Research Article

Spray Pyrolysis Deposition of Nanostructured Tin Oxide Thin Films

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Nanostructured SnO2 thin films were grown by the chemical spray pyrolysis (CSP) method. Homemade spray pyrolysis technique is employed to prepare thin films. SnO2 is wide bandgap semiconductor material whose film is deposited on glass substrate using aqueous solution of SnCl4·5H2O as a precursor. XRD (X-ray diffraction), UV (ultraviolet visible spectroscopy), FESEM (field emission scanning electron microscopy), and EDS (energy dispersive spectroscopy) analysis are done for structural, optical, surface morphological, and compositional analysis. XRD analysis shows polycrystalline nature of samples with pure phase formation. Crystallite size calculated from diffraction peaks is 29.92 nm showing nanostructured thin films. FESEM analysis shows that SnO2 thin film contains voids with nanoparticles. EDS analysis confirms the composition of deposited thin film on glass substrate. UV-visible absorption spectra show that the bandgap of SnO2 thin film is 3.54 eV. Bandgap of SnO2 thin film can be tuned that it can be used in optical devices.

1. Introduction

The tin oxide is a wide bandgap semiconductor (energy bandgap 3.6 eV), and it has only the tin atom that occupies the centre of a surrounding core composed of six oxygen atoms placed approximately at the corners of a quasiregular octahedron (Figure 1). In the case of oxygen atoms, three tin atoms surround each of them, forming an almost equilateral triangle. The lattice parameters are \( a = b = 4.737 \, \text{Å} \) and \( c = 3.186 \, \text{Å} \) [1].

SnO2 is a special oxide material because it has a low electrical resistance with high optical transparency in the visible range. Due to these properties, apart from gas sensors, SnO2 is being used in many other applications, such as electrode materials in solar cells, light-emitting diodes, flat-panel displays, and other optoelectronic devices where an electric contact needs to be made without obstructing photons from either entering or escaping the optical active area and in transparent electronics, such as transparent field-effect transistors [2, 3]. SnO2 owing to a wide bandgap is an insulator in its stoichiometric form. However, due to the high intrinsic defects, that is oxygen deficiencies, tin oxide (SnO2−x) possesses a high conductivity. It has been shown that the formation energy of oxygen vacancies and tin interstitials in SnO2 is very low. Therefore, these defects form readily, which explains the high conductivity of pure, but nonstoichiometric, tin oxide.

SnO2 thin films have been deposited using different techniques, such as spray pyrolysis [4], sol-gel process [5, 6], chemical vapour deposition [7], sputtering [8], and pulsed-laser deposition [9]. In the present investigation, the authors have used the spray pyrolysis technique to prepare thin films of SnO2 because the technique is simple and involves low-cost equipments and raw materials. Moreover, the deposition rate and the thickness of the films can be easily controlled over a wide range by changing the spray parameter. The technique involves a simple technology in which an ionic solution (containing the constituent elements of a compound in the form of soluble salts) is sprayed over heated substrates. Though a number of tin salts are available for this purpose, the most suitable is one whose decomposition temperature is not very high, the decomposition reaction leading to the formation of SnO2 is thermodynamically feasible, and no residue of the reactants is left behind in
the deposited material [10]. Keeping these in view, we have used an aqueous solution of SnCl₄·5H₂O as the precursor solution for spray pyrolysis in the present investigation. In this paper, we report the synthesis and characterization of nanostructured tin oxide thin films.

2. Experimental

SnO₂ thin films were deposited by the CSP technique from aqueous solutions containing 0.1 M tin chloride pentahydrate as a precursor, using compressed air as a carrier gas. A homemade assembly has been used to prepare thin film as described elsewhere [11]. Ultrasonically cleaned glass slides cut in small pieces are used as a substrate on which films are grown. Cleaned glass slides were then placed on a solid uniform thermal conductor surface to provide proper heating with uniformity to films. A heater is used as heat source to provide temperature of around 250°C. After spraying, films on glass slides were sintered at 550°C for 30 min inside the furnace. Total volume of the solution sprayed was 20 mL. The various process parameters in the film deposition are listed in Table 1. The scheme of the spray pyrolysis setup used in this study is presented in Figure 2.

The deposited thin films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), optical absorption spectra, and energy dispersive-spectroscopy (EDS) measurements. X-ray diffraction pattern was recorded on diffractometer (Miniflex Model, Rigaku, Japan) using CuKα radiation with a wavelength λ = 1.5418 Å at 2θ values between 20° and 80°. The average crystallite size (D) was estimated using the Scherrer equation [12] as follows: 

\[ D = \frac{0.9λ}{β\cosθ} \]

where λ, β, and θ are the X-ray wavelength, the full width at half maximum (FWHM) of the diffraction peak, and Bragg diffraction angle, respectively. A Hitachi S-4800 model was used to examine the surface morphology of the sample by FESEM and the percentage of constituent elements was evaluated by the energy dispersive X-rays analysis (EDX) technique. The optical absorption spectra of the films were measured in the wavelength range of 200–700 nm on a Shimadzu UV-2450 spectrophotometer.

3. Results and Discussion

Figure 3 shows X-ray diffraction pattern of the SnO₂ thin films. XRD pattern is compared with JCPDS standard database [13], which confirms the formation of SnO₂. XRD pattern of SnO₂ thin film deposited over glass substrate shows polycrystalline phases with calculated h, k, l indices (110), (101), (200), (111), (210), (211), and so forth, corresponding to peak positions 26.60, 33.90, 38.0, 39.00,
Figure 4: FESEM micrograph of SnO$_2$ thin film at different spots (a-b) and with different magnification (c-d).

Figure 5: EDS pattern of SnO$_2$ thin film deposited on glass substrate.

42.60, and 513.80 as shown in Table 2. Crystal structure of SnO$_2$ thin film is cassiterite and the average crystallite size calculated from diffraction peaks is 29.92 nm.

Figures 4(a) and 4(d) show FESEM micrograph of SnO$_2$ thin film at different spots and magnification. Deposited thin film shows pores on surface containing nanoparticles. Figure 4(d) shows the particles in pores.

Figure 5 shows EDS pattern of tin oxide thin film. EDS analysis confirms the composition of deposited thin film on glass substrate for the sample. Stoichiometrically expected at % of Sn and O is 33.3 and 66.7, respectively. Observed at % of Sn and O is 28.25 and 71.75, respectively. There is little deviation from stoichiometry of the prepared film.

Figure 6 shows optical absorbance spectrum of SnO$_2$ thin film. The bandgap energy calculated from the absorption spectra is 3.54 eV which is exactly matching with reported bandgap energy (3.6 eV) of SnO$_2$ [14, 15].
Table 2: X-ray diffraction analysis of the SnO₂ thin films.

<table>
<thead>
<tr>
<th>(h k l) planes</th>
<th>Angle, 2θ (degree)</th>
<th>d spacing (Å)</th>
<th>FWHM</th>
<th>Crystallite size (nm)</th>
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<tr>
<td>(1 1 0)</td>
<td>26.60</td>
<td>3.3484</td>
<td>0.163</td>
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<td>(1 0 1)</td>
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<td>0.171</td>
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<tr>
<td>(2 0 0)</td>
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<td>0.190</td>
<td>32</td>
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<tr>
<td>(1 1 1)</td>
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<tr>
<td>(2 1 0)</td>
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<td>2.1206</td>
<td>0.130</td>
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<tr>
<td>(2 1 1)</td>
<td>51.80</td>
<td>1.7635</td>
<td>0.159</td>
<td>32</td>
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<tr>
<td>(2 2 0)</td>
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</table>

4. Conclusions

In this study, we showed that SnO₂ thin films could be successfully deposited by the low-cost chemical spray pyrolysis method in air, using aqueous solutions containing SnCl₄·5H₂O.

(i) Homemade spray pyrolysis technique is a cheap and easy method to prepare thin films.

(ii) Crystallite size calculated from diffraction peaks is 29.92 nm showing nanostructured thin film formation.

(iii) FESEM studies film shows pores on surface containing nanoparticles and EDS analysis confirms purity of film.

(iv) Bandgap of SnO₂ can be tuned that it can be used in optical devices.

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References


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