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PURE AND Ni DOPED TIN OXIDE NANOPARTICLES PREPARED BY CO-PRECIPITATION METHODS

T.AMUTHA[1], S.SAHAYA SEETHA[2], M.VIDHYA[2] and K.PRABHA3[*]
[1,3]Department of Physics, Mother Teresa Women's University, Kodaikanal, Tamilnadu, India.
[2]Department of Physics, Fathima College (Autonomous), Madurai, Tamilnadu, India.
***Corresponding author :** Dr.K.Prabha, Department of Physics, Mother Teresa Women's University, Kodaikanal. 624101,India, Mob : 09486866383; E.mail: mtwprabha@gmail.com*

ABSTRACT: Pure and Ni–doped Tin Oxide (SnO_2) nanoparticles were synthesized by simple co-precipitation method. The structural, morphological and optical properties of these nanoparticles were investigated by using X-ray diffraction, UV-Vis spectroscopy, FTIR and Photo Luminescence Studies. The X-ray diffraction revealed that all samples are pure tetragonal rutile- structure with crystalline space ($P4_2$/mnm) and the nickel doping did not change the tetragonal structure of tin oxide. The optical band energies of pure and Ni doped SnO_2 nanoparticle were evaluated from UV-Vis-NIR studied and found to be ~2.16 eV and ~1.75 eV respectively.

Key Words: Tin Oxide, X-ray Diffraction, UV-Absorption, FTIR, PL Studies

1. INTRODUCTION

Among the various important categories of the functional materials like, polymers, magnetic, dielectric and semiconductors, the ferromagnetic semiconductors are emerged as attracting materials and driven a considerable attention in the recent years[1-2]. Tin oxide (SnO2) is one of the most intriguing materials to be investigated today, This is because tin dioxide is a well-known n-type semiconductor with a wide band gap of 3.6-3.8 eV [3-5], and for 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.,[6-12].Co-precipitation[13] is a suitable chemical method in a nanoparticles synthesis because it does not require high pressure and temperature and impure materials are eliminated by filtration and washing. In present study tin oxide nanoparticles were synthesized by co-precipitation method and ultrasonic waves irradiation was used to homogenize nanoparticles.

2. EXPERIMENTAL PROCEDURE

For preparation of Ni doped SnO_2, the appropriate amounts (1M of Ni (Ni(NO_3)2.9H_2O and 99M of Tin ($SnCl_2$.2H_2O) of two precursors of Tin chloride (Tin ($SnCl_2$.2H_2O) and Nickel nitrate (Ni (Ni(NO_3)2.9H_2O) were dissolved in de-ionized water, stirred for 2 hours hot using plate with a magnetic stirrer. Then, Ammonium Hydroxide (NH_4OH) was added into the solution (drop by drop), with stirring, until the white precipitates were obtained. After 30 minutes of stirring the resultant mixtures were rinsed, several times, with de-ionized water to remove chlorine and other ionic impurities, which may formed during the synthesis process. Then, washed precipitates were dried in air at 40^0C for 20 hours followed by natural cooling up to the room temperature and then final powder products were collected carefully. These precursors were ground in an agate mortar pestle for 30 minutes to obtain fine powder. These powders placed in a Al_2O_3 crucible for sintering in furnace at 450 °C for 5 hrs followed by furnace cooling at room temperature. To get the annealed powdered sample of Nickel doped SnO2.

3. RESULTS AND DISCUSSION

Fig.1(a) shows the XRD patterns of pure and nickel doped tin oxide nanoparticles synthesized by co-precipitation method.

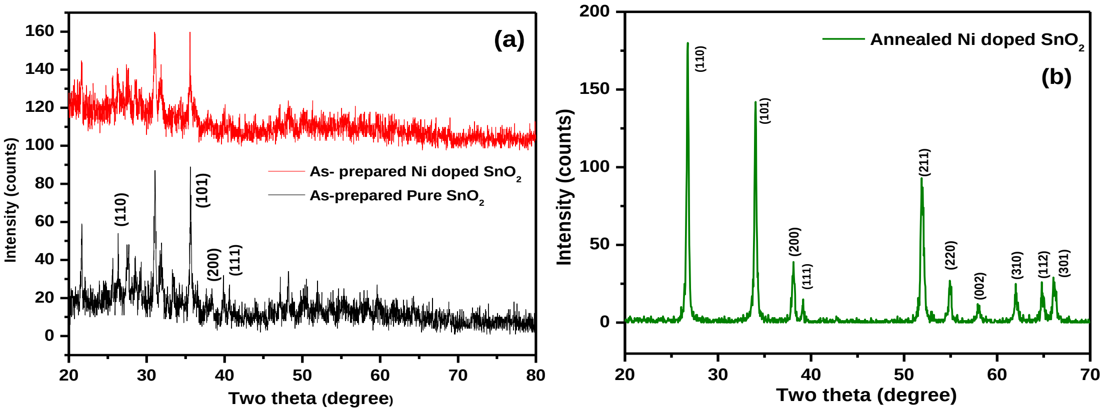

Fig.1 Shows the XRD patterns of (a) as-prepared pure SnO_2 and Ni doped SnO_2, (b) shows the Ni doped SnO_2 annealed for 400^0C for 2h sample

Fig.1(b) shows the XRD spectrum of Ni doped SnO_2 nanoparticles annealed at 400°C for 2 hr which showing well defined characteristics peaks. The observed values of 2θ and d-spacing's are in good agreement with the standard values of the JCPDS file no. 21-1250. The diffraction angle 2θ with corresponding diffraction planes (h k l) was observed at 26.81° (1 1 0), 34.04° (1 0 1), 38.07° (2 0 0), 39.13° (1 1 1), 51.93° (2 1 1), 54.90° (2 2 0), 57.98° (0 0 2), 62.01° (3 1 0), 64.82° (1 1 2) and 66.18° (3 0 1) correspond to tetragonal SnO_2 rutile structure with crystalline space group (P4 $_2$/mnm). Ni doped SnO_2 samples structure also a comparable similar pattern of pure-SnO_2 was observed except that the diffraction peak shifts slightly to the lower angle. Ni doping does not affect the original tetragonal unit cell of SnO_2. The diffraction planes are broadened. The peak position also shifts towards lower angle indicating the expansion of lattice. The crystalline size of the Ni doped SnO_2 samples were calculated by the Debye-Scherrer's equation which is given by d = kλ/β cos□, where 'k' is the shape factor, '□' is the wavelength of x-rays used, β is the full width half maximum of the peak and □ is the glancing angle. The annealed sample of Ni doped SnO2 determined the Crystalline size is about 23 nm of lattice constant a=4.738 and c=3.188 (Tetragonal).

PHOTOLUMINESENCE SPECTROSCOPY (PL) STUDIES

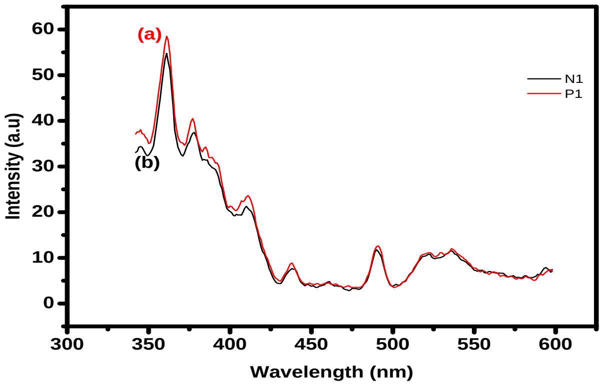

Figure 2. shows PL spectrum of (a) as-prepared pure SnO_2 sample, and (b) as-prepared Ni doped SnO_2 sample

The PL spectra of pure and Ni doped SnO_2 nanas emission bands at 361nm, 377nm, 412 nm, 438.71 nm, 491.73 nm, 521nm, and 537 nm excited at a wave length of 439 nm at room temperature are shown in Fig.(a). Figure (b) shows the photoluminescence spectra of samples with Ni doped SnO_2 annealed at 400 °C for 2 hour. The PL emission is directly related to the recombination of excited electrons and holes, so the higher PL intensity indicates a faster in recombination rate which in turn increase in the conductivity of the material.

UV-VISIBLE SPECTROSCOPY STUDIES: Ni doped SnO_2

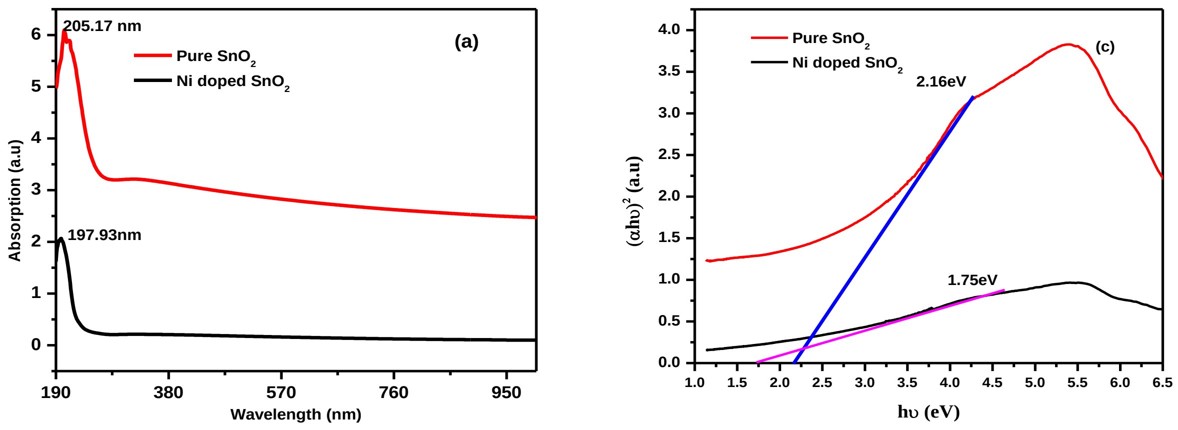

Figure 3. shows the (a) absorption spectrum of annealed Pure and Ni doped SnO_2 (b) energy band gap of annealed Pure and Ni doped SnO_2

Absorption spectra shows an ultraviolet cut-off around 190–250 nm Fig. 3(a) which can be attributed to the photo-excitation of electrons from valence band to conduction band. Generally, high absorption value is observed in the UV region and it becomes low at visible region. Optical transmittance spectra of pure SnO_2 and Ni-doped SnO_2 nanoparticles at annealed samples from 200 to 1000 nm are shown in Fig. 3(b). It is observed that the values of transmittance are high in the visible region and minimum at wavelength ~200 nm. The inset of the figure shows 3(c) the Tauc's plot for determining the band gap energy of nanoparticles. The estimated band gap energy of un - doped SnO_2 is ~2.16 eV, while, the band gap energy of the Ni doped compound found to almost same and is ~1.75 eV. The observed band gap energy of un - doped SnO_2 nanoparticles is quite higher than the band gap energy of bulk SnO_2 (3.6 eV). The decrease in the band gap energy may be due to the accumulation of donor energy levels of TM ions in the actual band gap of SnO_2.

FTIR- Studies

Fig shows that the FTIR spectra of tin oxide nanoparticles as prepared and annealing temperature at 450^0C by using deionized water as a solvent. As-prepared SnO2 powders exhibit an intense, very broad peak ranging from ca. 3565.58 to 3406 cm-1, which may be due to the adsorbed water and NH_3. After annealing, the peaks shift to higher wave numbers such as 3931.52 to 3416.28 cm-1. The band centered at 1622.26 cm-1 may also be related to water for without annealing temperature. After heating at 450^oC, other bands present are H-O-H stretching of water at 1629.89 cm-1, which is present in the environment or as impurity in the structure and at 2918.48 cm-1, corresponding to a C-H bond, possibly impurities of organic compounds involved in the washing process like ethylene. The band at 613.18 cm-1 confirmed purity of tin metal. After annealing the band was shifted to 625-630 cm-1. The absence of peaks such as 1189, 1125, and 1080 cm -1 were observed after annealing at 450oC indicated the absence of inorganic carbonates [14]. The FT-IR spectra of of Ni doped SnO2 as prepared and annealing temperatures at 450oC. The particle are given in Figure, in which the band located at 3404.94 cm-1 is owing to the vibration of O-H and the band located at 1699.32 cm- 1 is due to the H-O-H vibrating mode of the absorbed water. After annealing at 450^oC indicated that vibrational mode observed at 2921.17 cm – 1 is due to C-H stretching vibration. The characteristic band at 3415.28 cm– 1 corresponds to the stretching vibration of O–H groups. No additional absorption peaks were observed with Ni addition after annealing at 450^oC, indicating its homogeneous dispersion in the support material [15].

4. CONCLUSION

Pure and Ni-doped Tin Oxide nanoparticles have been synthesized by using co-precipitation method. The nanoparticles were synthesized without any requirements of special atmosphere and high pressure. Structural study reveals that the prepared samples have tetragonal structure. The band gap energy of doped SnO_2 nanoparticles was found to be lesser than the pure. This may due to the accumulation of donor energy levels of Ni ions in the bandgap of tin oxide.

REFERENCES

[1]. G.A. Prinz, Science 282,(1998) 1660.

[2]. S.A. Wolf, D.D. Awschalom, R.A.Buhrman,J.M. Daughton,S.V.Molnar,M.L.Roukes, A.Y. Chtcheljanova and D.M.Treger, Science 294, (2001) 1488.

[3]. GANESH E PATIL, D D KAJALE, 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., Vol. 34, No. 1, pp. 1–9. February 2011.

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

[5]. S. GNANAM, V. RAJENDRAN" LUMINESCENCE PROPERTIES OF EG-ASSISTED SnO2 NANOPARTICLES BY SOL-GEL PROCESS" , Digest Journal of Nanomaterials and Biostructures, Vol. 5, No 3, pp.699-704,July-September 2010.

[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., Vol.14, No.7,pp.2930-2953,2002.

[7]. Sipra Choudhury, C. A. Betty, K. G. Girija, and S. K. Kulshreshtha "Room temperature gas sensitivity 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. Tsamis a,A. Romano-Rodriguez b, J.R. Morante "Nanostructured oxides on porous silicon microhotplates for NH3 sensing" , Microelectronic Engineering,,Vvol. 85 ,pp.1116-1119,2008.

[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, Vol. 48,No. 5,pp.458-484, November 2010.

[10]. GANESH E PATIL,D D KAJALE, D N CHAVAN, N K PAWAR, P T AHIRE, S D SHINDE, V B GAIKWAD, G H JAIN "Synthesis, characterization and gas sensing performance of SnO2 thin films prepared by spray pyrolysis", Bulletin of Materials Science,Vol.34,No.1,pp.1- 9,2011.

[11]. Chunjoong Kim, Mijung Noh, Myungsuk Choi, Jaephil Cho,and Byungwoo Park "Critical Size of a Nano SnO2 Electrode for Li-Secondary Battery", Chem. Mater.Vol.17,pp. 3297-3301, 2005.

[12]. Paraguay-Delgado, F., Antúnez-Flores, W., Miki-Yoshida, M., Aguilar-Elguezabal, A., Santiago, P., Diaz, R., Ascencio, J.A." Structural

[13]. Hidalgo, P.,R.H.R. Castro, A.C.V. Coelbo and D. Gouvea, 2005, Surface Segregation and Consequent SO_2 Sensor Response in SnO_2 - NiO, Chemistry of Materials Journal , 17:4149-4153.

[14]. K.Nakamato, "Infrared and Raman spectra of inorganic and coordination compounds, "New York: John Wiley and Sons, 1, 978-226, 1986.

[15]. L. S. CHUAH, M. Y. YAACOB, M. S. FAN, S. S. TNEHa, Z. HASSANa "Synthesis, characterization and optical properties of Ni-doped nanocrystalline SnO2" OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 4, No. 10, October 2010, p. 1542 – 1545.