Growth, structure and photoluminescence properties of SnO$_2$-ZnO (TZO) micro cubes

S. Samal$^1$, A. B. Panda$^{2*}$, B.S. Acharya$^2$

1. Department of Materials Science, Indian Institute of Technology, Kanpur-208016
2. Department of Physics, CVRCE,Bidyanagar,Bhubaneswar-752054,INDIA

* A. B. Panda; e-mail id: atalabit@gmail.com

Abstract: Structural investigation from X-ray diffraction patterns of TZO revealed the presence of SnO$_2$ (cassiterite), ZnO (wurtzite) and ZnSnO$_3$ and ZnSnO$_4$ phases. The optical absorption spectra recorded for these powders dispersed in ethanol show the nature of the composite nanopowders to be semiconducting one having an optical absorption band around 280nm. Electron microscopy confirms a change in shape and size of the particles with a change in Sn/Zn ratio. The amorphous nature increases while going from Sn/Zn ratio of 0.87 to 3.75 and cubes of size ~ 2µm, rhombohedral and irregular shaped particles are also observed. The prepared tin zinc oxide samples (TZO) show excitation bands at 241, 287 and 351 nm and common emission bands at 448, 485, 462 and 531 nm for all excitation energies. The photoluminescence and other studies reveal the role played by composition in changing the shape.

Key words: SnO$_2$-ZnO (TZO), nano cubes, photoluminescence, Nano Composite oxide

1. Introduction

Out of all transition metal oxides, few oxides like, ZnO, In$_2$O$_3$, SnO$_2$ and TiO$_2$ have received considerable attention for their use in optoelectronic devices, sensors and catalytic application [1-5]. SnO$_2$ doped with Fluorine or Indium oxide has been extensively used as conducting media for determining the electrical properties of many solid state devices. There have been considerable studies on SnO$_2$ thin films for sensor application also [6-7]. The key to understand the nano SnO$_2$ surface properties is the dual valance state of Sn i.e., +2 and +4. This property of capturing electron and hole to become Sn$^{2+}$ and Sn$^{4+}$ introduces changes in the surface properties by changing the electronic structure thus making surface states to lie deep inside the band gap and lowering the work function. Since reduction of Sn$^{4+}$ to Sn$^{2+}$ depends on oxygen chemical potential of the system, systematic investigation of nano SnO$_2$ prepared through soft chemical solution route is desirable for understanding the basic mechanism of such reduction process. In addition, ZnO is a wide band gap (3.37 eV) n-type semiconductor with large exciton energy of 60 meV having interesting technological properties for applications in photovoltaic and functional coatings [4, 6]. Moreover both SnO$_2$ and ZnO exhibit diverse group of growth morphologies such as nanocombs, nanorings, nanohelixes/nanosprings, nanobelts, nanowires and nanocages at lower dimensions [4]. Due to the promising features and morphology dependant properties of SnO$_2$ and ZnO as well as their composites (TZO), it may be expected that their nanostructure forms represent building blocks for special nanodevices and may offer exciting opportunities for fundamental research and technological applications. The present investigation is an effort in this direction to measure the structural and optical properties of such nanoparticles.
2. Materials and methods

Appropriate amount of SnCl$_2$•2H$_2$O and Zn (O$_2$CCH$_3$)$_2$ (AR grade, Merck) were dissolved in distilled water to make the solution having pH 1.8 to 2.0. Required amount of Sodium Oxalate (AR grade, Merck) was dissolved in distilled water to make the pH of the solution to 8.0. Both these solutions were added drop wise from two burettes simultaneously, which took 15 minutes to make a solution of 300ml. The mixture was stirred with the help of magnetic stirrer and saddle for 75 minutes when it becomes the clear solution. To this clear solution, liquid ammonia solution having strength of 25 wt % of NH$_3$ was added drop by drop. In this way 30 drops were added when white precipitates were seen. Different such solutions having their final pH of 10.30 were subjected to precipitation, filtering and continuous washing with distilled water the final powders were obtained after drying these powders in the oven at 120°C for 2 hrs. Several samples were prepared with varying composition of Sn and Zn at different pH conditions. However, the present investigation deals with three samples which were prepared at pH =10.30 at varying Sn/Zn ratios in atomic % (S$_1$: 0.87, S$_2$: 1.75 and S$_3$: 3.75).

3. Result and Discussion

Phase analysis of the composite SnO$_2$-ZnO powders were made by using X-ray diffraction technique. The diffractometer used for this purpose was X-Pert Pro with copper target and other accessories given in our earlier work [8]. The patterns have been displayed in Figure 1. Three samples having different Sn/Zn ratio prepared under same conditions have been shown in this figure. The average crystallite size for each sample was calculated by using the Debye-Scherer formula, $D = \frac{0.89\lambda}{\beta\cos\theta}$ where ‘$\lambda$’ is the X-ray wavelength, ‘$\theta$’ is the Bragg diffraction angle and ‘$\beta$’ is the peak width at half maximum [9]. The phase analysis was made by comparing inter-planer spacing ‘d’ and intensity ‘I’ values with those of standard XRD patterns of ICDD (Ref. code: 98-000-6056). This has been given in Table-1. One can see that the crystallite size increases from (46±0.5) nm to (58±0.5) nm under Sn/Zn ratio goes from 0.87 to 1.75. But for Sn/Zn = 3.75, this size decreases to (34±0.5) nm.

![Figure 1. XRD patterns of S$_1$ (Sn/Zn = 0.87), S$_2$ (Sn/Zn = 1.75) and S$_3$ (Sn/Zn = 3.75)](image)

Further, the phase analysis indicates formation of pure SnO$_2$ casiterite phase for Sn/Zn = 3.75 whereas two phases of SnO$_2$ and ZnSn(OH)$_6$ are found for Sn/Zn = 1.75 [1, 6]. It is really interesting to see that a lower Sn/Zn ratio of 0.87 results in multiphase system having SnO$_2$, Zn$_3$SnO$_4$ and ZnSn(OH)$_6$ phase. For the SnO$_2$ casiterite phase, the “d” values are 3.349, 2.643 and 1.764 with corresponding (h k l) values (1 1 0), (0 1 1) and (1 2 1) respectively (ICDD: Ref. code: 98-000-6056). For the impurity
phases \([\text{Zn}_2\text{SnO}_4 \text{ and ZnSn(OH)}_6]\), the corresponding 2\(\theta\) values are found to be around 22, 32, 53, 58 and 19, 46, 68, 73 respectively [10,11].

Table 1. Average crystallite sizes and phase identified from XRD patterns

| Sample No. | Sn/Zn ratio | Average Crystallite Size (±0.5nm) | Phases Identified |
|------------|-------------|-----------------------------------|------------------|
| S\(_1\)    | 0.87        | 46.00                             | \(\text{Zn}_2\text{SnO}_4\), \(\text{SnO}_2\) (Cassiterite), \(\text{ZnSn(OH)}_6\) |
| S\(_2\)    | 1.75        | 58.00                             | \(\text{SnO}_2\) (Cassiterite), \(\text{ZnSn(OH)}_6\) |
| S\(_3\)    | 3.5         | 34.00                             | \(\text{SnO}_2\) (Cassiterite) |

To correlate these observations, the differential thermal analysis curves along with the weight loss during heating have been shown in Figure 2.

The results show two peaks (one strong endothermic peak around 256 °C and weak endothermic peak around 82 °C) for compound having Sn/Zn = 0.87 and one (endothermic peak around 254 °C) for Sn/Zn = 1.75 while one strong endothermic peak around 259°C and a weak endothermic peak around 88 °C for Sn/Zn = 3.5. This indicates the water molecules on the surface of the compounds go out while heating the sample whereas transformation of phase like \(\text{SnZn(OH)}_6\) taken place leading to \(\text{SnO}_2\) or \(\text{Zn}_2\text{SnO}_4\) phases. The peak temperature shifts from 254°C to 259°C when complete \(\text{SnO}_2\) is formed. This is in accordance with the XRD results presented in table 1 and figure 1. The optical absorption spectra of the samples taken in the ethanol medium have been shown in the Figure 3. The three samples taken for
observations show interesting structures in UV region. In Sn/Zn = 0.87 the band gap calculated from absorption spectra corresponding to maximum absorption peak at wavelength ($\lambda_m$ = 276 nm) was found to be 4.49 eV whereas for Sn/Zn = 1.75 the band gap was found to be 4.90 eV ($\lambda_m$ = 253 nm). In the third sample where Sn/Zn = 3.75, the absorption shows a flat structure with minimum absorption and the transmission in the UV region was found to be change thus to a constant value in the visible range of spectrum studied. However, the inset shows the magnified image showing the $\lambda_m$ = 275 nm giving the band gap to be 4.50 eV. Thus it is obvious that pure SnO$_2$ phase is responsible for such behavior.

Figure 3. UV – visible absorption spectra of S$_1$ (Sn/Zn = 0.87), S$_2$ (Sn/Zn = 1.75) and S$_3$ (Sn/Zn = 3.75). In-set shows the magnified image of absorption spectra of S$_1$ (Sn/Zn = 0.87).

The photoluminescence spectra of these samples were taken under different excitation energies (figures not shown) have been given in Table-II. The excitation spectra were taken in UV range i.e., 240 nm to 400 nm and the emission spectra were recorded in the visible range of 400 nm to 800 nm. For brevity typical emission and excitation spectra for sample having Sn/Zn = 1.75 have been shown in Figure 4(b) and Figure 4(b).

Figure 4. Typical photoluminescence (a) emission spectra and (b) excitation spectra for sample having Sn/Zn = 1.75.
There is several emission bands found in the photoluminescence spectrum. But excitation spectra have been recorded by placing the monochromator at 448, 462, 485, and 531 emission bands respectively.

Table 2. Details of PL (excitation and emission) spectra obtained for $S_1$ (Sn/Zn = 0.87), $S_2$ (Sn/Zn = 1.75) and $S_3$ (Sn/Zn = 3.75)

| Sample | Emission Spectra | Excitation Spectra |
|--------|------------------|-------------------|
| $S_1$  | $\lambda_{exc}$ (nm) | Peak position (nm) | $\lambda_{em}$ (nm) | Peak position (nm) |
| 241    | 405.64, 423.85, 441.42, 447.36, 460.45, 485.16, 531.12, 544.18, 574.31 | 448 | 238.76, 290.03, 325.32, 373.25 |
| 287    | 422.41, 435.94, 448.42, 461.95, 484.86, 530.66, 543.16 | 462 | 274.31, 353.81, 370.66 |
| 351    | 424.12, 462.21, 486.23, 530.18, 543.47 | 485 | 284.64, 344.46, 390.22 |
| 531    | | 206.64, 297.12, 320.14, 364.61, 395.95 |
| $S_2$  | 408.46, 424.21, 448.74, 461.12, 485.56, 530.16, 543.54, 573.68 | 448 | 238.74, 289.80, 317.33, 332.71 |
| 287    | 422.41, 448.43, 461.95, 485.12, 530.83, 543.32 | 462 | 278.36, 306.92, 333.75, 347.88 |
| 351    | 423.28, 462.19, 485.42, 509.34, 530.83, 543.64 | 485 | 284.00, 342.06, 368.47 |
| 531    | | 283.01, 341.14, 367.08 |
| $S_3$  | 408.76, 424.38, 448.91, 461.18, 484.61, 530.34, 543.71, 5556.14 | 448 | 238.87, 286.34, 317.06, 333.10 |
| 287    | 423.04, 448.02, 461.56, 474.05, 485.51, 531.31, 543.82 | 462 | 283.68, 303.24, 335.55, 347.60 |
| 351    | 424.85, 435.31, 442.58, 447.78, 462.35, 485.26, 531.06, 543.55 | 485 | 283.14, 345.54, 368.71 |
| 531    | | 283.61, 311.09, 367.67 |

The presences of several common bands were then taken for excitation purpose. In this way, the excitation wavelengths 241 nm, 287 nm, and 351 nm were chosen. The PL emission spectral bands have been given in the table after curve fitting of the complex spectra [12].

Scanning electron microscopic observations of the surfaces of nanopowders have been shown in Figure 6. The powders were found to be nanocrystalline in nature. The nanocrystals aggregate to form bigger agglomerates and these are homogenously distributed. One can find different shapes such as spherical, hexagonal and pyramidal etc which aggregate to give larger grains. This has been well defined in sample $S_1$ with Sn/Zn = 0.87.
When this ratio is increased to 3.75 well defined cubes are seen [10]. The size of the cubes varies from 2µm to 1µm. Also seen are rhombohedral shaped crystallites. On the rhombohedral shaped surface smaller crystallites are seen to be adherent [7, 12-14].

The transmission electron microscope photographs given in Figure 7 for sample S$_2$ and S$_3$ show the segregation of nanocrystallites leading to well defined grain boundaries and lattice fringes.

**Figure 5.** FESEM micrographs of S$_1$ (Sn/Zn = 0.87), S$_2$ (Sn/Zn = 1.75) and S$_3$ (Sn/Zn = 3.75)

**Figure 6.** The transmission electron microscope photographs sample S$_2$ (Sn/Zn = 1.75) and S$_3$ (Sn/Zn = 3.75). The insets show selected area diffraction pattern
The selected area diffraction pattern given in the inset for a particular grain shows spotty nature while these nonocrystallines give well defined diffraction pattern. From this and the lattice fringes, the lattice constant calculated for c-axis oriented grains to be 0.299 nm. When well defined nanocubes or rhombohedral shape crystallites were seen in SEM, their electron microscopic photographs and SAED patterns show the characteristic feature of crystallinity in the nano range.

4. Conclusion

From these above observations, one can conclude that,

a) composition plays an important role in nanostructure formation in SnO2-ZnO composite powders,
b) with a pH of 10.3 and Sn/Zn = 3.75, the powder shows cassiterite structure both through X-ray and electron diffraction,
c) the photoluminescence studies also support these results

More comprehensive studies with pH variation and composition change will be reported in detail in future publication.

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