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Improvement of the optoelectronic properties of tin oxide transparent conductive thin films through lanthanum doping

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ABSTRACT

This work highlights some physical investigations on tin oxide thin films doped with different lanthanum content (ratio La–to-Sn = 0–3%). Such doped thin films have been successfully grown by spray pyrolysis onto glass substrates at 450 °C. X-ray diffraction (XRD) patterns showed that SnO_2:La thin films were polycrystalline with tetragonal crystal structure. The preferred orientation of crystallites for undoped SnO_2 thin film was along (110) plane, whereas La-doped ones have rather preferential orientations along (200) direction. Although the grain size values exhibited a decreasing tendency with increasing doping content confirming the role of La as a grain growth inhibitor, dislocation density and microstrain values showed an increasing tendency. Also, Raman spectroscopy shows the bands corresponding to the tetragonal structure for the entire range of La doping. The same technique confirms the presence of La_2O_3 as secondary phase. Moreover, SEM images showed a porous architecture with presence of big clusters with different sizes and shapes resulting from the agglomeration of small grains round shaped. Photoluminescence spectra of SnO_2:La thin films exhibit a decrease in the emission intensity with La concentration due to the decrease in grain size. Optical transmittance spectra of the films showed high transparency (~80%) in the visible region. The dispersion of the refractive index is discussed using both Cauchy model and Wemple–Di-Domenico method. The optical band gap values vary slightly with La doping and were found to be around 3.8 eV. It has been found that La doping causes a pronounced decrease in the sheet resistance by up to two orders of magnitude and allows improving the Haacke's figure of merit (Φ) of the sprayed thin films. Moreover, we have introduced for a first time a new figure of merit for qualifying photo-thermal conversion applications. The obtained high conducting and transparent SnO_2:La thin films are promising to be useful in various optoelectronic applications.

1. Introduction

Transparent conductive oxides (TCO) thin films of compound semiconductor materials have been studied extensively in recent years because of their high transmittance and electrical conductivity in various optoelectronic devices, such as solar cells, light-emitting diodes, and panel displays. Tin oxide (SnO_2) thin films are considered one of the most suitable materials for these applications due to their physical properties such as high electrical conductivity, high transparency in the visible part of the spectrum and high reflectivity in the IR region [1].

Moreover, the attractiveness of SnO_2 is increased by its simplicity and the ease by which it can be synthesized in thin-film form a variety of techniques such as the chemical vapor deposition [2], the pulsed laser deposition [3], the spray pyrolysis [4] and the sol–gel process [5]. Among these techniques, the spray pyrolysis method seems suitable due to its simplicity, low cost, easy to add doping materials and promising for high rate and mass production capability of uniform large area coatings in industrial applications. The properties of the spray deposited SnO_2 thin films were found to be dependent on the processing conditions and the nature of precursors used. The precursors play a key role in the structure, the morphology, the growth as well as the electrical and optical properties of the deposited material.

Undoped SnO_2 is a highly transparent, widely applicable material with n-type conductivity and wide band gap energy (E_g = 3.6–4.0 eV) whose electrical properties critically depend upon its intrinsic defects (O vacancies or Sn interstitials). Also, there are a number of exhaustive papers published on SnO_2 itself, as well as its deposition in thin-film.

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However, for optoelectronic devices, particularly in flat panel displays and solar cell applications, mainly by reducing signal loss and delay, the conductivity should be improved without affecting the transmission. Indeed, to control and improve the physical properties of this oxide for a wider range of possible applications, various elements such as: Sb [6], F [4], Mo [7], Li [8] and Nd [9], have been tested as doping. Similarly, the investigations of SnO_2 coatings are interesting and can be used as a heat mirror suitable for application in solar photo-thermal conversion [7,10].

Recently, trivalent rare-earth ions such as Ce^{3+}, Er^{3+}, La^{3+} and Yb^{3+} doped semiconductors have attached much attention because their optical properties promising applications in optoelectronic devices [11]. It was established that these ions act as grain growth inhibitors and remain mainly localized as aggregates at the grain boundaries due to the limitation of solubility.

To date, there are few attempts using La element as doping in tin oxide thin films. To ovoid corrosive process that affects metal structures, the synthesis of $Sn_{(1-x)}La_xO_2$ (x = 1,3 and 5 mol%) ceramic thin film deposited on AISI 304 steel have been tested [12]. These films were deposited via dip-coating and spin-coating techniques to reach a real packing, and then heat-treated at temperatures ranging from 400 to 500 °C during two hours. Raman spectroscopy and scanning electron microscopy (SEM) revealed crack-free, single-phase, dense thin films with good adhesion to the metal substrate for the entire temperature range. No later, Gaik Tin Ang et al. [13] prepared La–SnO_2 catalytic pellets using modified sol–gel process. High sensitivities towards 500 ppm of ethanol, acetone and methanol were achieved for 5 at.% of La content with values lying in 55–59 domain. The average response time for the developed sensors is of the order of 15 s showing a fast response sensor that could be used for volatile organic compounds. Moreover, Fu et al. [14] attributed the effect of La doping on hindering crystallite growth to the solute drag and lattice distortion resulting from La dissolving in the bulk phase of SnO_2 to form solid solution, rather than the monolayer of La on the surfaces of SnO_2.

To the best of our knowledge, few works have been conducted on the effect of La doping on the optoelectronic properties of SnO_2 synthesized by spray pyrolysis route. Therefore, the aim of this present study is to fabricate SnO_2: La thin films from $SnCl_2$ precursor and explore the influence of La content on the crystallographic, morphological, electrical and optical properties of tin oxide. For each specific application, we used an appropriate figure of merit, whose one is introduced by us, to evaluate the performance of our prepared films. The results obtained are compared and discussed with the specified results by several researchers.

2. Experimental details

2.1. Films preparation

Undoped SnO_2 thin films were deposited by the spray pyrolysis technique. A solution of stannous chloride dehydrates ($SnCl_2.2H_2O$-0.1M) in a mixed solvent of 90% methanol and 10% deionized water was used as a precursor. A few drops of HCl were added to reach a clear solution and it was sprayed onto glass substrates. Before the deposition, the substrates were cleaned with alcohol and deionized water, then dried with nitrogen gas. The temperature was fixed at 450 °C using a digital temperature controller with a thermocouple located onto a metallic hot plate surface. Consecutively, under similar experimental conditions, lanthanum-doped SnO_2 thin films have been elaborated by adding lanthanum chloride heptahydrate ($LaCl_3.7H_2O$) as source of La in the starting solution. La-to-Sn molar ratios ([La]/[Sn]) were 0%, 1%, 2% and 3%. All the starting solutions were vigorously stirred at room temperature during 30 min in order to achieve the homogeneity of the solution. Nitrogen was used as the gas carrier (pressure at 0.35 bar) through a 0.5 mm diameter nozzle. As reported by Amlouk et al. [15], the nozzle-to-substrate plane distance was fixed at the optimal value of 27 cm. The nozzle movement speed in the plane (x,y) allows the control of the thin film surface uniformity. The total volume of solution sprayed was 50 ml and the rate of spray was 4 ml/min. After deposition, the coated substrates were allowed to cool down naturally at room temperature.

2.2. Characterization techniques

First, all sprayed thin films were characterized by X-ray diffraction (XRD) measurements using *Philips PW 1729 system* diffractometer with monochromatic CuK_α radiation (λ = 1.54059 Å). Surface morphology and grain sizes of SnO_2:La sprayed thin films were studied by means of Scanning electron microscopy (SEM). The SEM images were performed by *JEOL-JSM 5400* microscope at an operating voltage of 15 kV. Computer program *ImageJ* was used in the processing of SEM images to obtain particle size distributions. Second, Raman spectroscopy was recorded at room temperature by means of a Jobin Yvon HR LabRAM in backscattering co-focal configuration with a spatial resolution of 1 μm and spectral resolution less than 0.35 cm^{-1}. The light excitation is an Ar^+ laser at the wavelength of 488 nm. On the other hand, the optical transmittance T(λ) and reflectance R(λ) of SnO_2:La sprayed thin films were recorded using a *Perkin–Elmer Lambda 950* spectrophotometer in a 250–2000 nm wavelength domain. The photoluminescence spectra were performed at room temperature using a *Perkin–Elmer LS 55* Fluorescence spectrometer with 325 nm wavelength excitation. Finally, measurements of the electrical conductivity and the sheet resistance of all synthesized thin films were carried out by the well-known four probe method.

3. Results and discussion

3.1. Structural analysis

To investigate the crystal structure, lattice parameters and crystallite sizes of La-doped SnO_2 thin films, XRD analysis was used. Fig. 1 shows the XRD patterns of the undoped and La-doped SnO_2 thin films with various La concentrations. All the diffraction peaks matched well the tetragonal rutile structure of SnO_2 according to JCPDS 72–1147 card with a maximum intensity corresponding to

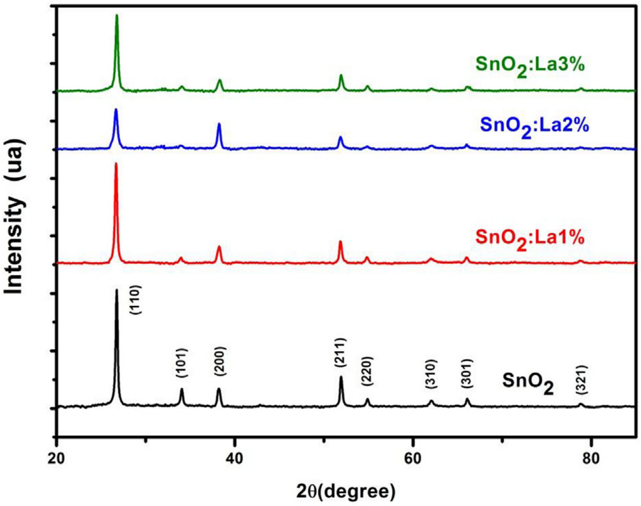

Fig. 1. X-ray diffraction pattern of La-doped SnO_2 thin films.