Applied Surface Science 258 (2012) 8902–8907

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

# Pulsed direct current magnetron sputtered nanocrystalline tin oxide films

A. Sivasankar Reddy, N.M. Figueiredo, A. Cavaleiro*

*SEG-CEMUC – Department of Mechanical Engineering, University of Coimbra, 3030-788, Coimbra, Portugal*

ARTICLE INFO

*Article history:*
Received 24 August 2011
Received in revised form 5 April 2012
Accepted 22 May 2012
Available online 27 May 2012

*Keywords:*
Oxides
Thin films
Sputtering
Electrical
Optical

ABSTRACT

The nanocrystalline tin oxide ($SnO_2$) films were deposited on glass substrates by pulsed magnetron sputtering technique and subsequently annealed from 200 to 500 °C. The structural, microstructural, electrical, and optical properties of as deposited and annealed $SnO_2$ films were studied. The crystallinity degree of the films increased with annealing temperature. Photoluminescence (PL) measurements showed that the emission peaks have low intensity and are positioned at 535 nm (2.31 eV) and 605 nm (2.05 eV) in as deposited $SnO_2$ films. The intensity of PL peak increases sharply with the increasing of annealing temperature. The as deposited films exhibited high electrical resistivity and low optical transmittance. After annealing at 500 °C, the electrical resistivity of the films decreased to the lowest value of 0.015 Ω cm, being the optical transmittance 90%.



## 1. Introduction

Tin oxide ($SnO_2$) thin films are attractive in a wide range of applications, e.g., gas sensors, transparent electrodes, heat mirrors, solar cells, thin films resistors, antireflection coatings [1,2], due to their unique properties of high optical transparency in the visible region with low electrical resistivity. Additionally, $SnO_2$ films are chemically and thermally stable, and mechanically harder than ZnO films [3]. In the past few years, nanocrystalline $SnO_2$ has been reported to have some different characteristics from the bulk crystals, and much attention has been focused on the synthesis and investigation of the novel properties of $SnO_2$ nanowires, nanorods, nanobelts, and nanotubes [4]. Various thin film deposition techniques including sputtering [5], laser-assisted chemical vapor deposition [6], pulsed laser evaporation [7], electrodeposition [8], and metalorganic chemical vapor deposition [9] have been used to deposit $SnO_2$ films. Among these techniques, pulsed magnetron sputtering has recently become a very popular method of thin film deposition, due to its versatility, high stability, controllability, repeatability, low environmental impact and ability to provide uniform coatings over large area substrates up to 4 m in width [10,11]. In this paper, $SnO_2$ films were deposited on unheated glass substrates by pulsed magnetron sputtering from a pure Sn target in the presence of oxygen and subsequently annealed in air at different temperatures. The structural, microstructural, electrical and optical properties of as deposited and annealed films were investigated.

## 2. Experimental

The $SnO_2$ films were deposited on cleaned glass substrates by pulsed magnetron sputtering using a Sn target (15 cm × 15 cm × 0.7 cm, 99.99% purity). The deposition was carried out in a reactive atmosphere in the presence of a mixture of pure Ar and $O_2$ gases, with a molar ratio Ar:$O_2$ of 0.5. The deposition pressure was fixed at approximately 0.7 Pa. The substrate holder was neither biased nor intentionally heated and it was set to a constant rotation speed of 20 r.p.m. The target to substrate distance was fixed at 6 cm. Before deposition, an ultimate vacuum pressure better than $7 \times 10^{-4}$ Pa was reached. The substrates surface was ion cleaned with an ion gun. The cleaning procedure included first an electron heating and afterwards an Ar+ bombardment, for 10 min each (ion gun settings at 20 A, 40 V and substrate bias progressively increased to −70 V). During the deposition of the films, the power on the target was fixed at 900 W. The as deposited films were post-annealed at 200, 300 and 500 °C in air. The films thickness was approximately ~200 nm. The chemical composition of the coatings was determined by an electron probe microanalysis (EPMA) apparatus equipped with wavelength-dispersive X-ray spectroscopy (WDX). The structural properties of the films were determined by X-ray diffraction (XRD). The surface morphology and microstructure was characterized by atomic force microscopy (AFM), and scanning electron microscopy (SEM), respectively. The photoluminescence (PL) spectra were measured with a LS55 fluorescence spectrometer (PerkinElmer) at room temperature. The electrical properties of the

* Corresponding author. Tel.: +351 239 790745; fax: +351 239 790701.
*E-mail address:* albano.cavaleiro@dem.uc.pt (A. Cavaleiro).

0169-4332/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2012.05.112

**Table 1**
Chemical composition of pulsed dc magnetron sputtered $SnO_2$ films.

| Sample history | Atomic percentage | | |
|---|---|---|---|
| | Sn | O | Sn/O |
| As deposited | 36.2 | 63.8 | 0.57 |
| 500 °C | 34.3 | 65.7 | 0.52 |

films were measured by four point probe technique and the optical transmittance was recorded using a UV–vis-NIR double beam spectrophotometer.

## 3. Results and discussion

The chemical composition of as deposited and annealed (500 °C) $SnO_2$ films is listed in Table 1. EPMA results show that the $SnO_2$ films contain tin and oxygen. The Sn/O ratio is close to the stoichiometric compound of $SnO_2$ after annealing the films at 500 °C.

### 3.1. Film structure and surface morphology

Fig. 1 shows XRD patterns of the as deposited and annealed $SnO_2$ films. From the results, neither Sn nor sub-stoichiometry $SnO_2$ phases were found in the as deposited and annealed films. The as deposited and annealed films were polycrystalline with tetragonal structure. The as deposited films exhibited broad peaks corresponding to the (1 1 0), (2 0 0), and (2 1 1) reflections. With the annealing temperature, the peaks became progressively narrower and new reflections appeared, (1 0 1) at 200 °C and (2 2 0) at 500 °C. The presence of broad peaks indicates that $SnO_2$ has very small crystallite sizes [12] which increase with annealing temperature. With this trend, the diffraction peaks were shifted to increasing higher angles. The lattice parameters $a$ and $c$ for the tetragonal structure were calculated from the equation, $\frac{1}{d_{hkl}^2} = \frac{h^2+k^2}{a^2} + \frac{l^2}{c^2}$ where $d_{hkl}$ is interplanar spacing, $h$, $k$, and $l$ are all integer indexes of the lattice plane, and $a$ and $c$ are lattice constants [13].

The lattice parameters $a$ and $c$, calculated from the (1 1 0) and (2 1 1) peaks, are listed in Table 2. It is observed that with increasing annealing temperature the lattice parameter $a$ decreases whereas $c$ increases. Chen et al. [4] suggested that in the as deposited films a large number of oxygen vacancies, vacancy clusters, and local lattice disorder can occur, which lead to an increase in $a$ and a decrease in $c$. With the annealing temperature, a progressive removing of the oxygen vacancies and lattice defects takes place

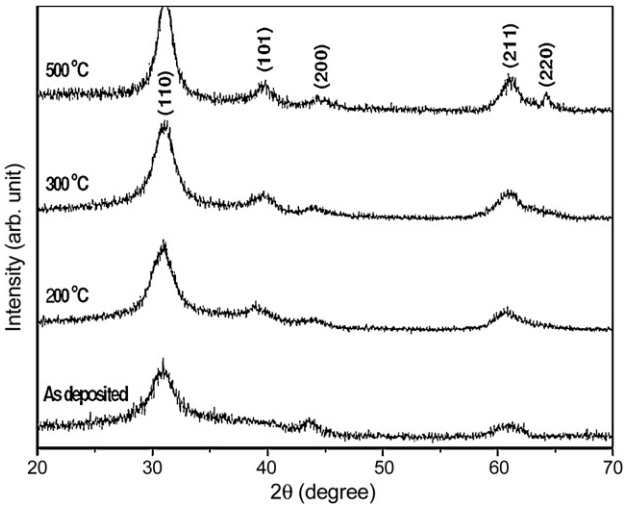


**Fig. 1.** XRD patterns of $SnO_2$ films as a function of annealing temperature.

**Table 2**
Lattice parameters of as deposited and annealed $SnO_2$ films.

| Annealing temperature (°C) | Lattice parameter (Å) | |
|---|---|---|
| | $a$ | $c$ |
| As deposited | 4.762 | 3.155 |
| 200 | 4.756 | 3.174 |
| 300 | 4.733 | 3.179 |
| 500 | 4.722 | 3.193 |
| ICDD (#88-0287) | 4.737 | 3.186 |

with the consequent decrease in $a$ and increase in $c$ parameters, tending toward the equilibrium $c/a$ ratio.

The grain size of the films was calculated from the Scherer's equation, neglecting the peak broadening due to residual stresses in the films, $L = 0.9\lambda/(\beta \cos\theta)$, where $L$ is the grain size, $\beta$ is full width at half maximum in radians, and $\lambda$ is the wavelength of X-rays(1.7903 Å). The as deposited film has average grain size of 4.1 nm which progressively increased, after annealing at 200, 300, and 500 °C to 4.6 nm, 5.4 nm, and 7.3 nm, respectively.

Scanning electron microscopy micrograph of the 500 °C annealed $SnO_2$ film is shown in Fig. 2(a). A very smooth and compact surface is observed without any particular feature detected. Within the resolution of the SEM used apparatus, no cracks and voids could be detected. Fig. 2(b) shows the atomic force microscopy image of the $SnO_2$ film annealed at 500 °C. It is seen that the film has a homogeneous and smooth surface, with a narrow distribution of small grains. The average RMS roughness of films was found to be 1.1 nm. From the histogram, we observed that the average grain size was ~5 nm.

### 3.2. Photoluminescence properties

The room temperature PL spectra of the as deposited and 500 °C annealed $SnO_2$ nanocrystalline films are shown in Fig. 3. The emission peaks have low intensity and are positioned at 535 nm (2.31 eV) and 605 nm (2.05 eV) in as deposited $SnO_2$ films. After annealing the films at 500 °C, the dominant peak was slightly red shifted to 538 nm and the intensity of the peaks sharply increased, especially the higher energy one. Transparent conducting oxides like $SnO_2$ are n-type because of the existence of intrinsic defects, such as oxygen vacancies and/or metal interstitials [14]. In poly- and nano-crystalline oxides, oxygen vacancies are the most common defects and usually act as radiative centers in luminescence processes [15].

The observed PL red shift can be attributed to a combined effect of larger crystallite size and compressive stress [14], in good agreement with the present structural and microstructural results. The residual compressive stresses are arising during cooling down from annealing temperature and they are due to the mismatch between the coefficients of thermal expansion of the film ($SnO_2$) and the substrate (glass). If the chemical composition of the as grown sample is taken into account, a very high number of oxygen vacancies should be present (O is sub-stoichiometric in relation to $SnO_2$), much more than in the annealed case. Therefore, in principle stronger PL emission would be expected for the as grown sample. However, the presence of an excessive amount of defects can lead to additional competitive non-radiative recombination paths, which weakens the transition between the donor and the acceptor levels [14]. As the number of excessive defects in the film diminishes with thermal annealing, the non-radiative recombination processes also diminishes. In this way the PL intensity can in fact increase for the sample annealed at 500 °C. On the contrary, the very low cooling rates used after the annealing process can affect the distribution of space charges in the nanoparticles with a vacancy migration from the bulk to the surface of the grains [16]. Therefore, despite the bigger