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Studies on the thick-film organic vapor sensors based on binary metal oxides

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Thick film sensors of binary mixtures of metal oxides: e.g. tin dioxide/zinc oxide; tin dioxide/indium oxide; and tin dioxide/tungsten oxide for isopropanol vapor detection were fabricated on alumina substrate via screen printing technique. The tin oxide/tungsten oxide thick films showed superior sensor properties (sensitivity and response time) at lower operating temperature (140°C).

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1. Introduction

Gas sensors based on wide band semiconductor metal oxides play an important role in the detection of toxic pollutants (CO, H_2S, NO_x, SO_2, etc) and combustible gases (H_2, CH_4 and flammable organic vapors, etc.). Metal oxide materials such as SnO_2, ZnO, TiO_2, WO_2, Ga_2O_3, and others have been examined for gas sensing applications and for control of industrial processes. Tin oxide (SnO_2) is one of the most extensively studied material among metal oxides [1-2]. Various techniques have been used to improve the sensitivity and selectivity of these sensors. A large part of the literature deals with characterization of sensors employing different forms of oxides, effect of catalytic or other additives, ion implantation, and use of masks and filters to improve selectivity and temperature programming techniques etc. [1-12]. However, a lack of consistency in sensor properties has been a major problem associated with various techniques used for the fabrication of sensors. Bulk, thick, and thin films of SnO_2 have been used in the fabrication of gas sensors. Thin-film sensors are of great interest because of relatively small geometry, low power consumption, and distinct sensing effect, etc. A sensor having a thin film of less than a few hundred nanometers has a reasonably good sensitivity, but usually shows poor stability due to weak mechanical strength. The dispersions of dopants, which enhances, the sensitivity over thin film is not as satisfactory as those for thick or bulk type sensors [13-15]. For thick-film or bulk type sensor, dopants (or additives) are usually mixed homogeneously with the powder precursors.

Recently, it has been reported that composite sensors incorporating differing proportions of tin oxide and zinc oxide exhibits higher sensitivity over a range of organic vapors [8]. Most importantly, the composite sensors have shown to have a significantly higher sensitivity than sensors fabricated from tin dioxide or zinc oxide, when operated under identical experimental conditions. It has been proposed that an increase in sensitivity is due to synergistic effects: complementary catalytic activity [9]; and formation of hetro-junctions and changes in microstructure on sintering [10].

Our aim for the present investigation is to fabricate thick-film sensors of binary mixtures of oxides: Tin oxide/Zinc oxide; Tin oxide/Indium oxide; and tin oxide/ tungsten oxide and investigate their response, such as sensitivity and response time to 2-isopropanol. The study was also performed to predict the detection capability of sensors for different concentrations.

2. Experimental

Sensors were fabricated on an alumina substrate by thick-film technology (TFT). Tin (IV) oxide powder (99.99% metals basis, Alpha Aesar), Tungsten (VI) oxide powder (99.8% metals basis Alpha Aesar), Zinc oxide powder (99.9% minimum -325 mesh powder Alpha Aesar) and Indium (III) oxide powder (99.99% metals basis Alpha Aesar) were used in the fabrication of the sensors. Composites incorporating 75:25 (wt%) tin oxide/tungsten oxides (TTO), 75:25 (wt%) tin oxide/zinc oxides (TZO), and 75:25 (wt%) tin oxide/indium oxides (TIO) were produced. In each case, oxides mixtures were grounded and milled. To prepare the ink/paste for screen-printing, a commercially available Terpineol-based vehicle ESL 449 and an active mixture was blended. The paste was then applied onto ultrasonically cleaned alumina substrate using screen-printing machine [16]. Film samples were then placed in the furnace and the temperature was ramped up at a rate of 2°C/min to a calcination temperature of 400°C, where the samples were held at 400°C for 2 hours. The

furnace was then ramped up again at rate of 2 °C/min to a sintering temperature of 800°C and held at 800°C for 6 hours. The furnace was then ramped down at a rate of 2 °C/min to the ambient conditions. The silver print electrodes were then deposited on the surface of sensing layer. Fig. 1 shows the sensor geometry. Typically, thickness of the sensor film was about 50 μm. The gas sensing properties were investigated under static conditions. The output resistance variations of the sensor were measured simultaneously with respect to temperature and time. The output- resistance was recorded using a Keithley's 617 programmable electrometer connected to a PC. The resistance variation was measured for different concentrations of test vapors ranging from 20 ppm to 100 ppm. The sensors were fixed onto a sample holder and the operating temperature of the film was determined with a thermocouple attached to the sensor.

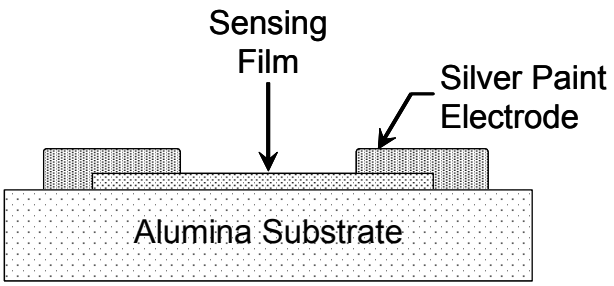

Fig. 1. Cross section of a sensor fabricated using alumina substrate.

Sensitivity was calculated using the following formula:

$$Sensitivity\,(S) = \frac{Ra - Rg}{Rg} \times 100$$

where *Rg* is the sensor resistance influenced by the isopropanol vapors, and *Ra* is the sensor resistance in the air.

3. Results and discussion

Fig. 2 shows the concentration of injected specie and respective sensitivity of binary oxides sensor operated at 140 ºC. There is a slight increase of sensitivity with the increase of injected concentration of vapors. The sensor fabricated with SnO_2/WO_3 (TTO) composite shows the highest sensitivity for 2-isopropanol, even at 20-ppm level among the other two sensors investigated. The sensitivity reaches saturation at about 100 ppm of vapors. With a fixed surface area, a lower concentration of gas implies a lower coverage of gas molecules on the surface. An increase in vapor concentration raises the surface coverage, eventually leading to a saturation level, thus determining the upper detection limit. Fig. 3 shows the response time of composites oxides to 20 ppm 2-isopropanol vapors.

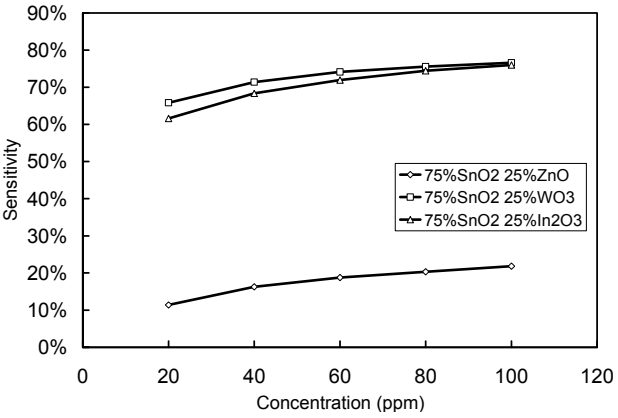

Fig. 2. Sensitivity of binary oxides of isopropanol vapors at 140 ºC.

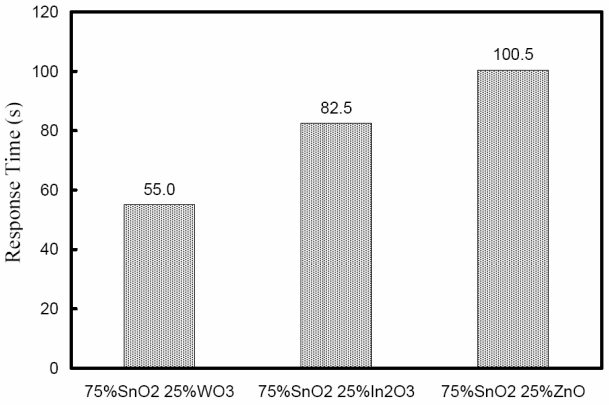

Fig. 3. Response time for binary oxides to 20 ppm isopropanol vapor.

To propose mechanisms for detection of isopropanol vapor, it is worth mentioning that ZnO, SnO_2, WO_3, have non-stoichiometric structures, free electrons originating from oxygen vacancies contribute to conductivity (n-type) by following equation:

$$O_o\,(bulk) = V_o + 2e^- + \tfrac{1}{2}O_2\,(gas) \qquad (1)$$

Thus in an n-type metal-oxide semiconductor, conduction electrons (e^-) arising primarily from point defects (oxygen vacancies and interstitial tin atoms) and play a major role in the gas sensing operation [1-2, 17], which is the combination of two adsorption reactions. First, the sensitizing reaction, some reactants gases are adsorbed with contact on the surface of SnO_2-MO (where M = Zn, W or Zn), to form a Schottky contact, electrical resistance of these materials is changed, thereby indicating the presence of the gas. Then as it is known practically, surface detection is done with participation of oxygen, which can be present in molecular (O_2^-) or atomic (O^-) forms to reduce the resistance of the SnO_2-MO layer in the presence of reducing gas. So, the reaction sequences on 2-isopropanol, $(CH_3)_2CHOH$, can be written in the following reaction steps with physical and chemical adsorption:

Step I for sensitizing reaction:

$$O_2(gas) + 2e^- \rightarrow 2O^- + \Delta H_1 \quad (2)$$

Step II for detection reaction:

$$(CH_3)_2CHOH + O^- + \Delta H_2 \rightarrow e^- + CH_3COCH_3 + H_2O + \Delta H_3 \quad (3)$$

Step III for net equilibrium reaction (the addition of Eqs. (1) and (2)):

$$O_2 + 2(CH_3)_2CHOH \rightarrow 2CH_3COCH_3 + 2H_2O + \Delta H_4 \quad (4)$$

Surface morphology of the films is an important issue, as the smaller the grain size, the larger the specific surface area, which results in the greater adsorption and higher sensitivity [18-19]. To seek an explanation for changes in sensor response of three binary composites investigated, pore size distributions have to be measured. Decrease of pores is likely to be responsible for decrease of sensor response [20]. Highly porous film sensors have high sensitivity [21]. The observed changes in the sensitivity of the binary oxides sensor elements may be attributed to porosity and particle size variation. However, catalytic effects of Tungsten, Zinc and Indium can not be ruled out. Further detailed study is in progress to conclude the possible response mechanisms and will be reported elsewhere.

4. Conclusions

Gas sensors based on binary oxides were prepared and characterized. It was experimentally demonstrated that the Tin oxide-Tungsten oxide film improved the sensor gas-sensing properties compared to other binary oxides investigated for 2-isopropanol, and produces a shorter response time. Furthermore, screen-printed binary oxides thick films could be appropriate for alcohols sensing at a relatively low temperature (140ºC), which is modest on the viewpoint of semiconducting gas sensors.

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