Optical Property Study of Electrodeposited Tin Oxide Thin Film

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Abstract.

Tin oxide (SnO_2), a common n-type semiconductor is extensively used in the detection of various gases due to its stable bandgap and excellent physical-chemical properties. In this paper, the SnO_2 is made by the electro-deposition method using a Zinc electrode on FTO glass. This reaction is done at room temperature with an acidic aqueous solution containing primary salt as $SnSO_4$.The optical properties of SnO_2 were investigated by utilising UV-VIS spectrophotometry.

keyword: Tin oxide, *thin film, UV-Vis Spectrophotometry*

1. INTRODUCTION

SnO_2, the first semiconductor material used commercially for methane detection [1] is a typical n-type metal oxide semiconductor with a broad and stable bandgap of 3.6eV [2]. Features like high transparency, high conductivity, and large mobility make SnO2 a widely accepted and appreciable gas-sensing material [3,4]. This rutile-type crystalline structure at room temperature [5] is not only used for gas sensing [6,7] but also as electrocatalytic anodes [8], solar cells [9] and catalysts [10,11]. Electrical conductivity can be enhanced by increasing the number of charged particles by doping [1]. Over the years researchers have used a number of techniques such as Chemical Bath Deposition (CBD) [12], Controlled Precipitation Method [13], Nitric Acid Leaching [14], Electrodeposition [15], Thermal Evaporation Technique [16], Sol–Gel [17] and Hydrothermal [1].

Chang et al 2002[18] successfully electrochemically deposited nanostructured SnO_2 on copper substrate and chose $SnCl_2$ as the tin-based salt at a temperature of 85° C followed by a heat treatment in a vacuum at 400°C for prominent crystallinity. Aditia et al 2011[12] deposited SnO_2 thin film by Chemical Bath Deposition on a glass substrate. Choosing the precursor as $SnCl_2.2H_2O$ and the catalyst as urea, varied the calcination temperature of the substrate and thereby proving that a higher calcination temperature would have been better for crystallinity. Kyoungkeun et al [14] leached Pb-free solder in nitric acid in a Pyrex glass reactor equipped with a heat sink to maintain the thermal equilibrium. The leaching efficiencies were directly proportional to temperature and HNO3 concentration thereby achieving 99.986% pure SnO_2. Junie Jhon M. Vequizo et al 2010[4] fabricated Sno2 thin film by electrodepositing SnSo4 and Nitric Acid on indium-tin-oxide (ITO) at room temperature with an acidic pH. The working solution was oxygen-bubbled which was used as an oxygen precursor for the better deposition of the substrate. Zheng et al 2021[1] doped graphene on Sno2 and obtained a 96.112 sensing response to methane at 243°C.SnO_2-NP was prepared hydrothermally using SnCl4.5H20 for 8 Hrs. Quaranta et al 1999[17] had a sol-gel setup for fabricating SnO_2/Os gas sensitive thin film. Os doping improved the sensitivity of tin oxide and made promising progress in order to make low-cost methane sensors. Ibarguen et al 2006[13] synthesized tin oxide nanoparticles by controlled precipitation. An optimal pH yielded the desired product with major phase 6.25 with potentiometric and conductimetric titrations at 350°C. Even at 600°C, it showed high reactivity. Naz et al 2020[19] conducted the experiment successfully using the chemical co-precipitation method on hydrated stannous salt followed by annealing them at 400°C,500°C, and 600°C.Elango et al 2015[20] green synthesized SnO_2 nanoparticles from Persia Americana seed extracts of size in the range of 4nm at low cost without doing any harm to the environment.

In this paper, we have synthesized tin oxide thin films by means of the electrodeposition method and optical characteristics have been investigated. We have chosen Electrodeposition because of its effectiveness, rapid synthesis time and low cost. The process was conducted at room temperature with optimal pH for better deposition. Further analytical study (UV-VIS) was done to verify the purity and other aspects of the thin films.

2. EXPERIMENTAL

2.1 Materials

In this experimental procedure, the materials utilized were stannous sulfate ($SnSO_4$), analytical reagent, tartaric acid($C_4H_6O_6$), analytical reagent, potassium nitrate (KNO_3), analytical reagent, nitric acid (HNO_3), distilled water (H_2O).

2.2 Synthesis of SnO_2 Thin Film

The tin oxide thin films were synthesized using the electrodeposition method. 0.1 M stannous sulfate was dissolved in 5ml distilled water and magnetic stirring was applied till a fine solution was obtained. 0.85 gm tartaric acid was added to the solution and a magnetic stir was applied for as long as a homogeneous solution was formed with fine white particles floating in it. 0.1 potassium nitrate was first dissolved in 5ml water and added dropwise to the above solution until the solution becomes just clear that is the solution at that very instant becomes transparent and no more drops were added. The pH of the solution was maintained at 2.2 using nitric acid (1:10 V/V). The solution was left for a few minutes to make sure that everything dissolves uniformly. Clean FTO glass and extremely clean, polished zinc rod were submerged and connected with wires. Figure 2.1 shows the experimental setup. The entire setup was kept undisturbed till a white crystalline layer is obtained on the FTO. The FTO was dried up and heat treated at 600°C for 2 hrs in order to oxidize the free tin ions that may be present in the thin film and to have a strong deposition of tin oxide over the FTO. In Figure 2.12 some of the thin films synthesized have been shown.

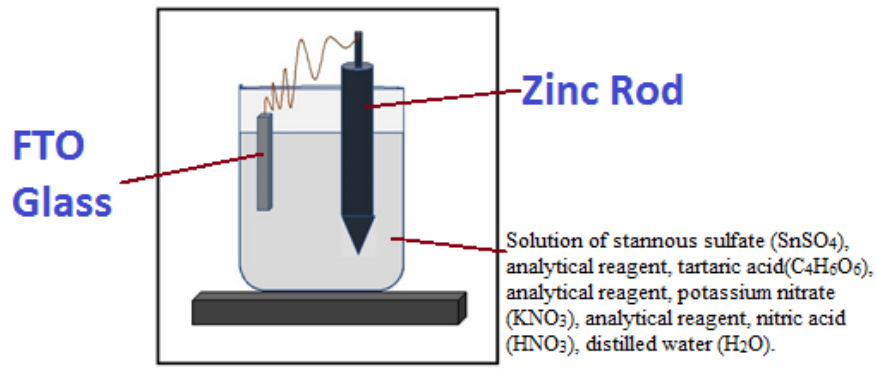

Figure 2.1. Schematic Representation of the Setup

Figure 2.12. Tin Oxide Thin Film

2.3 Characterization

The optical characterization of the thin film was performed with UV-Vis Spectrophotometry in the instrument JASCO UV, present in Jadavpur University under the model V-730. The measuring range was set at 800nm-200nm with a data interval of 0.2nm, bandwidth -1.0nm, and response time of 0.06s. So reasonable and accurate results could be made from this.

3. RESULTS AND DISCISSION

3.1 Optical Characterisation of SnO_2 Thin Film

3.11 UV-Vis absorbance

The optical properties were measured with JASCO UV by plotting a graphical relationship between absorbance wave spectra of tin oxide thin film and wavelength of UV. In figure 3.11, the graph can be divided into prominent two regions, one the region between the range of 200 nm-525nm where the absorbance was compatible to an extant and peak absorbance at 407.9 nm was observed which indicates a red shift or bathochromic shift with that respect to that of 312 nm found by Bhagwat et al 2015[21]. The other is between 525nm-800nm, in which there is a decrease in absorbance with an increase in wavelength, and a steady curve decrease is observed.

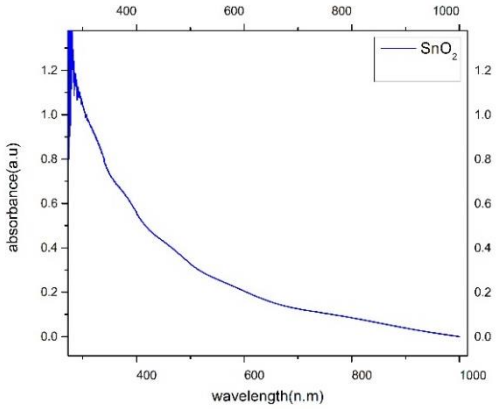

Figure 3.11. Absorbance Vs Wavelength

3.12 Band Width

The optical analysis of absorbance spectra is done by tauc plot, which gives the relationship between absorption coefficient(α) and photon energy(hv) by the equation 3.12 [21]

$$(\alpha h\nu)^n = K(h\nu - E_g) \qquad \textbf{(3.12) [21]}$$

Where α denotes the absorption coefficient, h is plank's constant (6.62×10^{-34} m^2kg/s),ν is the frequency, Eg is the estimated optical bandwidth of the thin film and n is the nature of transmission which in this case is taken as 2 due to the direct bandgap nature of tin oxide.[21] As we can see in Figure 3.12, the graph has x coordinates as $h\nu$ and y coordinates as $(\alpha h\nu)^2$,and a straight line is extrapolated which meets the energy axis at 3.04 eV. Thus, estimating the optical bandwidth of the synthesized material to be 3.04 eV which is within the range of (2.5– 3.4 eV) as stated by Elango et al 2015[20].

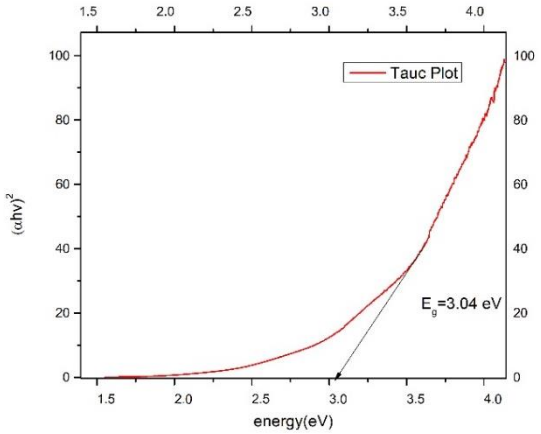

Figure 3.12. Tauc Plot of the Thin Film

4. CONCLUSION

A cost-effective and replicable procedure for synthesizing tin oxide has been demonstrated in this paper. Since the process is in an early phase, it needs to be optimized. A distinct redshift is seen in the bandgap of the substrate which could be reduced by controlling the amount of chelating agent (in this case tartaric acid) dissolved in the solution so that the speed of tin oxide deposition can be regulated. Or by heat treatment of the thin films for better oxidation. Nevertheless, the rough estimates indicated that the process is an advantageous one and can be further optimized.

5. FUTURE WORK

In the future, for better characterization XRD (X-ray Powder Diffraction), SEM (Scanning electron microscope), and other analysis techniques should be conducted to have a clearer idea about the morphological, elemental, etc characterization of the material. Tin oxide is used for a variety of applications especially gas sensors, which could be fabricated after the initial stages.

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8. Biographies

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