Synthesis and chemoresistive sensitivity to hydrogen of nanostructured CuO films

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Highly porous CuO films up to $1\,\mu$m thick consisting of vertically oriented nanowires ~ 50 nm in diameter were synthesized by copper evaporation in a vacuum arc discharge in an argon/oxygen atmosphere followed by deposition on heated substrates. The phase composition and polycrystalline nature of the films were confirmed by X−ray diffraction. On the example of gaseous hydrogen H_2 at a sensor operating temperature of $300°$C, sensory characteristics of CuO films were studied. The qualitative mechanism of the effect of gas on the electrical characteristics of the nanostructured CuO film is described.

Copper oxide is a subject of a great number of experimental papers and summary reviews [1–5] describing the mechanism for detecting various toxic gases. Those papers convincingly demonstrate that copper oxide behaves as a *p*-type semiconductor, which allows applying a relevant sensor−effect model to describe experimental results.

The operation principle of conductometric gas sensors is based on the ability of surface−adsorbed atmospheric oxygen to be an acceptor of electrons from the gas sensor sensitive layer. This significantly influences the electrical resistance of this layer that is a channel for current carriers flowing. Outstanding sensitivity and conductivity may be achieved by modulating the conduction channel resistance.

A great variety of the copper oxide morphological forms enabled creation of highly stable sensors with a low analyte detection threshold. However, there is only a finite number of works devoted to investigating hydrogen sensitivity of gas sensors based on copper oxide. This paper reports on experimental studies of resistive response to gaseous hydrogen (H_2) of the CuO film consisting of vertically oriented nanowires. Such information will provide enhancement of knowledge on the gas−sensor behavior of different copper oxide morphological forms. The advantage of the considered morphology is the combination of the sensor layer manufacturability with high sensitivity.

The background of this study was investigation of the copper oxide nanopowders by impedance spectroscopy performed by the authors earlier [6]. As it turned out later, significant variation in electrical resistance of powders annealed in air at $300°$C relative to the resistance of as−fabricated ones cannot be explained only by excluding the proton conductivity.

The CuO film was formed in the process of vacuum−arc sputtering of pure copper in argon−oxygen atmosphere followed by deposition on a heated ($400°$C) sapphire wafer having golden contacts of the interdigitated structure. The contact width and inter−contact distance were 0.5 mm. The procedure scheme is presented in Fig. 1, *a* [7,8]. The arc discharge current was 90 A, operating pressure was 80 Pa, the gas feed system ensured feeding the reaction gas (20 vol.% of O_2) and buffer gas (Ar) necessary for plasma−chemical reactions. The film formation time was 60 min.

Currents of the sensor structures were monitored and detected by using a precise sourcemeter Keithley 2400; the applied voltage was 5 V. In investigating the gas−sensitive properties, there were used synthetic air and its gaseous mixture with hydrogen in the preset concentrations (100−1000 ppm), which were prepared in an external vessel. The desired humidity (40% in all the experiments) was established by mixing dry air and air moistened by the air barbotage method. The flows were controlled and regulated by using a hygrometer with a capacitance−type sensor at the chamber temperature of $25°$C. The prepared gas mixture was supplied into the measurement chamber 900 cm^3 in volume wherein the experimental sensor was installed. In its turn, the chamber containing the sensor was put into the chamber of vacuum system NNV-6.6-I1. The initial evacuation rate was chosen so as to ensure a constant total flow through the gas sensor of 1000 cm^3/min at the atmospheric pressure in the chamber. The time of response and reduction was defined as the time during which the resistance changes by 90%. The initial duration of the chamber purging with air free of hydrogen was 30 min for stabilizing the samples as well as the synthetic air parameters and sensor temperature.

The substrate operating temperature was maintained in the experiments at $300°$C in order to intensify the
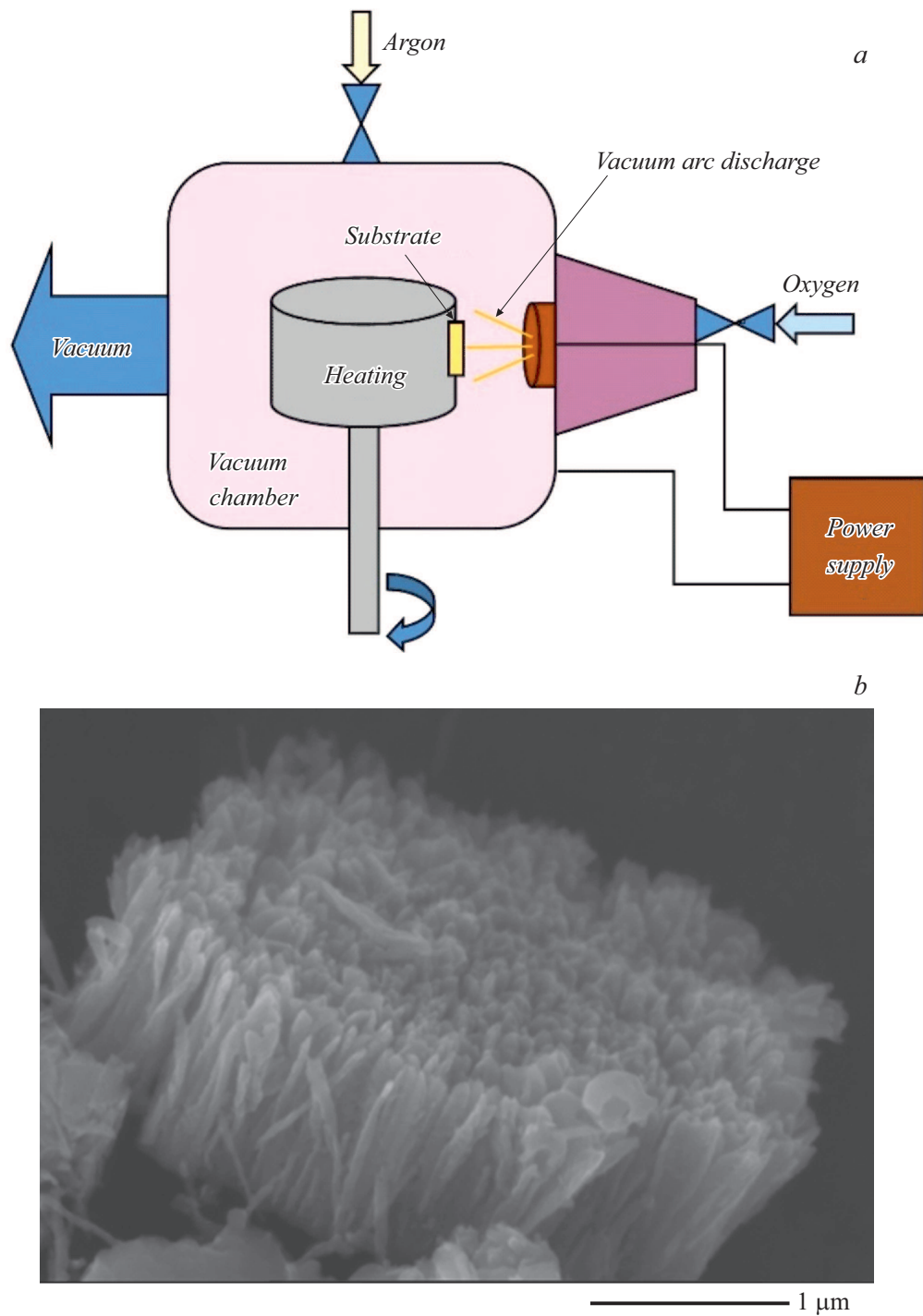
Figure 1. Schematic illustration of the procedure for fabricating experimental samples (*a*) and SEM image of a fragment of the CuO film detached from the substrate (*b*).

gas adsorption−desorption processes and also to prohibit the moisture condensation that prevents access to the gas−sensitive surface. Some ideas about the operating temperatures are presented, in, e.g. [9,10].

Fig. 1, *b* presents an image obtained by using scanning electron microscope Jeol JSM-7001-F (SEM image), which demonstrates the morphology of highly porous CuO films.

The latter are vertically oriented nanowires up to $1\,\mu m$ in length and $\sim 50\,nm$ in diameter. Individual nanowires grow from the substrate with a minimal buffer layer whose composition is also of the oxide type. This was confirmed by the energy−dispersive analysis of the top and bottom sides of the nanostructured film and also by the measurements of resistive characteristics ($\sim 1500\,\Omega$ at $300°C$). The presence
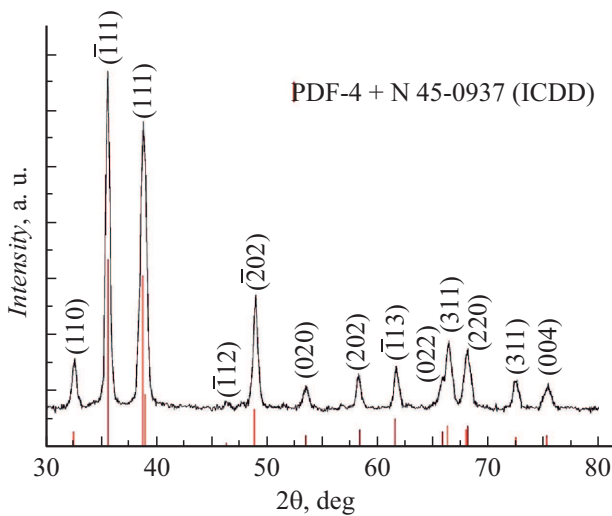
Figure 2. X−ray diffraction pattern of the CuO film sample. Vertical lines indicate the diffraction peak positions and relative intensities according the index ICDD data for the CuO monoclinic phase.

of even a thin metal copper layer could decrease the resistance to tens of ohms due to bypassing the interdigitated structure.

The problem of using nanostructures in sensory devices consists in ensuring detection of the resistive response, namely, in forming current−collection contacts. In this work, the copper oxide columnar structure is arranged so as to ensure both the current flow through the surface layers of individual nanowires and the contact between neighboring nanowires. This is why the structure becomes easily accessible for gas penetration. Along with this, individual nanowires can be arranged so densely as to have a good electrical contact between each other.

Fig. 2 presents an X−ray diffraction pattern (Bruker D8 Advance, monochromic CuK_α radiation, $\lambda = 0.15406$ nm) of the CuO sample detached from the substrate. The data confirms formation of single−phase CuO nanostructures. The samples also exhibit a large fraction of the crystalline phase and thus do not need post−fabrication annealing.

The film morphological parameters were obtained using the Meta Sorbi MS device. For the CuO film sample, specific surface area derived by the Brunauer−Emmett−Teller (BET) method from the isotherms of low−temperature adsorption−desorption of nitrogen appeared to be $30 \, \text{m}^2/\text{g}$, while porosity was 15%.

Fig. 3 demonstrates the time dependence of sensor response while adding gaseous H_2 in different concentrations at the sensor operating temperature of $300°$C. The sensor sensitivity increases proportionally to the increase in the H_2 concentration in the chamber. There were observed base resistance variations by 15, 33, 54, 76 and 92% at the concentrations of 100, 250, 500, 750 and 1000 ppm, respectively. The sensor response time also varied within the range of $35-10$ s depending on the hydrogen concentration of

100−1000 ppm, respectively. The reduction time increased linearly with the respective increase in the gaseous hydrogen concentration and belonged to the range of $10-45$ s.
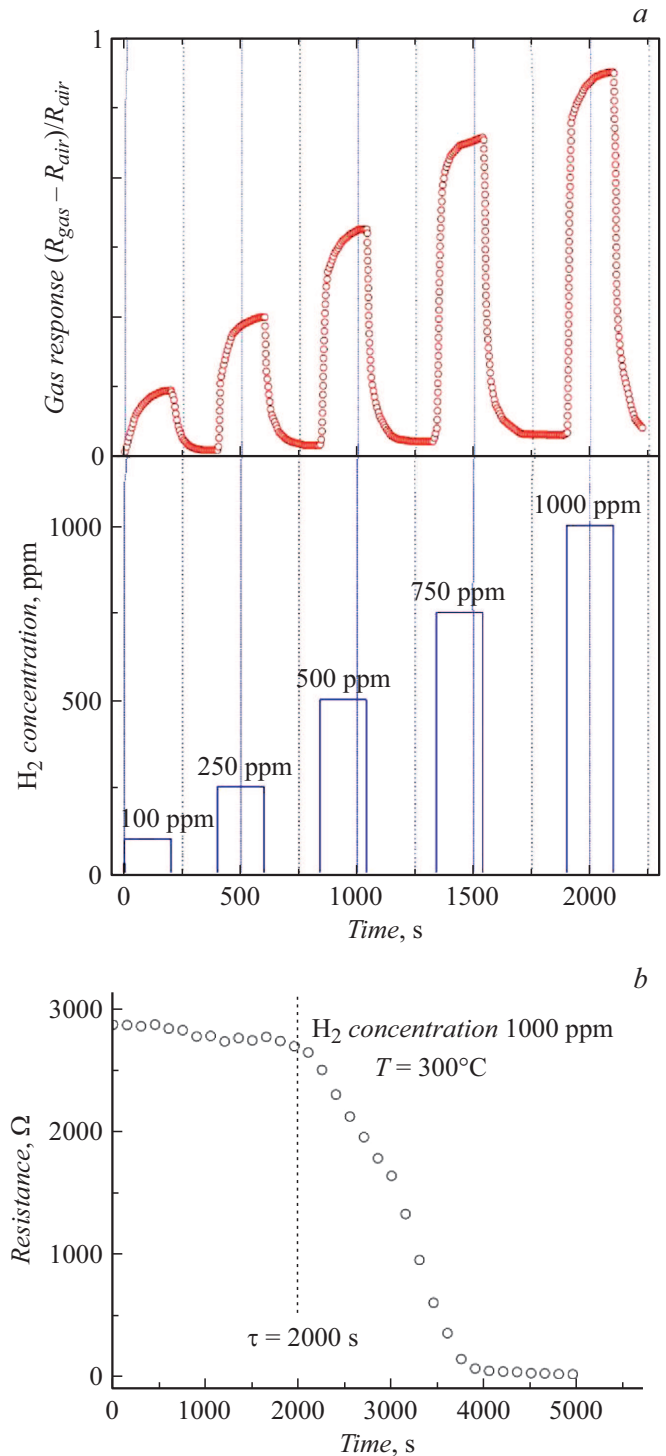

Figure 3. *a* — dynamic dependence of the CuO conductometric sensor response on the hydrogen concentration. R_{air} is the measured electrical resistance of the CuO sensitive layer in air, R_{gas} is that under the action of the gas under study. *b* — time dependence of the sensor resistance in the hydrogen−containing atmosphere.

The observed resistance variation is caused by modulation of the surface spatial charge region under the action of gas according to the following scheme [9–11]. When the sensor is installed in air, $O_2(gas) \rightarrow O_2(ads)$. Then oxygen physically adsorbed on the surface plays the role of acceptor of the CuO film electrons and turns to the chemosorbed negative forms: $[O_2(ads) + e^-] \rightarrow O_2^-(ads)$ or $[\ldots] \rightarrow 2O^-(ads)$ (at $T = 100-300°C$); $[\ldots] \rightarrow O^{2-}(ads)$ at $T > 300°C$.

These reaction result in formation in the CuO nanowire surface layers of a „hole" accumulation layer whose thickness (Debye length L_D) directly depends on the amount of chemosorbed oxygen. This layer defines to a high extent the oxide electrical resistance.

Once the CuO film is exposed to the gaseous hydrogen, it begins reacting with negative oxygen ions adsorbed on the surface (O^-, O^{2-}). Threat, electrons previously captured by oxygen release into CuO. The nanowire coating consisting of surface oxygen ions shrinks down. In the surface layer there occurs electron−hole recombination, the „hole" accumulation layer becomes thinner, and the electrical resistance increases. An important feature of such a sensor is the presence of oxygen under normal conditions, which defines the zero mark relative to which hydrogen is detected.

An observed base line drift was caused by incompletely reversible recovery of the base resistance due to a continuous increase in the H_2 concentration during the experiment. In our experiments, this variation did not exceed 7%. This may be associated with the desorption incompleteness caused by insufficiently long time intervals between hydrogen inflows.

An important feature of pure reducing gases is not only their ability to promote oxygen desorption from the surface of the sensor sensitive layer but also the possibility of chemical reduction of the sensor material under certain conditions. The CuO surface layers may be reduced as $CuO \rightarrow Cu_2O \rightarrow Cu$ with a significant decrease in the sensor electrical resistance (to $\sim 10\,\Omega$). We have not observed such a percolation phase transition in our experiments on the sensor response dynamic dependence. Probably, in our experiments such factors as morphological peculiar features of the film we studied, sensor operating temperature and time of exposure to gas were insufficient for the oxide reduction to metal copper.

This effect begins manifesting itself in case of long−term exposure to hydrogen. Fig. 3, b presents the time dependence of the sensor resistance under the impact of gas mixture with the hydrogen content of 1000 ppm at the operating temperature of 300°C. One can see that considerable resistance variation caused by formation of the Cu_2O and Cu phases starts after the sensor has stayed in the hydrogen−containing atmosphere for 33 min. The resistance decrease connected with this takes place despite the competing oxidation effect of oxygen permanently contained in the gas mixture. Kinetics of this reaction is associated with

thermal energy that activates the CuO reduction; at higher operating temperatures, hydrogen migration into the CuO bulk is faster [12]. Such a behavior was demonstrated in, e. g., [10] for branched networks of CuO nanowires where this feature was used to improve the sensors's selectivity.

Thus, the gas sensor morphology described in this paper ensures an access for oxygen and analyzed gas to a large area of the CuO surface during investigation of its gas−sensitive properties. The gas penetration induces variations in the p-type CuO electronic structure during formation of the surface „hole" accumulation layers. This results in a significant modulation of electrical resistance in conductometric measurements, which reaches 0.92 at the H_2 concentration of 1000 ppm. In the presence of hydrogen, the resistance variation is caused by a decrease in the hole−type conductivity of each individual nanowire and, along with this, by an increase in the contact resistance between neighboring nanowires.

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Conflict of interests

The authors declare that they have no conflict of interests.

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