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Tungsten Oxide Films with High Sensitivity to Nitric Oxide

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Abstract:
The subject of the study was to determine the tungsten oxide films' sensitivity to nitric oxide of the ppb level. High sensitive films development of chemical sensors for NO detection at low level can have practical application for advanced solutions in medicine. Films were obtained by two different methods: thick-film technology and by thermal sputtering in vacuum. The investigations were carried out under the sensor thermal stabilization conditions in the range 50 - 350 ^{0}C. The nitric oxide concentrations were measured in a range of 1 - 100 ppb. A temperature impulse mode effect on a sensitive layer was used for detection of NO low concentrations in the model gas mixtures.

Key words: nitric oxide, tungsten oxide, film

Introduction

Over the past years it was shown that nitric oxide (NO), which sometime toxic pollutant of the environment, plays a fundamental role in numerous biological processes in the body. Exhaled NO is widely accepted as non-invasive marker of airway inflammation for research. Inflammatory lung diseases are common and they are difficult to diagnose and characterize. Nitric oxide in low concentrations considerably regulates the physiological functions, but in high concentration may contribute to the pathogenetic process [1-2]. Advances in collection methods of biomarkers and development of more sensitive ways for detection can be useful in monitoring of body state.

High sensitive films development of chemical sensors for NO detection at low level can have practical application for advanced solutions in medicine. The oxides of transition metals are used as sensitive layers of sensors, owing to their high electrical and physical characteristics, i.e. good extrinsic ion conductivity, large forbidden gap, surface properties prevailing over those of bulk, widely variable stoichiometry [3]. Comparative study of WO_3 films' sensitivity to nitric oxide low concentrations was investigated. Films were obtained by two different methods, thick-film technology and by thermal sputtering in vacuum.

Experimental

The sensitive element consists of an alumina substrate with dimensions of 2 x 0.5 x 0.2 mm. One side of the substrate is covered with a gas sensitive film; the other side of the substrate has a film heater made of platinum paste. The film heater is at the same time a thermal resistor in the sensor. The sensitive layers were formed by two methods: the thermal sputtering in vacuum and thick-film technology. In the former, WO_3 films were thermally sputtered in vacuum. The thin films of 0.1 - 0.3 μm were obtained at evaporation temperature of 1100 ^{0}C and pressure in chamber 1,33 x 10^{-8} bar. In the latter, films were formed by thick film technology based on pastes. Thick-film pastes were prepared by adding of substance nanopowder in organic vehicle. After mixing a powder with a vehicle, paste was milled to homogenize the mixture. Then thick films were printed on substrates, dried and annealed.

The films' properties were examined on sample gas mixtures using a dynamic blender "Environics-4000" (Environics, USA) and Dräger test ampoules (Dräger, Germany). The investigations were carried out under the sensor thermal stabilization conditions in the range 50 - 350 ^{0}C with the constant values of the heater resistance and applied power. The nitric oxide concentrations were measured in a range of 1 - 100 ppb.

Results and Discussion

Both type films show top sensitivity for NO micro concentrations in the temperature range of 120 – 170 ^{0}C (see Fig. 1). The sensor films' characteristics can be purposely changed by varying conditions of film formation and by varying film temperature at measurements.

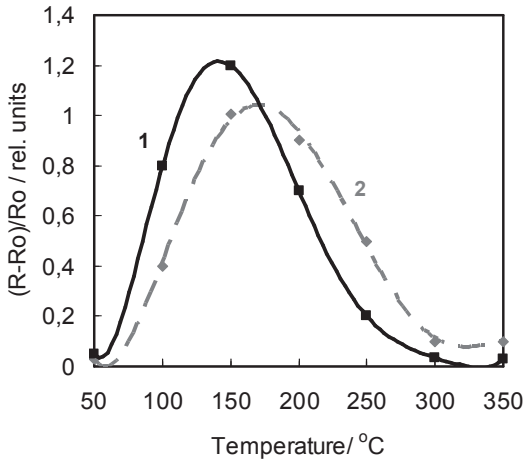

Fig. 1. Typical sensitivity dependence on temperature for thin (1) and thick (2) films at 50 ppb NO: R – resistance in NO/air, R_o – resistance in air.

Sensors showed high sensitivity to presence of NO micro concentrations at 20 ppb level in air (see Fig. 2). Response time of sensors depends on temperature and it is from 30 seconds to several minutes.

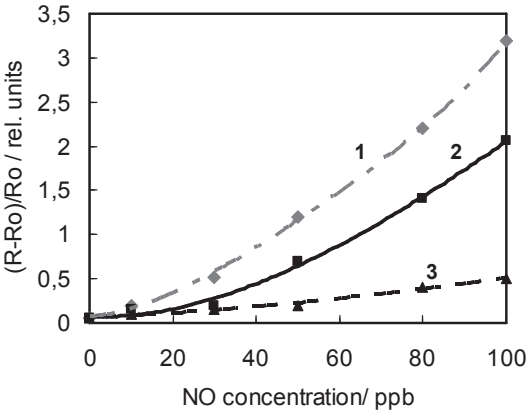

Fig. 2. Typical sensitivity dependence on NO concentration in air at different temperatures for thick film: 150 ^{0}C (1); 200 ^{0}C (2); 100 ^{0}C (3).

All films are mostly sensitive to the relative humidity when it is less than 40% at temperatures which are less than 200 ^{0}C (see Fig.3). Humidity dependence can be removed at collection of samples for detection.

The working temperature for detection of NO was choose at 150 ^{0}C. The sensor signal stabilization and repeatability are insufficient at such low temperature. Taking into account this fact there is necessity to keep a special temperature conditions for sensor working regime. Interaction products of sensitive layer with gas remain on the sensor surface if the sensitive layer temperature is too small. Surface is not able to be recovered, that interrupts the sorption of gas in the future measurements. But if the surface temperature is very high, an analyzed gas is not able to be adsorbed on the sensor surface. That is why it is necessary to try to find ways of heating regimes.

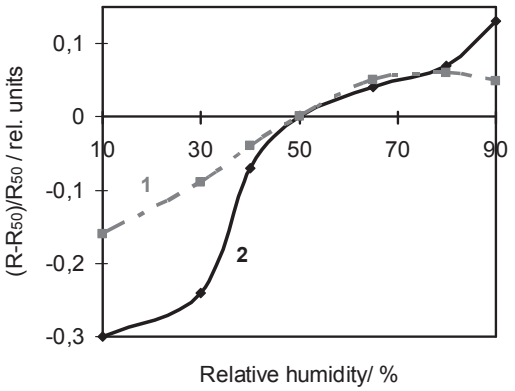

Fig. 3. Typical sensitivity dependence on humidity for thin (1) and thick (2) films at 150 ^{0}C: R – resistance at different humidity, R_{50} – resistance at 50% relative humidity in air.

A temperature impulse mode effect on a sensitive layer was used for detection of NO low concentrations in the model gas mixtures. The time of temperature cycle was equal from 1 to 5 minutes. Different temperatures were used. It is necessary to use optimal combination of these parameters to keep high sensitivity and don't lose in stability of sensors. The optimal cycle was 3 minutes at basic working temperature of 150 ^{0}C with sensitivity keeping of 20 ppb NO in air.

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