Annealing temperature effect on structural properties of tin oxide nanoparticles

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Tin oxide (SnO$_2$) nanoparticles were synthesized employing simple sol–gel method. Modification in the structural, morphological and optical properties of the as-synthesized tin oxide nanoparticles due to various solution pH (6–12) and thermal annealing at 400 °C (Experiment 1) was studied. X-ray diffraction results of the tin oxide nanoparticles prepared from the precursor solution pH 8 and annealed at 400 °C showed the formation of tin oxide tetragonal phase (SnO$_2$-t) and the surface morphology of the SnO$_2$-t nanoparticles studied by scanning electron microscope revealed the formation of spherical shaped agglomerations. Hence, the tin oxide nanoparticles prepared from the solution pH 8 were annealed at 200, 400, 600 and 800 °C in order to study the effect of annealing at various temperatures on the structural, morphological, optical and vibrational properties of tin oxide nanoparticles (Experiment 2). When the annealing temperature was increased to 600 and 800 °C, mixed phases of SnO$_2$-t and tin oxide orthorhombic system (SnO-o) were formed. Various solution pH and annealing temperatures influenced the direct band gap value. SnO$_2$-t phase synthesized from the solution pH 8 and annealed at 400 °C showed a direct band gap of ~4.50 eV. The tin oxide samples annealed at various temperatures showed a slight shift in the fluorescence peak observed at ~327 nm. Raman studies of the samples obtained from Experiment 1 and Experiment 2 showed a slight shift in the vibrational frequency. I–V studies carried out to investigate the electrical properties of the SnO$_2$ thin film formed by simple drop casting method revealed better ohmic contact and its suitability for gas sensing applications.

Keywords: Oxide; Temperature; Sol-gel.
1. INTRODUCTION

Metal nanoparticles prepared by different synthesizing process attracted the attention because they show modifications in the shape, size distribution, surface morphology and surface area of the nanoparticles; thus, they possess the potential to tune the physical and chemical properties of the semiconducting materials [1, 2]. Quantum confinement effect of nanomaterials paved ways to discover novel materials suitable for various applications [3, 4]. Semiconducting materials with modified optical and electronic properties possess wide range of applications and the materials with wide band gap are of specific interest in device fabrications. Thus tin oxide, an n-type semiconductor with wide direct band gap of 3.6 eV, possesses potential applications in many fields such as solid state gas sensors [5], dye sensitized solar cells [6, 7], photocatalysis [8], lithium ion storage batteries [9, 10], gas sensors [11] and phosphoproteomic research [12]. Further the Au and Ag dopants enhance the electrical and optical properties of tin oxide [13]. Tin oxide nanostructures such as nanowires [14], nanobelts [15], nanoribbons [16], nanoflowers [17], and nanorods play an important role in tuning the structural, electrical and optical properties [18]. Several methods such as mechano-chemical reaction method [19], hydrothermal method [18, 20], microwave method [21] and solid-state reaction method [22] and sol–gel method are adopted to prepare tin oxide nanomaterials. Among them sol–gel method is cost effective and produces better homogeneity in the preparation of nanoparticles [17, 23]. Hence, in the present work, sol–gel method is employed to synthesize tin oxide nanoparticles.

Among the various phases of tin oxides, SnO is the most metastable phase, which is mostly formed at high annealing temperatures (450 and 750 °C), whereas SnO2 is the stable phase [24]. SnO2 itself crystallizes in two phases, SnO2 tetragonal (SnO2-t) and SnO2 orthorhombic (SnO2-o). Meyer et al. [25] demonstrated that SnO phase exists due to reduction of SnO2 and hence the two phases of SnO2 and SnO coexist in the prepared samples. Nose et al. [26] also discussed about SnO oxidation to SnO2. Gu et al. [27] reported that the mixed phases of SnO2-t and SnO2-o mesocrystals show effective ethanol sensing behavior than that of the single SnO2-t phase. The calcination temperature also plays an important role in obtaining orthorhombic phase of SnO2 [28]. Diallo et al. [29] reported that annealing the single phase cassiterite SnO2 nanoparticles (synthesized via Aspalathus linearis) at different temperatures (400–900 °C) improved the crystallinity of the samples and controlled the size of the particles [30]. It is evidently shown that the solution pH used in the synthesis process can effectively tune the nanostructures. Further the size, morphology and phase of the tin oxide nanoparticles can be effectively modified by the process of annealing [31–33]. Hence in the present work, we report on the synthesis of tin oxide nanoparticles by sol–gel method at solution pH 6, 8, 10 and 12. As the nano-particles synthesized at pH 8 and annealed at 400 °C showed spherical structures they are further annealed at various temperature and their effect on the structural, morphological, optical and electrical properties are reported.

2. EXPERIMENTAL

Tin oxide nanoparticles were synthesized by sol–gel method using cost effective tin (II) chloride (SnCl2·2H2O) and ammonia (NH3) solution (EMerck A.R. Grade). In this process, 1.67 g of tin chloride was dissolved in ethanol (25 ml) and the solution was stirred for 2 h at 60 °C and then dried in oven at 60 °C for 5 h. On stirring the tin chloride solution, NH3 solution was added dropwise to adjust the solution pH to 6, 8, 10, and 12 in independent experiments. Then the product tin oxide was centrifuged, dried in hot air oven at 60 °C and then it was annealed at 400 °C for 2 h (Experiment 1). As the tin oxide nanoparticles synthesized at solution pH 8 employing the above method formed spherical shaped nanoparticles, the synthesized nanoparticles at pH 8 were annealed at 200, 400, 600 and 800 °C for 2 h (Experiment 2). Structural analysis (X-ray diffractometer (X’Pert PAN Analytical)) with CuKα radiation (λ = 1.5405 Å), surface morphology (FEI Quanta FEG 200
scanning electron microscopy), UV-DRS measurement (Shimadzu 2450), Raman analysis (NRS-7100 (JASCO)), fluorescence spectral studies (FP-8600 (JASCO)) and electrical studies (Keithley 2636B) of the synthesized tin oxide nanoparticles were carried out. The prepared sample from solution pH 8 and annealed at 400 °C was used to deposit thin film on the cleaned glass substrates (1 cm × 1 cm) using simple drop casting technique and then it was dried. Contacts were made using silver paste, and the electrical properties of the film were studied.

3. RESULTS AND DISCUSSION

X-ray diffraction pattern (XRD) of the as-synthesized (AS) tin oxide nanoparticles from the precursor solution of different pH values are presented in the Fig. S1 (given in Supplementary file) whereas XRD pattern recorded for the samples annealed at 400 °C are presented in Fig. 1a. Figure S1 evidently shows that XRD peaks of the as-synthesized nanoparticles are broad whereas annealing the prepared samples at 400 °C increased the intensity of the XRD peaks (Fig. 1a). Further it is also evident from the Fig. 1a that the XRD peaks of the tin oxide nanoparticles synthesized from the solution pH 8 and annealed at 400 °C become relatively intense and sharp. Since the nanoparticles synthesized at solution pH 8 and annealed at 400 °C acquired spherical structures shown in Fig. 2a, b. The tin oxide nanoparticles prepared from solution pH 8 was annealed at various temperatures (Tₐ) of 200, 400, 600 and 800 °C to investigate the modification in their properties (Experiment 2). XRD pattern presented in the Fig. 1b shows that the synthesized nanoparticles annealed at 600 °C (B3) and 800 °C (B4) consist of mixed phases of SnO₂-t (JCPDS Card No. 41-1445) and SnO-o (JCPDS Card No. 77-2296). The diffraction peak observed at 2θ = 39.67° [Fig. 1b (B3, B4)] is due to SnO-o phase [which is marked with the symbol (*)]. Thus, the results show that only SnO₂-t phase is formed up to the annealing temperature 400 °C (Fig. 1b; B2 = A2) and increase in the annealing temperature to 600 and 800 °C yielded the mixed phases of SnO₂-t and SnO-o. The intensity of XRD peak of (023) plane corresponding to SnO-o phase is relatively less. The various growth parameters used in the present work are not effectively influenced to improve the formation of SnO-o phase. Marikannan et al. reported on the formation of mixed phases of SnO₂-o/ SnO-o thin films prepared by sol–gel spin coating method using different solvents and disclosed that both oxidation and preparation methods were the major factors influencing the formation of mixed phases. Wang et al. [36] reported that, tin oxide nanoparticles prepared using carbon nanofibers (CNFs) by hydrothermal method for different reaction time have produced mixed phases of SnO₂-t and SnO₂-o and SnO₂/CNFs nanocomposite prepared was used for hydrogen sensor application. Gu et al. [27] reported that both SnO₂-t and SnO₂-o phases are resulted when annealing temperature is raised to 600 °C. Hu et al. [28] also reported that the simple chemical method yields the SnO₂-t and SnO₂-o phases of nanorods which are used for sensing Isopropanol gas. But the present work shows that the as-synthesized sample from solution pH 8 and annealed at 600 and 800 °C formed mixed phases of SnO₂-t and SnO-o.
Interplanar distance $d$ and the values of unit cell parameters $a$ and $c$ of SnO$_2$-t phase were calculated from the XRD peaks of (200) and (002) planes using the relation $1/d^2 = (4\sin^2\theta)/\lambda^2 = (h^2 + k^2)/a^2 + l^2/c^2$ [34] and the average crystallite size ($D$) was calculated from Debye–Scherrer formula, $D = 0.9\lambda/(\beta\cos \theta)$ [37], where $\lambda$ is the wavelength of X-rays used (1.5405 Å), $\beta$ is full width half maximum (FWHM) in radian and $\theta$ is the Bragg’s angle and $(h\ k\ l)$ are the Miller indices. The cell parameters calculated in the present work are given in Table 1 which reveals that cell parameter values obtained from Experiment 1 and Experiment 2 are nearly same. Further the present values compare well with the corresponding standard values of $a = 4.738$ Å and $c = 3.187$ Å (JCPDS Card No. 41-1445). Thus, the calculated values show that the $a$, $c$ and $d$ are not influenced effectively by the various precursor solution pH and annealing temperature. The calculated average crystallite size from the XRD peaks of (110), (101) and (211) planes of SnO$_2$-t phase (Experiment 1 and Experiment 2) are given in the Table 1. Experiment 2 shows when annealing temperature is increased, the XRD peak intensity becomes sharper and the crystallite size increases systematically (Table 1). Sathyaseelan et al. [38] and Muthukumar et al. [39] have also observed the same trend due to heat treatment in the synthesized TiO$_2$ nanoparticles. The increase in crystallite size is due to the diffusion of atoms from the grain boundary to the grain [1]. Thus, the present results reveal that the nanoparticles synthesized from the solution pH 8 and annealed at 400 °C show well-developed single-phase tin oxide (SnO$_2$-t) (Fig. 1b; B2). However, the tin oxide nanoparticles obtained from pH 8 and annealed at 600 and 800 °C show the signature of SnO-o phase along with the SnO$_2$-t phase. Thus, the annealing temperatures 600 and 800 °C seem to be critical which formed the SnO-o phase, a first report from this work.

Morphological variation due to the influence of solution pH and annealing temperatures obtained from the Experiments 1 and 2 is displayed in the Fig. 2a, b respectively. Morphology of the tin oxide synthesized from sol–gel method strongly depends on the amount of H$^+$ or OH$^-$ ions in the solution [40]. Tin oxide synthesized from the solution pH 6 and Ta 400 °C, contains slurry like morphology with no definite shape (A1). When the solution pH is 8 and Ta is 400 °C, the image B2 (= A2) shows agglomerated spherical shaped structures. This is enlightened by the projected image shown adjacent to image B2. On increasing the solution pH to 10 (A3) and 12 (A4), the size of the agglomerated structure is decreased and unevenly distributed for Ta 400 °C. The reason for modification of the surface morphology can be explained using the OH$^-$ and H$^+$ ions concentration in the solution as following:
when the solution pH is 6 (Ta = 400 °C), it becomes relatively more acidic and hence there will be more concentration of OH− ions. Reaction of NH3 with the precursor solution containing tin chloride leads to the formation Sn(OH)2 compound during the reaction process and later dissociates into Sn2+ and OH− ions. When the concentration of Sn2+ and OH− ions are more than the critical value, Sn2+ plays a major role in the formation of SnO2 nuclei. However, when pH is increased, changes in the OH− ions concentration occur and decrease the density of H+ ions than that at lower pH. Thus, on increasing the solution pH from acidic to basic the concentration of H+ ions decrease and increase in the OH− ions influences to form the desired structures [40]. In the basic medium (> pH 7) the OH− ions interact with positively charged Sn2+ and form SnO2. In the present work at higher pH (10, 12) hydrolysis and condensation process will be uncontrollable [40] and hence the samples A3 and A4 give irregular shape; subsequently in the Experiment 2 high annealing temperature (Ta = 600 and 800 °C) formed more agglomerated structures. Thus, the FESEM images clearly show that the SnO2-t nanoparticles prepared from pH 8 and on annealing at 400 °C yielded agglomerated spherical shaped nanoparticles (A2 = B2). EDS of sample (A2 = B2) confirms the presence of elements Sn and O (Fig. 2c).

**Figure 2** a FESEM images of tin oxide nanoparticles prepared from various solution pH and annealed at 400 °C; pH 6 (A1), 8 (A2), 10 (A3) and 12 (A4). B FESEM images of as-synthes- sized tin oxide nanoparticles from pH 8 and annealed at different temperatures 200 °C (B1), 400 °C (B2 = A2), 600 °C (B3) and 800 °C (B4). c EDS analysis of tin oxide nanoparticles synthesized from pH 8 and annealed at 400 °C.
Table 1 Comparison of cell parameters, average crystallite size and band gap energy of the tin oxide nanoparticles obtained from the Experiment 1 and Experiment 2.

<table>
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<th>Tin oxide nanoparticles</th>
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4. CONCLUSIONS

Sol–gel method based tin oxide nanoparticles were synthesized by varying pH of the precursor solution and the prepared samples were annealed at different temperatures. Overall, the prepared sample A2 annealed at 400 °C shows slightly agglomerated spherical shaped morphology and confirms the formation of single SnO$_2$-t phase. The formation of mixed phases SnO$_2$-t and SnO-o is due to annealing the samples at 600 and 800 °C. The absorption edge observed at 278 nm in the sample (A2) is shifted from the bulk value 337 nm due to quantum confinement effect. The Raman peaks appeared at ~621 and ~757 cm$^{-1}$ confirm the formation of SnO$_2$-t phase and the presence of weak FL emission peak at 409 nm is due to the oxygen vacancies in the prepared tin oxide nanoparticles. SnO$_2$-t phase nanoparticles prepared from solution pH 8 and annealed at 400 °C shows an average crystallite size of ~10 nm and hence increase in the band gap value to ~4.5 eV. I–V study shows ohmic contact nature and the resistance obtained is 1.6 MΩ for the sample A2 which may be useful for sensing application.

References
