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Research of temperature dependence of conductivity of arrays of ZnO/Au and ZnO/SnO_2 nanorods under the influence of combined visible and ultraviolet irradiation

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Abstract. Arrays of ZnO nanorods of vertical orientation were synthesized by hydrothermal method on quartz substrates. The nanorods had a length of 500–800 nm and an average cross-sectional size of 40–80 nm. On top of ZnO nanorods, by vacuum thermal evaporation and subsequent annealing at 300 °C, gold (Au) nanoclusters with average sizes of 9 ± 1 nm and 4 ± 0.5 nm and tin oxide (SnO_2) nanoclusters with average sizes of 30 ± 5 nm and 15 ± 3 nm. To fabricate resistive sensor elements, V-Ni contact metallization was formed over nanorods by vacuum thermal evaporation. The study of the electrophysical characteristics of arrays of ZnO/Au nanorods showed that the simultaneous effect of temperature and radiation from a LED with a wavelength of 400 nm leads to almost temperature independence of the conductivity of sensor elements.

Keywords: ZnO, nanorods, electrophysical properties, ultraviolet irradiation

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Материалы конференции
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Исследование температурной зависимости проводимости массивов ZnO/Au и ZnO/SnO_2 наностержней при воздействии комбинированного видимого и ультрафиолетового излучения

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Аннотация. Массивы ZnO наностержней вертикальной ориентации были синтезированы гидротермальным методом на кварцевых подложках. Наностержни имели длину 500–800 нм и средний размер поперечного сечения 40–80 нм. Поверх ZnO наностержней методом вакуумного термического испарения и последующего отжига при 300 °C были сформированы нанокластеры золота (Au) со средними размерами 9 ± 1 нм и 4 ± 0.5 нм и нанокластеры оксида олова (SnO_2) со средними размерами 30 ± 5 нм и 15 ± 3 нм. Для изготовления резистивных сенсорных элементов поверх наностержней методом вакуумного термического испарения формировалась V-Ni контактная металлизация. Исследование электрофизических характеристик массивов ZnO/Au наностержней показало, что одновременное воздействие температуры и излучения от светодиода с длиной волны 400 нм приводит практически к температурной независимости проводимости сенсорных элементов.

Ключевые слова: ZnO, наностержни, электрофизические свойства, ультрафиолетовое облучение

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Introduction

It is known that unmodified ZnO films and nanostructures (nanofibers, nanorods, nanosheets, etc.) show high sensitivity to NO_2 and other gases (no worse than 1 ppm) at operating temperatures of 200 °C and above. Modification of ZnO nanofilms and nanostructures with gold (Au) and tin (SnO_2) clusters can lead to a significant increase in sensitivity and selectivity, but the operating temperature decreases insignificantly. When ZnO-modified films and nanostructures are photoactivated by LED radiation in the UV and visible wavelength ranges, the sensitivity limit of sensors becomes at the level of 0.1–1 ppm even at room temperature or close to it [1, 2]. However, studies of the electrophysical characteristics of arrays of ZnO/Au and ZnO/SnO_2 nanorods under simultaneous exposure to temperature and ultraviolet irradiation have not yet been carried out. These studies are the aim of this work.

Materials and Methods

Arrays of ZnO nanorods of vertical orientation were synthesized by the hydrothermal method on quartz substrates. The nanorods had a length of 500–800 nm and an average cross section of 40–80 nm. On top of the ZnO nanorods, gold nanoclusters with medium sizes were formed by vacuum thermal evaporation (sample ZnO/Au(1)) and 4 ± 0.5 nm (sample ZnO/Au(2)) and tin nanoclusters 30 ± 5 nm (sample ZnO/SnO_2(1)) and 15 ± 3 nm (sample ZnO/SnO_2(2)). For the final formation and stabilization of the electrophysical characteristics of the ZnO/Au and ZnO/SnO_2 nanostructures, annealing was performed at a temperature of 300 °C for 2 hours. Further, to fabricate sensor elements, V-Ni contact metallization with a metal layer thickness of 0.2 µm was formed over the nanorods by thermal vacuum evaporation.

The study of the electrophysical properties of the obtained samples was carried out on a hardware-software measuring complex, which makes it possible to measure the electrophysical characteristics of sensor structures, including when exposed to an LED with a wavelength of 400 nm, the radiation of which contains both UV and visible components (UV-viz irradiation) [3, 4].

Results and Discussion

Figure 1 shows the temperature dependences of the conductivity (G) of samples of ZnO/Au and ZnO/SnO_2 nanorod arrays. Studies have shown a significant dependence of the conductivity of the sensor structure on the heating temperature. When heated from room temperature to 300 °C, the conductivity increases by one or two orders of magnitude.

As can be seen from Figure 1, the temperature dependences of the conductivity of samples of ZnO/Au and ZnO/SnO_2 nanorod arrays are approximated by a linear function. The conduction activation energy (E_a) was calculated based on the Arrhenius equation (1).

$$G = G_0 \cdot \exp^{-\frac{Ea}{k} \cdot T}, \quad (1)$$

where k is the Boltzmann constant, G_0 is the coefficient that considers the conductivity of the material [5].

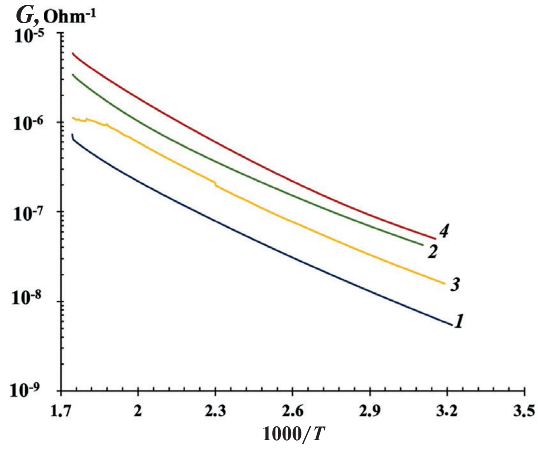

Fig. 1. Dependence of sample conductivity on reciprocal temperature: 1) ZnO/Au (1), 2) ZnO/Au (2), 3) ZnO/SnO_2 (1), 4) ZnO/SnO_2 (2) NRs

It was calculated that Ea is 0.25–0.27 eV for NR ZnO/SnO_2 samples and 0.23–28 eV for NR ZnO/Au samples 0.23 and 0.28 eV in the temperature range 35–300 °C.

In the present work, additional studies were carried out in which the samples were heated and simultaneously irradiated with UV-viz irradiation from a LED with a wavelength of 400 nm with an emission intensity of 133 μW/cm². Figure 2 shows the dependence of the conductivity G of the studied samples on the operating temperature under simultaneous exposure to UV-viz irradiation.

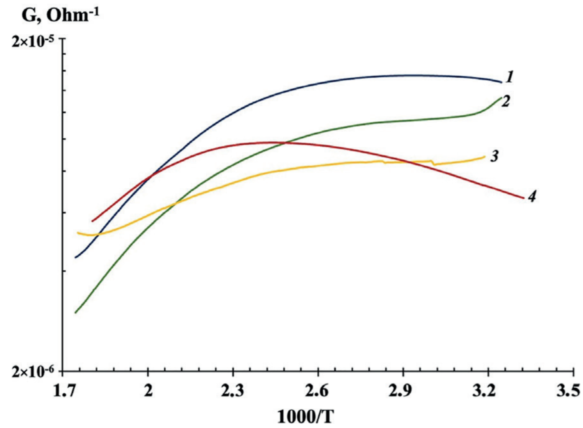

Fig. 2. Dependence of sample conductivity on reciprocal temperature under simultaneous exposure to UV-viz irradiation: *1*) ZnO/Au (1), *2*) ZnO/Au (2), *3*) ZnO/SnO_2 (1), *4*) ZnO/SnO_2 (2) NRs

Comparison of Fig. 1 and 2 showed that when exposed to UV-viz irradiation even at room temperature, the conductivity of the samples increases by two to three orders of magnitude. Further simultaneous heating and exposure to radiation showed that the conductivity of the ZnO/Au (1), ZnO/Au (2), ZnO/SnO_2 (1) samples in the temperature range of 35–170 °C is practically independent of temperature. This effect is a consequence of the fact that the generation of charge carriers in arrays of nanorods under the action of UV-viz irradiation is much higher than the temperature generation of charge carriers. An exception is the ZnO/SnO_2 (2) sample, in which the temperature generation of charge carriers leads to a slight increase in conductivity.

At temperatures above 170 °C, the conductivity of all nanorod samples begins to decrease. This may be due to the processes of ionization of oxygen molecules adsorbed on the surface of ZnO nanorods. As is known, in air at temperatures above 200 °C, oxygen molecules capture electrons from the conduction band with the formation of O_2^- [1, 6] as shown in equation (2).

$$O_2 + e^- \rightarrow O_2^-. \quad (2)$$

According to the phenomenological theory of photoconductivity, charge carriers arising in a semiconductor as a result of photoionization are nonequilibrium. The generation of nonequilibrium electrons (Δn) in ZnO nanorods leads, first of all, to a change in the specific conductivity of the semiconductor (σ), which should be written in the form (3):

$$\sigma = e \cdot \left(\mu_n \cdot n_0 + \mu_n \cdot \Delta n \right), \quad (3)$$

where e is the electron charge, n_0 is the equilibrium concentration of electrons, μ_n is the electron mobility.

Thus, when the sample is exposed not only to UV-viz irradiation, but also to temperatures in the range of 25—300 °C, the semiconductor conductivity can be written in the form (5):

$$\sigma = e\mu_n \cdot \left(n_0 + \Delta n^T + \Delta n^L - \Delta n^{O_x} \right), \quad (5)$$

where Δn^T is the concentration of non-equilibrium electrons under the influence of temperature, Δn^L is the concentration of non-equilibrium electrons under the influence of UV-viz irradiation; Δn^{Ox} is the change in the electron concentration due to the ionization of oxygen molecules.

An analysis of equation (5) and figures 1 and 2 shows that at an electron mobility of 10^{10} cm^2/(V·s), electron generation due to temperature can be estimated at 10^{10}—10^{13} cm^{-3} depending on temperature, Electron generation due to photoactivation can be estimated at 10^{13} cm^{-3}, and approximately at (1–4)·10^{13} cm^{-3} one can estimate the decrease in the electron concentration due to the ionization of oxygen molecules.

Conclusion

The studies performed have shown that simultaneous exposure to temperature and UV-viz irradiation leads to an insignificant temperature dependence of the conductivity of sensor structures based on arrays of ZnO/Au and ZnO/SnO_2 nanorods. This occurs due to the generation of electrons during the photoactivation of semiconductor structures. The concentration of non-equilibrium charge carriers is estimated at 10^{13} cm^{-3}. The discovered property is positive for the manufacture of industrial gas sensors, since the simultaneous exposure to temperature and UV-viz irradiation does not require special devices to stabilize their temperature.

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