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Rheotaxial growth and vacuum oxidation—Novel technique of tin oxide deposition—*In situ* monitoring of oxidation process

M. Kwoka [a,*], M. Krzywiecki [b]

[a] *Department of Microelectronics and Nanotechnology, Institute of Electronics, Silesian University of Technology, Akademicka 16, 44-100 Gliwice, Poland*
[b] *Institute of Physics – CSE, Silesian University of Technology, Konarskiego 22B, 44-100 Gliwice, Poland*

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ABSTRACT

Within this work a novel preparation method of SnO_2 nanolayers based on *in situ* rheotaxial growth and vacuum oxidation (RGVO) is presented for the first time. The SnO_2 films were characterized with the use of X-ray Photoelectron Spectroscopy (XPS), and Atomic Force Microscopy (AFM). A special emphasis was given to control the oxidation conditions in order to obtain the RGVO SnO_2 nanolayers of controlled stoichiometry/nonstoichiometry for potential application. Performed XPS studies demonstrated that the RGVO SnO_2 nanolayers are of extremely high purity and exhibit the controlled nonstoichiometry depending on the additional controlled oxidation. The variations of RGVO SnO_2 nanolayers' surface chemistry, determined also by XPS, were in a good correlation with the variation of their surface morphology controlled by AFM experiments.

1. Introduction

Tin dioxide (SnO_2) is a base material in resistive-type gas sensors for oxidizing and reducing gases [1] applied in commercial gas sensors. Nowadays, the research is focused on nanostructured materials [2]. The main effort was put to one-dimensional structures, like nanowires, due to their large surface-to-volume ratio, chemical stability and electrical performance [3–5]. However, thin film technology is still a core fabrication method for sensors because of the main advantages like simplicity, repeatability, and low power consumption [3].

Among various techniques for the preparation of SnO_2 thin films of thickness of several hundred nm the Rheotaxial Growth and Thermal Oxidation (RGTO) method [6,7] looks as one of the most effective for gas sensing applications. Rheotaxial means the natural tendency for some elements like Sn, In and Hg to create the droplets during deposition at the substrate.

In the recent studies it was observed that for deposition of Sn thin film on Si at 265 °C the majority of Sn droplets exhibited diameters ranging 200–500 nm corresponding to the highest substrate surface coverage. Accordingly prepared RGTO sample, due to maximum surface to volume ratio, showed the highest sensor response to nitrogen dioxide [8]. Studies of the RGTO SnO_2 thin films morphology and surface chemistry confirmed the existence of SnO_2 crystalline phase, however coexisting with SnO phase inside the films [9]. Moreover, using the X-ray Photoelectron Spectroscopy (XPS) method, it was observed that the surface of SnO_2 crystallites is under-stoichiometric as expected from the oxygen deficient termination of their facets. This statement was in contradiction to the X-ray diffraction data [10]. Which was more important, studies [9] additionally showed that the surface of SnO_2 crystallites is covered by a huge amount of undesired carbon contamination (species) coming from the atmosphere being a strong barrier for the diffusion of gas in the gas sensor working conditions. The same problem was observed for the SnO_2 nanolayers prepared by the Laser-enhanced Chemical Vapor Deposition (L-CVD) method in recently addressed studies [11].

The mentioned main disadvantages of RGTO technology forced us finding of the novel approach to obtain the pure SnO_2 nanolayers of controlled nonstoichiometry/stoichiometry based on the rheotaxial growth of Sn single nanolayers under ultrahigh vacuum condition combined with the simultaneous *in situ* vacuum oxidation (RGVO).

Here, the first results of XPS studies on the *in-situ* monitoring of the oxidation conditions in the novel RGVO technique for obtaining the tin oxide/dioxide nanolayers of controlled nonstoichiometry/stoichiometry are presented. The application of XPS method is crucial in investigation of the material's sensing properties because the attenuation length for photoelectrons is ~3 nm and the sensor effect takes place within the surface space charge layer which is also ~3 nm [3,4]. The photoemission studies were followed by the AFM method which allowed the observation of the nanograins expected at the surface of RGVO SnO_2 nanolayers.

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

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2. Material and methods

RGVO SnO_2 layers were obtained under UHV conditions (~5•10^{-9} h Pa) by thermal evaporation of Sn (Lesker, 99.999% purity) on heated n-type Si (110) substrates maintained at 265 °C with the oxygen partial pressure ~10^{-4} h Pa for 2 h. The thickness of SnO_2 nanolayers was ~20 nm, as determined *in situ* with a quartz crystal microbalance (QMB). To obtain stoichiometry towards SnO_2, additional *in situ* step-by-step vacuum oxidation was performed at increasing oxygen exposure in the range of 10^{-4}–10^{-2} h Pa (10^6–10^8 L) during 2 h.

The *in situ* control of the surface chemistry after each step of the SnO oxidation process was sequentially performed using the XPS method. A SPECS spectrometer equipped with an X-ray lamp (AlKα 1486.6 eV), and a hemispherical analyzer (PHOIBOS-100) was used. The system was operating at 10^{-7} Pa. The reported binding energies (BE) have been calibrated to the Au4f peak at 84.0 eV [12].

The AFM experiments were performed using the AFM Bruker MultiMode 8 system. The measurements were done using Brucker® SiAn tips operating in Tapping Mode. The data were filtered to eradicate scanner- and tip-induced distortions.

3. Results and discussion

Fig. 1a shows the XPS survey spectra of RGVO SnO_2 nanolayers after their additional oxidation with increasing oxygen exposure, described in Section 2. It was done for the monitoring of their general surface chemistry, including their purity and stoichiometry.

The O1s, Sn3d, Sn4s and Sn4d related core level XPS peaks were detected for all of the samples. Moreover, only a very weak C1s peak was observed. However, the C1s signal-to-noise (S/N) ratio ~2, hence it can be neglected. It means that additional oxidation at higher oxygen exposures give us the SnO_2 nanolayers of high purity without C contaminations. This is crucial while compared to the RGTO technology, for which the C contaminations were observed very deeply inside the thin films as detected using XPS ion depth profiling [9].

Fig. 1b shows the XPS O1s–Sn3d spectral windows of RGVO SnO_2 nanolayers after additional oxidation procedure with increasing oxygen exposure. Spectral windows were used for monitoring of surface chemistry of RGVO SnO_2 nanolayers. Based on the atomic sensitivity factors [13] and procedure from [3,6] one can determine the relative [O]/[Sn] concentration of RGVO SnO_2 nanolayers. The results are summarized in Table 1.

One can see from Table 1, that the as deposited RGVO SnO_2 nanolayers are understoichiometric even for the SnO nanolayers. Hence, additional *in situ* vacuum oxidation of the as deposited SnO nanolayers had to be performed in order to obtain the stoichiometry towards SnO_2. For the lowest oxygen exposure 10^6 L the relative [O]/[Sn] concentration reached a value close to the stoichiometric SnO similarly to the as deposited samples. This extorted further oxidation processes. The additional oxidation at 10^7 L resulted [O]/[Sn] concentration of 1.15. It was far from fully stoichiometric SnO_2 as for the L-CVD SnO_2 [14].

The evident increase of [O]/[Sn] concentration was only observed after the oxygen exposure at 10^8 L (Table 1). This information confirms that under applied oxidation conditions the RGVO SnO_2 nanolayers consist of a mixture of SnO and SnO_2, with a small domination of the latter.

However, it corresponds to subsurface region of a few nm and is related to the photoelectron inelastic mean free path which is for SnO_2 equal to 3 nm. The overall composition of the layer will be altered towards the interior of the SnO_2 layer. However, which has to be underlined, we are interested in the determination of the composition of only subsurface region of RGVO SnO_2 nanostructures up to ~3 nm, which corresponds to the Debye length at which SnO_2 gas sensing effect appears.

To prove such statement the decomposition of XPS O1s and $Sn3d_{5/2}$ peaks for the samples having the lowest and highest [O]/[Sn] concentration was performed (Fig. 2).

The as deposited RGVO nanolayers contain mainly the SnO (as confirmed by O–Sn^{2+} bondings in O1s and Sn^{2+} bondings in $Sn3d_{5/2}$),

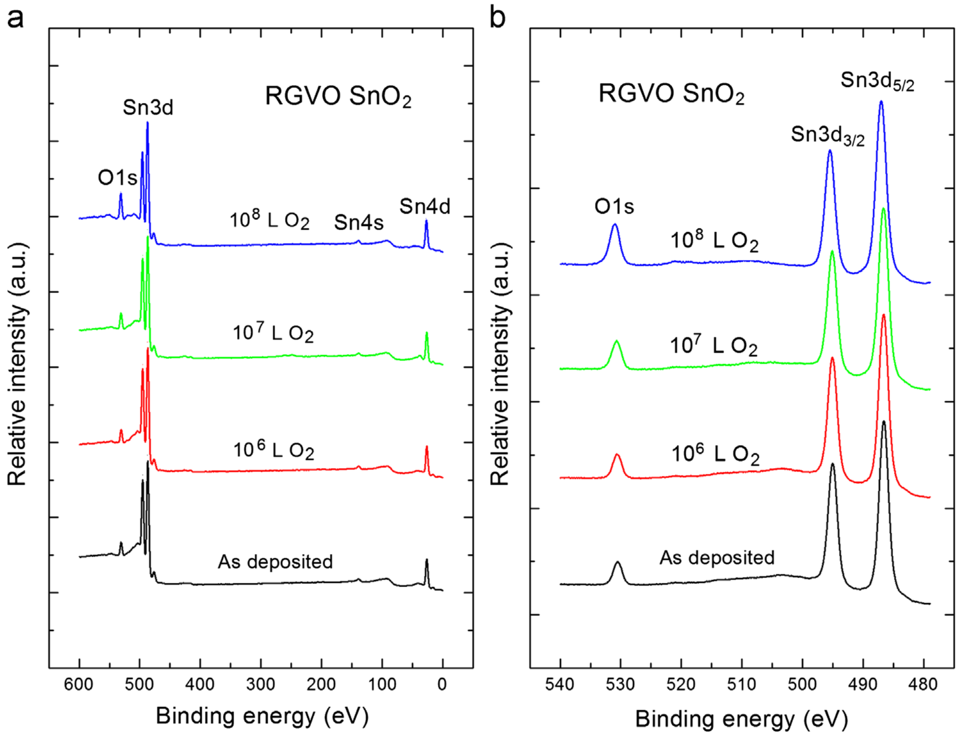

Fig. 1. (a) XPS survey spectra with the main core level lines of the *in situ* deposited nanolayers after subsequent oxidation. (b) O1s–Sn3d spectral windows.