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Effect of solvent volume on the physical properties of undoped and fluorine doped tin oxide films deposited using a low-cost spray technique

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ABSTRACT

Undoped and fluorine doped tin oxide films were deposited from starting solutions having different values of solvent volume (10–50 ml) by employing a low cost and simplified spray technique using perfume atomizer. X-ray diffraction studies showed that there was a change in the preferential orientation from (211) plane to (110) plane as the volume of the solvent was increased. The sheet resistance (R_{sh}) of undoped SnO_2 film was found to be minimum (13.58 KΩ/□) when the solvent volume was lesser (10 ml) and there was a sharp increase in R_{sh} for higher values of solvent volume. Interestingly, it was observed that while the R_{sh} increases sharply with the increase in solvent volume for undoped SnO_2 films, it decreases gradually in the case of fluorine doped SnO_2 films. The quantitative analysis of EDAX confirmed that the electrical resistivity of the sprayed tin oxide film was mainly governed by the number of oxygen vacancies and the interstitial incorporation of Sn atoms which in turn was governed by the impinging flux on the hot substrate. The films were found to have good optical characteristics suitable for opto-electronic devices.

1. Introduction

Transparent conducting oxides (TCO) such as SnO_2, In_2O_3, $CdSnO_4$, CdO and ZnO have been widely used in the optoelectronic devices, coating for energy conversion windows, detection of oxidizing and

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reducing gases [1], solid state gas sensor devices [2], heat reflecting mirrors, solar cells, defrost windows, anti static materials, touch panels and photo conductors [3–5] because of their wide range of band gap values (2.8–4.2 eV) which allow visible and reflect IR radiation, high electrical conductivity, excellent chemical stability and other useful characteristics [6,7]. Amongst them, tin oxide (SnO_2) is one of the prominent low cost conducting materials as well as window layers in these devices. Pure SnO_2 is either an insulator or an intrinsic semiconductor. In order to use it as a conducting layer, the resistivity of SnO_2 has to be reduced. To reduce the resistivity, dopants such as F, Cl, Sb, Br, Ni and Cu can be employed. In undoped SnO_2 also, the resistivity can be reduced by creating oxygen vacancies in the SnO_2 lattice.

Among the currently available TCO materials, fluorine doped tin oxide (FTO) is one of the most competing substitutes for indium doped tin oxide. Pure and fluorine doped tin oxide films have been prepared by various techniques such as electron beam evaporation (EBE) [8], chemical vapour deposition [9], pulsed laser deposition [10], sol–gel [11–13], thermal evaporation [14] and spray pyrolysis [15–18], etc. Among these techniques, spray pyrolysis is simple, inexpensive and has many other advantages such as easy doping and scaleable processing in industrial productions, etc. [19,20]. In the present study, pure and FTO films are fabricated by employing a further simplified spray technique using perfume atomizer which has several advantages over conventional spray technique [21,22]. Many researchers studied and reported the effect of concentration of the precursor solution on the physical properties of undoped and fluorine doped tin oxide films, but in this study, the effect of solvent volume on the properties of these films have been studied systematically and reported which is not available in the literature to the best of our knowledge.

2. Experimental method

Pure and fluorine doped tin oxide films have been produced by an easy, low cost and simplified spray pyrolysis method using perfume atomizer. The schematic diagram of the experimental set up and other details have been reported elsewhere [23]. An aqueous solution of high pure $SnCl_2{\cdot}2H_2O$ was used as the deposition solution. Fluorine doping was achieved by adding NH_4F (10 wt.%) with the starting solution. Different sets of starting solutions were prepared by dissolving 2 g of $SnCl_2{\cdot}2H_2O$ with different volumes of (10, 20, 30, 40, and 50 ml) doubly deionized water. A very small amount of HCl (0.1 mol/l) was used to dissolve $SnCl_2{\cdot}2H_2O$ and NH_4F. This solution was magnetically stirred for 1 h and it was followed by an ultrasonic agitation for 20 min. The precursor solution thus obtained was sprayed manually by means of a perfume atomizer on pre-heated (340 ± 5°C) glass substrates of dimensions 75 × 25 × 1.35 mm^3. The temperature of the substrates was monitored using a temperature controller with chromel–alumel thermo couple. The intermittent spray deposition followed in this study is a two step procedure: a spray and 5 s interval. The substrates were pre-cleaned ultrasonically with organic solvents and doubly deionized water for degreasing and to remove the contaminations if any, on the surface. The experiment was repeated several times to confirm the reproducibility.

X-ray diffraction patterns were recorded using X-ray diffractometer (PANalytical-PW 340/60 X'pert PRO) which was operated at 40 kV and 30 mA with X-ray source of CuKα radiation having wavelength 1.5406 Å. Scanning electron microscopy (SEM) images, atomic force microscopy (AFM) images and optical transmission spectra were obtained using a scanning electron microscope (HITACHI-S-3000H), atomic force microscope (Veeco-di CPII) and the UV–Vis-NIR double beam spectrophotometer (Perkin Elmer LAMBDA-35) respectively. The electrical parameters were measured with the use of a four-point probe and Hall effect apparatus (ECOPIA HMS-3000) with van-der Paw configuration.

3. Results and discussion

3.1. Structural studies

Fig. 1 shows the XRD patterns of the undoped tin oxide films grown from starting solutions having different solvent volumes. All the patterns fit well with the tetragonal structure of SnO_2 and contain the characteristic SnO_2 peaks only. The preferential orientation is along the (2 1 1) plane for the films