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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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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,