Effect of annealing temperature on structure-property correlations in Zn$_2$SnO$_4$ nanostructured films for optoelectronics

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Abstract

In the present work, the effect of annealing temperature on structural, optical and electrical properties for sol gel synthesized Zn$_2$SnO$_4$ nanostructured films has been investigated for their suitability in optoelectronics. These samples were probed by using XRD, UV-Visible spectroscopy, photoluminescence spectroscopy and Hall measurements. The x-ray diffraction study divulges the polycrystalline nature and phase transition from cubic inverse spinal Zn$_2$SnO$_4$ phase to pervoskite ZnSnO$_3$ phase in the synthesized films. The optical transmission of $\sim$43%–73% in the visible region while the optical gap varies from 3.61–3.95 eV has been observed for the annealed films. The defect related emission peaks at 423, 445 and 481 nm has been observed. The lowest electrical resistivity $(5.8 \times 10^{-3} \ \Omega \ cm)$ and highest figure of merit $(10^{-3} \ \Omega^{-1})$ for the films annealed at 600 °C has been observed. These results are very important for the development of new n-type transparent conductor for various optoelectronic devices.

1. Introduction

Binary metal oxides have been the area of attentiveness in scientific research owing to their ever increasing popularity in transparent electronics. Efficient binary oxides like ZnO, CdO, SnO$_2$ and TiO$_2$ have already made their mark in various technologies. They are being widely used in flat panel displays [1], solar cells [2], coatings [3], electrochromic devices [4], and gas sensors [5, 6]. A step ahead in this technology was made by making use of ternary oxides and multi component oxides, which offer the flexibility to tune the properties of resulting material. Besides being flexible, multi component system offer amalgamation of properties of different participating atoms to favour their stability to harsh chemical environments. Among the various ternary oxides available, Zn-Sn-O is considered to be promising to have characteristic optical and electronic properties as TCO material. Generally, the combination of ZnO and SnO$_2$ exists in two different crystallographic phases viz. Zn$_2$SnO$_4$ (cubic spinal) and ZnSnO$_3$ (orthorhombic), known as zinc stannate. It has been characterized with high electron mobility, low electrical resistivity and excellent transparency in the visible portion of the spectrum [7–11]. The existence and growth of these two phases depend on many factors. The growth of Zn$_2$SnO$_4$ and ZnSnO$_3$ films have been reported by using different techniques like hydrothermal synthesis, thermal evaporation, sol-gel based spin coating and high temperature calcination [12–18]. In case of hydrothermal process using the alkaline NaOH, it is basically the concentration of alkaline mineralizer and temperature of the process that determine the overall properties of the final product. Many scientific groups have worked on the selective growth of its particular phase i.e. the orthorhombic ZnSnO$_3$ phase decomposes into Zn$_2$SnO$_4$ and SnO$_2$ above 700 °C [19]. Another intermediate state, Zn$_2$Sn(OH)$_6$ is formed when Sn$^{2+}$ oxidizes to Sn$^{4+}$, and then decompose to Zn$_2$SnO$_4$ phase [20].

The precursor solvent such as methanol, ethanol, isopropanol and ethoxyethanol have found to greatly influence the structure property relationship for sol gel deposited films [21–23]. The use of different solvents has influence on the transmittance and average grain size of the sol gel coated metal oxide films [21, 22]. The use of different solvents viz. 2-methoxyethanol, iso-propyl alcohol, ethanol, and methanol have found to influence the phase formation temperature, phase formation and preferred orientation for the lead zirconate titanate (PZT)
fils [23]. This change in the properties can be ascribed to reign between volatility and viscosity of the solvents as well as the resulting sols. Many solvents are used for the sol-gel deposition of films, while very less literature is available for the use of acetylacetone which acts both as the solvent and stabilizer. Since the growth of specific ZTO phase strongly depends on precursors along with annealing temperature, therefore the structure-property relationship for the transformation should be explored. So, the present article make an effort to investigate the physical characteristics on temperature induced structural transformation of ZTO films.

2. Experimental details

The samples of zinc stannate (Zn₂SnO₄) nanocomposite films were deposited on well cleaned silica glass substrates using sol gel spin coating technique. The precursor solution of 0.2 M was prepared using the zinc acetate dehydrate [Zn(CH₃COO)₂.2H₂O, CDH, 99.5%] and tin chloride [SnCl₂, SD Fine Chemicals, 99%] in appropriate concentrations and dissolved separately in acetylacetone [CH₃COOH₂.CO.CH₃, LOBA CHEMIE, 98%]. Then, individual solutions were stirred at 60 °C for 1 hr and then both the solutions were mixed together. The resultant solution was further aged for 24 hr for the necessary hydrolysis process. The deposition of Zn₂SnO₄ films was accomplished by spin coating technique (Spin NXG-P1, Apex Instruments, India) on well cleaned silica substrates at 2000 rpm for 80 s. Each deposited layer was then dried in an oven maintained at 260 °C for 10 min. This coating process was repeated for fifteen times to get the films of desired thickness. These samples were further subjected to high temperature annealing in a muffle furnace for an hour, under normal air conditions.

The thickness of films was measured using a 2D surface profilometer (Alphastep D-100, KLA Tencor, USA) and thickness of the deposited films was found to be ~150 nm. Amorphous/crystalline nature of the samples was made by using x-ray diffractometer (D8 Advance XRD, Bruker, Germany) using Cu Kα radiation (λ = 1.5418 Å), operated at 40 kV and 40 mA. The surface topography was investigated by atomic force microscope (Tosca, Anton Paar, Austria). The film morphology and composition was studied by using scanning electron microscope (JSM-6610LV, JEOL) equipped with energy dispersive x-ray analyser [XFLASH 6/30, Bruker, Germany]. The optical transmission spectrum was recorded in the 300–900 nm wavelength range with the help of UV–Vis spectrophotometer (UV-1800, Shimadzu, JAPAN). The emission spectrum was recorded by using fluorescence spectrophotometer (Cary Eclipse, Agilent, USA) at excitation wavelength of 370 nm from xenon arc lamp. Electrical property was studied in van der Pauw’s geometry by employing a Hall measurement system (HMS 3000, Bridge technology, USA).

3. Results and discussion

Figure 1 shows the XRD patterns for zinc stannate Zn₂SnO₄ (ZTO) films annealed at different temperatures viz. 600, 800, 900 and 1000 °C, respectively. These patterns suggest the preferential growth along (311) plane of cubic spinal structure of Zn₂SnO₄ system except for samples annealed above 900 °C. A feeble intensity peak for (012) plane of ZnSnO₃ phase starts appearing for annealing temperature equal to or more than 800 °C and the annealing at 1000 °C lead to the formation of dominating pervoskite ZnSnO₃ phase instead of cubic spinel phase i.e. the temperature induced structural phase transition from cubic spinal to orthorhombic ZTO phase. These results are in harmony with the literature [24, 25]. The lattice constant for the cubic geometry was calculated using the relation [26]:

\[ d = \frac{a}{h^2 + k^2 + l^2} \]  

(1)

where ‘d’ is inter planar spacing for the planes represented by miller indices (h k l) and ‘a’ is lattice constant. Tabulate form of the calculated value of lattice constant is presented below, showing a variation in the lattice constant. The maximum value of lattice constant is for sample annealed at 800 °C with either side a lower value have been observed. A possible reason for a decrease in lattice parameter could be related to the decomposition of ZnSnO₃ phase into the grains of ZnSnO₂ phase formed at high annealing temperature. Also, the crystallite size is calculated using the Debye-Scherrer formula [22, 27]:

\[ D = \frac{0.9\lambda}{\beta \cos \theta} \]  

(2)

The study of other lattice parameters like micro-strain (ε) and dislocation density (Δ) can also be helpful in understanding the various crystallographic imperfections that assimilated during the deposition of films. These parameters are calculated with the help of following relation [28]:

\[ \]
The calculated values of these parameters are tabulated in Table 1. The crystallite size increases with the increase in annealing temperature and the largest grains are formed at 1000 °C. The other parameters viz. lattice strain and dislocation density decreases with annealing temperature, ensuring better structural properties of the films annealed at high temperature. It is suggested that with the formation of ZnSO₃ phase in the deposited films have largest crystallite size as well as less structural defects in the films.

Figure 2 shows the FESEM images and EDS spectra for the nanostructured ZTO films. The energy dispersive x-ray spectroscopy disseminates the presence of Zn, Sn and O elements in the deposited films. It has been observed that the annealing have great influence on the morphological features of the films annealed at high temperature. It is suggested that with the formation of ZnSO₃ phase in the deposited films have largest crystallite size as well as less structural defects in the films.

Figure 3 shows the 2D AFM images for the different samples. It has been observed that particle size first decreases with the increase in annealing temperature as a result of diffusion and decomposition of the Zn₂SnO₄ phase, restricting the growth of this phase. Further increase in annealing temperature results in sudden increase in the particle size and may ensure the formation of ZnSnO₃ phase. Yuan et al have also reported the growth of crystallite size with annealing temperature [29].

Table 1. Summary of structural parameters including FWHM (β), 2θ value, crystallite size (D), lattice constant (a), lattice strain (ε), dislocation density (Δ) and surface roughness (Ra) as a function of annealing temperature for Zn₂SnO₄ nanostructured films.

| T (°C) | β (rad) | 2θ (rad) | DₓRD (nm) | a (Å) | ε (×10⁻⁵) | Δ (×10⁻⁵) | DᵧAFM (nm) | Ra (nm) |
|-------|--------|----------|-----------|------|-------------|-----------|------------|-------|
| 600   | 0.0057 | 0.6028   | 22        | 8.60 | 1.4         | 2.0       | 14.9       | 1.68  |
| 800   | 0.0055 | 0.5972   | 23        | 8.68 | 1.3         | 1.8       | 11.2       | 1.44  |
| 900   | 0.0029 | 0.6024   | 44        | 8.61 | 0.7         | 0.5       | 9.5        | 1.04  |
| 1000  | 0.0016 | 0.6014   | 78        | 8.62 | 0.4         | 0.2       | 31.8       | 1.02  |

\[
ε = \frac{β \cos θ}{4}
\]

\[
Δ = \frac{1}{D^2}
\]

The calculated values of these parameters are tabulated in Table 1. The crystallite size increases with the increase in annealing temperature and the largest grains are formed at 1000 °C. The other parameters viz. lattice strain and dislocation density decreases with annealing temperature, ensuring better structural properties of the films annealed at high temperature. It is suggested that with the formation of ZnSO₃ phase in the deposited films have largest crystallite size as well as less structural defects in the films.
Figure 2. FESEM images for ZTO films for different annealing temperatures.

Figure 3. AFM images (2D) for ZTO films.
parameters in the table below. An increase in particle size with annealing temperature is also supported by AFM measurements.

Figure 4 represents the transmission spectra for ZTO samples. All the samples depict good transparency in the visible region of the spectrum for the sol-gel synthesized samples. The average transmission varies from 55 % to 75 % with the increase in annealing temperature. The least value of average transmission (55%) for sample annealed at 800 °C while the maximum transmission (75%) has been observed for sample annealed at 1000 °C. The variation optical properties can be attributed to the structural differences that occurred at the high annealing temperature, leading to the formation of the new ZnSnO3 phase. These values of high transparency obtained in case of ZTO are noteworthy for its use in optoelectronic devices [29]. The optical gap can be obtained with the help of the following relation [30]:

\[
(\alpha h\nu)^2 = B(h\nu - E_0)
\]

where ‘\(\alpha\)’ stands for the absorption coefficient, \(h\) is Plank’s constant, \(B\) is a constant related to nature of transition and \(E_0\) is the band gap energy. The value of optical gap is obtained by linear extrapolation of the curve \((\alpha h\nu)^2\) versus \(h\nu\) on the horizontal axis. The value of optical gap is tabulated in table 2. It is interpreted that the value of band gap energy increase from 3.61 eV (bulk sample) to 3.95 eV (for 1000 °C), which can be related to the formation of another phase of the zinc stannate (ZnSnO3). Since the reported band gap of the pure ZnSnO3 phase of zinc stannate (3.7–3.9 eV) is high as compared to the Zn2SnO4 phase of zinc stannate, increase in the band gap energy can purely be related to the phase reconstruction.

Figure 6 shows the photoluminescence spectra of zinc stannate films recorded at an excitation of 370 nm. All the films exhibit four major emission peaks occurring at 423 nm (violet), 445 nm (blue), 481 nm (yellow-green) and 511 nm (green) which are related to zinc vacancy, zinc interstitials, oxygen vacancy and oxygen anti sites respectively. Identical results have been reported by Mishra et al [31]. Thus, the defect related emission rules over the band edge emission (not observed) for ZTO system. The intensity of emission peaks increases with annealing temperature till annealing at 900 °C and thereafter the PL intensity falls for sample annealed at 1 000 °C. Further, it is found that there is no change peak position/shape, meaning no change in the type of defects but only change in the relative contributions for the emissions on annealing temperature.

The electrical parameters viz. electrical resistivity, charge density and their mobility are evaluated for Zn-Sn-O nanocomposite films by Hall measurement. The resistivity of the synthesized films is calculated using the following relation [32]:

\[
\rho = R_s t
\]

where \(R_s\) is sheet resistance and \(t\) is film thickness. The value of different parameters viz. electrical resistivity, carrier concentration and mobility with annealing temperature are tabulated in table 2. The electrical resistivity increases while an inverse relation between mobility and carrier concentration has been observed with annealing temperature. Therefore, the cumulative effect of carrier concentration and their mobility is related to an increase in electrical resistivity of ZTO films. The low value of electrical resistivity near to current industry standard i.e. indium tin oxide material is reported for spray paralysed ZnO-SnO2 films by Atay et al [33].
Figure 5. Tauc’s plot for Zn$_2$SnO$_4$ nanostructured films annealed at different temperatures.

Table 2. Variation of opto-electrical parameters containing transmission, band gap ($E_0$), resistivity ($\rho$), mobility ($\mu$), carrier concentration ($N$) and FOM as a function of annealing temperature ($T_a$) for spin coated Zn$_2$SnO$_4$ nanostructured films.

| $T_a$(°C) | T% @550 nm | $E_0$(eV) | $\rho$(10$^{-3}$ Ω-cm) | $\mu$(m$^2$/V.s) | $N$(10$^{19}$ cm$^{-3}$) | FOM (10$^{-4}$Ω$^{-1}$) |
|-----------|------------|-----------|----------------------|-----------------|-----------------|----------------------|
| 600       | 66.95      | 3.86      | 5.8                  | 56              | 8.74            | 1.1                  |
| 800       | 43.83      | 2.86      | 7.2                  | 97              | 1.52            | 0.6                  |
| 900       | 71.82      | 2.71      | 7.6                  | 151             | 0.17            | 0.9                  |
| 1000      | 73.40      | 2.39      | 8.0                  | 49              | 2.27            | 0.9                  |

Figure 6. Emission spectra for Zn$_2$SnO$_4$ nanostructured films annealed at different temperatures.
The parameter which can be related to the application as TCO material is known as figure of merit (FOM). It is calculated as the ratio of average transmission at 550 nm to the sheet resistance of the films and is formulated as

\[ \Phi = \frac{1}{\alpha \rho} \]

(7)

where, \( \alpha \) is the absorption coefficient and \( \rho \) is the sheet resistance of the film. The calculated value of FOM is also tabulated in Table 2. It is observed from this table that ZTO600 sample have the small value of electrical resistivity and hence largest FOM value (≈0.11 Ω\(^{-1}\)) to make it suitable for TCO applications. These values are four orders of magnitude greater than that reported for similar compositions (10\(^{-5}\) Ω\(^{-1}\)) by Bibi et al [35].

4. Conclusion

Structural, optical and electrical properties of sol–gel deposited nanocomposite Zn–Sn–O films as a function of annealing temperature has been carried out in the current work. Structural characterization reveals the polycrystalline, inverse spinel cubic structure, which changes to pervoskite structure at high annealing temperature. These films exhibit relatively good transmission in the visible region compared with sol-gel deposited films. The defect related emission at 423 nm dominates for the synthesized films. Hall measurements confirm the n-type conductivity with lowest resistivity (5.8 × 10\(^{-3}\) Ω cm) and highest figure of merit (1.1 × 10\(^{-1}\) Ω\(^{-1}\)) for the film annealed at 600 °C. These results are very important for the development of alternate TCO materials for future optoelectronic devices.

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