Thin Solid Films 517 (2009) 6161–6169

Contents lists available at ScienceDirect

Thin Solid Films

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

Local surface morphology and chemistry of SnO_2 thin films deposited by rheotaxial growth and thermal oxidation method for gas sensor application

L. Ottaviano [a], M. Kwoka [b,*], F. Bisti [a], P. Parisse [a], V. Grossi [a], S. Santucci [a], J. Szuber [b]

[a] Department of Physics, University of L'Aquila, 67100 Coppito, Italy
[b] Department of Electron Technology, Silesian University of Technology,44-100 Gliwice, Poland

ARTICLE INFO

Available online 6 April 2009

Keywords:
Tin dioxide
RGTO thin films
Local surface morphology
Local stoichiometry
XRD
SEM
AFM
XPS depth profiling

ABSTRACT

In this paper experimental results of a comparative X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM) and X-ray Photoelectron Spectroscopy (XPS) study of the crystalline structure, the local morphology, and the surface and in-depth chemistry of SnO_2 thin films obtained by Rheotaxial Growth and Thermal Oxidation (RGTO) method are presented. XRD rules out even a minor presence of a coexisting SnO phase. AFM and SEM show a fractal like morphology of nanograins (20 nm typical size) agglomerated in clusters of crystallites with a bimodal size distribution. XPS shows that the surface of the SnO_2 crystallites is slightly under-stoichiometric as expected from the oxygen deficient termination of their facets. Noteworthy, as evidenced by XPS depth profiles, there are no significant changes of the surface chemistry of the RGTO film with argon ion sputtering.

1. Introduction

Tin dioxide (SnO_2) serves as an important base material in a variety of resistive-type gas sensors. The widespread applicability of this semiconducting oxide is related both to its range of conductance variability and to the fact that it responds to both oxidizing and reducing gases [1,2]. Up to now, commercial gas sensors devices (mainly used for domestic applications in the gas alarm systems) based on SnO_2 have been fabricated with thick (about 1 mm) films, for which a fundamental limitation is large power consumption [3]. This limitation does not concern the thin solid film gas sensors [4].

Among various techniques for the preparation of SnO_2 thin films the Rheotaxial Growth and Thermal Oxidation (RGTO) method first proposed by Sberveglieri [5,6] looks as one of the most effective methods in view of gas-sensing applications. This technique is based on a two-step process. It consists of: i) a deposition of a thin Sn film on a substrate maintained at a temperature slightly exceeding the Sn melting point (231.8 °C) (first step); and ii) a subsequent long-term post-deposition oxidation at high temperature up to 700 °C (second step). In the first step a discontinuous Sn film is formed composed of isolated, almost spherical droplets. Due to the absence of percolation in the plane electrical resistivity of the thin film is infinite. The granular structure is preserved during the final oxidation but the Sn droplets undergo a significant increase in size due to oxygen incorporation. This results in an almost 30% increase of the film thickness. Moreover, the second step, via oxidation, creates connecting "necks" between the formerly isolated Sn droplets, and such necks open a percolation path for the flow of electric current in the RGTO SnO_2 based gas-sensing devices [5–7]. Even though, over the last decade, this deposition technique has become recognized as one of the most efficient method to obtain very sensitive SnO_2 thin films [8–16], however, few studies focused their attention on the physical parameters that during the RGTO growth affect the gas response of the thin film. Radecka et al. [17] showed that a distinct change in the surface morphology occurs when Sn is deposited on substrate maintained at temperature slightly exceeding its melting point. However, till very recently, there were no studies aimed to determine the optimal conditions (substrate temperature and metal film thickness) during the Sn thin film deposition to produce the largest surface to volume ratio and accordingly the optimal gas sensitivity. This was addressed in one of our recent papers [18], where we made a systematic SEM study of the influence of substrate temperature during Sn deposition on the droplets diameter, and the substrates surface coverage. There, it was observed, that for deposition of Sn thin film on Si substrate at 265 °C: i) the majority (above 80%) of the Sn droplets have diameters ranging between 200 and 500 nm and ii) this corresponds to the highest substrate surface coverage (exceeding 65%). Accordingly, such carefully prepared RGTO sample, due to its maximum surface to volume ratio, showed the highest sensor response to nitrogen dioxide (NO_2).

In this work, we propose a microscopic investigation of such optimized RGTO samples. X-ray Diffraction (XRD) data are presented and discussed in comparison with Scanning Electron Microscopy (SEM) images of unprecedented spatial resolution and with high energy resolution X-ray Photoelectron Spectroscopy (XPS) data.

* Corresponding author. Tel./fax: +48 32 2372057.
E-mail address: Monika.Kwoka@polsl.pl (M. Kwoka).

0040-6090/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2009.04.011

2. Experimental

Tin dioxide SnO_2 thin films were deposited according to the RGTO method at the Silesian University of Technology. As substrates we used Si(111) wafers with a native oxide layer. The wafers were cleaned according to a standard procedure involving degreasing in acetone and rinsing in deionized water. In particular, according to our recent optimized procedure [18], at the first step thin metallic tin layers (500 nm) were deposited by classical vacuum thermal evaporation (10^{-3} Pa) from 99.99% pure Sn on a resistively heated substrate maintained at a temperature of 265 °C. The second step, involving the thermal oxidation of Sn thin layer, was performed in two sub-steps: 6 h at 600 °C and 1 h at 700 °C in dry air atmosphere inside a reaction chamber of a diffusion furnace (type SDO125).

The crystallinity and the crystalline phases present in the films were checked by XRD using an X-ray diffractometer with CuK_α radiation (model Seifert XRD 3003 TT RD).

The local surface morphology of the samples was investigated by SEM and Atomic Force Microscopy (AFM). For SEM we used a Zeiss LEO 1530 microscope equipped with a field emission electron gun operated at a beam energy of 5 keV. For AFM we used a Digital Dimension 5000 system with a Veeco NANOSCOPE IV controller, operating in tapping mode (Si cantilevers with 300 kHz resonance frequency). XPS was performed with a home brewed Ultra High Vacuum system equipped with: a PHI monochromatized Al K_α (300 W) X-ray source (photon energy 1486.6 eV) and a concentric hemispherical analyzer (CHA) (PHI 10360 Model) spectrometer set to a pass energy of 5 eV and a sample analysis area of 800×800 μm^2. The residual gas pressure in analyzing chamber was typically less than 10^{-7} Pa. XPS depth profiling analysis of the RGTO SnO_2 thin films was performed with 2 keV Ar^+ sputtering scanning ion gun. The incident primary ion beam was inclined 60° to the normal, to reduce the penetration depth of collisional cascade and to maximise the sputtering yield. The raster area was 3×3 mm, and the etching rate estimated was equal to 0.04 nm/s.

3. Results and discussion

3.1. Surface structure and morphology

The RGTO thin film crystalline structure has been investigated with XRD. Fig. 1 shows a typical Bragg–Brentano spectrum taken on an identically prepared film grown on Al_2O_3. Diffraction data show the presence of the [110], [101], [200], [211], [220], and [002] diffraction peaks from crystalline SnO_2 in the cassiterite rutile phase. The diffraction pattern perfectly matches with the SnO_2 reference crystal structure JCPD file No. 21-1250. The XRD peaks at $2\theta = 34.80$, 43.0, and 54.0 are related to the alumina substrate. The shaded area in the spectrum covers the spectral window where, if present, the main diffraction line from a coexisting SnO phase should be observed. Thus our results are in line with what already reported in literature (i.e. absence of coexisting SnO phase) and with the expectation of a complete transition to a SnO_2 phase upon annealing in oxygen at temperatures above 550 °C [19]. From the analysis of the width of the XRD peaks (Scherrer formula) it can be derived that the thin film is composed of SnO_2 crystallites with an average size of 20 nm. This is in line with the SEM investigation reported hereafter.

The SEM investigation of the RGTO SnO_2 thin film shows an extremely complex morphological landscape. To the best of our knowledge our images show an unprecedented spatial resolution. SEM images in (Figs. 2, 4 and 5) refer to the RGTO SnO_2 thin film after exposure to air. Images in Figs. 6 and 7 have been acquired after UHV Ar^+ sputtering. It is worth stressing that, the morphology of the RGTO film may depend on many factors (for example — substrate type, its temperature, deposition rate, oxygen partial pressure in the deposition chamber etc.) whose influence is not addressed in this paper. Accordingly many results reported here (such as fine details of morphology of the deposit) may be slightly different under different preparation conditions of the RGTO film. Nonetheless, we focus in this work on the correlation between morphology, gas sensitivity, and surface chemistry, coming to conclusions that can be considered of rather general validity.

Fig. 2 shows the RGTO SnO_2 thin film morphology at decreasing length scales. Fig. 2(a) shows the overall sample morphology. Larger area images (not reported for brevity) indicate such a morphology which is self-similar on a length scale of the overall macroscopic sample surface (width and height 1 cm). The layer is formed by partly connected irregular structures (hereafter referred as spongy-like) with sizes typically ranging from 1.0 to 5.0 μm. The average size of such spongy-like agglomerates is 3.2 μm as determined from a statistical analysis of a SEM image containing one hundred agglomerates. Fig. 2(b) shows such mesoscale spongy-like agglomerates with higher magnification. Most of the agglomerates are interconnected. On the other hand the film surface is also occupied by few μm sized patches with no such large agglomerates. Such patches are not exposing the bare substrate, rather they are characterized by a quite different morphology where agglomerates are present with a completely different shape (more regular) and have also a completely different size distribution. The framed area in Fig. 2(b) is reported with higher magnification in Fig. 2(c)

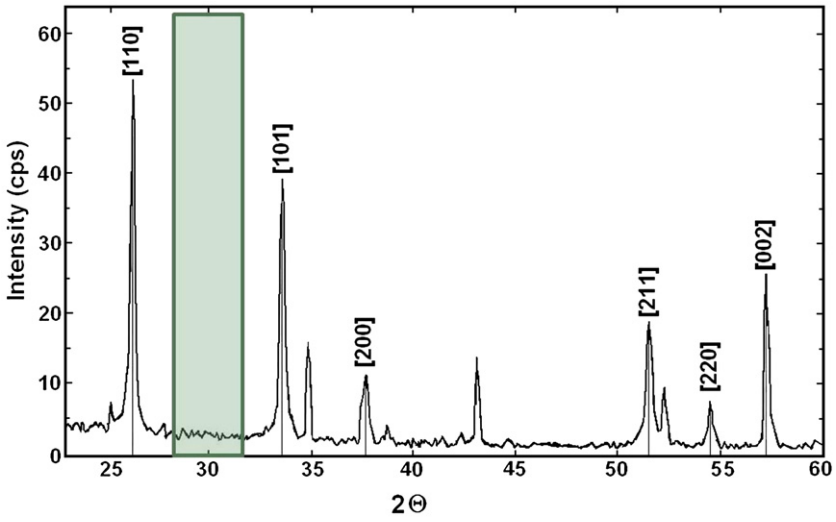

Fig. 1. XRD spectrum of the RGTO SnO_2 thin film. The shaded area covers the spectral window where the occurrence of SnO is expected.