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Effect of intermittent time on structural, optoelectronic, luminescence properties of sprayed antimony doped tin oxide thin films

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ABSTRACT

By implementing spray pyrolysis technique the influence of intermittent time on to the structural, optical and electrical properties of the antimony doped tin oxide (ATO) thin films were analyzed. It is seen that all the films exhibit tetragonal crystal structure with a preferential growth along the (2 1 1) and (3 0 1) planes. The crystallite size of the film estimated from the XRD pattern decreases with increase in intermittent time. The pyramidal crystallites formed due to coalescence are observed from SEM images. The average optical transmittance in the visible range is 75%. The calculated IR reflectivity was found to be in the range of 92–97%. For the typical film deposited with 15 s intermittent time, the values of sheet resistance and resistivity of about 3.12 Ω/□ and 4.2×10^{-4} Ω cm, respectively. The films deposited with 15 s intermittent time has higher φ (23.95×10^{-3} Ω^{-1}) than the values of φ reported in literature for ATO films prepared by spray pyrolysis technique. All the above mentioned properties of the ATO films deposited by spray pyrolysis technique are useful for the production of low-cost, large area coatings of ATO films.
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1. Introduction

Now a days, tin oxide (SnO_2) doped materials is attracting great attention for their potential application as one of the Indium tin oxide (ITO) substitution. Due to high transparency to visible light, relatively high electron concentration and mobility makes (ATO) as an important material in the field of transparent conducting oxides (TCOs). It is also observed from literature that tin oxide thin films doped with antimony exhibit interesting electrochemical properties in different electrode processes [1], such as low temperature electrochemical combustion of organic pollutants, ozone production and organic electro-synthesis [2]. Also ATO is a transparent conducting oxide (TCO), which has been focus of intensified study due to its technological importance as a solar energy material (i.e., energy generation and energy savings), electrochemical properties, thermal and environmental stability, low cost and easy fabrication [3]. The coexistence of optical transmission and electrical conductivity in undoped tin oxide is related to oxygen deficiency; in fact intrinsic SnO_2 stoichiometric samples are highly resistive [4]. The structural tolerance to a high concentration of donor oxygen vacancies is possible due to the multivalence of tin [5]. Usually SnO_2 is doped with Sb because the substitution of Sn^{4+} by Sb^{5+} leads to a donor center very close to the conduction band. Thus ATO exhibits interesting properties, which arise from the coexistence of oxygen vacancies with antimony doping. ATO coatings can also act as heat mirrors owing to their high reflectivity in the infrared range. Studies of Sb doping in SnO_2 should focused on increasing the electron concentration without film degradation and drastically reduced mobility will aid TCO research. The current research on ATO thin films has focused on the improvement of coating process, the influence of doping in order to improve optoelectronic properties and the extensions of ATO thin film application fields. Some of the researcher's premeditated ubiquitous and immediate goal of doped SnO_2 research is to improve transparent contacts for light emitting diodes and solid-state lasers [6]. Beyond these technological applications, diminutive effort has been focused on enhancing and controlling the fundamental properties of SnO_2 by doping with antimony for low cost and also allows further studies of its material properties.

It is found that ATO thin films have been deposited by using a wide variety of physical and chemical techniques. It is possible to modify the properties by controlling the preparative conditions, which in turn makes ATO suitable for a particular application. Therefore, the preparation technique plays a vital role. Various

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deposition techniques such as electron beam evaporation [7], radio-frequency magnetron sputtering [8], chemical vapor deposition (CVD) [9] and sol–gel [10] have been employed. Although ATO in thin film form can be obtained from a wide variety of deposition techniques, we are principally interested in films deposited by chemical techniques, such as spray pyrolysis deposition. Spray pyrolysis (SP) is a simple and inexpensive technique having advantages like ease of adding dopant material, reproducibility, high growth rate and mass production capability for uniform large area coatings, which are desirable for industrial, solar cell and gas sensor applications.

The properties of chemically sprayed SnO_2 thin films can be modulated mainly by (i) the substrate temperature, (ii) the nature of the dopant, (iii) quantity, (iv) spray rate and (v) nozzle to substrate distance (NSD) and (vi) intermittent time. In spray pyrolysis, the droplets are transported to the substrate in an ideal fashion, i.e., as the droplet approaches the surface, the solvent in the droplet vaporizes completely. The time available for warm up in the vicinity of the substrate depends upon the droplets velocity, which in turn depends upon the propelling and retarding forces acting on them. In many experimental situations, the control on the retarding forces operating on the droplets is limited, which seriously restrict the frequency at which the droplets are transported to the substrate and thus the growth rate. The optimum velocity for the droplets is often obtained by adjusting the nozzle to substrate distance and intermittent time. In this respect, the effect intermittent time in ATO has received much attention as compared with other parameters. The intermittent spraying may promote this process by placing intervals between repeated depositions [11].

In the present paper, we have studied effect of intermittent time (sec) in producing ATO films of lower electrical resistivity and higher optical transmittance as well as highest figure of merit. The objective of present work to synthesize ATO thin films by spray pyrolysis method so as to achieve relatively high optical transmittance and with suitable electrical conductivity ($\sim 2.38 \times 10^3\ \Omega^{-1}\ cm^{-1}$).

2. Experimental

ATO thin films were deposited onto ultrasonically cleaned preheated corning glass substrates using the chemical spray pyrolysis technique. Spraying solution (2M) of optimized doping concentration, quantity and nozzle to substrate distance [12,13] was prepared by mixing the appropriate volumes of pentahydrate stannic chloride ($SnCl_4{\cdot}5H_2O$) powder (L.R. grade, Thomas Baker) and $SbCl_3$ (L.R. grade, s d fine) in double distilled water. The ATO thin films were prepared in different sets of experiment to see the effect of intermittent time. The all other process parameters were kept constant and critically studied the effect of intermittent time on physical properties of ATO thin film. The intermittent time was varied from 5 to 20 s at the interval of 5 s. All other preparative parameters were kept at their optimum values.

The structural properties were studied by a Philips X-ray diffractometer PW-1710 (λ, 1.5405 Å) using Cu-Kα radiation in the span of 10–80°. Surface morphology of the thin film was studied with JEOL JSM 6360 scanning electron microscope (SEM). Optical absorption study was carried out in the wavelength range 300–1100 nm using spectrometer Systronic Model-119. The room temperature PL spectra were recorded using a PerkinElmer luminescence spectrometer (model: LS55) equipped with a xenon flash lamp and a grating to select the source of excitation. The excitation and emission spectra were recorded in the fluorescence mode over the wavelength range 225–700 nm. The electrical parameters such as sheet resistance and figure of merit were measured at room temperature by Hall Effect set-up, in Van der Pauw configuration, supplied by Scientific Instruments, Roorkee, India.

2.1. Deposition of ATO thin films

In spray pyrolysis, the droplets are transported to the substrate in an ideal fashion, i.e., as droplet approaches the surface, solvent in the droplet vaporizes completely. The droplets undergo vaporization if their residence time in the vicinity of hot substrate surface is sufficiently long so as to warm it up to the ambient temperature. The time available for warm up in the vicinity of the substrate depends upon the droplet velocity, which in turn depends upon the propelling and retarding forces acting on them. The optimum velocity for the droplets is often obtained by adjusting the control parameters such as solution and gas flow rates, NSD and intermittent time.

During spray deposition, the substrate temperature falls due to continuous spray. Therefore, it is necessary to stop the spraying process to attain the optimum temperature. We have studied the effect of waiting time (i.e., intermittent time) on film properties. The process involves spraying cycles of 5 s followed by 5 s without spray, to avoid cooling of the substrate.

2.2. Growth process and reaction mechanism

A close control of the spraying parameters such as doping, substrate temperature, uniformity of temperature throughout the substrate etc., produces films with the required properties like high visible transmittance and low resistivity.

Generally in spray pyrolysis, the chemical reaction of thin film formation of SnO_2 is as follows:-

$$SnCl_4 + 2H_2O \rightarrow SnO_2 + 4HCl \quad (1)$$

If the reaction is completed, the resulting SnO_2 would become an insulator. Since the films obtained by pyrolytic decomposition are conducting, the expected reactions are,

$$2SnCl_4 + 4H_2O \rightarrow SnO_2 + Sn\,O + 7HCl + \frac{1}{2}O_2 + \frac{1}{2}Cl_2 + \frac{1}{2}H_2 + e^- \quad (2)$$

$$2SnCl_4 + 4H_2O \rightarrow SnO_2 + Sn\,O + 8HCl + \frac{1}{2}O_2 + 2e^- \quad (3)$$

Therefore, the conductivity of undoped SnO_2 is attributed to a combination of chlorine ion and oxygen vacancies which result from incomplete decomposition of $SnCl_4$ and incomplete oxidation of the films. These defects are considered to be electron donors.

The addition of a trivalent cation such as Sb^{3+} to SnO_2 increases the number of oxygen vacancies. This causes an increase in the conductivity of the film according to the following mechanism

$$2Sb^{3+} \rightarrow 2Sb_{Sn} + V_o^{\cdot\cdot} \quad (4)$$

where Sb_{Sn} denotes an Sb occupying a Sn position, generating a negative charge. If Sb^{5+} is present, the SnO_2 conductivity increases due to the presence of free electrons

$$2Sb^{5+} \rightarrow 2Sb_{Sn} + 2e^- \quad (5)$$

In both cases, antimony cations will form a solid solution with tin oxide and the conductivity will depend on the doping level [14]. These facts show the importance of controlling the preparation conditions of tin oxide, such as the oxide stoichiometry and deposition temperature. It is directly responsible for the oxide conductivity Moreover; the preparation conditions will also affect the crystallinity [15], morphology [16] and electrocatalytic activity [17] of SnO_2 films.

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