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Sensor for Detection of Chemical Agents Made of Co-Doped SnO_2

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Abstract. SnO_2+2at.% Co gas sensitive thin films with different thicknesses were deposited on alumina substrates and on the Multi-Sensor-Platforms by the rf magnetron sputtering method using SnO_2 doped with 2 at.% Co ceramic target prepared by us. Palladium catalytic particles and interdigital gold contacts (when the alumina substrate was used) were deposited by ion beam sputtering method on the surface of the sensing layers. The response of semiconductor films to dichloroethane, dichloromethane, dimethylformamide, propylene glycol, sarin and yperit vapors was measured at different operating temperatures. It was found that the SnO_2 doped with 2 at.% Co sensor with film thickness of 160 nm has high response to different concentrations of above mentioned chemical agents.

Keywords: gas sensor, chemical agents, thin film, magnetron sputtering, SnO_2

1. Introduction

Threat of military operations and terrorist acts with application of chemical agents is not only maintained, but also unfortunately rises in the modern world. Two sarin gas attacks in Japan (Matsumoto and Tokyo, 1994-1995) and recent military operations in Syria confirm this horrible reality. Therefore, the researchers in all countries continue to investigate the possibility of developing of sensors for detection of chemical agents. Note that chemical agents include chemical warfare agents (e.g., sarin, soman, tabun, ethyl sarin, sulfur mustard, nitrogen mustard, hydrogen cyanide, arsine, chlorine, phosgene et.al.) and toxic industrial chemicals (hydrogen cyanide, nitrous oxide, carbon monoxide, dichloromethane, phosphorus pentafluoride et al.). Sensors for detection of chemical agents should be sensitive to very low concentrations of agents – considerably lower than immediately dangerous to life or health concentrations. Note also that because of extremely high toxicity of chemical warfare agents (CWAs) their handling in laboratory, when testing the related sensor, is very dangerous risk. Therefore, many researchers in place of CWAs usually utilize appropriate stimulants for the testing of sensor devices. For example, dimethyl-methyl-phosphonate is often studied as a stimulant of nerve agents such as sarin and soman, 1.5-dichloropentane and di(propyleneglycol) methyl ether are considered as stimulants of mustard gas (vesicants agents), acetonitrile known as a stimulant for cyanide agents.

Several techniques such as infrared spectrophotometry, Raman spectroscopy, colorimetric indicators, ion mobility spectrometer and mass spectrometers combined with gas chromatographs have been developed to detect the CWAs and toxic industrial chemicals (TICs). Several kind of gas sensors have been developed based on different sensing materials and various transduction platforms. The main classes of gas-sensing materials include metal oxide semiconductors, metal-oxide/polimer composite, carbon nanotube, graphene and other novel materials. Now arrays of chemically sensitive micro resistors of above-mentioned gases produced from semiconductor metal oxide are considered as one of the most promising basic technologies for detection of chemical agents. These metal oxide based chemiresistive semiconducting sensors offer advantages such as their very low cost, high

sensitivity, fast response and recovery times, easy in manufacturing, small size, simple electronic interface, low power consumption and portability [1].

SnO_2 is the most studied material and SnO_2-based gas sensors have been used to detect CWAs and TICs [2-8], but other semiconductor metal oxide such as TiO_2, WO_3, ZnO, CuO, In_2O_3 have also been considered [9-11].

In this paper, we report the development of technology and fabrication of a Co-doped SnO_2 nanostructured films based sensors for detection of CWAs such as sarin and yperite, as well as TICs such as dichloroethane, dichloromethane, dimethylformamide and propylene glycol. The Co-doped SnO_2 thin films were synthesized by the high-frequency magnetron sputtering method and their sensing properties were investigated.

2. Materials and measurements methods

Ceramic targets made of metal oxide SnO_2 doped with 2 at.% Co were synthesized by the method of solid-phase reaction in the air. The powders of initial oxides (SnO_2 and Co_2O_3) were weighed in the applicable quantities. This mixture was carefully intermixed and pressed. The compacted samples SnO_2<Co> were exposed to thermal treatment in the programmable furnace Nabertherm, HT O4/16 with the controller C 42. The annealing was carried out at 500 °C (five hours), 700 °C (five hours), 1000 °C (five hours) and 1100 °C (five hours) consecutive. Then, the synthesized compositions were subjected to mechanical treatment in the air in order to eliminate surface defects. Thus, smooth, parallel targets with a diameter of ~ 40 mm and thickness ~ 2 mm were prepared.

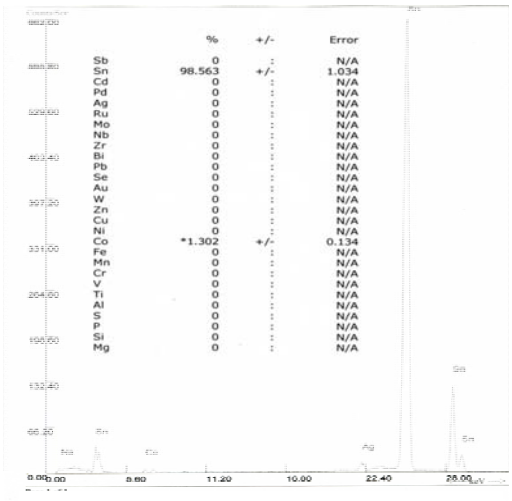

Fig. 1. The result of chemical analysis of the SnO_2<Co> target.

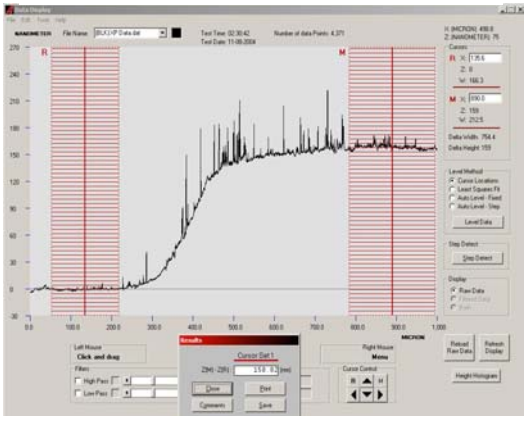

Fig. 2. The thickness measurement result for the Co-doped SnO_2 film.

Chemical composition of prepared SnO_2 <Co> targets was studied using Niton™ XL3t GOLDD+ XRF Analyzer. The results of this investigation have shown that the real content of cobalt's atoms on the surface of the prepared ceramic targets was equal to 1.3 % (Fig. 1).

Prepared semiconductor SnO_2<Co> targets had sufficient conductance and were used for deposition of nanosize films using the high-frequency magnetron sputtering method. An alumina or Multi-Sensor-Platforms (purchased from TESLA BLATNÁ, Czech Republic) were used as a substrate for films. In the last case, when the Multi-Sensor-Platforms were used as substrates, the chip was kept at constant temperature using heat resistance. The platform integrates a temperature sensor (Pt 1000), a heater and interdigital electrode structures of platinum thin film on a ceramic substrate. The heater and temperature sensor are covered with an insulating glass layer. Gas sensitive layer made of SnO_2<Co> was deposited onto the non-passivated electrode structures. Then, the Multi-Sensor-Platform was converted into gas sensor.

The following working conditions of the high-frequency magnetron sputtering were chosen: the power of the magnetron generator unit was 60 W; the substrate temperature during sputtering was 200 °C; duration of the sputtering process was equal to 20 minutes for SnO_2<Co>. The sensing device was completed through the ion-beam sputtering deposition of palladium catalytic particles (the deposition time ~ 3 seconds). The interdigital gold contacts were deposited (the

deposition time was 1 hour) by ion beam sputtering method on the surface of the sensing layers when the alumina substrate was used. Further annealing of the manufactured structures in the air was carried out at the temperature of 350 °C during 2 hours to obtain homogeneous films and eliminate mechanical stress.

The thickness of the deposited doped metal oxide films was measured by Ambios XP-1 profilometer (see Fig. 2). The thickness of the SnO_2<Co> films was equal to 160 nm.

The morphology of the deposited Co-doped SnO_2 films was studied by scanning electron microscopy using Mira 3 LMH (Tescan). The result of the study of morphology for the deposited doped metal oxide films is presented in the Fig. 3. The average size of nanoparticles was equal to18.7 nm.

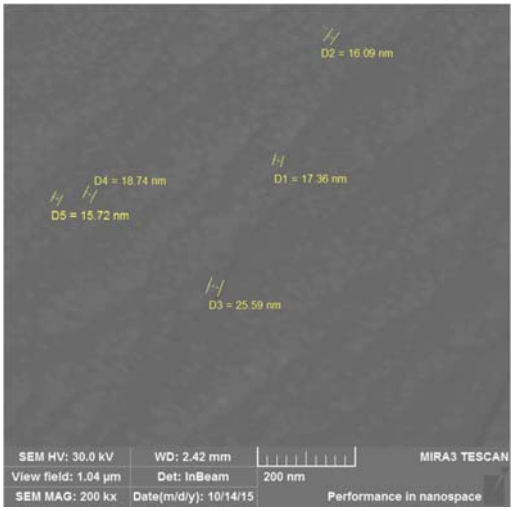

Fig. 3. The SEM image for the SnO_2<Co> film.

Gas sensing properties of prepared sensors made of Co-doped SnO_2 metal oxide films under the influence of TICs were measured in YSU using homemade developed and computer-controlled static gas sensor test system [12]. The sensors were reheated and studied at different operating temperatures. When the electrical resistance of sensors was stable, the vital assigned amount of compound in the liquid state for sensors testing was injected in measurement chamber by a microsyringe. Moreover, the target matters were introduced into the chamber on the special hot plate designed for the quick conversion of the liquid substance to the gas phase. After its resistance reached a new constant value, the test chamber was opened to recover the sensors in the air. The sensor on alumina substrate is put on the heater, which allows raising temperature of the sensor active area up to 350 °C. Testing of the SnO_2<Co> semiconductor sensors responses to the different gases such as dichloroethane, dichloromethane, dimethylformamide and propylene glycol vapors was carried out at the different operating temperatures (from room temperature up to 350 °C). All measurements were carried out at 0.5 V applied voltage on sensor electrodes.

Investigations of the sensitivity of the prepared sensors made of Co-doped SnO_2 films to CWAs such as sarin and yperite were carried out at University of Defense (Vyshkov, Czech Republic). Measuring system for gas sensor testing works as vacuum-type, where gaseous sample from sample bag flows through 3-way valve to glass measuring chamber and then through flow meter to membrane pump, which generates vacuum. Sample bags are multi-layer foil chromatography bags (Supelco brand) with aluminum foil. Measuring glass chamber can be equipped by four different gas sensors connected via electrical feed troughs. Resistance of a sensitive layer is recorded by DC measurement by Agilent 34970A data logger unit with multiplexer card. Gaseous sample with concentration in ones of ppm are prepared by procedure, where in the first step we fill the sample bag with defined volume of ambient air (the same air we fill also to the second bag as reference), then we inject calculated volume of liquid agent by Hamilton syringe via septum to the sample bag. Sample bags were kept for at least an hour prior measurement until injected agent evaporates in the bag fully. Prepared sample bags with contain of agent and with reference air are connected to 3-way valve, by which we can switch desired atmosphere. These measurements were performed at the operating temperature of 210 °C.

3. Results and discussion

We investigated the sensitivity of prepared SnO_2<Co> sensors to such TICs as dichloroethane ($C_2H_4Cl_2$), dichloromethane (CH_2Cl_2), dimethylformamide (C_3H_7NO) and propylene glycol ($C_3H_8O_2$). The sensors manufactured by us are resistive, i.e., their operation is grounded on changes

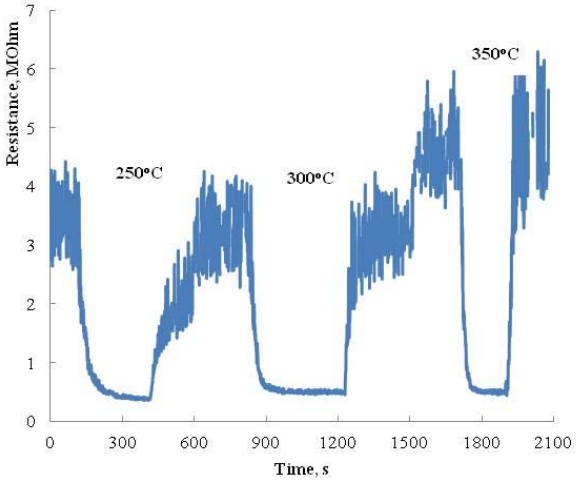

Fig. 4. The SnO_2<Co> sensor resistance variation under the influence 200 ppm of dichloromethane at different work body temperatures.

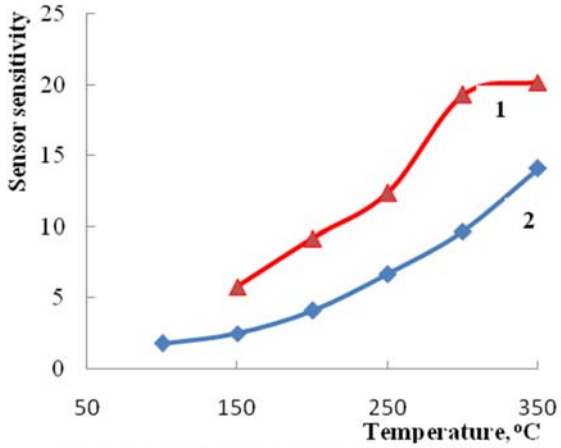

Fig. 5. The SnO_2<Co> sensor sensitivity dependence on temperature to 500 ppm dimethylformamide (1) and 350 ppm dichloroethane (2).

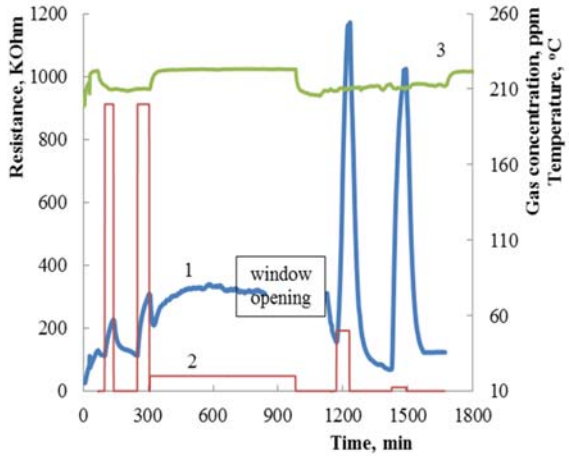

Fig. 6. The resistance variation under influence of sarin for the Co-doped SnO_2 sensor (1). Curves (2) and (3) - gas concentration and work body temperature, accordingly.

in the resistance of gas sensitive semiconductor layer under the influence of target gas due to an exchange of charges between molecules of both the semiconductor film and adsorbed target gas. As known, there are ions such as O_2^-, O^- and O^{2-} on the surface of semiconductor films. They originate due to electrons, which are captured by adsorbed oxygen on the surface of oxide:

$$O_2\,(gas) \leftrightarrow O_2\,(ads) \quad (1)$$

$$O_2\,(ads) + e^- \leftrightarrow O_2^-\,(ads) \quad (2)$$

$$O_2^-\,(ads) + e^- \leftrightarrow 2O^-\,(ads) \quad (3)$$

$$O^-\,(ads) + e^- \leftrightarrow O^{2-}\,(ads). \quad (4)$$

The exchange of charges takes place between these surface oxygen species and target gas molecules. So, the reaction between oxygen species and dichloroethane, dichloromethane, dimethylformamide and propylene glycol can be simply described by reactions (5), (6), (7) and (8), respectively. A variation of the sensor resistance takes place as a result of such exchange of electrons. This variation of resistance was fixed as sensor response.

$$C_2H_4Cl_2 + 3O^- \rightarrow 2HCl\uparrow + 2CO_2\uparrow + H_2O\uparrow + 3e^- \quad (5)$$

$$CH_2Cl_2 + 2O^- \rightarrow 2HCl\uparrow + CO_2\uparrow + 2e^- \quad (6)$$

$$2C_3H_7NO + 21O^- \rightarrow 6CO_2\uparrow + 4NO_2\uparrow + 7H_2O\uparrow + 21e^- \quad (7)$$

$$C_3H_8O_2 + 8O^- \rightarrow 3CO_2\uparrow + 4H_2O\uparrow + 8e^-. \quad (8)$$

The typical curve demonstrating the changing of the sensor resistance under the influence of the target gas at invariable work body temperature is presented in Fig. 4.

The sensor sensitivity was determined as the ratio of R_{air}/R_{gas}, where R_{gas} is the sensor resistance in the presence of target gas in the air and R_{air} is the sensor resistance in the air without target gas. The dependence of the SnO_2<Co> sensor sensitivity to 350 ppm dichloroethane and 500 ppm dimethylformamide on the work body temperature is presented in Fig. 5. Investigated Co-doped SnO_2 metal oxide sensors demonstrate response to 350 ppm dichloroethane starting from 100 °C. The resistance of the SnO_2<Co> sensor was changed more than one order under the influence of 500 ppm dimethylformamide at operating temperature of 300 °C.

The SnO_2<Co> sensor sensitivity to 200 ppm dichloromethane and 650 ppm propylene glycol at different work body temperatures is presented in Table 1. The response to 200 ppm dichloromethane and 650 ppm to propylene glycol was detected for prepared SnO_2<Co> sensors starting at 150 °C. The best sensitivity was achieved at operating temperature of 200 °C and 300 °C to 200 ppm dichloromethane and to 650 ppm propylene glycol, respectively.

Table 1. The Co-doped SnO_2 sensor sensitivity

Temperature	dichloromethane (200 ppm)	propylene glycol (650 ppm)
150 °C	3.5	2
200 °C	36	22.7
250 °C	10.4	282
300 °C	9	417
350 °C	13.5	207

The sensitivity of our SnO_2<Co> sensors to vapors of sarin and yperit was measured in the University of Defense (Vyskov, Czech Republic). As shown from the presented results of these measurements (Fig. 6 and Fig. 7), the sensor was exposed comparatively greater concentration of target gas (200 ppm sarin and 100 ppm yperite) at the beginning of the measurements. Thus, the stabilization of the sensor parameters occurred. After that the SnO_2<Co> sensor was sensitive to yperite starting from 25 ppm. The sensitivities to 50 ppm and 12.5 ppm sarin were equal ~8 and ~15, accordingly, at the operation temperature of 210 °C.

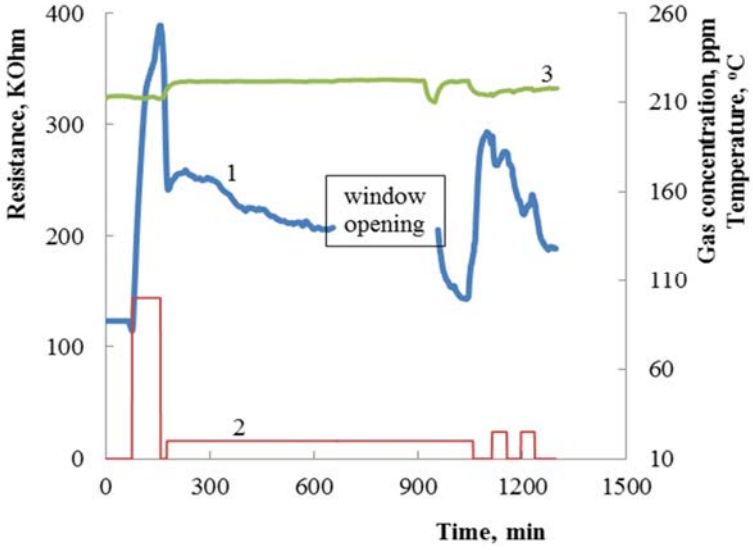

Fig. 7. The resistance variation under influence of yperite for Co-doped SnO_2 sensor (1). Curves (2) and (3) - gas concentration and work body temperature, accordingly.

4 Conclusions

The technology for the manufacturing of semiconductor sensor made of Co-doped SnO_2 was developed. Nanostructured SnO_2<Co> films were deposited onto the alumina substrate and Multi-Sensor-Platforms using the high-frequency magnetron sputtering method. The thickness of sensitive layer was measured, as well as its chemical composition and surface morphology were studied. Specimens detecting CWAs and TICs were manufactured and investigated. The response of the prepared thin film Co-doped SnO_2 sensors to different concentrations of the vapors of sarin and yperite was measured at the operating temperature of 210 °C. The responses to various TICs (propylene glycol, dichloroethane, dichloromethane and dimethylformamide) were measured at different work body temperatures of the SnO_2<Co> sensor.

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