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Effect of the fluorine content on the structural and electrical properties of SnO_2 and $ZnO–SnO_2$ thin films prepared by spray pyrolysis

Arturo I. Martinez*, Dwight R. Acosta

Thin Films Laboratory, Institute of Physics-UNAM, A.P. 20-364, 01000 Mexico D.F., Mexico

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Abstract

Transparent conducting oxide thin films of SnO_2 (TO) and of $ZnO–SnO_2$ binary–binary system (ZO–TO system) have been prepared by the spray pyrolysis method. In this work, we study the influence of fluorine doping concentration on the structural, optical and electrical properties of films above mentioned. Fluorine doped tin oxide (FTO) thin films on glass present resistivity around to 4×10^{-4} Ω cm, high optical transmission close to 80% and optical band gap close to 4.5 eV. X-ray diffraction measurements show that the FTO films are highly oriented along the (200) plane parallel to the substrate. ZO–TO films deposited at substrate temperature of 450 °C using alcoholic solutions of $ZnCl_2/SnCl_4$ with a Zn/Sn=0.40 atomic ratio, presented polycrystalline structures with a mixture of zinc oxide and tin oxide phases (ZO–TO system). These films present a resistivity close to 6 Ω cm and an optical transmission in the visible range of 82%. Further addition of NH_4F to the starting solution lowered the resistivity of ZO–TO thin films to 2.43×10^{-1} Ω cm as a consequence of fluorine incorporation. From electrical and optical measurements, the Moss–Burstein effect was found in both TO and ZO–TO thin films.

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1. Introduction

Transparent conducting oxides (TCO) are wide band gap semiconductors ($\geq$3.1 eV) whose properties strongly depend on the stoichiometric deviation, e.g. oxygen deficiency (SnO_{2-x}) and on the nature and quantity of impurities trapped into the host lattice, such as in Sn:In_2O_3 and F:SnO_2 (FTO) materials [1]. Tin oxide and zinc oxide, in thin film configuration are technologically important materials because its use in photovoltaic cells [2], gas sensors [3], electrochromic devices and low-e windows [4], photocatalysis [5], etc. In order to combine and to stabilize the properties of TCO films, it is proposed in the literature as an alternative to fabricate TCO materials based in multicomponent oxides, which consist in a combination of binary or ternary compounds such as: $In_2O_3–ZrO_2$, $SnO_2–ZrO_2$[6], $ZnO–SnO_2$ [7], $In_2O_3–Sc_2O_3$ [8], $ZnO–V_2O_5$ [9].

The TCO thin films can be prepared by a variety of methods such as chemical vapor deposition (CVD), sputtering, sol–gel process and spray pyrolysis (SP). The sputtering and evaporation processes often prove to be too expensive for some industrial applications. The chemical spraying offers a competitive alternative for the massive production of these coatings. The SP method presents some noticeable advantages, such as: a wide possibility of varying the films properties by changing the composition of the starting solution (introduction of dopants and change the film microstructure) and low cost when large-scale production is needed.

$ZnO–SnO_2$ system has been prepared by sputtering [7] and very recently, by SP method [10]; this material combines the thermal stability in a hydrogen environment of ZnO and the good chemical stability of SnO_2. By sputtering Minami, et al. [7] deposited amorphous films with a resistivity of 4–

* Corresponding author.
E-mail addresses: artmtz@correo.unam.mx (A.I. Martinez), dacosta@fisica.unam.mx (D.R. Acosta).

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5×10^{-3} Ω cm and average transmission of about 80% using a target with a Zn content of about 33 at.%. By spray pyrolysis, Bagheri et al. [10] found polycrystalline films with high resistivity of 2 Ω cm and an optical transmission of 80%. In a similar way to tin oxide thin films, it can be expected that the higher resistivities found in films deposited by spray pyrolysis can be lowered by doping the oxide with fluorine.

The aim of this work is to study the effect of the fluorine concentration on the structural, optical and electrical properties of TCO thin films of tin oxide (TO) and zinc oxide–tin oxide (ZO–TO system). We present results of undoped and fluorine doped TO and ZO–TO thin films deposited by an optimized spraying procedure which let us to fix important parameters such as concentration of precursors in the solution, substrate temperature, solution flow rate and nozzle to substrate distance. In a first step, we studied the effect of the substrate temperature on the physical properties of TO thin films and after finding an optimal substrate temperature, we proceeded to study the effect of the fluorine concentration on the physical properties of TO and ZO–TO thin films.

2. Experimental details

The deposition of the films was performed as follows: The substrate was placed in contact with an aluminum hot plate and its temperature (T_s) was monitored by a temperature controller using a standard thermocouple system. Prior to deposition, the substrate was kept at different temperatures between 350 to 550 °C in steps of 50 °C. The spraying process was done with an especially designed glass atomizer, which has an output nozzle of 0.5 mm in diameter. 25 ml of the starting solutions was sprayed on glass or sapphire substrates, using compressed air (345 kPa) with a solution flow rate of 5 ml/min and a nozzle to substrate distance of 30 cm. The process involves spraying cycles of 1 s, followed by short periods with no spray of 20 s, to avoid a too strong cooling of the substrate. The schematic diagram of the SP apparatus used in this work is shown in Fig. 1.

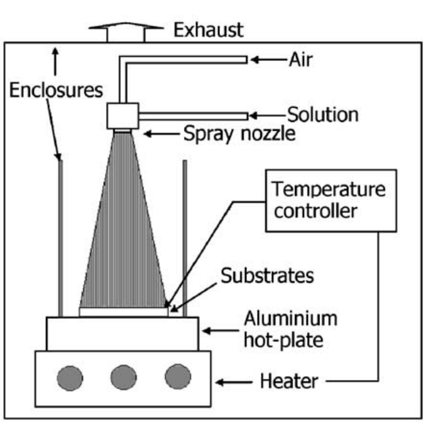

Fig. 1. Schematic diagram of the spray pyrolysis apparatus used for the deposition of TO and ZO–TO films.

Pure and fluorine doped TO layers were prepared spraying an alcoholic solution of $SnCl_4$ with different amounts of fluorine. The solutions used were 0.2 M alcoholic solutions of $SnCl_4.5H_2O$ with different concentrations of NH_4F, so that the proportions of fluorine to tin (F/Sn) run from 0 to 100%. Undoped and fluorine doped ZO–TO thin films were deposited by spraying an alcoholic solution containing 0.2 M of $SnCl_4.5H_2O$ and 0.08 M of $ZnCl_2$ in a Zn/Sn=0.40 atomic ratio, with different concentrations of NH_4F, so that the fluorine to tin at. ratios, (F/Sn), was varied from 0 to 100%. Hydrochloric acid was added to increase the stability of the solutions [10].

The film thickness was measured with an Alpha Step 200 profilometer. The electrical resistivity, Hall mobility and carrier concentration were determined at room temperature using the van der Pauw method using a MMR Technologies equipment, Hall effect parameters were measured in a magnetic field of 0.3–0.5 T. The optical transmission (T) spectra of the films were obtained using an Agilent 8453 UV–visible spectroscopy system, all the T values reported along this paper were measured without subtract the absorption of the substrate. The structural characterization was carried out with an AXS D8 Advance X-ray diffractometer operating in Bragg–Brentano θ–θ geometry with Cu K_α radiation. Compositional studies were done with energy disperse X-ray spectrophotometer (EDS) attached to a LV-JEOL 5600 scanning electron microscope (SEM), in this study small pieces of coated glass without the typical gold film were mounted on the SEM holder. Also a JSPM-5200 atomic force microscope was used to study the surface in tapping mode using a commercial silicon cantilever with a spring constant of 40 N/m, all measurements were made at ambient conditions.

3. Results and discussion

3.1. Tin oxide thin films

From the X-ray diffraction (XRD) patterns, the lattice constants, grain sizes and its orientation in our films were determined. All XRD patterns present in Fig. 2 contain only SnO_2 peaks. TO thin films deposited at 350 °C show an amorphous nature with (110) and (101) peaks of very low intensity corresponding to the SnO_2 cassiterite structure according to the joint committee on powder diffraction standards (JCPDS) 41–1445 card [11], see Fig. 2(a). When T_s increases, the amorphous background diminished and the intensity of the diffraction peaks increased, this behavior is due to the fact that at low T_s the starting materials ($SnCl_4$) and undesired by-products (HCl, CO_2, CO, etc.) are present in the films, suggesting that the T_s is not enough for completing the chemical reaction, e.g. the droplet hit on the hot substrate removing a lot of heat causing a partial decomposition of the starting materials. TO and FTO thin films prepared at 450 °C are polycrystalline materials and present a single phase with a