Investigation into the Gas Sensitivity in Nanostructured Films Based on Tin Dioxide by Impedance Spectroscopy

V. V. Tomaev, L. N. Gar’kin, V. P. Miroshkin, and V. A. Moshnikov
St. Petersburg State University of Electrical Engineering, ul. Professor Popova 5, St. Petersburg, 197376 Russia
Received April 12, 2004

Abstract—It is demonstrated that, in principle, it is possible to prepare polycrystalline films of the composition 0.9SnO₂·0.1CuO with one-dimensional nanoparticles on the surface and to fabricate highly sensitive gas sensors on their base. The films thus prepared are characterized by a high sensitivity to gases, to strongly polar molecules of water and ethanol, and also to oxygen.

INTRODUCTION

Metal-oxide polycrystalline semiconductors have found a wide use in fabrication of gas-sensitive sensors [1]. It should be noted that materials based on tin dioxide are most promising due to a number of advantages [2].

The aim of this work was to investigate the sensitivity of tin dioxide–based nanostructured metal oxides to polar gas molecules by impedance spectroscopy.

TECHNIQUE FOR PREPARING CALIBRATION GAS MIXTURES FOR USE IN INVESTIGATION OF THE GAS SENSITIVITY OF FILMS BASED ON TIN DIOXIDE

In order to investigate the gas sensitivity of semiconductor metal-oxide materials, we designed a setup (schematically drawn in Fig. 1) for preparing calibration gas mixtures. The setup was constructed according to the principle of dynamic dilution of gas flows with the use of gas extraction [3].

In the preparation of calibration mixtures, the gas concentration in a measuring vessel was controlled by producing the corresponding flows of a gas (a reference gas mixture). In turn, the concentration of liquid vapors (including water vapor) was controlled by saturating the gas with vapors of the studied compound (for example, helium, nitrogen, air) in a special bubbler at room temperature.

This makes it possible to prepare gas mixtures with a precisely predetermined and controlled concentration. Volatile and weakly volatile compounds can be used as solvents.

The gas flow saturated only with one component can be produced by bubbling a gas through a pure liquid. In this case, the vapor concentration in the gas mixture is constant with time (for a steady flow of the noble gas) and depends on the temperature of the bubbled liquid.

According to the reference data [4], the vapor pressure over the liquid for C₂H₅OH at 293 K is \( p = 5.33 \times 10^3 \) Pa. This pressure was used for calculating the conditions for the preparation of a mixture of dry air with alcohol (C₂H₅OH) in a ratio of 99 : 1 (vol %).

The setup (Fig. 1) involves the following components. Compressor 1 is intended for the gas intake from atmosphere, production of a necessary pressure in a gas line, and transfer of the tested mixture to the surface of a sensitive semiconductor film. Drier 2 removes an excess moisture from the sampled gas. Tee 3 provides the separation of the gas flow and its passage through two lines. Rotameters 4 serve for recording the velocities of individual gas flows and their mixtures. The gas from the ambient medium and vapors of the tested compound are mixed in mixer bubbler 5. Tee 6 provides the mixing of two gas flows (with different compositions) in one line. Cock 7 is used for regulating the gas feed into thermostat 8. Studied sample 9 is placed in the thermostat on a special support. Flexible leads are attached to the sample for measuring electrical signals from the active film through contacts 10. The temperature in the thermostat is measured by thermocouple 11 with the use of millivoltmeter 12. Admittance meter 13 (Tesla BM 507 or Tesla BM 538 instruments depending
INVESTIGATION INTO THE GAS SENSITIVITY

FILM PREPARATION

Nanostructured polycrystalline films were grown on 22-XC ceramic substrates by the hydropyrolytic method described in detail in our earlier work [5].

Under the conditions providing the vapor–liquid–crystal mechanism, we fabricated the SnO$_2$-based nanocrystalline films with a filamentary morphology. The films were prepared on pressed 22-XC ceramic substrates with a mean grain size of 500 nm. In this case, an SnO$_2$ thin film was preliminarily deposited on the substrate. The mismatch of the crystal lattice parameters of the substrate and the deposited film leads to the formation of a granular material with a mean grain size of ~25–100 nm.

In order to modify the operating surface of the film in the course of formation and to change its electrical properties, the copper chloride was used as the dopant.

The micrograph of SnO$_2$–CuO one-dimensional filamentary nanocrystals grown by the hydropyrolytic method is shown in Fig. 2. The mean diameter of nanofibers and their length are approximately equal to 50–100 nm and 2–4 µm, respectively.

The analysis of the micrograph in Fig. 2 permits us to assume that the metal-oxide films prepared by the hydropyrolytic method should possess a high sensitivity to different gas media. Subsequent investigations confirmed our assumption.

DESIGN OF SAMPLES FOR MEASUREMENTS

The design of typical samples used in experiments is shown in Fig. 3. A 22-XC ceramic plate of the composition (mol %) 97Al$_2$O$_3$·3SiO$_2$ (6 × 15 × 0.3 mm$^3$ in size) served as the substrate. A nickel film deposited on the substrate surface by vacuum evaporation was used as electrodes.

It was noted in our previous work [6] that, when studying the dielectric loss, the sample can be conveniently described in terms of different equivalent circuits composed of a set of “ideal” capacitors and resistors. If the studied sample is an “active” element of the circuit (for example, converter), the equivalent circuit can involve current or voltage oscillators.

EXPERIMENTAL TECHNIQUE, RESULTS, AND DISCUSSION

The admittance of the metal-oxide films in different gas mixtures was measured with the use of the experimental setup (Fig. 1) on the Tesla BM 507 and Tesla BM 538 instruments. These instruments provided the measurements in the total frequency range 5 Hz–110 MGz.

The samples were examined under the following conditions: (I) a moist air atmosphere at a temperature of 293 K and a pressure of ~10$^5$ Pa, (II) a dry air atmosphere at a temperature of 623 K and a pressure of ~10$^5$ Pa, and (III) an atmosphere of a mixture containing dry air and ethanol (C$_2$H$_5$OH) in a ratio of 99 : 1 (vol %) at a temperature of 623 K and a pressure of ~10$^5$ Pa.

The initial measured impedance $Z$ was determined as the modulus $|Z|$ and the phase angle $\phi$, which were directly recorded with pointer instruments.

It should be noted that, according to the generalized Ohm’s law, the impedance $Z^*$ of the sample is defined as follows [7]:

$$Z^* = Z(\cos \phi - i\sin \phi) = Z' - iZ''$$

(1)

where $Z'$ and $Z''$ are the active and reactive impedance components, respectively.

The impedance of polycrystalline samples is characterized by a complex behavior, because it involves the contributions of individual particles, grain boundaries, insulating fragments (such as pores), and contacts.