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Effect of F doping on physical properties of (211) oriented SnO_2 thin films prepared by jet nebulizer spray pyrolysis technique

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ABSTRACT

Transparent conducting fluorine doped tin oxide (FTO) thin films have been prepared jet nebulizer spray pyrolysis technique at 500 °C for different doping concentrations. The X-ray diffraction spectra confirm the polycrystalline nature of SnO_2: F with tetragonal structure. All the films show a preferred growth orientation along (211) diffraction plane. Scanning electron microscope images show that the films have a uniform surface morphology with well defined pyramid like grains. The AFM results of the films indicate that the surface roughness is increased with F doping. The optical transmittance of FTO films is improved from 75 to 92% in the visible region of the solar spectrum and the optical absorption of the films is very low. The blue shift of optical band of the films is explained by Burstain–Mass effect. The observed blue shift of the UV emission band in the photoluminescence spectra confirms the incorporation of F into tin oxide crystal lattice. The presence of functional groups and chemical bonding were confirmed by FTIR. Hall Effect measurements show that the prepared films having n-type conductivity with low resistivity (2.3×10^{-4} Ω-cm) and high carrier concentrations (6.9×10^{20} cm^{-3}).

1. Introduction

In general the transparent conducting oxide (TCO) semiconductors exhibit a high transmission in the visible region and high electrical conductivity. Due to these properties, the TCO materials have been used in a wide range of applications in science and technology. Among the available TCOs the Tin oxide (SnO_2) is a promising candidate for optoelectronic applications such as solar window layers of thin film solar cells, light emitting diode (LED), photo transistors and gas sensors [1–4]. It has a tetragonal structure with a wide band-gap of >3.6 eV and behaves as n-type semiconductor [5]. The nature of the properties of the crystalline SnO_2 depends on different kind of defects and impurities that are present in the structure of this material. These defects could affect its structural, optical and electrical properties of thin films. The conductivity of SnO_2 can be increased by doping with group III, V–VII elements of the periodic table; some of which are Al, Sb, B and F. Among these elements, the most widely used dopant is fluorine because of the fact that the resultant fluorine-doped tin oxide (FTO) film is highly stable both chemically and thermally. Also the F^- has ionic radii (1.17 Å), which is lower than the ionic radii of anion

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O^{2-} (1.22 Å) in SnO_2 and the fluorine may substitute for the anion (O^{2-}) in SnO_2 and acts as a donor in SnO_x:F [6]. Either doped or undoped SnO_2 thin films can be synthesized by numerous techniques such as Sol–Gel Process [1], APCVD [7,8], DC Reactive Sputtering [9], Thermal Evaporation [10], Pulsed Laser Deposition [11], Spray Pyrolysis [12–14]. Several researchers successfully prepared the thin films by Nebulizer Spray Pyrolysis (NSP) technique [15–17]. All of these methods have advantages and disadvantage, but jet nebulizer spray pyrolysis has a noticeable advantage, it is a low-cost and non-vacuum technique for large area applications and can produce high quality film with low precursor volume. The working of NSP method is based on the Bernoulli principle. When a pressurized flow of air is directed through a constricted orifice; the velocity of the airflow is increased and creates a jet stream. The impact of a jet stream with liquid produces aerosol particles (particle size ~2.5 μm). The mist form of solution is helping to improve the quality of film and can obtain a uniform growth due to gradual nucleation with minimum wastage.

In the present work, the structural, morphological, optical, and electrical properties of fluorine doped tin oxide thin films deposited by jet nebulizer spray pyrolysis technique. The prepared films were characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM), Atomic force microscopy (AFM), UV–Vis spectrophotometer, Room temperature PL, Fourier transform infrared spectroscopy (FTIR) and Hall Effect measurements.

2. Materials and method

In this work, the jet nebulizer spray pyrolysis apparatus (Fig. 1) is used to prepare SnO_2: F thin films, which consists of a jet nebulizer, L tube to convey the aerosol, substrate holder with heater and air compressor. We have used the following materials to prepare tin doped indium oxide thin films. Tin (II) Chloride dehydrates ($SnCl_2 \cdot 2H_2O$) with a purity of ≥98%, Ammonium Fluoride (NH_4F) with a purity of ≥96% and Acetic acid (CH_2COOH) with a purity of ≥99% supplied by MERCK company. The doubly distilled water and Borosilicate glass (1.35 mm thickness) is used as solvent and substrate respectively.

First the Tin (II) Chloride dehydrate is dissolved in 100 ml double distilled water to make 0.4 M starting solutions. Doping of Fluorine was achieved by adding Ammonium Fluoride in the starting solution. A few drops of acetic acid were added to obtain a clear and homogeneous solution. The doping level in the solution varied from 0 to 20 wt% in steps of 5 wt%. The mixture was stirred under constant speed for 1 h with a magnetic stirrer. Prior to the deposition, glass substrates (1 sq inch) were cleaned with acetone, isopropyl alcohol, and distilled water successively for 15 min in ultrasonicator. The substrate temperature for each deposition was kept at 500 °C in the air atmosphere. The prepared solution was sprayed with a jet nebulizer (HUDSON RCI micro mist, droplet size is ~2.7 μm) on the heated substrate with spray rate 0.5 ml/min using compressed air as a carrier gas. The nebulizer was kept at a distance of 5 cm from the substrate surface.

The structural parameters of spray coated SnO_2: F films were analyzed by X-ray diffractometer (XRD) using the PANalytical system with Cu $K\alpha_1$ radiation (k = 1.54056 Å). Surface morphology and topography was carried out by the Scanning Electron Microscope (ESEMQUANTA200, FEI-Netherland) and Atomic Force Microscopy in contact mode (Agilent 5500) respectively.

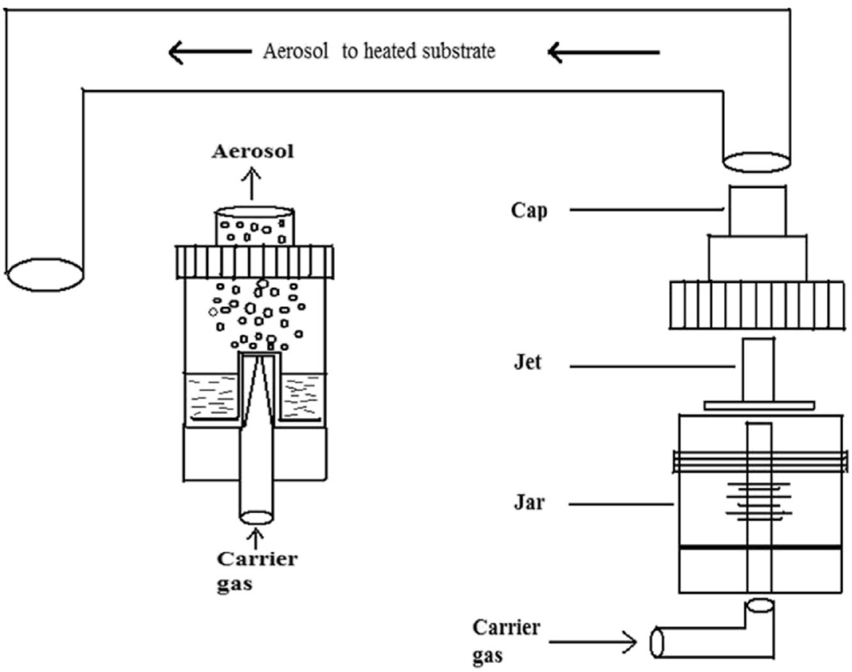

Fig. 1. Schematic diagram of jet nebulizer apparatus.