UV-assisted Chemiresistive Alcohol Sensor Based on Cobalt Doped Tin Dioxide

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***Abstract*—In this paper, a sputtering ceramic target based on SnO_2 doped with 2 at.% Co was synthesized by solid-phase reaction method. A chemiresisive alcohol vapor sensor based on SnO_2<Co> was manufactured by the high-frequency magnetron sputtering method. The alcohol sensing properties of the SnO_2<Co> sensor under the ultraviolet (UV) illumination were examined at room temperature. The UV-assisted alcohol sensor showed a sufficient response to low concentrations of alcohol vapor at room temperature. The Co-doped SnO_2 sensor has also demonstrated a good response to alcohol vapors at elevated operating temperature (200 °C).**

Keywords - gas sensor; alcohol; UV radiation; room temperature; metal oxides.

I. INTRODUCTION

Today, alcohol vapor sensors have a great demand in various fields. Ethanol sensors are used in food industry, medicine and biotechnology. Ethanol sensors are also extremely important during the production of ethanol and alcoholic drinks to monitor the wine quality. They are used in processes such as: food–packages, clinical analysis, agronomic, vinicultural and veterinary analysis, also toxic waste and contamination analysis, fuel processing, Trends in Analytical Chemistry (TRAC) management and societal applications, as well as chemical processing in industry [1]-[5]. Several methods and strategies have been reported for the detection of ethanol, e.g., gas chromatography, liquid chromatography, refractometry and spectrophotometry, semiconductor gas sensors and so on [2][6][7].

The solid-state gas sensors based on Metal Oxide Semiconductors (MOSs) with different nanostructures have played an important role in environment monitoring, domestic and car safety, control in chemical processing due to their distinct advantages, such as simple implementation, low cost, high sensitivity, stability and reproducibility, low detection limit, easy production, nontoxicity, easy-achieved real-time response and compatibility with micro-fabrication processes [8]-[10]. Various MOSs materials, such as SnO_2, In_2O_3, WO_3, ZnO, TiO_2, Fe_2O_3, CuO, Ga_2O_3, CTO (CrTiO) with different nanostructures and dopant have been studied and showed promising results for detecting Volatile Organic Compounds (VOCs) [11]. Among these materials, the SnO_2 has good electrical and chemical properties. It is an n-type semiconductor with tetragonal rutile structure and it has a large energy band gap of 3.6 eV at 300 K. It has been widely exploited as an ultrasensitive gas sensor for the detection of carbon monoxide (CO), ammonia, ozone, carbon dioxide, hydrogen, hydrogen peroxide, nitrogen dioxide, ethanol and so on [12]-[14]. The wide range of possible applications has attracted many researchers to work on this material with different nanostructures, such as nanograins, nanorods, nanowires and nanofibers synthesized by various methods. It has a high sensitivity to reducing and oxidizing gases, fast response and recovery behavior and low sensitivity to humidity [15]-[17].

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Although many conductometric gas sensors made of MOSs have been commercialized for the last decades, a lot of problems still need to be solved in order to improve the performance of gas sensing devices. The main issues are related to sensitivity, selectivity and stability but the lowering of sensor's operating temperature is still one of the main concerns. Resistive metal oxide based gas sensors normally operate at an elevated temperature (in a range of 200 ºC to 400 ºC). This results in higher power consumption, limits the use of the sensor in explosive environments, and causes difficulties for the sensor to be attached to electrical systems [18][19].

There are many studies aimed at applying new technologies and reducing operating temperatures. To ensure a low operating temperature, several techniques have been used, such as doping the metal oxides with additives, using catalytic particles, applying a high electric field across the sensor terminals and illuminating the sensors with UV radiation [20][21]. The irradiation of UV-assisted MOS sensors is an important alternative to activate chemical reactions on metal oxide surface and reduce the resistance of the thin sensing layer instead of the more common use of energy-demanding heating. Almost completely replacing the effect of thermal energy, UV irradiation greatly influences the adsorption and desorption processes of the gas on the semiconductor surface enhancing their reactivity with the analyte gas. Under the influence of UV illumination, as a result of the formation of electron–hole pairs, more neutral atoms and molecules of absorbed oxygen on the surface of the semiconductor become ions, which then interact with analyte gas. UV irradiation can also be used to clean the active surface of a gas sensing layer, but the more important function is to improve the sensitivity and selectivity of the gas sensor by reducing the operating temperature. If it is not possible to lower the operating temperature to room temperature by using UV irradiation, UV irradiation combined with heating can be used to stimulate the gas sensor [22]-[24].

In this paper, we focus on low temperature sensing of SnO_2 based thin film sensors under UV illumination. In Section 2, the fabrication steps of SnO_2<Co> sensor are presented. In Section 3, the studies of sensing properties of UV assisted ethanol sensor are presented. The conclusions are outlined in Section 4. The sensor exhibited good sensitivity to low concentration of ethanol vapors. Fabricated sensors have also sufficient selectivity and stability over time.

II. SENSOR FABRICATION

Sensitive layers based on SnO_2<Co> were deposited by RF magnetron sputtering technique. Firstly, appropriate quantities of the corresponding metal oxide powders (SnO_2+2 at.%Co_2O_3) were weighed and mixed thoroughly for 10 hours. Then, the mixture was subjected to pre-heat treatment at 800 ^{0}C for 5 hours (the initial annealing temperature was chosen based on the composition of the compound). The preheating of mixed powder eliminates the moisture of the metal oxide raw materials, which facilitates homogeneous mixing and milling of the powders (when the ceramic tablet is made of dry powders, it reduces the probability of formation of mechanical cracks during final annealing). Then, the mixed powder was milled for 20 hours until becoming fully homogeneous and pressed (with 2000 N/cm^2 pressure) in a form of a tablet (with 50 mm diameter). The sputtering ceramic target based on SnO_2 doped with 2 at.% Co (using the pressed tablet) was synthesized by solid-phase reaction method using thermal treatment in the atmosphere by the programmable furnace Nabertherm, HT O4/16 (with the controller of C 42). The final annealing was carried out at temperature range of 500 °C-1100 °C for 20 hours. The synthesized semiconductor solid solution was subjected to mechanical treatment in order to eliminate surface defects. So, a smooth and parallel target with a diameter of 40 mm and thickness of 2 mm was prepared as a magnetron sputtering target (see Figure 1).

The thin sensing layers were deposited on Multi-Sensor-Platforms by RF magnetron sputtering method using synthesized SnO_2<Co> target. The Multi-Sensor-Platforms were purchased by TESLA BLANTA (Czech Republic). The platform has a temperature sensor (Pt 1000) for controlling operating temperature. There are platinum heater and interdigitated electrodes on the ceramic substrate of the Multi-Sensor-Platform (see Figure 2). The heater and temperature sensor were covered with an insulating glass layer. Gas sensitive SnO_2<Co> layer was deposited onto the non-passivated electrode structure, so the Multi-Sensor-Platform was converted into gas sensor. Then, palladium catalytic particles are deposited on the surface of the magnetron sputtered sensing layer by ion-beam sputtering method for sensitization of active layer. The working conditions of the high-frequency magnetron sputtering and ion-beam sputtering are presented in Table I (the base pressure was 2×10^{-4} Pa for both cases). The manufactured sensors were annealed in the air at 350 °C for 4 hours for homogenization of sensing films and stabilization their parameters. The fabrication steps of photo-assisted gas sensor are presented in Figure 1.

The thickness of the SnO_2<Co> thin film was measured by the Alpha-Step D-300 (KLA Tencor) profiler. The result of the study of the film-substrate transition profile is shown in Figure 3. The thickness of the SnO_2<Co> film was equal to 180 nm.

The electrical and gas sensing properties of the SnO_2<Co> thin layer was measured using a home-made computer-controlled gas testing system. The testing system has a test chamber, pressure sensor (Motorola-MPX5010DP) and a data acquisition system (PCLD-8115) [25]. For measurement of alcohol vapor concentration, the SnO_2<Co> based sensor (the Multi-Sensor-Platform) was attached in the test chamber connecting the six pins (two pins of temperature sensor, two pins of heater and two pines of resistance measurement electrodes, see Figure 2) with the corresponding inputs on sensor holder. The UV LED (λ=365 nm) was attached 0.5 cm away from the active layer with illumination of 2 mW/cm^2. The gas sensing properties of the SnO_2<Co> sensor were measured at room temperature in the dark and under UV illumination. The

response of the sensor was measured also at 200 ^{0}C operating temperature in the dark. The working temperature of the sensor was adjusted by changing the voltage across the platinum heater. To have the necessary concentration of

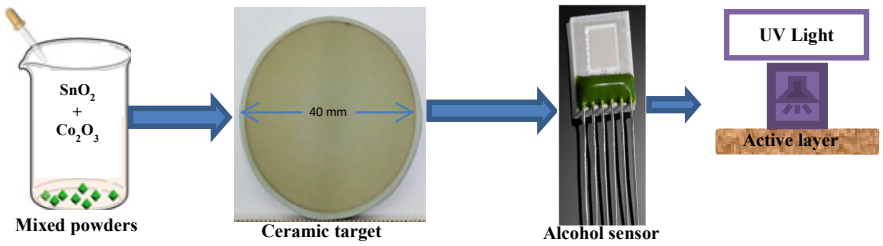

Figure 1. Schematic block diagram of the photo-assisted gas sensor fabrication.

TABLE I. THE WORKING CONDITIONS FOR DEPOSITION OF THIN LAYER AND CATALITIC PARTICLES.

Process	Sputtering duration	Working pressure	Power of generator	Substrate temperature	Cathode current	Anode voltage	Sputtering gas
Magnetron sputtering (RF)	20 m	2×10^{-1} Pa	60 w	200 ^{0}C	---	---	Ar
Ion-beam sputtering (DC)	3 s	5×10^{-1} Pa	---	100 ^{0}C	65 A	25 V	Ar

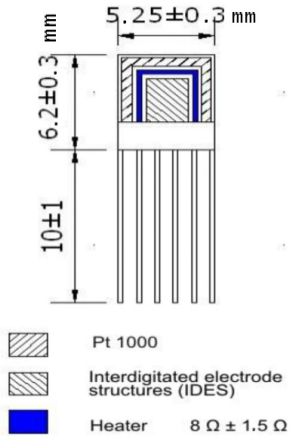

Figure 2. The schematic diagram of the Multi-Sensor-Platform.

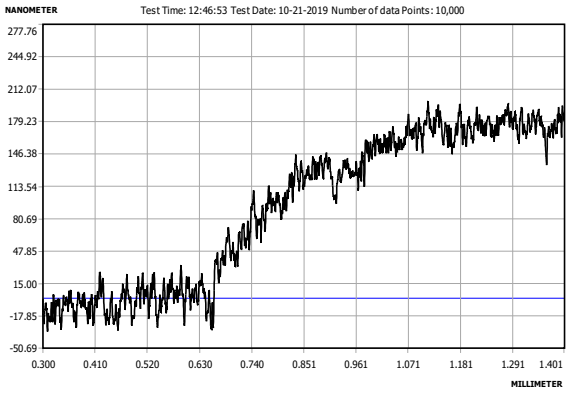

Figure 3. The thickness measurement result for the Co-doped SnO_2 film.

alcohol vapor in the chamber, the liquid ethanol was introduced into the chamber on the special hot plate designed for the quick conversion of the liquid ethanol to the gas phase. The response of the sensor is defined as $[(R_a-R_g)/R_a]\times100$ %, where R_a and R_g are the electrical resistances of active layer in air and target gas, respectively.

III. GAS SENSING PERFORMANCES

Initially, we tested the influence of the UV illumination on the baseline resistance of the SnO_2<Co> sensor at room temperature. It can be seen from Figure 4 that the value of R_0/R_{UV} (~350) ratio is larger than 1, indicating the decrease of the sensor baseline resistance under UV illumination. The response time of the Co-doped SnO_2 thin film under UV irradiation is a few minutes.

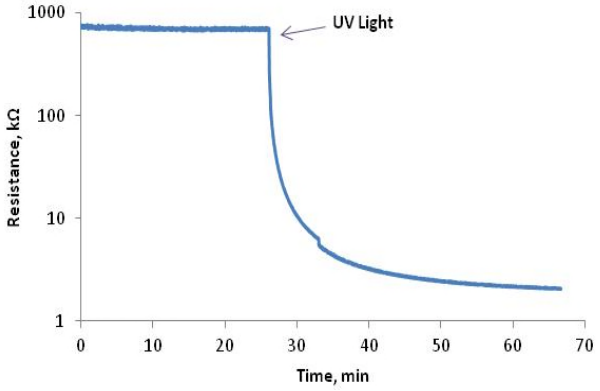

Figure 4. Resistance variation of the Co-doped SnO_2 sensing layer under the influence of UV irradiation at room temperature.

The manufactured sensor is resistive and its operation is grounded on changes of resistance of gas sensitive semiconductor layer under the influence of ethanol vapors caused by an exchange of charges between molecules of the semiconductor film and absorbed ethanol. The high operating temperature of these types of sensors is mainly due to the high activation energies of chemical reactions. For this reason, these types of sensors mainly do not sensitivity at room temperature. The UV light promotes the gas adsorption and desorption on the surface of the semiconductor participating to the sensing mechanisms [23].

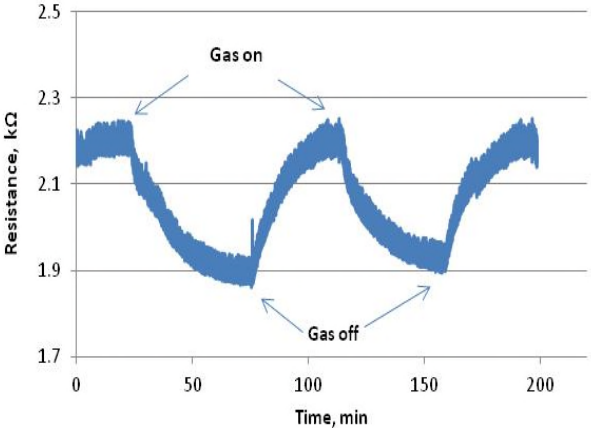

Figure 5. Resistance variation of the SnO_2<Co> sensor under the influence of UV irradiation at room temperature in the presence of 150 ppm ethanol vapors.

The thin film SnO_2<Co> based sensor did not show sensitivity to ethanol vapors at room temperature without UV irradiation. We measured the resistance variation (also the signal repeatability) of the SnO_2<Co> sensor in the presence of ethanol vapors under the influence of UV irradiation at room temperature. The resistance of the thin film changes by almost 400 Ω in the presence of 150 ppm ethanol vapors (see Figure 5).

Sensor response and recovery times are in minutes and it is clear that recovery times are faster because UV light more stimulate the desorption processes from the surface of the sensing layer.

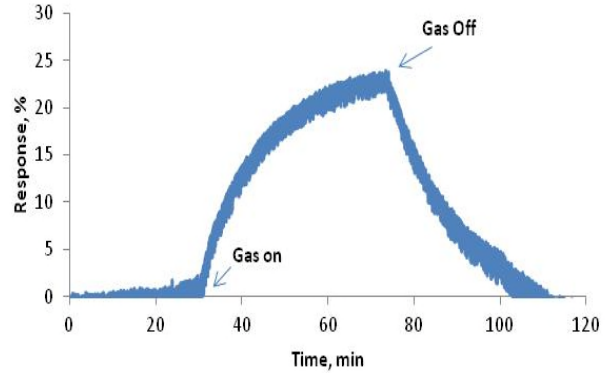

Figure 6. The SnO_2<Co> sensor response to 900 ppm of ethanol vapors under the influence of UV irradiation at room temperature.

Figure 6 shows the transient response of the SnO_2<Co> sensor in the presence of ethanol under UV light at room temperature. The response to 900 ppm ethanol vapors under UV illumination is sufficiently high (24 %).

We extracted the response vs. concentration curve for the Co-doped SnO_2 sensitive film. Figure 7 shows the dependence of response on the ethanol vapor concentration under the influence of UV irradiation at room temperature. The dependence has almost linear characteristic, which will allow not only to detect of ethanol vapors but also to accurately measure the low concentrations of this gas.

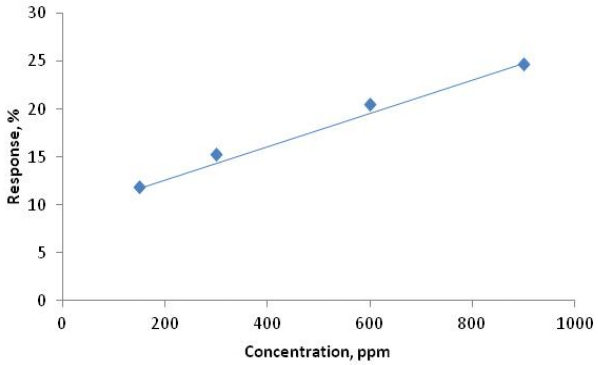

Figure 7. The dependence of response on the ethanol vapor concentration under the influence of UV irradiation at room temperature.

The resistance change of the Co-doped SnO_2 sensor under the influence of ethanol vapors at high operating temperature in dark conditions was also measured. The sensitive layer resistance decreases more than 25 times in the presence of 150 ppm ethanol vapors at 200 ^{0}C operating temperature (see Figure 8). The response and recovery times

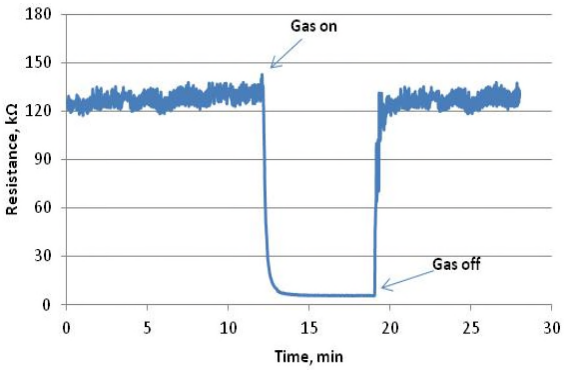

Figure 8. Resistance variation of the SnO_2<Co> sensor in the presence of 150 ppm ethanol vapors at 200 °C operating temperature in the dark.

of the sensor at high operating temperature are a few seconds. At high operating temperature in dark condition, the sensor performance is quite promising but the power consumption of fabricated sensor at 200 ^{0}C is about 2.5 W. It is more than two orders high then the power consumption (24 mW) needed the sensor operating with UV irradiation at room temperature.

IV. CONCLUSION

In summary, a simple technology has been used to manufacture semiconductor thin film sensor based on SnO_2 doped with 2 at.% Co. The fabricated SnO_2<Co> chemiresistive gas sensor showed a good sensitivity to different concentrations of ethanol vapor (from 150 to 900 ppm) at room temperature with the activation of low-powered UV LED (24 mW, 365 nm). The sensor displayed a good signal repeatability and long-term stability. These sensing characteristics made the present SnO_2<Co> based sensor a promising candidate for practically detecting ethanol vapors at room temperature.

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