Light-activation of gas sensitive layers based on zinc oxide nanowires

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Abstract. In this work, a sensor layer based on zinc oxide nanowires was synthesized by low-temperature hydrothermal method. The gas sensitivity of sample to isopropyl alcohol vapor was studied both during heating and under ultraviolet radiation. It was shown that depending on the presence of moisture on the surface of zinc oxide nanowires, isopropyl alcohol vapor can act as a reducing or oxidizing gas upon activation of gas sensitivity by ultraviolet irradiation. It was shown that there is an optimal intensity of irradiation, which determines the maximum response of sample. The gas sensitivity under moist air conditions demonstrates the possibility of practical application of adsorption resistive gas sensors with light-activation at room temperature.

1. Introduction
Gas sensors play an important role in many applications from medical diagnostics to industrial process control. Among them chemoresistive gas sensors possess advantages of high sensitivity, ease of miniaturization for portable devices and relatively low cost. Definitely, the sensor layers based on zinc oxide nanowires synthesized by low-temperature hydrothermal method (at \( t \approx 86 ^\circ C \)) are characterized both low cost and high sensitivity due to the small diameter of the nanowires (\( \approx 50 \) nm). It is worth noting that the analytical response depends not only on the influence of water vapor, but also on the deviation from stoichiometry in the surface layers. For this purpose, we study deviations from stoichiometry in gas sensitive layers under electron-beam irradiation [1] and special sacrificial doping [2, 3]. Chemoresistive gas sensors usually operate at high temperatures (\( \approx 300-400 ^\circ C \)) [4]. At the same time, high operating temperature sacrifices the lifetime of gas sensors and long-term stability of sensing performance, as well as limits the use of chemoresistive gas sensors for the detection of flammable and explosive substances. An obvious way to reduce the operating temperature of gas sensors to room one is to replace the mechanism for generating charge carriers with light-generation [5,6]. Thus, the study of light-activation of the gas sensitivity of layers based on zinc oxide nanowires at room temperature is prospective for expanding of application areas and increasing the stability of resistive gas sensors in general. In this work, a sensor layer based on zinc oxide nanowires was synthesized. The gas sensitivity of the sample to isopropyl alcohol vapor was studied both at elevated temperature (\( t \approx 300 ^\circ C \)) and at room one (\( t \approx 23 ^\circ C \)) under UV-light irradiation (\( \lambda \approx 365 \) nm). An important feature of this study is the use of ambient air (i.e. having a relative humidity of 30-50%) as a carrier gas.
2. Experiment

Sensor layer based on zinc oxide nanowires was synthesized by a low-temperature hydrothermal method with the suppression of nucleation in the solution volume at a temperature of \( t \approx 86 ^\circ C \) for 1 hour in an autoclave on substrate coated with seed nanocrystals [7]. The ceramic wafer with interdigitated electrodes (Sensor Platform, Tesla Blatna, a. s.) was used as a substrate. The width of the interdigitated electrodes and the distance between them is about 25 microns, the electrodes are NiCr/Ni/Au multi-layer structure (the top layer is gold). Seed nanocrystals were formed by spin-coating of an alcoholic solution of zinc acetate (5 mM in isopropyl alcohol). After three cycles of spin-coating the sample was annealed at 500 °C. After hydrothermal synthesis the sample was also annealed at 500 °C to remove surfactants and organic reaction products from the surface of the nanowires.

The sensitivity of the sample to isopropyl alcohol vapor (a typical reducing gas for n-type semiconductors) was studied in the measuring cell with the possibility of heating and irradiating the sample. All measurements were performed at a bias voltage of 5 V; the current flowing through the sample was measured using a picoammeter (Keithley 6485). The concentration of isopropyl alcohol vapor was set by adjusting the flow of carrier gas and the flow of isopropyl alcohol vapor obtained by passing the air flow through the bubbler. The concentration of target gas \( n \) in the output mixture was determined as:

\[
n = \frac{P_{\text{gas}} \cdot F_{\text{gas}}}{P_{\text{atm}} (F_{\text{gas}} + F_{\text{air}})},
\]

where \( P_{\text{gas}}, F_{\text{gas}} \) - saturated vapor pressure of the bubbling liquid, air flow rate through the bubbler; \( P_{\text{atm}} \) - atmospheric pressure (accepted as 760 mm Hg), \( F_{\text{air}} \) – carrier gas flow rate. Saturated vapor pressure is calculated from the Antoine equation:

\[
P_{\text{gas}} = 10^{A - \frac{B}{C + T}},
\]

where \( A, B, C \) - tabular approximation parameters, \( T \) – fluid (isopropyl alcohol) temperature. Thus, the concentration in all measurements was maintained equal to 1500 ppm. The light-activation of the gas sensitivity of the sample was studied using an ultraviolet (UV) LED with a wavelength of 365 nm, which corresponds to a photon energy of 3.4 eV, which exceeds the band gap of zinc oxide \( E_g \approx 3.3 \) eV. The LED irradiation intensity was controlled using pulse-width modulation (PWM) with a duty cycle of 0.01 to 0.8. The PWM period time was about 2 milliseconds, which is much less than the sample response time to irradiation (tens of seconds). Before gas sensitivity measurements in the first case, the sensor layer was stored in air (for 48 hours), in the second case, it was preheated to 300 °C (for 10 minutes).

The response to reducing gas was calculated as

\[
S = \left( \frac{R_a - R_g}{R_g} \right) \cdot 100\%,
\]

where \( R_g \) - resistance when exposed to target gas, \( R_a \) - resistance when exposed to air.

The response to oxidizing gas was calculated as

\[
S = \left( \frac{R_g - R_a}{R_a} \right) \cdot 100\%,
\]

where \( R_g \) - resistance when exposed to target gas, \( R_a \) - resistance when exposed to air.

3. Results and discussion

The results of the gas sensitivity study of the layer based on nanowires at 300 °C are presented in Figure 1.
Figure 1. The resistance changes of the sensor layer based on zinc oxide nanowires with heating up to 300 °C under cyclic exposure to isopropyl vapor (1500 ppm).

As can be seen from Figure 1, isopropyl vapor acts as a reducing gas, leading to a decrease in the sample resistance due to the capture of electrons by oxygen ions on the surface of the nanowires and a decrease in the thickness of the depletion layer. The response of the sensor layer in the standard operating mode (i.e. under heating) to isopropyl alcohol vapor (1500 ppm) calculated using eq. (3) was about 370%, which is sufficient for practical applications. The influence of UV-activation on gas sensitivity of the sample at room temperature after storage in air is shown in Figures 2, 3.

Figure 2. The resistance changes of the sensor layer based on zinc oxide nanowires after storage in air under cyclic exposure to isopropyl alcohol vapor (1500 ppm) at room temperature and UV irradiation with different intensities (duty cycle).

Isopropyl alcohol vapor exposure under UV irradiation after storage in air leads to an increase in the resistance of sensor layer. Thus isopropyl alcohol vapor acts as an oxidizing gas, further increasing the thickness of the depletion layer of nanowires. In this case, the reaction with isopropyl alcohol vapor is also reversible, as in the case of heating. Thus, the response to the oxidizing gas (in this case) was calculated using eq. (4). As can be seen, the sensitivity of the sensor layer increases with a decrease in the irradiation intensity in the range from 0.8 to 0.1, however, a decrease in the intensity to 0.01 leads to a slight decrease in the sensitivity. Thus, there is an optimal value for the intensity of UV-irradiation of the sensor layer. The response of the sample to isopropyl alcohol vapour (1500 ppm)
is a few percent, which is certainly not enough for the practical use of this sensor layer. Nevertheless, samples with greater sensitivity under heating are likely to exhibit greater sensitivity under UV-irradiation at room temperature. The sensitivity of sample under heating and UV irradiation is related to the structural features of the material, i.e. defects, adsorbed molecules, which, in turn, determines the change in the depleted charge region when interacting with gas molecules. It should be noted that without UV-irradiation, the sample did not show a gas sensitive response. Therefore, the sensitivity of the studied layer is due not only to the physical adsorption of isopropyl alcohol molecules, but also to photocatalytic reactions on the surface of nanowires. The results of measuring the sensor layer response after preheating (at room temperature and UV-irradiation) are presented in Figure 4. The response to isopropyl alcohol vapor calculated using eq. (3) is 18%.

**Figure 4.** The resistance changes of the sensor layer based on zinc oxide nanowires after pre-heating the sample to 300 °C under exposure to isopropyl alcohol vapor (1500 ppm) at room temperature and UV-irradiation with an intensity (duty cycle) of 0.4.

As can be seen, after preheating the sample, the isopropyl alcohol vapor again acts as a reducing gas under UV-irradiation at room temperature. The sensitivity of the preheated layer is significantly higher than the one after storage in air without preheating. The processes of current (conduction) change during heating and UV-irradiation are presented in Figure 5.

**Figure 5.** Processes of current change (at the bias voltage of 5 V) during a) heating and b) UV-irradiation of the sensor layer (in air).

The processes of the resistance change of the sensor layer upon heating and UV-irradiation in an air atmosphere differs significantly, as can be seen from Figure 5. It is known that, below 150 °C adsorbed oxygen exists predominantly in the form of $O_2^-$ ions, at higher temperatures the predominant ions are $O^-$, $O_2^-$ [8-10]. It is obvious that the sensor layer adsorbs water molecules when it is in the air at room temperature. During heating (Fig. 5a), the resistance decreases due to an increase in the concentration of charge carriers in the first section, then desorption of water molecules prevails, as well as a change...
in the predominant type of ions from $O^-_2$ to $O^-$ and $O^{2-}$, which leads to an increase in the thickness of the depletion layer of ZnO nanowires and an increase in the resistance. The generation of electron-hole pairs under UV-irradiation also leads to a decrease in the resistance of the sample, while there is no desorption of water molecules, as well as no change in the predominant type of oxygen ions. The generated holes reacting with chemisorbed $O^-_2$ ions lead to their desorption, at the same time, new adsorbed oxygen molecules capture photogenerated electrons, forming $O^-_2(hv)$ ions, thus achieving a new stable state. Preheating before measurements under UV-irradiation at room temperature causes desorption of water molecules from the surface of zinc oxide nanowires. In the absence of moisture on the surface of ZnO nanowires, isopropyl alcohol vapor acts as a reducing gas (as with heating). The lower sensitivity than in the case of heating is probably due to the predominant form of $O^-_2(hv)$ ions instead of $O^-$, $O^{2-}$ on the surface, and hence the smaller thickness of the depletion region. In the presence of water molecules on the surface of the nanowires, isopropyl alcohol vapor acts as an oxidizing gas, further increasing the resistance of the sensor layer. Over time, moisture is absorbed on the surface of the sensor layer, so to achieve long-term stability of the gas sensitive response, it should be preheated every few days.

4. Conclusion
The study of light-activation of the sensor layers based on zinc oxide nanowires showed that, under UV-irradiation, the sensor layer responds to isopropyl alcohol vapor (with a concentration of 1500 ppm) both in the presence of water molecules on the surface of nanowires and after their preliminary desorption by heating up. In the presence of moisture on the nanowires surface, a typical reducing gas (for an n-type semiconductor) acts as an oxidizing gas, further increasing the resistance of the sensor layer. There is an optimal radiation intensity, that determines the greatest response of the sensor layer to the target gas. The gas sensitivity of the sample in the presence of moisture on the surface of nanocrystals demonstrates the practical use of adsorption gas sensors with light-activation at room temperature.

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