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Sensing performance of heterojunction gas sensors based on SnO_2, WO_3 and ZnO metal oxides

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Abstract:

Thick film heterojunction gas sensors based on SnO_2, WO_3 and ZnO were fabricated. Their response to the presence of isopropyl alcohol was investigated. The sensing structures were studied using temperature stimulated conductance and cyclic voltammetry. The results of measurement shows, that the prepared structures exhibit current-voltage characteristics like a Schottky diode. This behavior result in strong influence of polarization voltage on the sensing parameters of those structures.

Key words: gas sensors, semiconductor metal oxides, heterojunction, thick film technology

Introduction

Measurements of gas mixture compositions becomes more and more important for modern industry. Currently is increasing demand for cheap and small gas sensing systems for the detection of volatile organic compounds (VOC) and inorganic gases.

Semiconductor gas sensors play a major role in this field [1]. During the last few decades the sensing performance of such sensors increase significantly. Nowadays detectors show great sensitivity [2,3], long life time and good stability [4]. Nevertheless, the problem of their poor selectivity is still not solved, which limits their application. To overcome this problem, multilayer structures are investigated. In most cases, the additional layers are used as active or passive filters. They are placed above the sensing layer [5,6] in order to minimize the effect of cross selectivity by protecting against unwanted compounds, which may affect the sensor response

Another way to improve the gas sensor performance is based on the use of interfaces formed between two single-phase metal oxide semiconductors [7-9]. In this work the authors present the construction and sensing properties of heterocontacts created between SnO_2 and WO_3 + 0,8% Au, WO_3 and SnO_2, ZnO and SnO_2 + 0,8% Au.

The proposed heterojunctions are build from different n-type semiconducting metal oxides. In contradistinction conventional semiconductor gas sensors, these materials forms layers and acts as simple resistors, which resistance depends on the composition of the ambient atmosphere. The detection mechanism of such devices is well known and discussed in many papers [10,11]. Change in conductance in such systems mainly depend on the phenomena which occurring at the surface and in volume of the gas sensing layer. Effects that occur at the electrode-gas sensing material interface plays a secondary role.

In the case of structures based on heterojunctions the sensor response carries the information about the interactions of target gas molecules with the single phase metal oxide regions and the heterocontact area.

Sensor fabrication

The heterojunction gas sensors were prepared by standard thick film technology on an alumina substrate (96% Al_2O_3). The integrated heater and the sensing structure were deposited on the opposite sides of the substrate (fig. 1). For the electrode materials and heater a commercially available gold and platinum pastes from ESL were used.

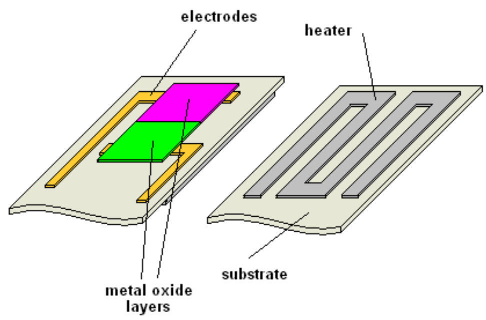

Fig. 1. Schematic view of the heterojunction gas sensor with the integrated heater.

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Thick film pastes for the gas sensing layers are composed of an organic binder (ESL 403 vehicle) and the respective metal oxide powder. The SnO_2 powder was synthesized by the modified Okazaky method. To get the ZnO powder a $Zn(NO_3)_2$ precursor was used. WO_3 was obtained by thermal decomposition of silicotungstic acid ($H_6[Si(W_2O_7)_6] \cdot nH_2O$) by heating it for 5 hours at 650°C.

The doping process of the gas sensing materials with gold particles was performed by mixing the respective metal oxide powders together with the right amount of ESL 8081-C metallo-organic gold conductor paste giving finally a composition of 0,8% wt gold.

Finally, the prepared thick film pastes for the heterojunction structure were screen printed at the electrodes and fired at 850°C for 2 hours.

Sensor characterization

The behavior of the prepared heterojunction gas sensors and their response to the presence of isopropyl alcohol in the target atmosphere was studied. The measurements were performed using temperature stimulated conductance (TSC) and cyclic voltammetry methods. The schematic diagram of the test setup is shown in fig. 2. The sensors were placed in a chamber. The measured atmospheres were composed of clean air with the appropriate content of isopropyl alcohol in the range of 10 ppm to 500 ppm. The flow rate of the gas mixture thought the chamber was set to 0.6 L/min.

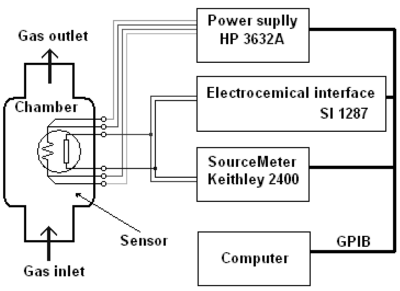

Fig. 2. Sensor test setup.

The TSC measurements were carried out using a HP 3632A power supply, to control the temperature of the sensor heater and a Keithley 2400 sourcemeter, to measure the conductance of the sensing structures. The working temperature of the heterojunctions was changing linear from 250°C to 700°C with a scan rate of 2°C/sec. To investigate the effect of polarization voltage on the *G=f(T)* characteristics, the structures were polarized with bias voltages in different directions.

During the TSC measurements the ZnO, WO_3+0.8% Au and SnO_2 layer respectively to the ZnO|SnO_2+0.8 wt. % Au, WO_3+0.8 wt. % Au and SnO_2|WO_3 heterostructure were connected to zero potential (GND). At the second electrode a voltage of -2 V or 2 V was applied.

For the cyclic voltammetry studies an SI 1287 electrochemical interface was used to register the current-voltage behavior of the structures. The measurements were performed in a two electrode setup. In each cycle the polarization voltage was changing from 0 V → -3 V → 3 V → 0 V.

The complete test setup was controlled by a PC class computer equipped with the respective software.

Results and discusion

To identify the optimal working temperature for the detection of isopropyl alcohol, the characterization of the structures was started with the TSC method. The obtained characteristics of conductance as a function of the heater temperature changes (*G=f(T)*) were used to calculate the sensitivity of the sensors for the presence of isopropyl alcohol. This parameter is defined by the equation (1) as a ratio of the sensor conductance measured in the atmosphere of isopropyl alcohol to the conductance measured in the reference atmosphere:

$$S = \frac{G_{gas}(T)}{G_{air}(T)} \qquad (1)$$

The achieved *S=f(T)* characteristics for the three samples exhibit several maxima in the investigated range of temperatures. As is shown in figure 3, the maximum sensitivity to isopropyl alcohol and the temperature T_{opt} at which the maximum is located depend on the polarization direction of the structures.

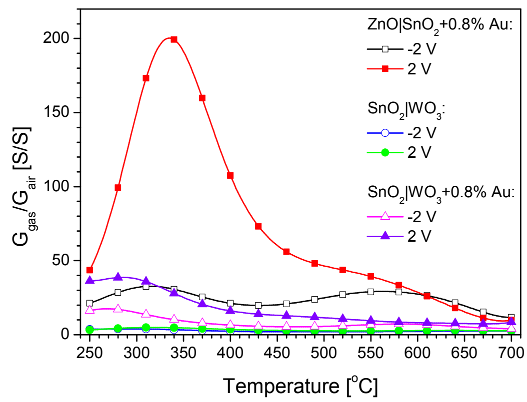

Fig. 3. Temperature dependence of sensor sensitivity to the presence of 200 ppm isopropyl alcohol in target atmosphere plotted for different polarization directions.

The highest response to isopropyl alcohol was observed by the $ZnO|SnO_2$+0.8 wt. % Au heterojunction sensor at a polarization voltage of 2 V.

The influence of the voltage polarization on the sensing performance was investigated using cyclic voltammetry. The obtained current-voltage (I-V) curves (fig. 4a,b,c) shows, that sensors behave like a Schottky diode. The current density flowing through the structure depend on the polarization direction. Such relation explain the different sensitivity level obtained from TSC.

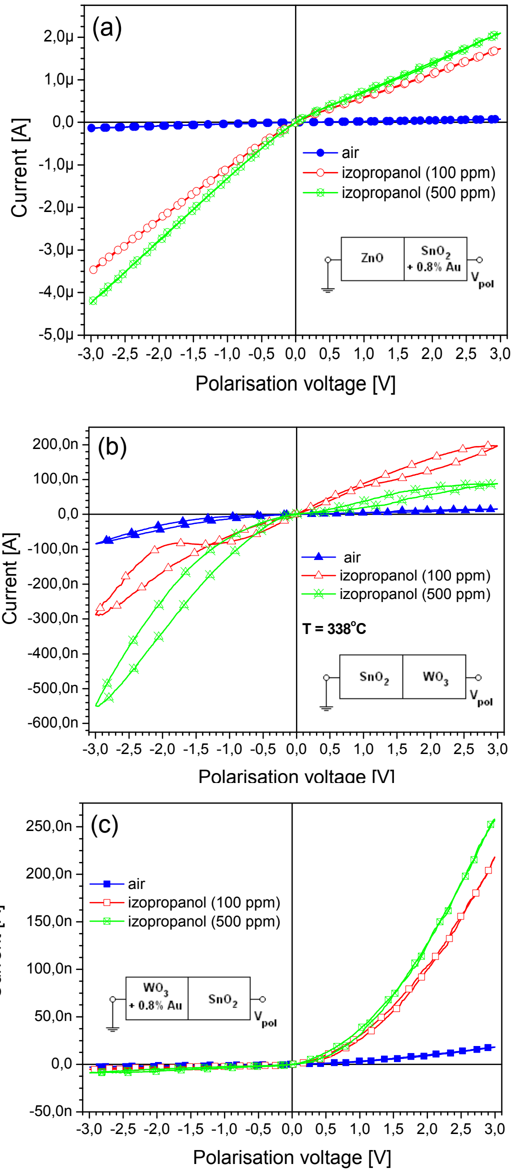

Fig. 4. Current-voltage characteristics measured in clean air and isopropyl alcohol by using the following structures: a) $ZnO|SnO_2$+0.8 wt. % Au, b) $SnO_2|WO_3$, c) $SnO_2|WO_3$+0.8 wt. % Au.

Based on the achieved results, authors plot the relationship of the sensor conductance to the concentration of isopropyl alcohol at temperatures were the local sensitivity maxima was found (fig. 5a,b,c). In logarithmic scale the relation between those factors is linear, like in a conventional single layer semiconductor gas sensor and can be described by equation (2) [12]:

$$G = G_0 p_{gas}^n \quad (2)$$

where G is the measured conductance, p_{gas} is the partial pressure of the target gas, G_0 and n are experimentally determined values, which are calculated by fitting the measured points with a linear equation (3):

$$\log G = \log G_0 + n \log p_{gas} \quad (3)$$

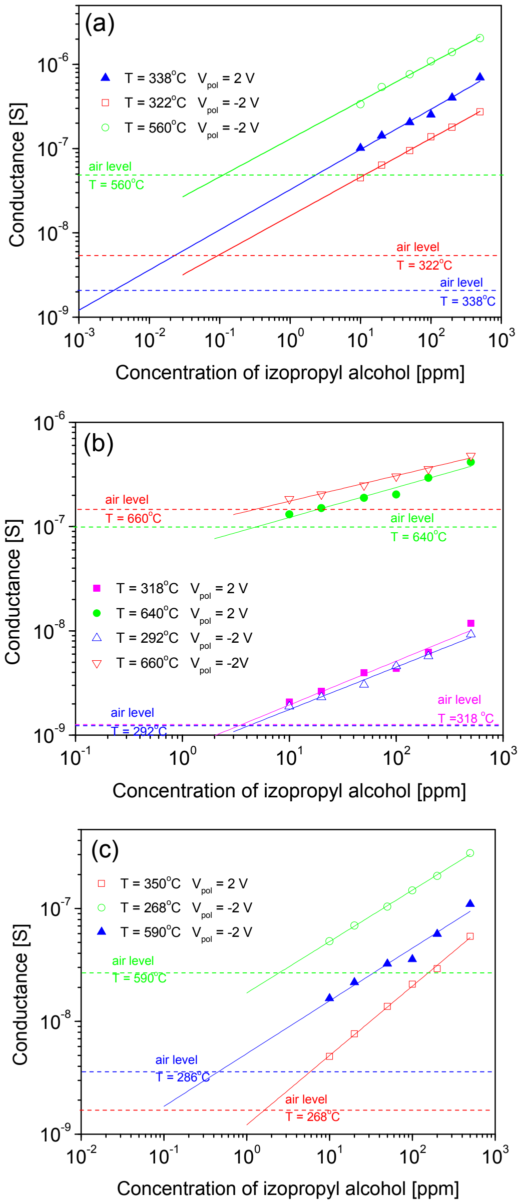

Fig. 5. Dependence of sensing structure conductance versus partial pressure of isopropyl alcohol: a) $ZnO|SnO_2$+0.8 Au, b) $SnO_2|WO_3$, c) $SnO_2|WO_3$+0.8 Au.

One should consider, that in the case of heterocontact gas sensors the coefficients G_0 and n doesn't represent the properties of a single layer as it could be conclude from the formula (2). Those factors correspond to an equivalent circuit which elements describe the interaction of the target gas with the gas sensitive materials in the junction region and in the two single phase metal oxides areas.

At a stable polarization voltage and temperature this equivalent circuit can be express as a single impedance element and lead to the equations (2) and (3).

Conclusions

The sensing properties of thick film ZnO|SnO_2+0.8 wt. % Au, SnO_2|WO_3 and SnO_2|WO_3+0.8 wt. % Au heterocontact gas sensors were investigated. The response of the devices to the presence of isopropyl alcohol has been shown.

The obtained current-voltage characteristics show rectifier properties for all three heterojunctions.

The highest sensitivity of about 200 was achieved by the ZnO|SnO_2+0.8 wt. % Au which work at a polarization voltage of 2 V and a temperature of 338°C. Its lower detection limit was estimated to be at about 3 ppb.

The rectifying properties of such heterojunction gas sensors give a an additional degree of freedom for the manipulation of sensor parameters. By combination of changes in polarization voltage with heater temperature modulation it is possible to control the sensor sensitivity and selectivity.

Acknowledgements

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