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SnO_2/TiO_2 thin film n-n heterostructures for H_2 and NO_2 gas sensing

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Abstract:
Pure SnO_2 and SnO_2/TiO_2 heterostructure based gas sensors for reducing H_2 and oxidizing NO_2 in the temperature range of 80 – 400^{O}C were investigated. SnO_2 thin films were prepared by RF magneton sputtering, whereas TiO_2 layers were deposited using a relatively less exploited Langmuir-Blodgett (L-B) technique. TiO_2 thin films were characterized with different spectroscopy and imaging methods (XPS, XRD, EDS, SEM, optical profilometry) which confirmed the presence of TiO_2 on the SnO_2 surfaces. The resistance change of SnO_2/TiO_2 system is higher than that of pure SnO_2 thin films for both H_2 and NO_2 gases. Additional TiO_2 layers significantly improve the response of SnO_2/TiO_2 gas sensors (in comparison to pure SnO_2) in the range of 200-400^{0}C even for low concentrations of NO_2. It suggests SnO_2/TiO_2 heterostructure based sensors obtained using combined sputtering/L-B methods can be highly sensitive for H_2 and NO_2.

Key words: gas sensors, n-n heterostructures, SnO_2/TiO_2, thin films, nitrogen dioxide

Introduction

TiO_2 and SnO_2 materials are among the most common metal oxides used for gas sensing [1-3]. The possibility to use different structures and preparation methods (physical and chemical) of TiO_2 and SnO_2 based gas sensors was widely investigated [4-6]. In this paper we discuss the Langmuir-Blodgett (L-B) method - an emerging technique [7] in electronic applications which allows to prepare TiO_2 ultra-thin films at room temperature without modification of the substrate. In this paper we compare properties of pure SnO_2 and SnO_2/TiO_2 heterostructures, and their responses to reducing H_2 and oxidizing NO_2 gases.

Material preparation and measurements

SnO_2 thin films were deposited onto special substrates with defined interdigital electrodes by RF magnetron sputtering from Sn target (20% O_2,180^{O}C, 50 W, 30 min). The SnO_2 layer was 200 nm thick. The TiO_2/SnO_2 structures were obtained by depositing TiO_2 thin films on previously prepared SnO_2 substrates using Langmuir-Blodgett technique (nanopowder of rutile was a starting material). The processes were performed using Langmuir KSV NIMA trough (Biolin Scientific company, Sweden) at room temperature and under normal pressure.
Gas sensitivity measurements were carried out in a gas chamber with a volume of about 30 cm^3 over the range of temperatures between 80 and 400^{O}C [5]. The sensors were exposed to NO_2 and H_2 gases at different concentration levels.

Results

Thin layers of TiO_2 obtained using the L-B method were characterized with SEM, XPS, XRD, EDS and optical profilometry methods. The XPS spectrum and SEM image of the TiO_2 layer is presented in Figure 1.
The SnO_2/TiO_2 heterostructure shows higher resistance than that of pure SnO_2 thin films but an additional TiO_2 layer increases the response to both reducing and oxidizing gases. Figure 2 shows the response of the SnO_2/TiO_2 system compared to pure SnO_2 based sensor at 400^{0}C within the H_2 concentration range from 15 to 325 ppm. It was observed that even for the smallest H_2 concentrations, there is an increase in the response of the SnO_2/TiO_2 sensor in relation to the pure SnO_2 thin film. Both

materials are n-type semiconductors thus the resistance R of the sensors drops under exposure to reducing H_2 gas, while it rises under exposure to oxidizing NO_2 gas.

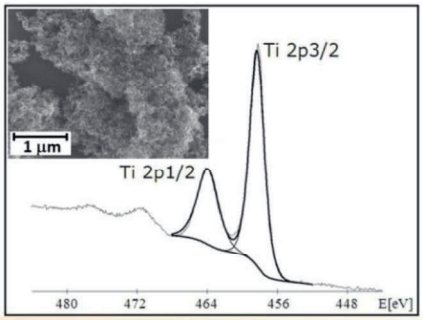

Fig. 1. Characteristic XPS peaks for Ti^{4+} in TiO_2 thin film obtained from nanopowder of rutile, SEM of TiO_2 layers on the silica substrate (inset)

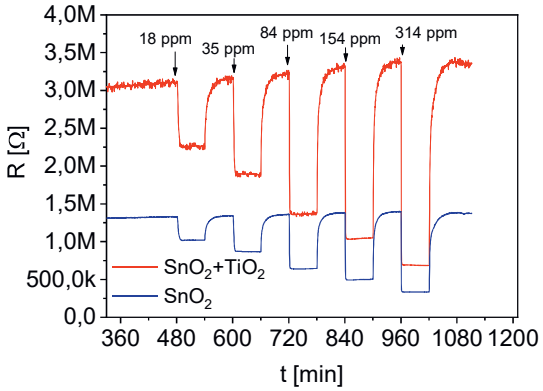

Fig. 2. Resistance changes of SnO_2/TiO_2 and pure SnO_2 thin films to H_2 at 400°C

Despite the significant increase in the SnO_2/TiO_2 system resistance compared to pure SnO_2 sensor the response was improved by the TiO_2 thin layer addition (Figure 2).

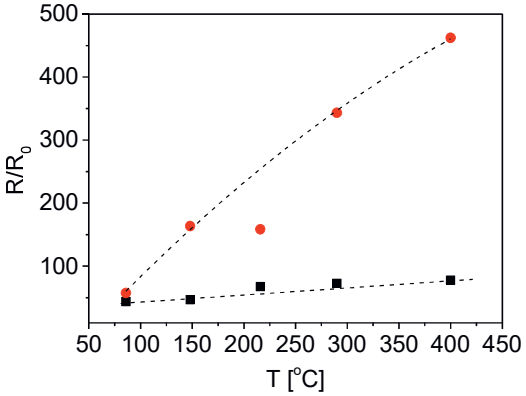

Fig. 3. The responses of pure SnO_2 and SnO_2/TiO_2 heterostructure based gas sensors to 20 ppm of NO_2 at 400°C

For SnO_2 sensors, the response defined as a ratio of sensor resistance R in NO_2 to resistance R_0 in air is of about R/R_0 = 70, whereas for SnO_2/TiO_2 system R/R_0 increases to 450 (at 400°C).

Conclusions

Spectroscopy and imaging methods used to characterize the investigated samples clearly indicate the proposed L-B technique is effective for depositing of TiO_2 thin films. Moreover, L-B, in contrast to physical vapour methods, is a non-destructive procedure which does not damage the SnO_2 substrates. The heterostructures obtained by depositing an additional TiO_2 thin layer on SnO_2 thin films have higher gas response than pure SnO_2 for both reducing (H_2) and oxidizing (NO_2) gases. It seems that SnO_2/TiO_2 based gas sensor is highly sensitive even to low concentrations of NO_2 gas. The significant response increase was observed especially over the range of 200°C - 400°C.

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