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THE GAS-SENSITIVE PROPERTIES OF TIN DIOXIDE FILMS

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This study investigates the fabrication and performance of SnO_2 thin films for gas sensing applications, utilizing a deposition method at 2 bar pressure and 8 ml/min flow rate. A multilayer structure was developed, comprising 14 layers, each with a thickness of 250 nm, optimized for sensitivity and stability. The gas sensor, featuring a film heater and sensitive elements doped with a 1% silicon additive, demonstrated a wide operational temperature range (20-370 °C). Characterization of resistance changes revealed significant hysteresis before isothermal annealing, with resistance values stabilizing after prolonged exposure to 370 °C. Post-annealing, the sensor exhibited three orders of magnitude higher resistance, indicating improved stability and electronic transport properties. Doping with a 1N $AgNO_3$ solution significantly enhanced sensitivity to ammonia, with a detection threshold of 500 ppm, while sensitivity to alcohol vapors decreased, indicating selectivity. Experimental results confirm that local doping and thermal treatment effectively enhance the metrological characteristics of SnO_2-based sensors, making them suitable for detecting toxic gases.
Keywords: *Gas sensor; Tin dioxide; Silver; Ammonia; Alcohol; Temperature; Tin dioxide*
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INTRODUCTION

Gas sensors of the resistive type based on metal oxide semiconductors (tin dioxide, zinc oxide) offer a number of advantages compared to other gas sensors: they allow for the detection of many inorganic and organic gases in the air, have a fast response time, and high sensitivity [1-3]. However, the problem of integrating such sensors into mass production remains unresolved, as it is quite difficult to simultaneously achieve stability, selectivity, and high sensitivity [4, 5].

Typically, tin dioxide (SnO_2) is deposited on a cold substrate, resulting in an amorphous film structure, and prior to working with a long-stored sensor, an extended high-temperature annealing process (above the sensor's operating temperatures) is necessary for the crystallization of the film, desorption of residual gases, and stabilization of its electrical parameters [6-8].

The aim of this study is to investigate the influence of isothermal annealing modes and Ag doping on the stability of gas sensing properties of tin dioxide films and to improve the metrological characteristics of gas sensors.

MATERIALS AND METHODS

The experimental method involved the deposition of SnO_2 films at an air pressure of 2 bar with a speed of 8 ml/min. The distance from the spraying head to the preheated silicon substrate was 85 cm [9]. The SnO_2 film was applied in a single layer for 18 minutes. Multilayer deposition of the SnO_2 film occurred every 1 minute with a subsequent 30-second break to restore the substrate temperature. In this way, 14 layers were obtained. The sample for investigation is a gas sensor crystal with dimensions of 1×1 mm^2, manufactured using microelectronic technology [10]. Its structure includes a film heater, two sensitive elements based on tin dioxide with a 1% atomic silicon additive (film thickness 250 nm, sensitive element area size 200×320 μm^2), and contacts for the sensitive layer in the form of a platinum pin structure with a distance of 10 μm between contacts [11-13].

Studies were conducted on the dependence of resistances of sensitive elements on the voltage at the heater U = 0 V, Ohm: alpha-temperature power supply) during heating and cooling. The temperature of different crystals at the same applied voltage may vary, so calibration of the sensor heater was carried out before starting the work. The following formula is used to convert the value of the heater voltage to temperature [14]:

$$R_{\text{н}} = R_{HO}(1 + \alpha(T - T_{20})) \quad (1)$$

where R_H - resistance of the heater when voltage is applied to it. R_{HO} - resistance of the heater when U = 0 V, α - temperature coefficient of resistance, C^{-1}; T — temperature of heating, °C; T_{20} = 20°C, room temperature.

The Table 1 shows the operating temperature of the sensor under corresponding voltages applied to the heater. The operating temperature range of this sample is within 20-370°C.

Table 1. Relationship between temperature and voltage on the heater (power supply).

U, V	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5	5.5
T,°C	19	50	60	95	127	146	204	245	282	326	367

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RESULTS AND DISCUSSION

Figure 1 shows the dependencies of R(U) obtained before annealing. It should be noted that the resistances during both heating and cooling do not return to their initial values. The difference in resistance values of the SE amounts to 115% (52 kOhm). Isothermal annealing allows achieving less dispersion in resistance values.

Investigation of the change in resistances of the SE sensor over time during isothermal annealing (Fig. 2) has been conducted. Annealing was carried out at T_{const} = 370°C. It is evident that the resistance of the SE increases, and after 4 hours of annealing, stabilization occurs. The annealing time of the sensor after storage may vary from half an hour to several hours of continuous exposure to high temperature.

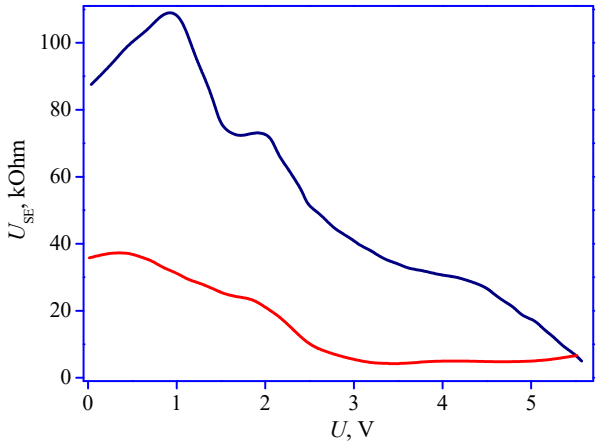

Figure 1. Relationship between R_{SE} and the heating voltage U during the heating and cooling processes conducted prior to annealing the sensor (Red-heating, blue-cooling)

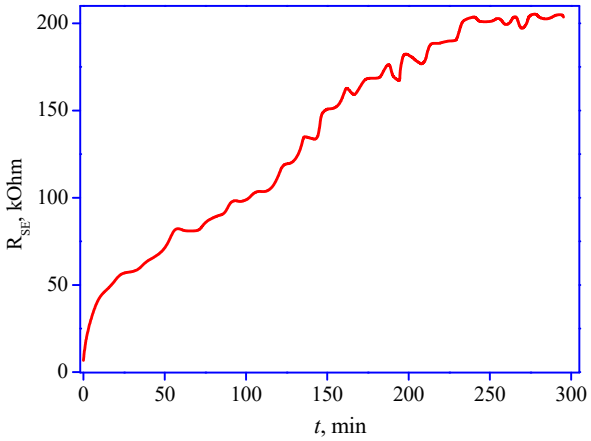

Figure 2. Relationship between the resistance of the sensor R_{SE} and time during isothermal annealing

Furthermore, the dependence of the R_{SE} values on U after isothermal annealing was investigated (Fig. 3). It was found that as a result of annealing, the resistance of the sensitive element returns to its original state after heating and cooling. However, compared to the values obtained before annealing, the resistances are three orders of magnitude higher. In order to determine the range of controlled gas concentrations, it is necessary to study the dependence of sensitivity on gas concentration [15-17]. Experiments have previously been conducted to investigate the influence of doping with various concentrations of silver, and a 1N solution of Ag was chosen as optimal. Figure 4 shows the dependencies of gas sensitivity on ammonia concentration within the range of 500 to 5000 ppm. At room temperature, a sample with doping of the sensor layer with a 1N solution of Ag ($R_{SE,1}$) and a control layer without doping ($R_{SE,2}$) was investigated.

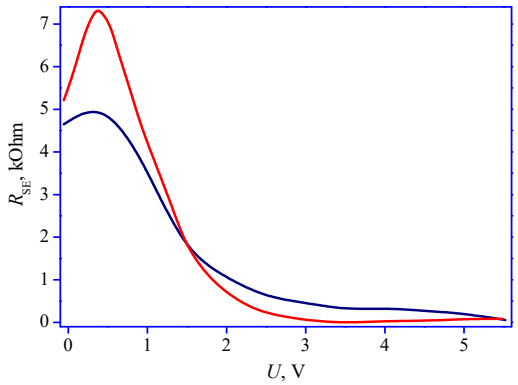

Figure 3. Relationship between R_{SE} and the voltage on the heater U_{BP} during heating and cooling processes conducted after the annealing of the sensor. (Red-heating, blue-cooling)

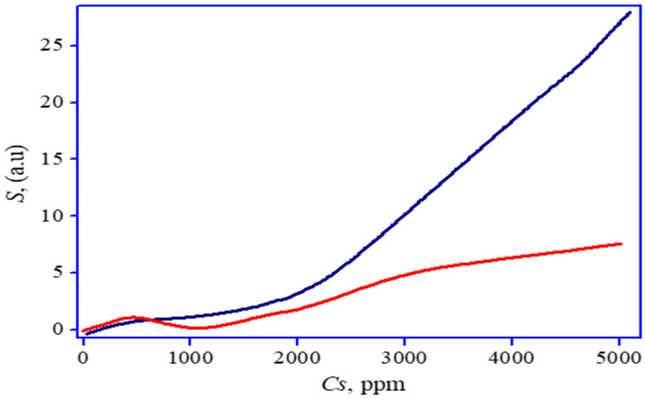

Figure 4. Dependence of the gas sensitivity of the doped sample 1N solution on the introduced concentration of ammonia vapors at T=210°C: $R_{SE,1}$ - sensitive sensor element with an undoped surface (control sample - red curve); $R_{SE,2}$ - sensitive sensor element with a doped surface (blue curve)

It has been established that the change in resistance of the doped sample ($R_{SE,2}$) is 20% at an ammonia concentration in the air of 500 ppm, while $R_{SE,1}$ (control) shows no reaction within this range. Additionally, the graph demonstrates a significant difference, approximately threefold, when comparing the sensitivity of the two elements at higher ammonia concentrations.

During the measurements, it was noted that after silver doping, the sensor's sensitivity to alcohol vapors decreases. An experiment was conducted to establish this relationship, as depicted in Fig. 5, to determine the influence of C_s = 3000 ppm when applying voltage to the gas sensor.

As shown in Fig. 4, after doping the surface of SnO_2, its sensitivity decreased by a factor of 3, while the temperature of maximum sensitivity remained practically unchanged, making it possible to create a selective microelectronic sensor for ammonia and alcohol.

A series of experiments was conducted to study the effect of doping on the selectivity of the sensor to different gases. The first part of the experiments involved determining the saturation time of the film with toxic ammonia vapors and, consequently, the maximum sensitivity. For this purpose, the sample was placed under a sealed dome, into which toxic gas vapors with concentrations of Cs=2000 ppm were introduced. The processes of interaction between ammonia and the semiconductor surface represent a prolonged process with a time delay of approximately 10-12 minutes.

The second part of the research involves establishing the dependence of S_g on the applied heating voltage and the operating modes of the sensor element, where the highest sensitivity to alcohol vapor (Cs=2000 ppm) is observed. The gas sensor's built-in heater was supplied with voltages ranging from 0.5 to 5 V in steps of 0.5 V, using the DC Power Supply HY3005 for heating the sensor's active surface. Resistance values were measured from the sensitive elements using Mastech MY64 multimeters [18]. It was found that the same sensor exhibits sensitive properties to different gases in different modes. Therefore, the next step was to conduct an experiment to determine the sensitivity of the doped sensor to two toxic gases simultaneously.

The gas sensor with the application of a doping substance at a concentration of 1N was investigated. Subsequently, samples were placed under the sealed dome of the measuring setup, and vapors of gases such as alcohol and ammonia were introduced at concentrations of 2000 ppm. The results of the effect of $AgNO_3$ impurities and operating modes on the sensitivity of the tested sample are shown in Figure 5.

Figure 6 can be divided into 3 parts: I - far left, II - central/middle, III - far right. In the first part, the steady state of the gas sensor is demonstrated without any external influences. In the second part of the graph, two toxic gases were introduced. The behavior of the curve in this segment indicates that the sensor film exhibits a sensitivity peak at room temperature (response to ammonia). Then, in segment 3, voltages ranging from 0.5 V to 5 V were applied in steps of 0.5 V. Subsequently, from the behavior of the curve, it is evident that the sensitive element's surface undergoes annealing and thermal stabilization. At a voltage value of U=5 V, a second peak appears, corresponding to the reaction of the semiconductor film SnO_2 to alcohol vapors.

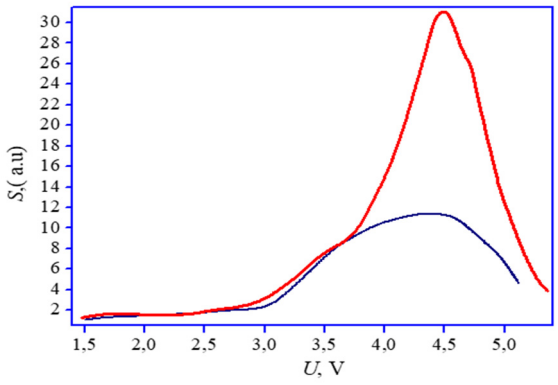

Figure 5. Effect of doping (1N solution) on the sensitivity to alcohol vapor Cs=3000 ppm when applying voltage to the gas sensor. (before – red curve, after – blue curve)

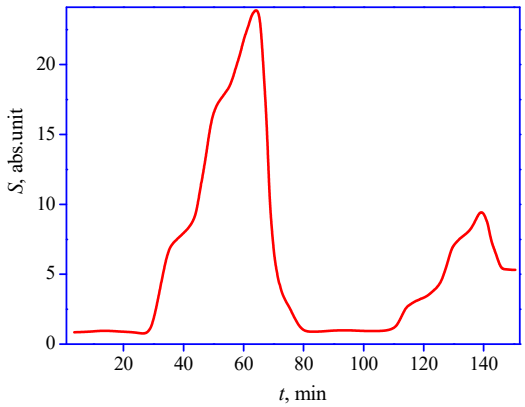

Figure 6. Sensitivity of the gas sensor doped with silver to a mixture of two gases - alcohol (2000 ppm) and ammonia (2000 ppm)

As a result of the research, a technique for local doping of SnO_2 sensing layers in microelectronic sensors has been developed. It has been demonstrated that SnO_2 sensing layers doped with $AgNO_3$ are sensitive to ammonia vapors at room temperature. The type of dependence of gas sensitivity on the concentration of ammonia in the range of 50 ppm to 5000 ppm has been determined. Sensitivity thresholds of SnO_2 films doped with 1N solution have been identified, which amounted to 500 ppm of ammonia in the air. Through experimentation, the selective response of the microelectronic sensor to vapors of two toxic gases simultaneously has been proven.

CONCLUSION

Therefore, these studies confirm that isothermal annealing improves the stability of gas sensor operation, increasing R_{SE} and releasing oxygen chemical bonds on the surface of the sensitive SnO_2 layer, thereby enhancing the electronic transport properties of the film. Doping Ag into the sensor layers of SnO_2 in gas sensors allows to improve the metrological characteristics (sensitivity, selectivity, power consumption) of the samples and makes them a good material for creating a selective indicator of toxic and explosive gases.

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ГАЗОЧУТЛИВІ ВЛАСТИВОСТІ ПЛІВОК ДІОКСИДУ ОЛОВА

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У цій роботі досліджується виготовлення та ефективність тонких плівок SnO_2 для датчиків газу з використанням методу осадження при тиску 2 бар і швидкості потоку 8 мл/хв. Було розроблено багатошарову структуру, що складається з 14 шарів, кожен з яких має товщину 250 нм, оптимізованих для чутливості та стабільності. Газовий датчик, який має плівковий нагрівач і чутливі елементи, леговані 1% добавкою кремнію, продемонстрував широкий діапазон робочих температур (20-370°C). Характеристика змін опору виявила значний гістерезис перед ізотермічним відпалом, а значення опору стабілізувалися після тривалого впливу 370°C. Після відпалу датчик продемонстрував на три порядки більший опір, що вказує на покращену стабільність і електронні транспортні властивості. Допування 1N розчином $AgNO_3$ значно підвищило чутливість до аміаку з порогом виявлення 500 ppm, тоді як чутливість до парів спирту знизилася, що свідчить про селективність. Експериментальні результати підтверджують, що локальне легування та термічна обробка ефективно покращують метрологічні характеристики датчиків на основі SnO_2, роблячи їх придатними для виявлення токсичних газів.

Ключові слова: *газовий датчик; діоксид олова; срібло; аміак; спирт; температура; діоксид олова*