

H₂S Sensor Studied by Electrochemical Impedance Spectroscopy

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Summary:

In the present work we studied by an electrochemical impedance spectroscopy, EIS, of the SnO₂ thin films as a hydrogen sulphide sensor. It was found that EIS is a useful technique for characterization of metal oxide sensors based on nanostructural materials.

Keywords: Thin films, reactive sputtering, tin dioxide, electrochemical impedance spectroscopy, sulphide gas sensor.

Background, Motivation and Objective

Hydrogen sulphide (H₂S) is a flammable, corrosive and lethal gas even at low concentrations (ppm levels). It is produced by various emitting sources (such as oil and gas processing facilities, natural emissions, sewage treatment plants, landfills and other industrial plants) [1]. Its limit of exposure of humans of concentration ranges from 10-100 ppm at time of exposure from 1-10 min. Therefore, there is an urgent need to develop some devices that allow fast, portable and low-cost monitoring of the H₂S responsible for air pollution and danger to human health [1,2].

Successful development of H₂S gas sensors for commercialization requires achieving three 'S': sensitivity, selectivity and stability. Recently, metal oxide semiconductor thin films of H₂S gas sensors have been studied extensively because of their simple fabrication process and low cost [2]. Commonly, direct current measurements have been used for determination of the sensor properties, such as three 'S'. Impedance spectroscopy, however, in addition to the same information, can also determine of individual properties of the sensing materials such as grain boundary, grain bulk and interface between electrode contact and sensing material [2-6]. In this work we describe impedance spectra of SnO₂ thin films recorded on air and H₂S gas atmospheres.

Experimental

Sample preparation

The thin films SnO₂ thin films were deposited by rf reactive sputtering from a metallic Sn target in a Ar-O₂ gas flow-controlled at-

mosphere. Corundum CC2 type supports (BVT Technologies, Czech Republic) were used as a target.

Impedance measurements

Impedance spectra were taken by two-probe technique with FRA Solatron 1260 using the Solatron Dielectric Interface 1296. Frequency range was from 1 Hz to 1 MHz. Amplitude of sinusoidal disturbance was 10 mV. Measurements were carried out in dry air - H₂S of the concentration range between: 0, 0.75, 1.5, 2.25, 3 ppm at 347°C.

Results

Figure 1 shows an example of the impedance spectra of the sensor SnO₂ thin film plotted as Nyquist form, at 374°C, under air and H₂S gas. The diameter of the semicircles decreases drastically with the increase in the concentration of H₂S.

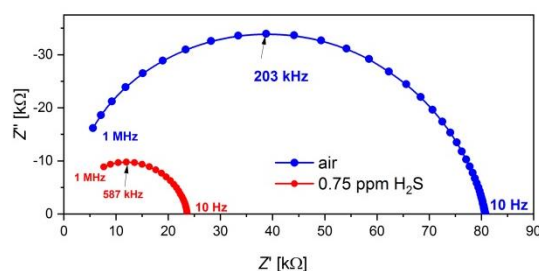


Fig. 1 Experimental impedance spectra of SnO₂ thin film at 347°C under air and 0.75 ppm H₂S.

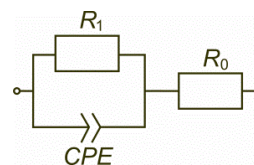


Fig. 2 Equivalent circuit used for the analysis of the impedance spectra.

The simplest equivalent circuit for measured spectra is presented in Fig. 2. It is composed of the resistor R_0 connected in series with the element composed from resistor R_1 and a constant phase element, CPE connected parallel. The impedance Z_{CPE} is given by the formulas [8]:

$$Z_{CPE} = A(2\pi f j)^{-\frac{1}{n}} \quad (1)$$

Where: A , n – constants, f - frequency [Hz], j - imaginary unit.

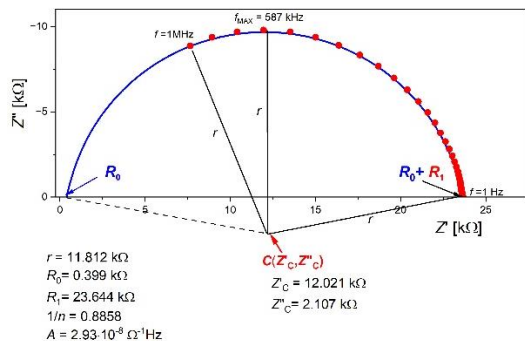


Fig. 3 Determination parameters of the equivalent circuit for SnO₂ thin film at 347°C under 0.75 ppm H₂S.

Figure 3 illustrates experimental points (red symbols) and fitted curve obtained based on the hypothetical equivalent circuit. The agreement is quite good. The method for determining the parameters of the equivalent circuit as well as their values are depicted in Fig. 3.

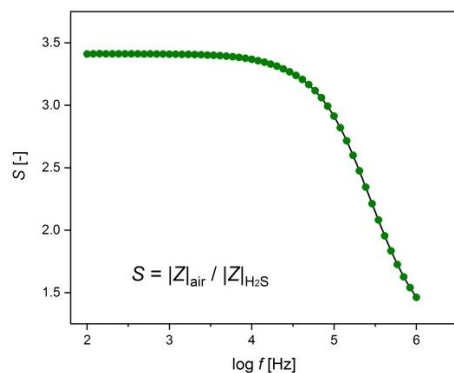


Fig. 4 Sensor signal, S of SnO₂ thin film at 347°C under 0.75 ppm H₂S.

The sensor signal S is done by the following equation:

$$S = \frac{|Z|_{AIR}}{|Z|_{H_2S}} \quad (2)$$

Where $|Z|$ is a modulus of impedance at air and H₂S, respectively. Fig. 4 illustrates sensor signal as a function of frequency.

Conclusions

In the present work we studied by an electrochemical impedance spectroscopy, EIS of the SnO₂ thin films as a hydrogen sulphide sensor. It was found that the EIS is a useful technique for characterization of metal oxide gas sensors based on nanostructural materials.

References

- [1] Y.C Chan, S.S. Mun Lock, M. K. Wong, C. L. Yiin, A. C. Minh Loy, K. W. Wai Cheah, S. Y. Wang Chai, C. Li, B. S. How, B. L. Fui Chin, Z. P. Chan, S. S. Lam, A state-of-the-art review on capture and separation of hazardous hydrogen sulfide (H₂S), *Env. Pol.* 314 (2022) 120219, doi.org/10.1016/j.envpol.2022/20219.
- [2] V. Balaubramant, S. Chandraleka, T. Subba Rao, R. Sasikumar, M.R. Kuppusamy, T.M. Sridhar, Review- Recent advances in electrochemical impedance spectroscopy based toxic gas sensors using semiconducting metal oxides, *J. Electrochem. Soc.* 167 *Semiconductor* (2020) 037572, doi:10.1149/1945-7111/ab77a0.
- [3] F. Vyslouzil, V. Myslik, M. Kovanda, R. Frycek, M. Jelinek, Impedance measurements of chemical gas sensors, *The Forth International Conference on Advanced Devices and Microsystem*, Slovenia, Slovakia 2002 pp 317-320: doi:10.1109/ASDAM.2002.1088532.
- [4] S. Luo, G. Fu, H. Chen, Y. Zhang, Gas sensing properties and complex impedance analysis of La₂O₃-added WO₃ nanoparticles to VOC gases, *Materials Chemistry and Physics* 109 (2008) 541-546, doi: 10.1016/j.matchemphys.2008.01.015.
- [5] J.M. Rheaume, A.P. Pisano, A review of recent progress in sensing of gas concentrations by impedance change, *Ionics* (2011) 17:99-108, doi 10.1007/s11581-010-0515-1.
- [6] T. Tasaki, S. Takase, Y. Shimizu, Impedance characteristics of acetylene gas sensing properties of Sm-Fe based perovskite-type oxide-based thick-film device, *Sensors and Actuators B:Chemical* B 187 (2013) 128-134, http://dx.doi.org/10.1016/s.snb.2012.09.086.
- [7] S.N. Shkerin, A.S. Tolkacheva, A.V. Nikonov, N.B. Pavzderin, Impedance spectroscopy of cell with Pt electrodes on oxygen-conducting material with matenite-related structure, *Ionics* (2016) 0593.
- [8] J. Ross, in *Impedance spectroscopy*, John Wiley & Sons 1987.

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