Synthesis and Characterization of Zn-doped and un-doped SnO\textsubscript{2} nanostructures for PV Applications

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ABSTRACT

Tin oxide nanostructures, un-doped and Zn-doped, have been prepared by conventional sol-gel technique. Research grade tin chloride (SnCl\textsubscript{2}.2H\textsubscript{2}O) and zinc acetate (Zn(O\textsubscript{2}C\textsubscript{2}H\textsubscript{3})\textsubscript{2}) were used as tin and zinc sources. Ethylene glycol and alcohol were used as solvents under different synthesis conditions. Transparent un-doped and Zn-doped SnO\textsubscript{2} sol was prepared after continuous stirring and refluxing at 40\textdegree{}C. Thin films, prepared from SnO\textsubscript{2} sol, have also been deposited on glass substrate by spin coating at 500 rpm for 10 seconds and then at 3000rpm for 30 seconds. Scanning electron microscopy results show the formation of nanodiamonds (~40nm) and nanorods (~30nm) after annealing at 300\textdegree{}C for 60 minutes. It is important to mention here that we have prepared SnO\textsubscript{2} nanostructures without the use of any surfactant and ligand during sol synthesis. X-ray diffraction (XRD) patterns show that the preferred orientation was (111) with orthorhombic crystal structure. Crystallite size was calculated to be ~8 nm from XRD results. Optical properties measured by using spectroscopic ellipsometer have shown a band gap of 3.87 eV, which is larger than the band gap of SnO\textsubscript{2} in bulk form (3.6eV). More than 90\% transmission was observed in these sol-gel deposited SnO\textsubscript{2} thin films. Electrical properties were studied using four-probe method and Hall effect. Thin films show room temperature conductivity of the order of $10^3$ $\Omega^{-1}$cm$^{-1}$. These optical and electrical values are comparable to values reported in literature. Zn-doped SnO\textsubscript{2} films show conductivity slightly better than the undoped one.

1. INTRODUCTION

Due to their unique electronic, optical and mechanical properties (Zheng 2001) one dimension (1D) nanoscale materials have gained many scientist’s attention. At this structural level, nanosized semi-conducting oxide materials show the properties such as super-conductivity, ferro-electricity and magnetism etc. covering all the aspects of material science.

Conductive oxides are promising materials for the manufacture of transparent electronics and optoelectronic devices in the ultraviolet (UV) region due to their wide band gap and high mobility. In the fast growing field of nano-technology, there is an urgent need of specially designed semiconductors to better match the properties of promising materials. Thus, it has led to a renewed interest in ternary oxide semiconductors (II–IV–VI oxides) of the form A\textsubscript{2}BO\textsubscript{4}, such as cadmium stannate.
(Cd₂SnO₄), generally known as cadmium tin oxide (CTO), and zinc stannate (Zn₂SnO₄), which is mostly called zinc tin oxide (ZTO). Zn₂SnO₄ is recognized for having high electron mobility (Tsaroucha 2011, Erslev 2008), high electrical conductivity, and desirable optical properties that make it suitable for an extensive range of applications such as in solar cells (Li 2012, Lana-Villarreal 2007), negative electrode material for Li-ion battery (Kim 2012, Srivastava 2007), sensors for the detection of humidity and various combustible gases (Yadav 2012), and as a photocatalyst for the degradation of organic pollutants (Cun 2002). Compared with binary oxides, the complex ternary oxides like Zn₂SnO₄ are chemically more stable making them ideal for applications involving extreme conditions (Zhang 2007). Zn₂SnO₄ has been successfully used as a flame retardant and smoke suppressant (Horrocks 2012).

The control of sizes and shapes of nanostructures is crucial as it may affect their electrical and optical properties (Lim 2011, Baruah 2009). For controlling the size of particles we have used sol-gel method. There are many advantages of sol-gel method such as it allows the production of new hybrid organic-inorganic materials, which do not exist in nature. Furthermore, it is cost-effective and large-area scalable technique.

In this paper, we report on the sol-gel prepared undoped and ZnO doped SnO₂. Stannous chloride hydrate (SnCl₂.2H₂O) was used as a precursor. The structural and morphological characterization was carried out by XRD, SEM and AFM. Effect of doping and synthesis parameters on the optical properties were also studied.

2. EXPERIMENTAL DETAILS

a. Synthesis of undoped and Zn-doped SnO₂ sol:

In this technique tin chloride hydrate SnCl₂.2H₂O was used as starting material. A solution of 0.1 mol % SnCl₂ in ethylene glycol was prepared by dissolving appropriate amounts of SnCl₂ under vigorous stirring at 60°C until colorless and transparent sol was obtained. Before gelation process thin films were also prepared on glass substrate by spin coating. Samples were dried at room temperature for 24h and then annealed at 300°C for 1h.

For doping purposes ZnO sol was synthesized by following the route mentioned in our previous paper (Riaz 2011). ZnO doped SnO₂ sol was prepared under the same conditions used for un-doped SnO₂ sol with Zn/Sn/O molar ratio of 2:1:2. Thin films of SnO₂ and ZnO doped SnO₂ were deposited with varying thicknesses. Doped films were also annealed at 300°C to obtain stable Zn₂SnO₄ structure.

b. Characterization:

Crystallographic structure along with the phase variation and crystallite size of undoped and doped SnO₂ samples was studied by Rigaku D-MAX/IIA X-ray diffractometer (XRD). CuKα (Ni filtered) radiations (λ=1.5405 Å) were used to obtain the XRD pattern. Surface morphology was observed using Hitachi S-3400N scanning electron microscope (SEM). Bruker CP-II atomic force microscopy (AFM) was used to characterize the surface nanostructure. Optical properties in the UV-VIS-IR range were obtained by using JA Woollam’s variable angle spectroscopic ellipsometer (VASE).
3. RESULTS AND DISCUSSION

Fig. 1 shows XRD pattern of undoped SnO₂ thin films. The films were deposited with varying thickness of 80-200nm in order to study the effect of variation in thickness on structural and optical properties at nanoscale. All the peaks are well consistent with JCPDS card no. (29-1484), which confirmed the samples as pure orthorombic crystalline SnO₂. Moreover, it can be seen that with increased thickness the FWHM of the (1 1 1) peak increased indicating a decrease in crystallite size.

XRD plot of as deposited samples confirm the crystalline structure of SnO₂ without any heat treatment. To obtain more quantitative information, the XRD pattern was analyzed with Gaussian function where full widths at half maxima [FWHM] were determined. The grain size of SnO₂ thin film (D) can be estimated by the Debye-Scherrer formula.

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

Fig. 1 XRD pattern of undoped SnO₂ thin films within the thickness range of 80-200nm
Where, $D$ = Crystalline grain size, $B$ = FWHM of the diffracted peak, $\lambda$ = wavelength of the X-rays, $\theta$ = Angle of diffraction.

Using Scherrer formula the average crystallite size of the deposited films are calculated to be 2.4nm, 3.9nm, 5.6nm, 6nm, 4nm. Fig. 2 shows the relation between thickness and crystallite size.

Fig. 2 Variation in crystallite size of SnO$_2$ samples

In the polycrystalline thin film structures, generally the major structure or orientation mainly depends on the processing parameters. During the coalescence of two differently oriented nuclei the structural changes occur by surface diffusion and migration of grain boundaries. In such cases, smaller nuclei may easily rotate on coalescence that causes the structural changes. The lowest surface energy, the grain boundary energy and the diffusion of surface atoms influence the stable polycrystalline state of a material.

The reports by Lee (2008) reveal that the preferred orientation of grain growth and the final texture of thin films depend on the strain energy minimization and surface energy minimization. The level of these energy states depends on the thickness of the films. The minimization of strain energy supports one type of texture while the minimization of surface energy promotes another. Furthermore, surface energy dominates at a lower film thickness, whereas at the higher film thickness strain energy will be significant. The surface structure of the substrate forces the nuclei to grow along a specific orientation. It can be concluded from the above discussion that the interaction at the film and substrate interface could be high at lower thickness values. So with increasing thickness of the thin films, strain energy dominates which results in the broadening of peaks. In our XRD patterns, peak broadening is observed with increase in thickness. The relationship between the broadening produced and stress/strain can be found by differentiating the Bragg’s law as given in Fig. 3 (Cullity 1978)
\[ b = \Delta 2\theta = -2\Delta d/d \tan \theta \]

Where, \( b \) = extra broadening and \( \Delta d/d \) = variation in strain

Fig. 3 Variation in Stress / Strain of SnO\(_2\) samples

Fig. 4 shows XRD pattern of Zn\(_2\)SnO\(_4\) thin films. All the peaks are well consistent with JCPDS card no. (29-1484) for pure SnO\(_2\) and with JCPDS card no. (24-1470) for doped SnO\(_2\).

Fig. 4 XRD pattern of Zn\(_2\)SnO\(_4\) thin films
Appearance of (311) characteristic peak of Zn$_2$SnO$_4$, under as-deposited condition, shows that ZnO has been successfully incorporated into the SnO$_2$ matrix. Further investigations of doped SnO$_2$ samples are under progress.

Fig. 5 shows SEM micrographs of SnO$_2$ and Zn$_2$SnO$_4$ thin films. Free large-area growth of nanorods and nanodiamonds of diameter 30nm and 40nm respectively is seen in case of SnO$_2$ thin films (Fig. 5 (a,b)). While on doping different structure was observed due to difference in ionic radii of Zn and Sn. Spherically shaped nanoparticles and long tubular structure is observed with diameter of 20nm and 50nm respectively (Fig 5 (c,d)). Pal (2009) reported SnO$_2$ nanostructures with use of cationic surfactant but it is worth mentioning here that these nanostructures are formed without the use of any surfactant during sol synthesis.

Fig. 5 SEM micrographs of (a-b) SnO$_2$ (c-d) Zn$_2$SnO$_4$

Fig. 6 shows surface morphologies of un-doped SnO$_2$ thin films with thickness of 80-200nm. It can be seen that films are extremely smooth with RMS surface roughness of
less than 3nm for all the films. Grain sizes along with the average and root mean square roughness values, obtained from AFM, are shown in Fig. 7.
The transmittances of doped and undoped films with different thicknesses are shown in Fig. 8, where (a) shows the results of undoped thin films with different thicknesses. The average transmittance of thin films at 339 nm is above 85% for all films regardless of film thickness, which is in good agreement with the reported values (Shamala, 2004). Generally the required transmittance of transparent conductive thin film for solar cells is over 85% and as such these results indicate that SnO$_2$ thin films are a good candidate to be used as a window layer in solar cells. When zinc is incorporated into the structure a slight increase in average transmission of the films is observed as shown in Fig. 8 (b).
Figs. 9 and 10 show refractive indices and extinction coefficient values for SnO$_2$ and Zn$_2$SnO$_4$ thin films with different thicknesses. The peak of refractive index at ~350nm corresponds to direct band gap transition. Variations in refractive index are observed with changes in thickness. For undoped thin films the refractive index increases till a thickness of 100nm after which the refractive index decreases. Refractive indices are in the range of 1.55-1.75 for undoped thin films while refractive index increases when Zn is incorporated into the structure. Refractive index of doped films is greater than the undoped ZnO and SnO$_2$. Generally, the refractive index of zinc stannate thin films is higher than those of ZnO and SnO$_2$ (Cetinorgu 2007).
Fig. 9 Variation in refractive index ‘n’ of (a) SnO$_2$ (b) Zn$_2$SnO$_4$ thin films
The direct band gap is extracted by linear extrapolation of $\alpha^2$ vs. $E$ (eV) plot to zero on the energy axis. Fig. 11 shows the band gap of doped and undoped SnO$_2$. Band gap for undoped thin films is in the range of 3.66-3.68 eV while with incorporation of Zn into SnO$_2$ structure causes an increase in band gap as expected due to Burstein-Moss shift. The band gap of Zn$_2$SnO$_4$ thin films are within the range of 3.75-3.78 eV. Wang (2007) reported band gap of 3.9-4.06 eV. Our results are in good agreement with those reported in literature.
Thin films showed room temperature conductivity of the order of $10^3 \ \Omega^{-1} \text{cm}^{-1}$. These optical and electrical values are comparable to the ones reported in literature. Zn-doped SnO$_2$ films showed conductivity slightly better than the undoped ones as shown in Fig. 12.
Undoped and zinc doped tin oxide nanostructures are prepared via cost effective and application oriented sol-gel route. Thin films with different thicknesses are deposited on glass substrate in order to study the structural and optical properties. SEM images show the formation of nanorod (30nm) and nanodiamond (40nm) on the surface of thin films. AFM results show the formation of granular films with average grain sizes of less than 8nm and with RMS surface roughness of less than 3nm. The most important thing is that these uniformly distributed nanostructures are formed without the use of any surfactant. Band gap values are in the range of 3.65-3.68 eV for un-doped films, whereas 3.75 – 3.78 eV was observed for doped SnO\textsubscript{2} thin films. Burstein Moss shift of band gap to high energies is observed in case of zinc doped SnO\textsubscript{2} thin films.

**REFERENCE**


