Co-DOPED SnO_2 SENSOR FOR DETECTION OF CHEMICAL AGENTS

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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, in all countries the researchers 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 CWAs their handling in laboratory, when testing the related sensor, is very dangerous risk. Therefore, many researchers in place of SWAs usually utilize an appropriate simulants for the testing of sensor devices. For example, dimethyl-methyl-phosphonate is often studied as a simulant of nerve agents such as sarin and soman, 1,5-dichloropentane and di(propyleneglycol) methyl ether are considered as simulants of mustard gas (vesicants agents), acetonitrile known as a simulant for cyanide agents. Several techniques have been developed to detect the chemical warfare agents (CWAs) and toxic industrial chemicals (TICs) such as infrared spectrophotometry, raman spectroscopy, colorimetric indicators, ion mobility spectrometer and mass spectrometers combined with gas chromatographs. 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/polymer composite, carbon nanotube, graphene and other novel materials. Now arrays of chemically sensitive micro resistors 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 [1-4]. SnO_2 is the most studied material and SnO_2-based gas sensors have been used to detect CWAs and TICs [5-8], 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 about the development of technology and fabrication of a Co-doped SnO_2 nanostructured films based sensors for detection such CWAs as sarin and yperite, and such TICs 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 ~ 40 mm and thickness ~ 2 mm were prepared.

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 atom on the surface of the prepared ceramic targets was equal 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 substrate for films. In last case, when the Multi-Sensor-Platforms were used as substrates, the chip can be kept at constant temperature using heat resistance. The platform integrates a temperature sensor (Pt 1000), a heater and interdigitated electrode structures in platinum thin film on a ceramic substrate. Heater and sensor are covered with an insulating glass layer. Gas sensitive layer made of SnO_2<Co> was deposited onto the non-passivated electrode structures. That way 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

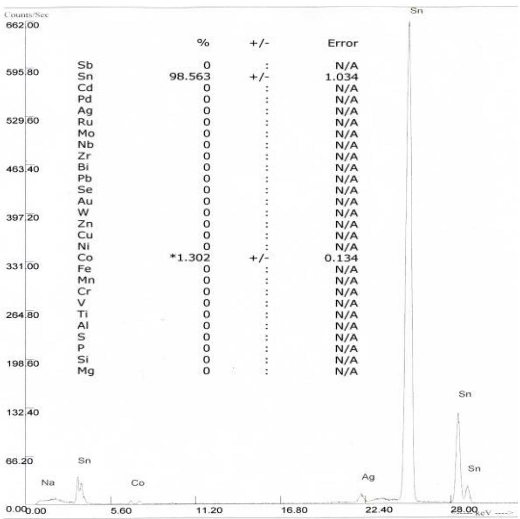

Fig. 1. The result of chemical analysis of the SnO_2<Co> target.

particles (the deposition time ~ 3 seconds). The interdigited 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 temperature 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 160 nm.

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 on the Fig. 3. The average size of nanoparticles was equal 18.7 nm.

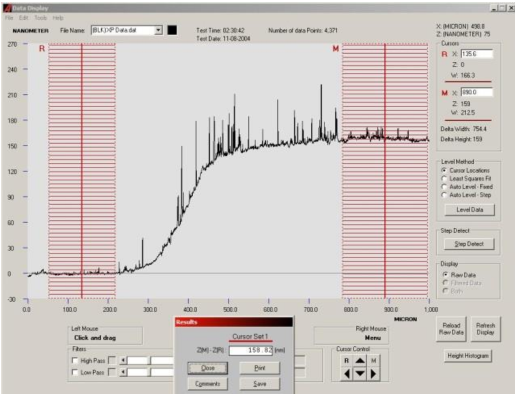

Fig. 2. The thickness measurement result for the Co-doped SnO_2 films.

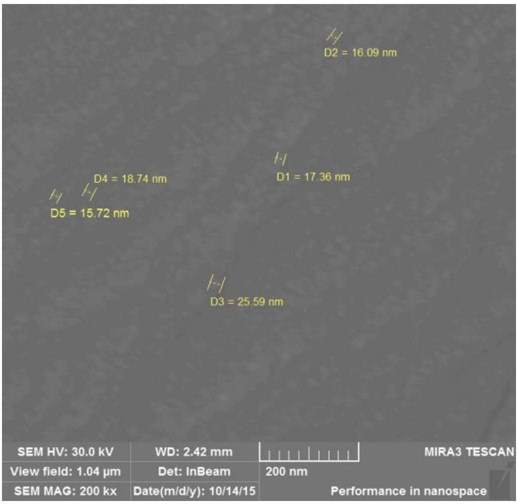

Fig. 3. The SEM image for the SnO_2<Co> films.

Gas sensing properties of prepared sensors made from Co-doped SnO_2 metal oxide films under the influence of TICs were measured in YSU using home-made 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 its 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 working body 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 sensor applied voltage 0.5 V. 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 Defence (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 flowmeter 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 4 different gas sensors connected via electrical feedthroughs. Resistance of 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 carried out at the operating temperature 210 °C.

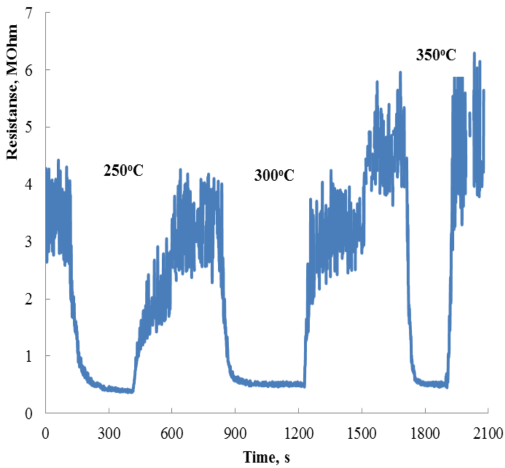

Fig. 4. The SnO_2<Co> sensor resistance variation under the influence 200 ppm of dichloromethane at different work body temperatures.

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 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 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.

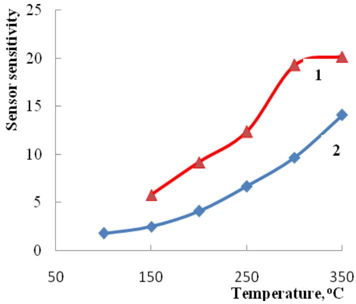

Fig. 5. The SnO_2<Co> sensor sensitivity dependence on temperature to 500 ppm dimethylformamide (1) and 350 ppm dichloroethane (2).

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

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

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

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

A variation of the sensor resistance takes place variation of resistance was fixed as sensor response.

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

The sensor sensitivity was determined as the ratio 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 temperature of the work body is presented on the 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 on order under the influence of 500 ppm dimethylformamide at operating temperature 300 °C. The SnO_2<Co> sensor sensitivity to 200 ppm dichloromethane and 650 ppm propylene glycol at different work body temperatures is presented on the 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 200 °C and 300 °C to 200 ppm dichloromethane and 650 ppm to propylene glycol, respectively. The sensitivity of our SnO_2<Co> sensors to vapours of sarin and yperit was measured in the University of Defence (Vyskov, Czech Republic). As shown from the presented results of these measurements (Fig. 6 and Fig. 7), the sensor is exposed comparatively greater concentration of gas (200 ppm sarin and 100 ppm yperite) in the beginning of the measurements. Thus, the stabilization of the sensor parameters occurs. After that the SnO_2<Co> sensor was sensitive to yperite starting from 25 ppm. The sensitivity to 50 ppm and 12.5 ppm sarin were equal ~8 and ~15, accordingly, at the operation temperature 210 °C.

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

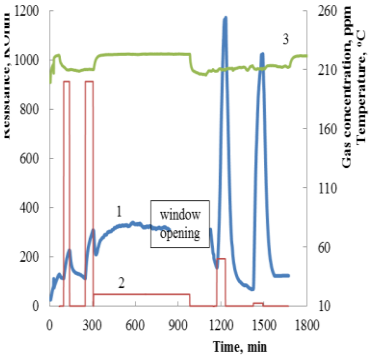

Fig. 6. The resistance variation under influence of sarin for the Co-doped SnO_2

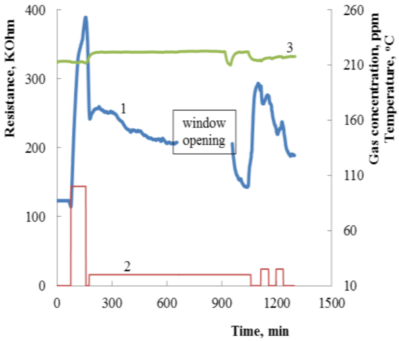

Fig. 7. The resistance variation under influence of yperite for Co-doped SnO_2 sensor (1). Curves (2) and (3) - gas concentration and work body temperature, accordingly.

3. Conclusions

The technology for the manufacturing of semiconductor sensor made of Co-doped SnO_2 was developed. Nanostructured films SnO_2<Co> were deposited onto the alumina substrate and Multi-Sensor-Platforms using the high-frequency magnetron sputtering method. The thickness of sensitive layer was measured; 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 sarin and yperite was measured at the operating temperature 210 °C. The responses to various TICs (propylene glycol, dichloroethane, dichloromethane and dimethylformamide) were measured at different temperatures of the SnO_2<Co> sensor work body.

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