

# Enhancement of SnO<sub>2</sub> for gas sensing applications

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## ABSTRACT

Thin films of SnO<sub>2</sub> were deposited by reactive RF magnetron sputtering. It was shown that the films possess gas sensitivity to ethanol vapor at room temperature. XRD, SEM, and EDX measurements of thin films were investigated. Annealing of SnO<sub>2</sub> thin films at 800 °C is polycrystalline and grain size of SnO<sub>2</sub> in the range about 12 nm. The growth of SnO<sub>2</sub> with annealing to 800 °C leads to the percolation nanorods structure. EDX clearly explains the rich of Sn reached 70% annealing. The conductivity of SnO<sub>2</sub> nanorods has been increasing at room temperature for ethanol vapors.

**KEYWORDS:** SnO<sub>2</sub> gas sensor, Magnetron sputtering; nanomaterials; conductivity; sensitivity.

## INTRODUCTION

Tin dioxide films are promising materials for the implementation of solid-state gas sensors with improved characteristics [1]. There is also an opportunity of integrating the gas sensors with subsequent signal processing structures on the same substrate which opens a new perspective for the development of miniaturized gas-sensing devices [2]. Recently, branched nanostructures have attracted great interest because they can provide means for improving parallel connectivity, enhancing device performance [3]. Nanostructures and thin films have been employed as sensing materials for building high-performance sensors due to their high specific surface area and novel electron transportation properties [1, 4-9]. Another makes use of the Joule heat produced by the sensor itself to achieve the optimum temperature rather than an external heater and hence reduce the total power consumption. In this complex situation, the number of processes that take place at the semiconductor surface makes it difficult to determine the actual reason for the conductance variance [10]. Usually, the higher temperature would lead to higher sensing performance due to the lowering of activation energy for gas

adsorption and desorption. However, the sensitivity reached the best value and then decreased with the increasing temperature in some reports [11, 12], and then the temperature stability should be taken into account, especially for the sensors. Maybe a little higher temperature would be better to render the required stability [13]. Present work supported the use of gas sensors at room temperature without risks for sensing the gases at high temperatures. Annealing of SnO<sub>2</sub> thin films improved the sensitivity for gas sensor application devices.

## MATERIALS AND METHODS

The samples were prepared by magnetron high-frequency sputtering method in a PVD 600 installation (Vac-Tec, Republic of Korea). The films for gas sensors were deposited onto Si (100) substrate at 250 °C. The target was a disc with a diameter of 100 mm and a thickness of 3 mm, obtained by pressing a powder of tin dioxide of a chemically pure grade followed by sintering at a temperature of 1200 °C. The target was sputtered at a pressure of  $1.3 \times 10^{-5}$  bar in a high-frequency Ar/O<sub>2</sub> discharge with a 3:1 ratio. The target-substrate distance was 60 mm. The deposition rate

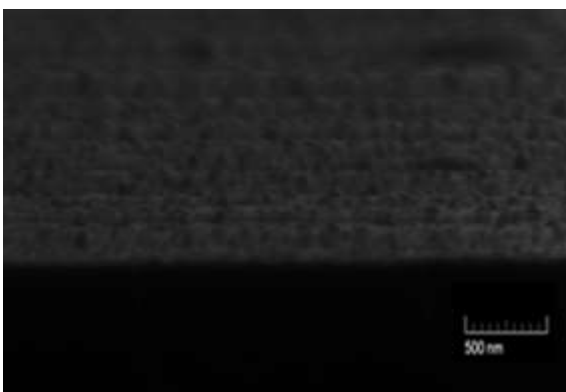
was maintained at a level of 0.4nm/s with a deposition time of 5 min.

The growth of SnO<sub>2</sub> nano roads becomes by annealing to 800°C. A measurement control program was implemented using the LabVIEW software.

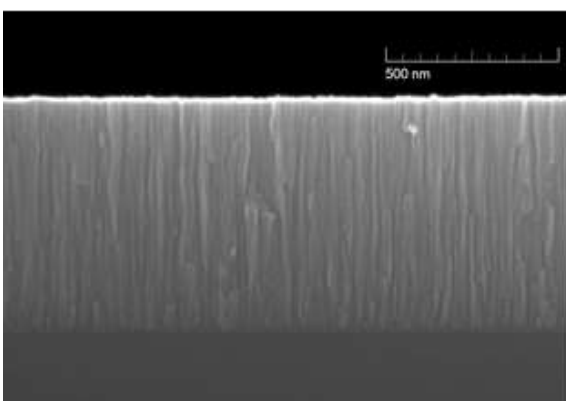
It allows easy control of the different experimental conditions used in gas sensor characterization such as the I-V characteristic, sensitivity, and response time measurements. The response of semiconducting metal oxides to various gases has most commonly been investigated by DC voltage measurements. The surface morphology and the thickness of the coatings were investigated using Scanning Electron Microscope (MIRA 2 LMU). As in an EDX study, the composition at a point is being analyzed, it should be conducted at several points to confirm that the composition analysis is valid for the whole surface of the film.

## RESULTS AND DISCUSSION

The growth of SnO<sub>2</sub> with annealing to 800 °C leads to the formation of a film consisting of vertically oriented rods, which in turn also consist of crystallites Figure 2.



**Figure 1.** SnO<sub>2</sub> film consists of grains to the substrate surface before annealing.



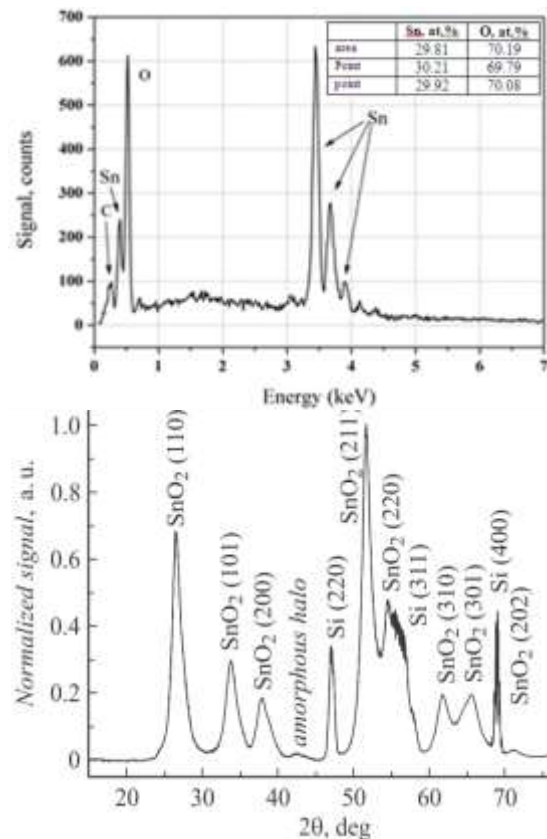
**Figure 2.** SnO<sub>2</sub> film consists of grains oriented perpendicular to the substrate surface after annealing to 3h for 800 °C.

The resulting image is processed using the Gwyddion 2.20 program [7].

It can be seen from the presented image that the films consist of grains oriented perpendicular to the substrate surface. The film thickness is about 300 nm. Pores with a characteristic transverse size of about 20 nm are located between the grains.

There are only 2 peaks at EDX spectra oxygen and tin. Thus, bulk consists of SnO<sub>2</sub> with excess oxygen.

The following results were calculated:



**Figure 3.** EDX and XRD of SnO<sub>2</sub> thin film gas sensor.

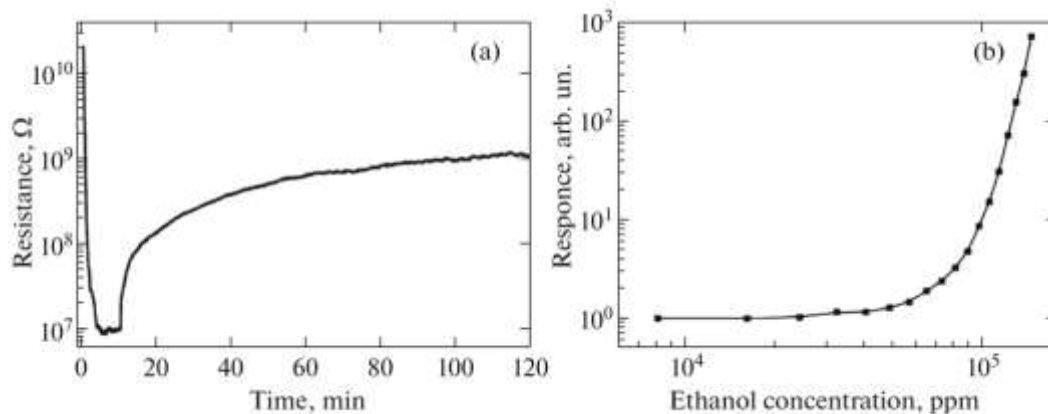
Silicon peak appears in EDX and XRD of SnO<sub>2</sub> thin film gas sensors as electron penetration depth is higher than the film thickness. Therefore, silicon peaks correspond to substrates.

Measurements by X-ray diffraction analysis showed that the crystal structure of the films corresponds to tin dioxide as shown in figure 3.

Determination of the influence of the composition of the surrounding atmosphere on the resistance of the samples showed that the introduction of saturated ethanol vapors into the measuring chamber leads to a decrease in the resistance of the sample by more than three orders of magnitude, and the subsequent blowing with clean air leads to a partial restoration of the resistance of the sample (Figure 4a). The dynamics of the sensor's response to the effect of ethanol vapors is

characterized by two exponential processes: fast, with a characteristic time of 8 s, and slower, with a characteristic time of 40 s (Figure 4b). The restoration of resistance during blowing with dry

air occurs linearly at a rate of 200kOhm/s in the first 50 min, then the rate of change in resistance decreases to 150 kOhm/s.



**Figure 4.** (a) Change in the resistance of SnO<sub>2</sub> film when ethanol vapors are introduced into the chamber, followed by blowing with clean air. (b) Dependence of the response of the resistance of SnO<sub>2</sub> to the presence of ethanol vapor in the surrounding atmosphere on the concentration of ethanol vapor

It is assumed that during the crystallization of deposited films during thermal annealing, the surface of microcrystals forms bonds with lattice oxygen.

Adsorbed oxygen ions create a space charge region near the surface of SnO<sub>2</sub> grains by extracting electrons from the material. Ethanol, being by nature a reducing gas, reacts with adsorbed O<sup>-</sup> ions and removes them from the surface of the grains, re-injecting electrons back into the material and thus lowering the resistance of the film [14].

## CONCLUSIONS

Thin film sensors SnO<sub>2</sub> annealed at 800 °C, have shown good sensitivity to ethanol. Measurements of the composition and crystal structure showed that the grains are composed of SnO<sub>2</sub>. The film thickness and the grain size 300 nm, 12nm. The electrical study reveals that the films have degenerate and exhibit n-type electrical conductivity. The obtained results revealed that the structures and properties of the films were greatly affected by annealing temperature.

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