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Electrical and structural properties of aluminium doped tin oxide codoped with sulphur for solar energy

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Abstract

Thin films of Tin Oxide co-doped with 28 atomic percentages of Aluminium (i.e. 28 at% Al) and varied concentration of Sulphur were prepared on 1 mm thick, 1 cm by 1 cm glass substrates at 470 0C by Spray Pyrolysis technique. Films were produced from 2.0 M solution of hydrous Tin Chloride dissolved in Ethanol with 38 % Hydrochloric acid concentration, 1.5 M aqueous Aluminium chloride and 2.0 M aqueous solution of Ammonium Sulphide. The effects of Sulphur concentration on structural and electrical properties of transparent Tin Oxide thin films were investigated in the atomic percentage of Sulphur content ranging from zero to fifty (i.e. 0at%S -50at%S) with a fixed 28at%Al content. Polycrystalline structures without any second phases were observed with preferential orientations along the (110), (101), (200) and (211) planes. The average grain size as determined from the (110) peaks lay in the range 19.2 nm-47.7 nm. The minimum resistivity was found to be 1.15x10-3 Ωcm for the Tin Oxide films doped with 32 at% Al content and 9.59x10-3 Ωcm for Tin Oxide films co-doped with 28 at% Al and 20 at% S content. It was observed that Aluminium doping lowered the grain size significantly but doping to optimum level of 32 at% Al content increases electrical conductivity of tin oxide. When Sulphur was intentionally introduced in the crystal structure of 28 at% Al doped Tin Oxide, the electrical conductivity decreased appreciably and the grain size increased.

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Keywords: Spray pyrolysis; transparent conductors; co-doping.

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1. Introduction

Thin films of Transparent Conducting Oxide (TCO) found many applications among poly-crystalline thin films in technology and industry [1] e.g. in optoelectronic devices, solar cells, electromagnetic shielding functional glasses and gas sensors. According to published results, the best n-type TCOs are Tin-doped Indium Trioxide (In_2O_3: Sn), Fluorine-doped Tin Dioxide (SnO_2:F), Aluminium-doped Zinc Oxide (ZnO: Al) thin films and Niobium-doped Titanium Oxide (TiO_2:Nb) [2]. The most commonly used materials are some heavily doped, wide band gap oxide semiconductors like Zinc Oxide doped with Indium or Aluminium, Tin Oxide doped with Antimony or Fluorine, Indium Oxide doped with Tin and Cadmium Stannate. The basic point in chemical design of p-type TCOs is to reduce strong localization of positive holes to Oxygen ions on the valence band edge. Indeed, a positive hole localizes on a single Oxygen atom and cannot migrate within the crystal lattice and therefore it constitutes a deep acceptor level [3]. The usual method of solving this problem is to use a cation of closed shell levels which degenerate with Oxygen 2p states. Copper and Silver have appropriate 10d states for this purpose, which yield a more dispersive band above the non-bonding oxygen 2p or cation 3d state. This has lower effective mass [4]. Practically, a donor impurity in the TCO films e.g. Antimony or Fluorine in the tin oxide, Tin in Indium Oxide and Aluminium in Zinc Oxide increase free electron concentration and therefore the n-type conductivity. However, a lower valence cation as acceptor impurity e.g. Zinc or Copper in Indium Oxide, and Indium or Aluminium in Tin Oxide produce a hole and increases the hole concentration and, therefore the p-type conductivity [5]. SnO_2:F thin films, due to their high conductivity, lowest cost, best thermal stability, best mechanical and chemical durability and lowest plasma frequency, are the most widely used in different applications [3]. The objective of this research is therefore to synthesise improved solar energy material from tin oxide co-doped with aluminium and sulphur using a vacuum free process of Spray Pyrolysis, which is cheapest compared to other processes. The produced film was an improved structure though with low conductivity.

2. Methodology

2.1. Sample Preparation

Aluminium co-doped with Sulphur Tin Oxide i.e. SnO_2:(Al+S) and undoped Tin Oxide films were pyrolytically deposited onto 1 mm thick, 1 cm by 1 cm glass substrates by Spray Pyrolysis. The detailed description of the Spray Pyrolysis reactor and the optimization of the film growth is given elsewhere [4]. The heterogeneous reaction involved in the film formation is [1,4]:

$$SnCl_{4(aq)} + 2H_2O_{2(s)} \Rightarrow SnO_{2(s)} + 4HCl_{(aq)} \quad (1)$$

of which the film would be an insulator if the reaction is complete. However, since the films obtained by pyrolytic decomposition are conducting, the expected reactions are:

$$2SnCl_{4(aq)} + 5H_2O_{(l)} \Rightarrow SnO_{2(s)} + SnO_{(s)} + 7HCl_{(aq)} + O_2 + 1/2Cl_2(g) + 3/2H_{2(g)} + e \quad (2)$$

$$2SnCl_{4(aq)}) + 5H_2O_{(l)} \Rightarrow SnO_2 + SnO_{(s)} + 8HCl_{(aq)} + O_{2(g)} + H_{2(g)} + e \quad (3)$$

The SnO_2:(Al+S) films were produced from 2.0 M solution of hydrous Tin Chloride ($SnCl_4.5H_2O$) in Ethanol mixed with a few millilitres of Hydrochloric acid, 1.5M aqueous dopant solution of hydrous Aluminium Chloride ($AlCl_3.6H_2O$) and Ammonium Sulphide (NH_4S). The deposition apparatus for spray pyrolysis in fig.1 with a separate spray nozzle is used for the dopant solution.

The doping concentration was varied by a carrier-gas flow rate ratio of x: 5 for NH_4S to $SnCl_4.5H_2O$ (+$AlCl_3.6H_2O$) solutions, where (x = 0.00, 1.00, 1.36, 1.60, 2.00, 2.65) i.e. variation in doping concentration was achieved by increasing the NH_4S flow rate. Compressed air was used as the carrier gas. For the different samples,

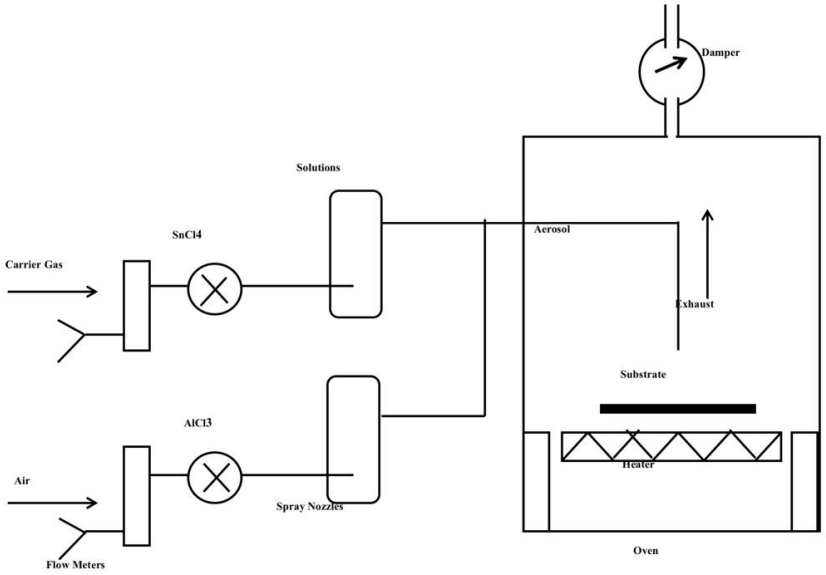

Fig. 1. Schematic diagram for spray pyrolysis oven used to prepare SnO2:Al thin films.

the substrate temperature was maintained at 470^0C, which is known to be the optimum temperature for formation of Tin Oxide films [4].

2.2. Sample Characterization

The structural properties were determined using Siemens D5000XRD system with CuK_α(λ=1.54056nm) radiation. The effective grain size was determined from the Full-Width at Half-Maximum (FWHM) of X-ray peak lines of the (110) plane using Scherer formula of equation (4) and the Williamson-Hall formula of equation (5).

$$g = \frac{180 \times \lambda}{\beta\pi \cos\theta_{hkl}} K \qquad (4)$$

where g is grain size, β is FWHM and K is a constant (0.9) with the grazing incident angle of 10 in parallel beam geometry of diffraction angle (2θ) between 200 and 700. The information on strain (ε) and grain size was obtained from the relation:

$$\frac{\beta\pi\cos(\theta)}{\lambda \times 180} = \frac{1}{g} + \frac{\varepsilon \sin(\theta)}{\lambda} \qquad (5)$$

The practical method for measuring electrical film resistance for the deposited film is by use of R-square probe (which is the most accurate for homogeneous sample with low resistivity). Hall measurements in conjunction with resistivity measurements were used to determine charge carrier concentration, charge mobility and charge carrier type (p-type or n-type)**.** The experimental results were compared with simulated results from Drude and Kim modelling. Electrical resistivity of the films was calculated from two adjustable parameters of Drude free electron model: plasma frequency (Ω_p) which is oscillation strength; and damping constant γ. The plasma frequency is proportional to the square root of the carrier density and the damping constant is proportional to the inverse of the mobility. The Drude dielectric susceptibility, χ_{Drude}, expressed as a function of frequency ω, is given as (6):

$$\chi_{\text{Drude}(\omega)} = \frac{\Omega_p^{\ 2}}{\omega^2 + i\omega\gamma} \quad (6)$$

The parameters of that model related the concentration of the charge carriers and their mobility to properties of the dielectric function. After a model parameter fit of the simulated spectrum to measured data, the carrier concentration and the mobility or resistivity were computed. The Drude model relates the macroscopic susceptibility to the microscopic quantities of carrier concentration n_e and mobility μ:

$$n_e = \frac{4\pi^2 c_o^2 \varepsilon_o m}{e^2} \Omega_p^2 \quad (7)$$

$$\mu = \frac{e}{m} \frac{1}{c_o \Omega_\tau} \quad (8)$$

Where e is the charge ($1.6\text{x}10^{-19}$C), c_o is the speed of light in a vacuum ($3.0\text{x}10^8$ m/s) and m the effective mass of the charge carriers (m is 0.3 times the mass of an electron ($9.1\text{x}10^{-31}$ kg). Resistivity was computed using the formula:

$$\rho = \frac{\Omega_\tau}{2\pi c_o \varepsilon_o \Omega_p^2} \quad (9)$$

Similarly, from equations (7), (8) and (9), charge mobility was expressed as:

$$\mu = \frac{2\pi}{\rho n e} \quad (10)$$

3. Results and Discussion

The choice of maintaining Aluminium dopant at 28 at% in Tin Oxide was made after considering previous research on SnO_2:Al. It is from this doping that indicated improvement in structural and electrical properties of Tin Oxide with dopant ranging between 28 at% Al and 32 at% Al. It was therefore expected that co-doping Tin Oxide with Aluminium and Sulphur will further improve these properties of the oxide. We can therefore start this investigation by starting with the 28 at% Al with varied concentration of Sulphur.

3.1. Structural properties

The orientation of the peaks was towards (110), (200) and (211) planes as illustrated in X-ray diffractograms in figure 2 with peaks generally decreasing with introduction of Sulphur dopant.

The intensity of peaks drops significantly and they become less conspicuous as co-doping with sulphur increases, keeping aluminium constant at 28 at%. No extra peaks are observed ruling out the possibility of phase separation. Moreover, there is no change of position of XRD peaks with change of co-doping concentration implying no alloying between Aluminium, Sulphur and Tin Oxide [1,2]. The slope of the graph $\beta\cos(\theta)/\lambda$ versus $\sin(\theta)/\lambda$ of figure 3 depicts the strain as being (0.004 – 0.152) compared to the literature value 0.0135 for sprayed SnO_2 films [3].

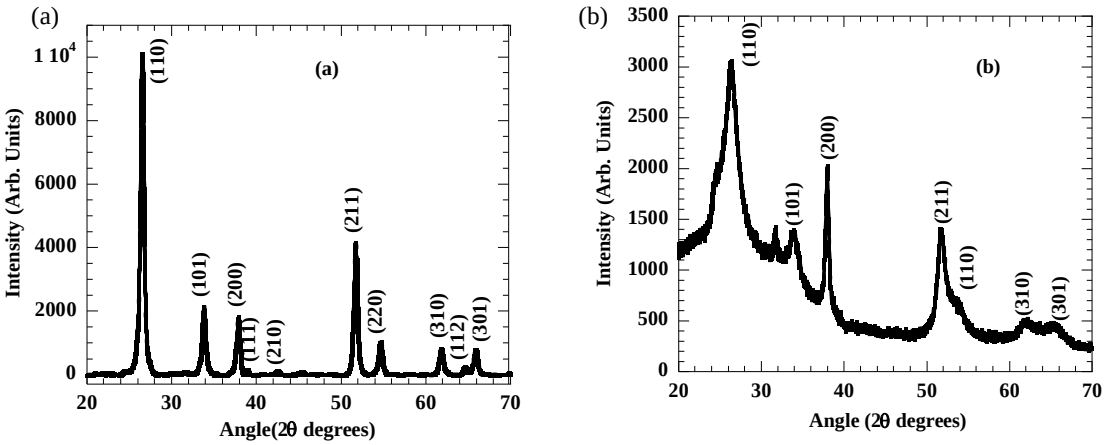

Fig. 2. X-ray Diffractograms of SnO2 co-doped with 28 at% Al (a) without Sulphur and (b) with 20at % Sulphur

The intercept on the y-axis gives the crystallite size of (19.24– 47.68) nm for the 28 at% Al, 50 at% S doped SnO_2 and undoped SnO_2, respectively from Scherer formula while from Williamson Hall formula, grain size is in the range (21.4 – 53.0) nm compared to the literature value of 25 nm for undoped Tin oxide [3]. Figure 4 shows that S doping lowers the grain size. With increasing S dopant in the Tin Oxide film, the crystallinity of SnO_2 decreases as strain increases.

3.2. Electrical properties

From the simulated and experimental values of resistivity and electron density of co-dopan**t**, it is illustrated that these materials were better conductors with lower co-dopant. However, the Aluminium doped was best if compared with Sulphur co-doped material. Resistivity increases with co-dopant concentration as illustrated in figure 5 for both experimental and calculated resistivity. This makes the co-doped material to be a lesser conductor. The electron density seemed to increase with the co-dopant concentration up to 28 at% Al co-doped with 20 at% S. This trend however changed thereafter as the electron density decreased with increase in co-dopant as illustrated in figure 6. The charge mobility seems to play a significant role in increasing the conductivity of the co-dopant as illustrated in figure 7. The best co-dopant had concentrations 28 at% Al, 20 at% S with hall mobility of 4.04 $cm^2V^{-1}s^{-1}$.

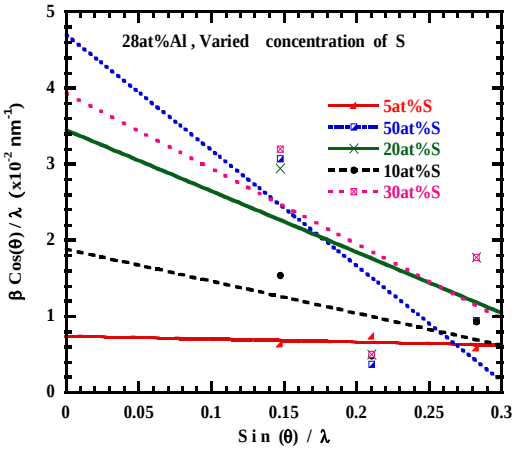

Fig. 3. Graph of βCos(θ)/λ versus Sin(θ)/λ for Al and S doped Tin Oxide

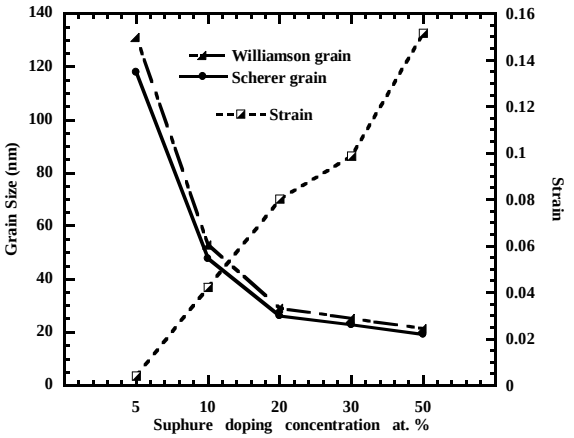

Fig. 4. Grain size/ Strain versus Sulphur doping concentration

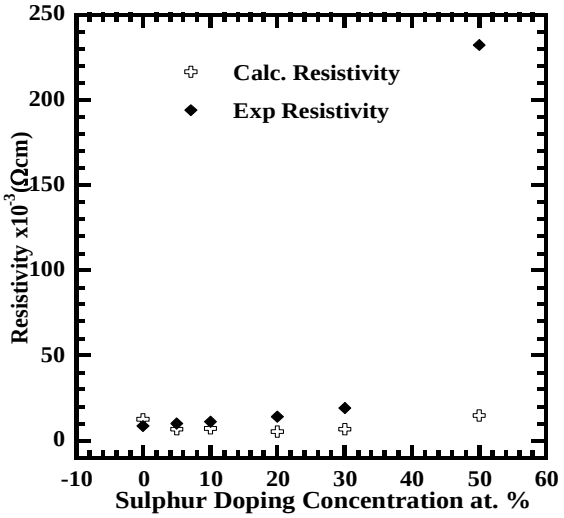

Fig. 5. Resistivity versus doping concentration of Sulphur

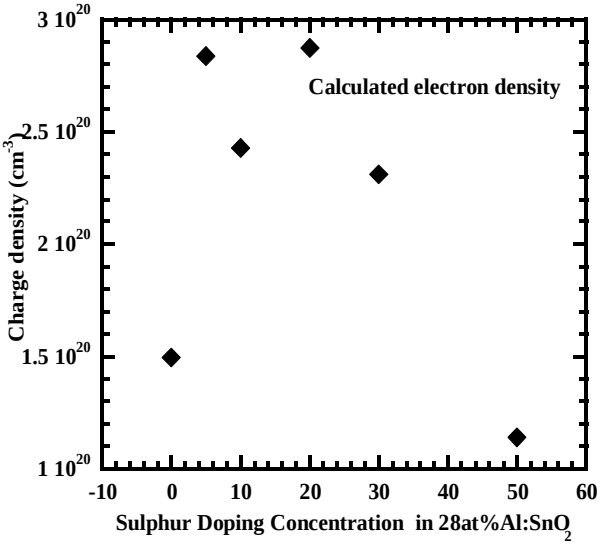

Fig. 6. Charge density versus doping concentration of Sulphur

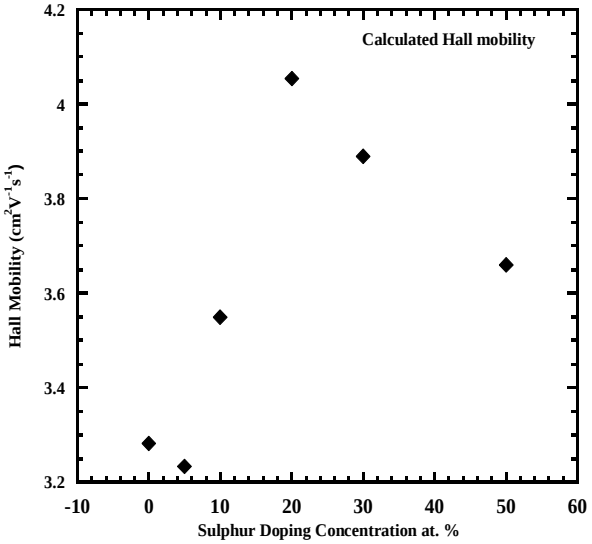

Fig. 7. Hall mobility versus doping concentration of Sulphur

4. Conclusions

From the XRD diffractograms, co-doping Tin Oxide with Sulphur and Aluminium does not cause alloying and phase separation. Hence, there is no shift in lattice parameters. The structure of the Oxide is however improved as depicted with increased strain and reduced grain sizes with increased doping concentration. The resistivity of the (Al+S) co-doped SnO2 increased with increasing Sulphur concentration, which lay in the range from 8.70x10-3 Ω cm to 2.327x10-5 Ω cm. The highest Hall mobility of 4.05 cm2V-1s-1 was obtained. The highest charge density of 2.87x1020cm-3 was recorded. Generally, for conductivity of Aluminium Tin Oxide codoped with Sulphur, the hall mobility was more of a determining factor than the carrier concentration.

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