J. Cho, S. Seal and L. Ludwig, 2007. Room temperature hydrogen response kinetics of nano-micro-integrated doped tin oxide sensor. Sensor. Actuat. B-Chem., 120(2): 573-583.

Shuping, G., X. Jing, L. Jianqiao and Z. Dongxiang, 2008. Highly sensitive SnO_2 thin film with low operating temperature prepared by sol-gel technique. Sensor. Actuat. B-Chem., 134: 57-61.

Tauc, J., 1974. Amorphous and liquid semiconductors. Plenum Press, London.

Thangaraju, B., 2002. Structural and electrical studies on highly conducting spray deposited fluorine and antimony doped SnO_2 thin films from $SnCl_2$ precursor. Thin Solid Films, 402(1-2): 71-78.

Vasiliev, R.B., M.N. Rumyantseva, N.V. Yakovlev and A.M. Gaskov, 1998. CuO-SnO_2 element for highly sensitive and selective detection of H_2S. Sensor. Actuat. B-Chem., 50: 186-193.

Yamazoe, N., J. Tamaki and N. Miura, 1996. Role of hetero-junctions in oxide semiconductor gas sensors. Mater. Sci. Eng. B-Adv., 41(1): 178-181.

Young, D.L., H. Moutinho, Y. Yan and T.J. Coutts, 2003. Growth and characterization of radio frequency magnetron sputter-deposited zinc stannate, Zn_2 SnO_4, thin films. J. Appl. Phys., 92(1): 310-319.