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Article

Electrical Characterization of Fluorine Doped Tin Oxide Deposited by Spray Pyrolysis Technique and Annealed under Nitrogen Atmosphere

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Abstract: Spray pyrolysis technique has been used to deposit Fluorine doped Tin Oxide (FTO) thin films. The deposited thin films were then annealed under Nitrogen atmosphere for 60 minutes at temperatures of 423K, 573K and 723K respectively. Four-point probe method was used to measure the electrical properties of the FTO thin films. The average sheet resistance was found to be within the range of 3.62×10^5 to $1.22 \times 10^4 \Omega/\text{cm}^2$. The resistance and the resistivity of the films were also investigated. It has been observed that as the annealing temperature increases the values sheet resistance and the resistivity decreases.

Keywords: Fluorine doped Tin Oxide (FTO), Electrical properties, annealing condition.

1. Introduction

Transparent conductive oxides (TCO) have become increasingly important in a large variety of applications due to demands for optically-transparent, conductive materials. Fluorine-doped tin oxide

(FTO) is an ideal candidate for applications requiring TCO due to its ability to adhere strongly to glass, resistance to physical abrasion, chemical stability, high optical visible transparency, and electrical conductivity. In the case of FTO, fluorine (F) is doped into tin oxide where fluorine substitutes for O^{-2} and acts as an electron donor, resulting in an n-type degenerate semiconductor. Fluorine is an ideal substitution for oxygen because the anionic sizes are rather similar R_0^{2-} = 1.32 Å and R_F^- = 1.33 Å and the energy of the Sn−F bond (∼ 26.75 D^o /kJ mol^{-1}) is similar to that of the Sn−O bond (∼ 31.05 D^O/kJ mol^{-1}). FTO is frequently used as an alternative to ITO when chemical and electrical stability at elevated temperatures is required for device fabrication or application. FTO is more thermally stable because it does not depend on oxygen vacancies to provide charge carriers (Russo and Cao, 2008). The doped SnO_2, due to its wide band gap (3.67 eV), high optical transmittance in the visible range and good substrate adherence, has many potential applications such as gas sensors, solar energy conversion, infrared-reflecting glass, antistatic coatings and transparent electrode preparation (Wu, 2010). Unlike many other film deposition techniques, spray pyrolysis is a very simple and relatively cost-effective processing method (especially when considering the equipment costs). It is an extremely easy technique for preparing films of any composition. Spray pyrolysis does not necessitate high-quality substrates or chemicals. The method has been employed for the deposition of dense films, porous films, and for powder production (Khanaa and Mohanta, 2013). Spray pyrolysis has been used for several decades in the glass industry and in solar cell production. Among the various deposition techniques, spray pyrolysis is well suited for the preparation of doped tin oxide thin films because of its simple and inexpensive experimental arrangement, ease of adding various doping materials, reproducibility, high growth rate and mass production capability for uniform large area coatings (Hadi, 2014).

2. Materials and Methods

2.1. Cleaning of the Materials

The soda lime glass, the beakers, and measuring cylinder were washed first with detergent and rinsed with distilled water, then washed with acetic acid and finally rinsed with ethanol.

2.2. Preparation of Fluorine Doped Tin Oxide (FTO)

10.0g of tin tetrachloride pentahydrate ($SnCl_2.5H_2O$) was measured using the digital weighing machine (balance) and dissolved in 100ml of ethanol in a closed container. The solution was stirred continuously until all the tin chloride pentahydrate was completely dissolved in the ethanol. The solution was labeled A.

2.0g of ammonium chloride was measured and dissolved in 4.0ml of ethanol in another container; the solution was stirred continuously until all the salt dissolved. And then the solution labeled B.

After both solutions have been allowed to fully stir, the tin chloride penthydrate solution is placed in a water bath and heated to 60°C. Next, the ammonium fluoride solution is then admixed. The combined solution is allowed to stir overnight to ensure complete mixing, and the resulting solution is clear and stable.

2.3. Synthesis of Fluorine Doped Tin Oxide (FTO) Thin Films

The spray pyrolysis technique was employed to deposit the fluorine doped tin oxide thin films. Soda lime glass was used as substrate. The precursor solution was the mixture tin chloride pentahydrate solution and ammonium fluoride solution. The solution was sprayed on the heated glass substrate using KM – 150 spray pyrolysis deposition machine (SPD). The deposition temperature and solution flow rate were maintained at 723K and 1.5ml/min respectively. Other parameters were kept constant. Film thickness of 100nm was deposited on the glass substrate at a nozzle – substrate distance of 11.0cm. The growth rate was approximately 25nm/min. The film thickness was measured using a taly step profilometer (roughness detector with a stylus Taylor Hobson model).

Four samples were prepared and labeled as F_1 : as deposited sample, F_2: sample annealed under nitrogen atmosphere at 423K, F_3: sample annealed under nitrogen atmosphere at 573K, and F_4: sample annealed under nitrogen atmosphere at 723K.

2.4. Annealing of the Samples

Three samples designated as F_2, F_3, and F_4 were taken and inserted into a horizontal cabolite oven one after the other and heated at temperatures 423K, 573K and723K respectively under nitrogen atmosphere for one hour. The samples were allowed to cool at room temperature before characterization. The sample marked F_1 was unannealed to serve as reference sample.

3. Results and Discussion

The electrical properties of the films were measured at room temperature. The resistivities of the four samples were measured using four – point probe method (SDY- 5 machine). Four-point probe method is an electrical resistance measuring technique that uses separate pairs of current-carrying and voltage-sensing electrodes to make more accurate measurements than traditional two-terminal (2T) sensing. A probe head with tungsten carbide tips with a point radius of 0.002", a probe spacing of 0.05" and a probe pressure of 70 to 180 grams was used for all measurements. Current was supplied by a

Crytronics model 120 current source with a range of applied currents between 1μA to 100 mA. Voltages were measured by a Keithley model 181 nanovolt electrometer with an input impedance of greater than 1 GΩ. Sheet resistance (Rs in units of Ω/sq.) and resistivity (ρ in units of Ω cm) were calculated from (Valdes, 1954):

$$\rho = 2\pi s \frac{V}{I} \qquad (1)$$

3.1. Electrical Studies

Figures 1a and 1b show the film resistivity and sheet resistance against annealing temperature plotted for as-deposited and annealed FTO films; as can be seen, the films are all conductive and as the annealing temperature increases the resistivity and sheet resistance values decreases. This decrease is due to the formation of FTO at higher temperatures, which is not possible at low temperatures. The change in the sheet resistance is attributed to the excess fluorine atoms that lie in the grain boundary regions Sn-F bonds and cannot act favorably for the growth of SnO_2 nanocrystals (Wu, 2010). The decrease in resistance indicates an enhancement of the carrier density in the film, and the increased carrier density is expected to lead to higher optical scattering and absorption in the spectral range (Kang, 2011). According to Russo and Cao (2007), as the annealing temperature increases, the crystallinity of the thin film also increases. This increase in grain size allows for superior charge mobility, thereby improving the electrical performance. The resistivity increases from $1.22\times10^{-1}\Omega$cm to $9.31\times10^{-1}\Omega$cm, according to Yousaf and Ali (2009), fluorine atoms incorporates at the interstitial sites and crystal structure of the films start to deteriorate, hence decreases the mobility of the free electrons and increases the electrical resistivity.

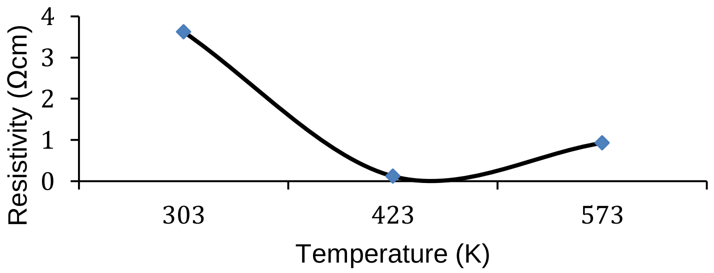

Figure 1a. Resistivity of FTO films as a function of annealing temperature

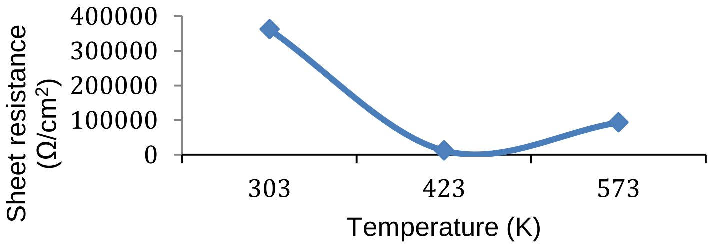

Figure 1b. Sheet resistivity of FTO films as a function of annealing temperature.

Table 1 shows the values of resistance, sheet resistance, and resistivity for as-deposited FTO films, FTO films annealed at 423K and FTO films annealed at 573K.

Table 1. Values of Resistivity ρ, sheet resistance R_S and Resistance R of FTO films annealed at different temperature.

Temperature	Resistance, R	Sheet resistance, R_s	Resistivity, ρ
303K	$7.99\times10^{4}\Omega$	$3.62\times10^{5}\Omega/cm^{2}$	$3.623\Omega cm$
423K	$2.69\times10^{3}\Omega$	$1.22\times10^{4}\Omega/cm^{2}$	$1.22\times10^{-1}\Omega cm$
573K	$2.05\times10^{4}\Omega$	$9.30\times10^{4}\Omega/cm^{2}$	$9.31\times10^{-1}\Omega cm$

4. Conclusions

This work reports the preparation and characterization of fluorine doped tin oxide thin films annealed under Nitrogen atmosphere at various temperatures. These films were deposited by spray pyrolysis technique. The annealing temperature and the annealing condition influenced the electrical properties of the thin films.

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