Industrial Engineering Journal
ISSN: 0970-2555
Volume : 49, Issue 6, June : 2020

Effect of nickel doping on the structural optical and magnetic properties of SNO2thin film for solar cell and electronics applications

[1]Sandhya Boosani, [2]Dr.Anuradha Gupta, [3]Dr Arunbalaji
[1,2]Assistant Professor, [3]Professor, [1,2,3] Department of Physics, Rishi MS Institute of Engineering and Technlogy for Women, Kukatpally, Hyderabad.

Abstract:
To improve the characteristics of SnO2 thin films for incorporation into solar cells and in spintronics applications, a comprehensive investigation on the fabrication of pure and Nickel (Ni) doped Tin oxide (SnO2) thin films with various doping concentrations has been carried out. By using X-ray diffraction (XRD), scanning electron microscopy (SEM), ultraviolet-visible spectrophotometers, and vibrating sample magnetometers, researchers examined the effects of Ni doping at various concentrations on the structural, optical, and magnetic properties of the various synthesized samples of SnO2 thin films (VSM). SnO2 displayed tetragonal structure in all of the Ni-doped samples. The crystal is defective due to the fusing of Ni into the SnO2 lattice, and the existence of additional peaks demonstrates that the nickel domination is clearly visible. Reduction in the optical band gap was observed with increase of Ni doping levels. The vibrating sample magnetometer measurements revealed that the ferromagnetic signal is progressively enhanced with increase in doping concentration.

Key Words: SnO_2 Thin Films, Spray Pyrolysis, Ferromagnetism, Nickel, Doping, Solar Cell, Spintronics.

1. Introduction

One of the largest difficulties facing humanity is ensuring a long-term energy source for a sustainable global environment. Fossil fuels and our present energy supply are the key things on which we rely. The use of fossil fuels causes environmental damage through air pollution and global warming. To develop solutions for an energy system that is really sustainable, much research is being done. The research focuses on improving technologies and infrastructure for a smooth transition to renewable energy sources, such as nuclear power, solar power, wind power, geothermal power, biomass and bio fuels, and hydropower, as well as increasing production efficiency, transmission, and utilization of the remaining fossil fuels, positive environmental impacts,[1,2]. From the beginning of the invention of nano structured dye-sensitized solar cell (DSSC), many experiments have been done to improve the performance of the solar cell by utilizing solar energy. Small amount of materials and low-cost manufacturing technologies are used in thin film solar cells. The transparent electrode, which is commonly made of transparent conductive oxides (TCO)is the critical part of the thin film solar cell and there has been current significance on developing new semiconductors for flexible thin-film solar cells[3].Tin oxide (SnO_2) is one among the most intriguing materials to be investigated today as it is a well-known n-type semiconductor having a wide band gap of 3.6-3.8eV [4,5] and due to its potential application in transparent conductive electrode for solar cells, a gas sensing material for gas sensors devices, transparent conducting electrodes, photochemical and photoconductive devices in liquid crystal display, gas discharge display, lithium-ion batteries, etc., [6-9]. Solar cells based on Tin demonstrates optical properties which are superior and good efficiency solar cell materials are exhibited by its alloys[10] having high optical transparency in the visible region and high electrical conductivity which are considered to be the most essential features for solar cells applications, gas sensors, and liquid crystal displays[11]. In addition to theseproperties SnO_2

http://doi.org/10.36893/IEJ.2020.V49I6.028-035

exhibits ferromagnetism and finds applications in novel magnetic optoelectronic devices. Doping of SnO_2 with metal ions has been used to alter the properties of the base material which results in an improvement of the device performance [12].The specific area of SnO_2 has been increased due to the addition of dopants such as Pt., Pd., Co, Fe and Ni. Of these dopants, nickel has been widely employed to enhance the performance of tin oxide [13]. Due to their close ionic radii: Ni2+ =69 nm and Sn2+ = 71 nm nickel ions can be easily doped into the tin sites. Depending on the doping level there occurs decrease in electron density and increase in oxygen vacancies [14, 15]. SnO_2: Ni the transparent conducting oxide semiconductor is a direct band gap energy material with nontoxic constituent materials and having abundance in nature. As not much work has been reported on Ni doped SnO_2 semiconductors as per the authors knowledge, an attempt has been made to synthesis Ni doped SnO_2 thin films and to study the influence of Nickel doping on structural, optical and magnetic properties.

2. Experimental methods

Synthesis of Ni doped SnO_2 thin films

Deposition of undoped and Ni-doped (SnO_2) films on glass substrates at calcined temperature of (500ºC) was made by self-assembled spray pyrolysis technique A homogeneous solution was prepared by dissolving ($SnCl_{4.5}H_2O$) and ($NiCl_{2.5}H_2O$) powders in distilled water at the concentration of 0.1 M at room temperature in which the volumetric ratios of Ni were (0, 1, 2, 3 and 4) %. The resultant solution was sprayed on glass substrate. Substrates made of glass and having dimensions 2.5 x 7.5cm^2 (Microscopic glass slides Lab tech medico (P) Ltd, Mumbai) was used for deposition of SnO_2:Ni thin films. To remove moistures and other organic substance present on the substrate surface, Substrates were washed with distilled water and HCl for several times .Other deposition conditions such as syringe needle substrate distance (8cm), spray time (5s), spray interval (10s), Film thickness (500nm) are employed.

Characterization Techniques

Scanning electron microscope (HITACHI S-4500H) was employed to obtain SEM images. The structural properties of the prepared SnO_2 thin films were examined by X-ray diffractometer (SHIMADZU-XRD 6000 diffractometer system with X-ray (Cu–Ka) of wavelength 1.5406Å). Unico 4802.UV–Vis double beam spectrophotometer in the wavelength range of 300nm–1100nm was used to measure the optical absorption and transparency of the films. FTIR spectra were recorded by means of SHIMADZU1800-UV Fourier transform infrared spectrometer. Magnetic study was made using a Vibrating Sample Magnetometer (VSM 7410).

3. Result and Discussion

Structural Properties

X-ray diffraction patterns were recorded for Pure and Ni doped SnO_2 thin films using Cu Kα radiation of wavelength 1.54 Å. Fig. 1 shows the diffraction peaks obtained for the SnO_2 and Ni doped SnO_2 thin films. The highest diffraction peaks are (110), (101), (200), (211), (220) and (301).The coincidence of diffracted peaks with tetragonal structure of SnO_2 (JCPDS card number: 41-1445) is observed for all the recorded peaks of Ni doped SnO_2 thin films.Ni doping causes no change in the tetragonal structure of SnO_2. No change in the position of the peak has been observed in XRD spectra which indicates that there is no considerable change in the structure. It is confirmed that nickel was doped into the host SnO_2 lattice as no other peaks related to nickel and nickel oxides were identified. The fusion of Nickel into the SnO_2 lattice makes imperfection in the crystal for 4at% of the dopant concentration and the presence of additional peak confirms that the nickel domination is well observed which is evident from the SEM image and the diffraction pattern. Though the doping level of Ni was increased from 1at% to 3 at% Nickel oxide phases were not dominated in Ni doped SnO_2 thin films. The intensity of the peak corresponding to the predominant plane (110) in the primary phase is increased on Ni doping until 3 at % of doping concentration and further addition of 1

Industrial Engineering Journal
ISSN: 0970-2555
Volume : 49, Issue 6, June : 2020

at% doping concentration the intensity decreases due to the replacement of $Sn4^{+}$ ions with Ni ions in the lattice of SnO_2 film, whereas the intensity of the plane (211) in the secondary phase rapidly increases. Which shows better atomic arrangement and lower scattering in these planes. The crystallite size of pure SnO_2 and Ni doped SnO_2 thin films for all the dopant levels was calculated using Debye-Scherrer formula [16]

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

Where k is a constant, λ is the diffraction wavelength of CuKα (λ = 1.5406 Å).β is the full width at half maximum (FWHM), and θ is the diffracted angle, respectively and it is found to be 45nm, 40nm, 35nm, 30nm and 30.5nm.

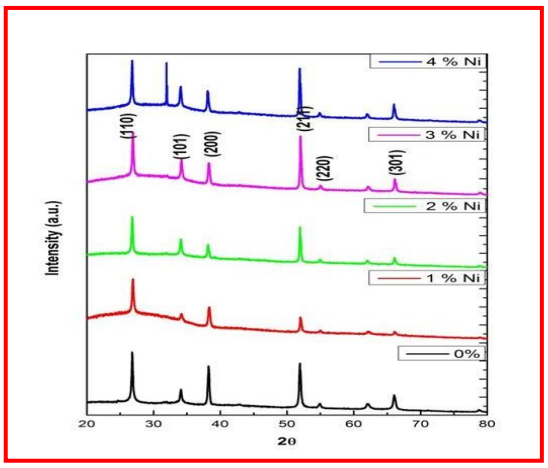


Fig.1. X-ray diffraction spectra of pure SnO_2 and Ni- doped SnO_2 thin films.

Morphological Analysis

Fig.2. shows the variation in the surface morphology of SnO_2: Ni thin films deposited at a calcined temperature of 500^0C with different Nickel content concentration. It can be seen in Fig.2.that there is a significant change in the morphology of the films. The presence of uniform sized grains are seen in the undoped film. The evolution in the structure of the films as a function of the dopant concentration is evident from the SEM images. The presence of the dopant Nickel and the quantity that goes into each sample influences the change in microstructure.1at% of Nickel doping influences the change in the morphology of SnO_2 film. In the recorded image of 2 at% of Ni doped SnO_2 thin films grain size decreases and there occurs agglomeration at certain places due to attractive forces between Ni doped SnO_2 Nanoparticles. Thin film of good surface morphology with a smooth surface having smaller grain size is observed for 3 at % of Ni doped SnO_2 thin films. Above 3 at % of doping concentration, lot of large irregular grains with different shapes have been identified as Nickel domination is more effective which is also evident from the XRD pattern.

http://doi.org/10.36893/IEJ.2020.V49I6.028-035

Industrial Engineering Journal
ISSN: 0970-2555
Volume : 49, Issue 6, June : 2020

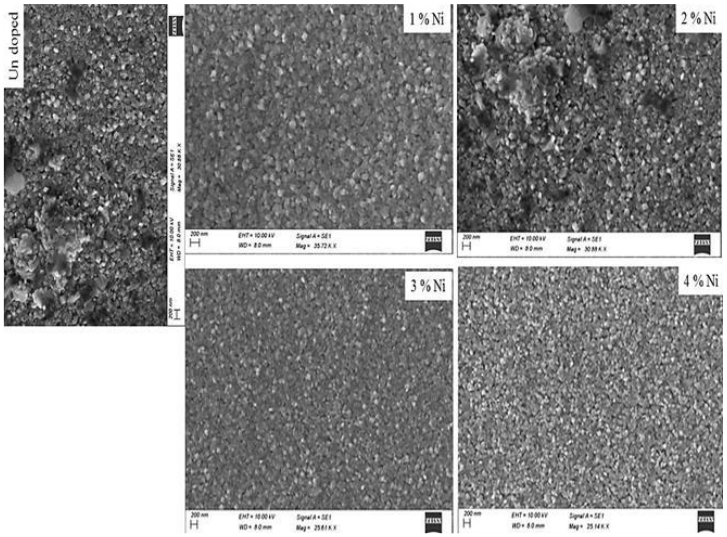


Fig.2. SEM images of pure and Ni doped SnO_2 thin films.

Optical properties

Optical transmittance spectra of undoped and Nickel doped tin oxide thin films are shown in fig. 3. It can be seen that transparency in the visible region (400–700 nm) is about ~30–90%. Minimum Transmittance is observed for undoped SnO_2 thin films. Due to homogenous and smooth surface as evident from the SEM image, maximum transmittance is observed for 3 at% Ni doped SnO_2 thin film indicating a good quality thin film for disposing it to be used as an electrode material in solar cell. According to Beenaet. al., [17] the decrease of transmittance arises due to many factors like increase in thickness, existence of oxygen vacancies and defects, roughness of the surface, permeable nature of the films, scattering in grain boundary etc. but in the present case the decrease of transmittance may be due to the irregular grains.

The absorbance spectra of pure SnO_2 and Ni doped SnO_2 thin films at different concentrations are depicted in fig.4. The recorded spectra shows an ultraviolet cut-off around 300nm–400nm which may be due to the photo-excitation of electrons from valence band to conduction band. High absorption value is observed in the UV region and it becomes low at visible region. The observed absorbance is almost constant over the higher wavelength region. The band gap is an important property which determines the quality of the deposited thin films. Fig.5 displays $(\alpha h\upsilon)^2$vs$h\nu$ usingTauc's plot for determining the band gap energy . The band gap values ranges from 3.46 to 3.65eV. Kuppanet. al.,[18] reported the energy band gap of Nickel doped Tin oxide lies between 3.70eV and 3.76eV and this is contrary to our present findings. In our previous results the band gap energy of pure SnO_2 deposited at a calcined temperature of 500^0C was found to be 3.5eV [19] which is in close agreement with the value obtained by Pan et al [20] is found to be 3.42eV and it is contrary to our present findings (3.65eV) for undoped polycrystalline SnO_2 thin films. Doping concentrations of Nickel Causes shrinking in band gap energies due to Moss-Burstein effect. In the present case good quality film was obtained in 3at% of Nickel doping concentration with the band gap energy of 3.43eV.

http://doi.org/10.36893/IEJ.2020.V49I6.028-035

Industrial Engineering Journal
ISSN: 0970-2555
Volume : 49, Issue 6, June : 2020

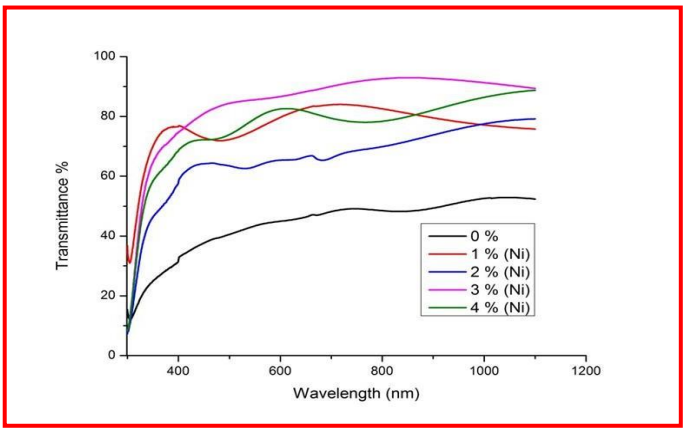


Fig.3. Transmittance spectra of pure $SnO_2$and Ni- doped SnO_2 thin films.

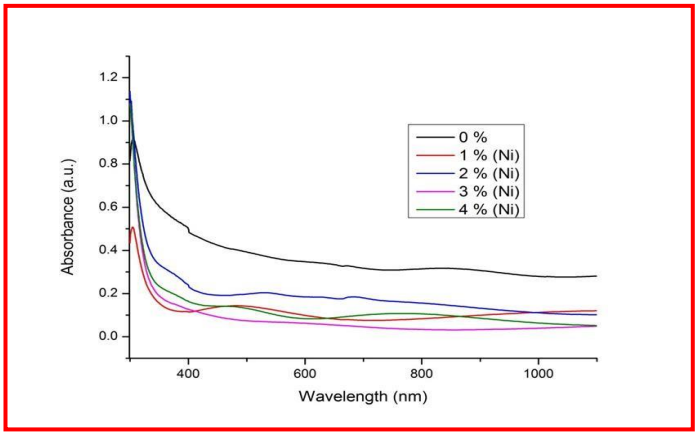


Fig.4. Absorption spectra of pure SnO_2 and Ni- doped SnO_2 thin films.

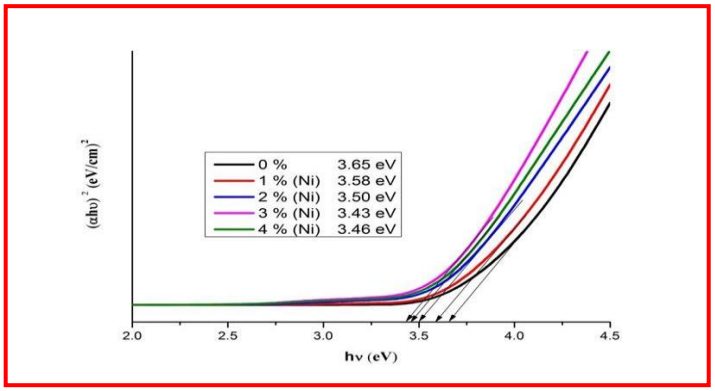


Fig.5. Tauc's plot for pure SnO_2 and Ni doped SnO_2 thin films.

FTIR analysis

Fig.6. shows the FTIR spectra in the range 500cm^{-1} to 4000cm^{-1} of pure SnO_2 and Ni doped SnO_2 deposited by self-assembled spray pyrolysis technique. Usually the range between 300cm^{-1} and 800cm^{-1} have been detected as Sn-O stretching vibration [21]. The peak appearing around 490cm^{-1} seems to be O–Sn–O and Ni bond vibration. The band located at 1620cm^{-1} is due to H-O-H vibrating mode of the absorbed water. Peaks observed at 1050cm^{-1}, and 1320cm^{-1} may be assigned to stretching vibrations of C-O and C-H bond. The band 1900 cm^{-1} is attributed to Sn-OH vibrational mode.

http://doi.org/10.36893/IEJ.2020.V49I6.028-035

Industrial Engineering Journal
ISSN: 0970-2555
Volume : 49, Issue 6, June : 2020

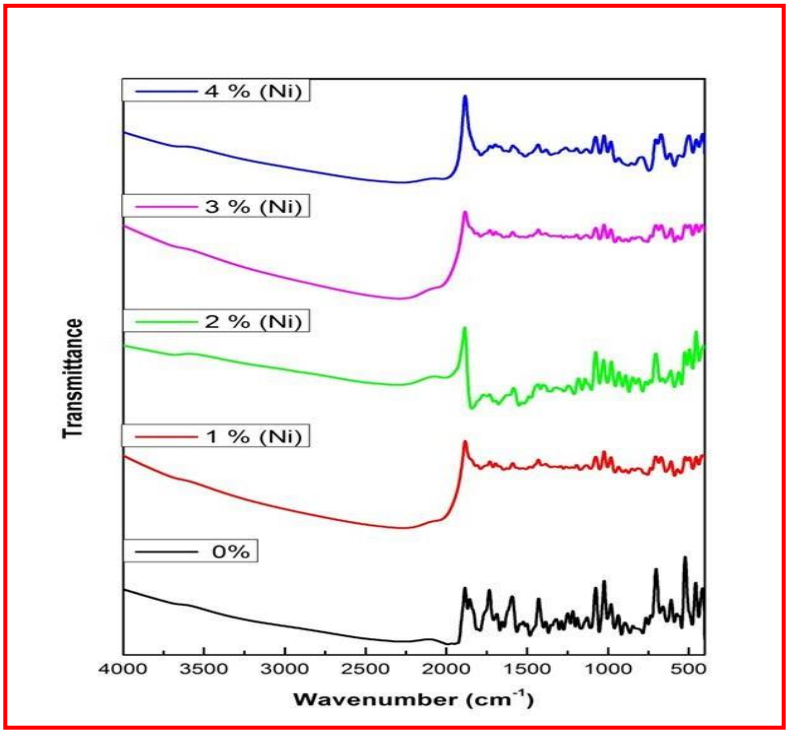
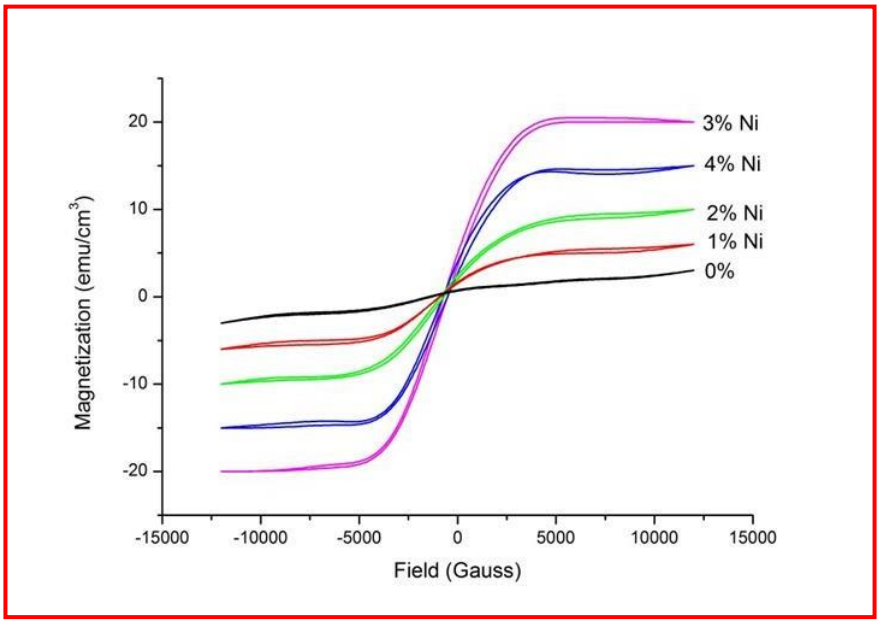


Fig.6. FTIR spectra of pure SnO_2 and Ni- doped SnO_2 thin films.

Magnetic properties

Fig.7. shows the curves of magnetization versus magnetic field of the pure and Nickel doped SnO_2 samples. The nanoparticles of SnO_2 are diamagnetic in nature and this was confirmed by several groups [22]. While Hays et al. found that nanoparticles of SnO_2 are non-ferromagnetic [23]. In the present case pure SnO_2 exhibits diamagnetic property. Doping of Ni results in the change of magnetization as the property transforms from diamagnetic to ferromagnetic state due to substitution of Ni ion with SnO_2 matrix. The ferromagnetic signal is progressively enhanced upto 3at % of dopant. The saturation magnetization (M_s), coercivity (H_{ci}) and retentivity (M_r) were summarized in the table.1.From the table it is observed that for 3at % dopant level the saturation magnetic moment was high. This may be due to the replacement of Ni^{2+} with Sn^{4+} leading to the increase of oxygen vacancies available for electron trapping and hence saturation magnetic moment increases. Low retentivity (M_r) and coercivity (H_{ci}) for 3at% concentration implies that resistance of the ferromagnetic material to become demagnetized is low.



http://doi.org/10.36893/IEJ.2020.V49I6.028-035

Fig.7. Magnetic property study (M-H curve) at Room temperature for pure and Ni doped SnO_2 samples.

Table.1.Summary of doping concentration, Saturation Magnetisation, Coercivity, Retentivity of SnO_2thinfilms.

Doping Concentration	M_s (emu /cm^3)	H_{ci} G	$M_r$emu/ cm^3
0	2.34	188.35	1.09
1at%	3.08	165.22	1.89
2at%	8.62	276.92	2.69
3at%	20.03	96.71	2.16
4at%	15.24	146.37	4.76

4. Conclusion

Using the self-assembled spray pyrolysis process, Ni doped SnO2 thin films with doping concentrations of 1at%, 2at%, 3at%, and 4at% were effectively produced. The grain size was found to be dependent on the dopant concentration based on the surface morphology of the films. Numerous outstanding characteristics were found in our findings, including crystallinity, high transmittance (90%), a band gap value of 3.43 eV, increased ferromagnetic behaviour, low retentivity (Mr), and low coercivity (Hci). Therefore, a possible contender for solar cells and spintronics applications is nickel doped at a 3 at% concentration in thin SnO2 films.

References

[1] H. Ramsurn and R. B. Gupta. Nanotechnology in Solar and Biofuels. ACS Sustainable Chem. Eng 2013,1, P.779−797.

[2] A. Purwanto, H. Widiyandari, and A. Jumari. Fabrication of high-performance fluorine doped–tin oxide film using flame-assisted spray deposition. Thin Solid Films,2012,520, P.2092-2095.

[3] Supriyonoa ,HediSurahmana , YuniKrisyuningsihKrisnandia , and JarnuziGunlazuardia Preparation and characterization of transparent conductive SnO2-F thin film deposited by spray pyrolysis: relationship between loading level and some physical properties, Procedia Environmental Sciences, 2015 28, P. 242 – 251.

[4] Ganesh E Patil, D DKajale, D N Chavan, N K Pawar, P T Ahire, S D Shinde, V B Gaikwad and G H Jain "Synthesis, characterization and gas sensing performance of SnO2 thin films prepared by spray pyrolysis", Bull. Mater. Sci., 2011, Vol. 34, No. 1, P. 1–9.

[5] L. C. Nehru, V. Swaminathan, C. Sanjeeviraja, "Photoluminescence Studies on Nanocrystalline Tin Oxide Powder for Optoelectronic Devices" , American Journal of Materials Science, 2012,Vol.2,No.2,P.6- 10.

[6] A. Kay, M. Gratzel, "Dye-Sensitized Core−Shell Nanocrystals: Improved Efficiency of Mesoporous Tin Oxide Electrodes Coated with a Thin Layer of anInsulating Oxide", Chem. Mater., 2002, Vol.14, No.7,P.2930-2953.

[7] SipraChoudhury, C. A. Betty, K. G. Girija, and S. K. Kulshreshtha "Room temperature gassensitivity of ultrathin SnO2 films prepared from Langmuir-Blodgett film precursors"Appl. Phys. Lett.vol. 89,No.7, 071914, 2006.

[8] R. Triantafyllopoulou a, X. Illa b, O. Casals b, S. Chatzandroulis a, C. Tsamisa,A. Romano- Rodriguez b, J.R. Morante "Nanostructured oxides on porous silicon microhotplates for NH3 sensing" , Microelectronic Engineering, 2008,Vol. 85 ,P.1116-1119.

[9] Huiyong Liu, V. Avrutin, N. Izyumskaya, Ü. Özgür, H. Morkoç "Transparent conducting oxides for electrode applications in light emitting and absorbing devices", Superlattices and Microstructures, 2010, Vol. 48,No. 5,P.458-484.

http://doi.org/10.36893/IEJ.2020.V49I6.028-035

[10]Toshiyuki, Y., Jiro, M. and Akira, Y. Thin films of CuInSe2 prepared by RF sputtering from various compositional powder targets: Solar Energy materials and solar cells, 1991, 27, P.25-35.
[11]S. H. Mohamed, "SnO2 dendrites-nanowires for optoelectronic and gas sensing applications," Journal of Alloys and Compounds, 2011,Vol. 510, no. 1, P.119–124.
[12]GetnetKachaDeyu , David Muñoz-Rojas , LaetitiaRapenne , Jean-Luc Deschanvres , Andreas Klein , Carmen Jiménez and Daniel Bellet. SnO_2 Films Deposited by Ultrasonic Spray Pyrolysis: Influence of Al Incorporation on the Properties, Molecules 2019, 24, 2797, doi:10.3390/molecules24152797.
[13]S. Singkammo, A. Wisitsoraat, C. Sriprachuabwong, A. Tuantranont, S. Phanichphant and C. Liewhiran, ACS Appl. Mater. Interfaces, 2015, 7, P.3077–3092.
[14]Q. Zhou, W. Chen, L. Xu, R. Kumar, Y. Gui, Z. Zhao, C. Tang and S. Zhu, Ceram. Int., 2018, 44, P.4392–4399.
[15]W. T. Li, X. D. Zhang and X. Guo, Sens. Actuators, B, 2017, 244, P.509–521.
[16]H. Klug, L. Alexander, X-Ray Diffraction Procedures: For Polycrystalline and Amorphous Materials, (New York, USA: John Wiley and Sons: 1974).
[17] Beena, D.; Lethy, K.J.; Vinodkumar,] R.; Pillai, V.P.Mahadevan; Ganeshan, V.; Phase, D.M.; Sudheer, S.K. Appl. Surf. Sci. 2009, 255, P. 8334.
[18] Kuppan, M., Kaleemulla, S., Madhusudhana, R. N., Sai Krishna N., Rigana, B. M., andShobana,M.(2014). Structural and Magnetic Properties of Ni Doped SnO2. Research Article.