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Review

Influence of the oxygen pressure on the physical properties of the pulsed-laser deposited Te doped SnO_2 thin films

E. Chan y Díaz[a,*], Juan M. Camacho[b], A. Duarte-Moller[a], R. Castro-Rodríguez[b], P. Bartolo-Pérez[b]

[a] Centro de Investigación en Materiales Avanzados, S.C. (CIMAV), Miguel de Cervantes Saavedra 120, Complejo industrial Chihuahua, Chihuahua 31109, México
[b] Applied Physics Department, CINVESTAV-IPN, Unidad Mérida, 97310 Mérida, Yucatán, México

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ABSTRACT

Tellurium doped tin oxide (Te:SnO_2) thin films were prepared by pulsed-laser deposition (PLD) on glass substrates at different oxygen pressures, and the effects of oxygen pressure on the physical properties of as-grown and post-annealed Te:SnO_2 films were investigated. The as-grown films deposited between 1.0 and 50 mTorr showed some evidence of diffraction peaks, with electrical resistivity of $\sim 8 \times 10^{1}\ \Omega$ cm, but increasing the oxygen pressure up to 100 mTorr, three diffraction peaks (1 1 0), (1 0 1) and (2 1 1) were observed containing the SnO_2 tetragonal structure, at 100 mTorr the electrical resistivity decreased abruptly at minimum value of $4 \times 10^{-2}\ \Omega$ cm, and increased reaching values of $\sim 4 \times 10^{-1}\ \Omega$ cm. The optical transmittance of the films increased with increasing oxygen pressure and high transmittance (~87%) in VIS region by the films prepared at 100 mTorr and higher. The band gap of as-grown films was ~3.5 eV corresponding at of the SnO_2. After of post-annealed at 500 °C at atmospheric pressure for 30 min all films showed crystallization, and notable electrical resistivity changes were observed. The carrier density increased monotonically in the range of oxygen pressure between 1.0 and 100 mTorr, reaching values of $\sim 2 \times 10^{18}\ cm^{-3}$, then, it decreased abruptly in films grown at 125 mTorr. While the mobility of the free-carrier decreased in the range of oxygen pressure between 1.0 and 100 mTorr, reaching minimum values of $\sim 5.8\ cm^2\ V^{-1}\ s^{-1}$. The optical transmittance showed similar characteristic like the as-grown films. The figure of merit at 100 mTorr of as-grown films had value $\sim 1.2 \times 10^{-5}\ \Omega^{-1}$, and for post-annealed films at 100 mTorr the figure of merit was similar $\sim 1.7 \times 10^{-6}\ \Omega^{-1}$, indicating they were the better films.

Contents

1. Introduction

Transparent conducting oxides (TCOs) are widely used for a variety of applications, including transparent electrodes for flat panel displays and for photovoltaic cell, low emissivity windows, windows defrosters, transparent thin films transistor, light emitting diodes, and semiconductor lasers [1–7]. Undoped tin oxide (SnO_2), which is a wide band gap (E_g) *n*-type semiconductor (3.6 eV) [8], belongs to the important family of oxide materials that combine low electrical resistance with high optical transparency (>80%) in the visible range (VIS) of the electromagnetic spectrum. SnO_2 films have some practical advantages over transparent conducting oxides (TCOs) films that contain indium or cadmium, as they are less expensive and non-toxic.

There are many different techniques used for deposition SnO_2 films: spray pyrolysis [9], reactive electron beam evaporation [10], rf-sputtering [11,12], dc-magnetron sputtering [13], chemical vapor deposition [14], reactive ion assisted deposition [15], filtered vacuum arc deposition [16] and pulsed-laser deposition (PLD) [17]. However, all methods require high substrate temperature or post-annealed in order to fabricate good-quality polycrystalline films. PLD has emerged as one of the simplest and most versatile meth-

* Corresponding author. Tel.: +52 614 439 1127; fax: +52 614 439 4884.
E-mail address: enrique.chan@cimav.edu.mx (E. Chan y Díaz).

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ods for the deposition thin films of a wide variety of materials [18]. A major advantage of PLD is that the stoichiometry of the target can be retained in the deposited films. In particular PLD in oxidizing gases is one of the promising methods of preparing complex oxide films, and has been applied to the deposition of TCOs films as various high-quality SnO_2 thin films with low resistivity [19–21]. In all the techniques used for the fabrication of SnO_2 films, the structural, optical and electrical properties of the films have been found to depend critically on the oxygen partial pressures (PO_2) and the substrate temperature (T_s) [22,23].

As we know, TCOs have conductivity (σ) in the range 10^2–10^6 $S\,cm^{-1}$. The conductivity is due to doping either by oxygen vacancies (V_O) or by extrinsic dopant. In the absence of doping, these oxides become very good insulators, with resistivity (ρ) > $10^{10}\,\Omega\,cm$. The electrical conductivity of *n*-type TCOs thin film depends on the carrier density in the conduction band and on their mobility: $\sigma = \mu ne$, where μ the electron mobility, n is the carrier density and e is the electron charge. Due to $E_g > 3.0$ eV separating the valence band from the conducting band, the conduction band cannot be thermally populated at room temperature ($kT \sim 0.03$ eV, where k is Boltzmann's constant), hence, stoichiometric crystalline TCOs are good insulators [7]. In the case of intrinsic materials, the density of conducting electrons has often been attributed to the presence of unintentionally introduced donor centers, usually identified as metallic interstitials (M_i) or oxygen vacancies (V_O) that produce shallow donor or impurity states located close to the conduction band. The excess of donor electrons is thermally ionized at room temperature, and move into the host conduction band. However, experiments have been inconclusive as to which of the possible dopants is the predominant donor [24]. Extrinsic dopant has an important role in populating the conduction band, and some of them have been unintentionally introduced.

On the other hand, a great variety of dopants have been studied in order to improve the electrical properties of SnO_2 for certain applications. The common extrinsic *n*-type dopants [11,12] are Sb, F, As, Nb and Ta. However, the electrical conductivity control of this material is not developed yet because there are problems that normally grown SnO_2 films seriously suffer from donor-type defects such a tin interstitial (Sn_i), V_O and these dopants impurities, which could deteriorates the mobility of the electron as consequence of a structural distortion due at the excess from a critical value of these donor-type defects. Tellurium is a semi metallic element with valence states of −2, +4 and +6 and is often used alloyed to Sn as SnTe, the multiple valences of the tellurium and its affinity with Sn can be used to tellurium doped SnO_2 as donor-type defect such a tellurium interstitial into SnO_2 structure and as consequence improve the electrical properties of the SnO_2.

Recently, it has been reported that the post-annealed process is also effective to reduce the residual donor-type defects on grown SnO_2 films in addition to the growth parameters such as surface treatment, substrate temperature, and Sn/O ratio [16]. In dependence of the technique of growth, usually the electron concentration varies with the annealing temperature and reaches minimum or maximum values in dependence of its temperature. This suggest that the increase and decrease of electron concentration is caused by to generation and reduction of V_O, also it suspected that this behavior is due to the reduction of Sn_i as has been observed in SnO_2 films grown by pulsed-laser deposition that electron concentration continuously decreases with the increase of annealing temperature [8,25]. These reports commonly refer that the annealing process under certain conditions is helpful for improve the structural properties of the films.

In this paper, we report on the investigation of the heat treatment on the physical properties of the Te-doped SnO_2 thin films grown by pulsed-laser deposition and the behavior of structural, electrical and optical properties.

2. Experimental procedure

Te-doped SnO_2 thin films were deposited on 25 mm × 25 mm glass substrates (Corning 2947) using a Nd:YAG laser (1064 nm, 10 ns full width at half-maximum) at a repetition rate of 5 Hz on a target with rotation of 30 rpm in order to avoid pitting of target at any given spot and to obtain uniform thin films. The substrate is attached with a stainless steel mask to the substrate holder which was heated by a tungsten lamp. The laser was focused through a 50 cm focal length lens onto a rotating target at a 45° angle of incidence. The energy density of the laser beam on the target surface was maintained at ~2.0 J/cm^2. The target-to-substrate distance was 60 mm. Before laser irradiation the deposition chamber is evacuated down to a base pressure of 10^{-6} Torr using a diffusion pump and a rotary pump. The target was prepared from 1.0 wt.% Te powder (6 N) mixture with SnO_2 powder (5 N) and sintered (thickness of 0.5 mm and diameter of 15 mm). During deposition, high purity oxygen (99.997%) was introduced into the chamber at different pressures (ranging from 1.0 to 150 mTorr). Substrate temperature for all growths was maintained at 500 °C. The ablations shots for all films were 10^3. The substrates were carefully cleaned in an ultrasonic bath for 10 min with acetone and methanol, rinsed in deionized water, and subsequently dried in air before deposition.

After deposition, the substrate was maintained at 500 °C for 30 min with same PO_2 was grown and was cooled to room temperature in the base pressure. The film was divided into two equal parts, one was annealed at 500 °C for 30 min at atmospheric pressure in a muffle in order to compare their physical properties as-grown and after of post-annealed.

The thickness (d) of the films was measured by a surface profilometer Dektak-8, Veeco. The electrical properties were determined at room temperature by Van der Pauw-Hall method. For a uniform thickness, the electrical resistivity (() can be determined using the relation (= $R_{Sheet}d$, where R_{Sheet} is the sheet resistance. All sheet resistance and resistivity values were determined as the average of three measurements of three different films deposited at same conditions. The optical transmittance measurements were performed using VIS-near-IR spectrophotometer. The value of the direct band gap was calculated using transmittance measurements and the Tauc formalism for direct transitions and parabolic bands [26].

$$\left\{ h\nu \ln\left[\frac{T}{T'}\right]\right\}^2 = (Ad)^2 (h\nu - Eg) \quad (1)$$

where T is the film transmittance, T' is the substrate transmittance, A is a constant that depends on the material, d is the film thickness, $h\nu$ the photon energy and Eg the band-gap energy. In $\{h\nu \ln[T/T']\}^2$, $h\nu$ coordinates expression (1) is a straight line. The line intercept corresponds to the band-gap energy. The structural properties were determined by measurements in the grazing incidence geometry with an inclination of 1° in the X-ray diffraction beam (XRD) using CuKα wavelength monochromatic radiation (λ = 1.5405 Å), at 40 kV with 35 mA and with an aperture diaphragm of 0.2 mm, using a D5000 Siemens X-ray diffractometer. XPS analyses were performed in a Perkin-Elmer PHI 560/ESCA-SAM system, with a base pressure of 2×10^{-9} Torr. Argon ion sputtering was performed with 4 keV energy ions and 0.36 μA/cm^2 current beam, yielding to about 3 nm/min sputtering rate. All XPS spectra were obtained without erosion and after 10 min of Ar^+ sputtering. The spectrometer was calibrated using the Cu $2p_{3/2}$ (932.4 eV) and Cu $3p_{3/2}$ (74.9 eV) lines. Binding energy calibration was based on C 1s at 284.6 eV.

3. Results and discussion

Fig. 1 shows the XRD patterns of as-grown films at 500 °C in different PO_2. The films deposited between 1.0 and 50 mTorr show evidence of three diffraction peaks around 2θ at 26.6° (1 1 0), 33.8° (1 0 1) and 51.7° (2 1 1), but when increasing the PO_2 up to 100 mTorr these orientations becomes more evident. All the films up to 100 mTorr are polycrystalline and contain the SnO_2 tetragonal structure [27]. It is observed the effect of PO_2 on the crystallinity of the Te:SnO_2 films, the intensity of (1 1 0) and (1 0 1) diffraction peak increases with increasing PO_2, but the (1 1 0) diffraction peak decreases for PO_2 = 125 mTorr, increasing the (1 0 1) diffraction peak. A strong peak signal of the (1 1 0) was observed for the 100 mTorr film, while the less intense was for the film prepared at 125 mTorr.

Fig. 2 shows the XRD patterns as a function of PO_2, of the post-annealed films. As it can be observed in the figure, all films have better crystallization than those without treatment, so the heat treatment improves the crystalline properties. At particular, the grown film at 10 mTorr has high orientation in the plane (1 1 0), but at higher pressures than 50 mTorr the peaks (1 1 0) decrease and the plane (1 0 1) increases evidently, indicating the crystal reori-