Synthesis and study of the gas sensitive properties of composite thin films of copper oxide and linear chain carbon

A V Smirnov, V A Kazakov, P S Platonov and E S Tyunterov

Department of Applied Physics and Nanotechnology, The Chuvash State University, Cheboksary 428015, Russia

E-mail: fizteh21@yandex.ru

Abstract. The possibility of synthesizing semiconductor films of copper oxide and films of copper oxide with linear chain carbon, which have good sensitivity to methanol and ethanol vapors, is shown in the work by a thermoresistive method. The proposed gas sensitivity mechanism describing the increase in resistance in methanol and ethanol vapors shows good agreement with the obtained experimental results.

1. Introduction
The possibility of synthesizing semiconductor films of copper oxide and films of copper oxide with linear chain carbon, which have good sensitivity to methanol and ethanol vapors, is shown in the work by a thermoresistive method. The proposed gas sensitivity mechanism describing the increase in resistance in methanol and ethanol vapors shows good agreement with the obtained experimental results.

Recently, nanostructured p-type semiconductor metal oxides have been investigated to determine reducing as well as oxidizing hazardous, flammable and toxic gases. The ratio of morphology, surface to volume ratio, cationic and anionic surface defects, porosity, particle size, degree of agglomeration and crystallographic orientation of these metal oxides of nanomaterials are strongly influenced by various gas sensing parameters [1].

To obtain excellent gas-sensitive properties, metal oxide nanomaterials with a high surface area to volume ratio are obtained, which are necessary for a better adsorption / desorption phenomenon of the analyzed gas [2].

A number of synthesis methods have been reported in the literature, such as solvothermal, thermal evaporation, hydrothermal and microwave hydrothermal, ultrasonic spray pyrolysis and electrodeposition to develop gas sensors using p-CuO semiconductor nanostructures, such as nanowires, nanorods, mesoporous films, nanocubes, nanosubes, nanosubes nanoruchins, nanoribbons, hollow spheres, etc. [3,4]. P-type metal oxides are attractive in that they can easily exchange their oxygen lattices with air to maintain their stoichiometry. This is a very useful property for maintaining the long-term stability of the sensor.

Due to these properties, nanostructured CuOx materials can be used for the manufacture of sensors, especially for ethanol, which is widely used in biomedical applications, the food industry, and alcohol quality analysis [5].

In [6], CuOx films were fabricated to create an ammonia sensor using the citrate sol – gel method. As a result of the study of gas-sensitive properties, reactions to ammonia were detected at a temperature of 180 °C in the concentration range of 25-150 ppm, which is characterized by stability and
reproducibility. From the typical response dynamics of the sensor element, it was found that the response time and recovery time are 4-6 seconds and 80-120 seconds, respectively.

In the study [7], a nanostructured film of copper (II) oxide deposited by reactive DC magnetron sputtering was studied for a static response to methanol and ethanol at operating temperatures from 350 °C and 400 °C, respectively. The maximum sensitivity observed for 2500 ppm methanol and ethanol is 29% and 15.4%, respectively. The response time to methanol and ethanol vapors was 235 s and 247 s, respectively.

The aim of this work is to study the gas-sensitive properties of thin-film semiconductor structures based on copper oxide at room temperature with a good response and recovery time.

2. Methodology
Copper films were deposited on glass substrates by thermoresistive evaporation in vacuum on a UVR-3M vacuum apparatus at a pressure of about 10⁻² Pa, then samples were annealed in an MIMP-VM furnace in an atmosphere of air at a temperature of 250°C for 20 minutes and at a temperature of 400°C. For another group of samples for preparing metal-carbon-carbon systems, copper films were deposited on the substrates and then linear-chain carbon (LCC) films were deposited by ion-plasma synthesis [8] and were thermally oxidized in an oven at a temperature of 400°C. The structure of the LCC films consists of many layers, each of which consists of chains of carbon atoms in sp1 hybridization, oriented normally to the layer surface. The chains are combined by van der Waals forces into a hexagonal structure with a distance between them of about 5 Å. The chains are curved, at the ends of the bends of which the H atoms are attached. The presence of delocalized electrons belonging to the entire molecule of the LCC provides metallic conductivity along the chain. The lack of coupling between the chains makes the film in the perpendicular direction a dielectric. This unique electrical property of the film is the record anisotropy of electrophysical properties.

An X-ray photoelectron spectroscopy (XPS) study was performed on a LAS-3000 (Riber) instrument equipped with a hemispherical analyzer with a delay potential OPX-150. To excite the photoelectrons, we used x-ray radiation from an aluminum anode (AlK = 1486.6 eV) at a voltage of 12 kV tube and an emission current of 20 mA. Calibration of the photoelectron peaks was carried out along the C1s carbon line with a binding energy (Esb) of 285 eV.

3. Experimental results

3.1. Study of XPS spectra
The previously obtained results of the optical and electrophysical properties of samples [9], with films of linear chain carbon deposited on them, raise the question of the interaction of copper and carbon atoms. One can try to explain this phenomenon by the fact that the linear-chain carbon film interacted with copper after heat treatment. This is evidenced by the XPS spectrum for copper in Figure 1.
3.2. Investigation of the dependence of resistance on temperature
A test sample was placed on a stage, which was pressed by two aluminum contacts connected to a KEITHLEY 2400 multimeter. The multimeter itself is connected to a personal computer. Using the LabTracer software, voltage parameters were set at which the experiment was conducted. According to the temperature dependence of electrical resistance, it is determined that when samples are heated, the resistance decreases, which indicates the receipt of films with semiconductor properties.

3.3. Investigation of the gas sensitive properties of copper oxide films
The test samples were placed on a stage, covered under a cap and alternately saturated with ethanol and methanol vapors (resistance changes are shown in Figures 2-5).

![Figure 1. Graph of XPS analysis of Cu-LCC films after annealing in the atmosphere at 400°C.](image1)

![Figure 2. The dependence of the resistance of the film of CuO-LCC on the exposure time in ethanol vapor.](image2)
Figure 3. The dependence of the resistance of the film of CuO-LCC on the exposure time in methanol vapor.

Figure 4. The dependence of the resistance of the Cu$_2$O film on the exposure time in ethanol vapor.

Response and recovery time are defined as the time required to reach 90% of the maximum signal level and the return time to 90% of the initial value, respectively. The sensitive layer shows the reaction time, recovery and sensitivity for Cu$_2$O samples for methanol vapors 1600 sec., 565 sec. and 2.1%, for ethanol vapors 1035 sec., 407 sec. and 2.1%, respectively; for CuO + LCC samples for methanol vapors 548 sec., 117 sec. and 2.1% and for ethanol vapors 169 sec., 65 sec. and 8.8%, respectively.

Adsorption of O$_2$ gas molecules, dissociation into an oxygen atom, and oxygen ionization by taking electrons from the surface of Cu$_2$O (or CuO + LCC) nanostructures lead to the formation of negatively charged surface oxygen ions:

\[
\begin{align*}
O_2 (g) + e^- & \leftrightarrow O_2^- \text{ (chemisorbed)} \\
O_2 (g) + 2e^- & \leftrightarrow 2O^- \text{ (chemisorbed)}
\end{align*}
\]
Figure 5. The dependence of the resistance of the Cu2O film on the exposure time in methanol vapor.

Negatively charged oxygen adsorption on p-type oxide semiconductors such as CuO leads to the formation of a hole (h+) storage layer near the surface. When reducing gases such as C2H5OH, CH3OH, etc. are present in the surrounding atmosphere, the reaction between the reducing gas and negatively charged surface oxygen releases an electron into the holes (h+), which, in turn, increases the resistance of the p-type semiconductor by electron hole recombination according to the equation:

\[ C_2H_5OH_{(chemisorbed)} + 6O^-_{(chemisorbed)} \rightarrow 2CO_2(g) + 3H_2O(g) + 6e^- \]

For comparison with our work, a CuO-based sensor manufactured by Mitesh et al. [10], the response time and recovery time are 3.91 min and 4.25 min to a methanol vapor concentration of 2500 ppm.

4. Conclusions

It is shown in the work that it is possible to synthesize semiconductor films of copper oxide and copper oxide with linear chain carbon, which have good sensitivity to methanol and ethanol vapors. The proposed gas sensitivity mechanism, which describes the increase in resistance in methanol and ethanol vapors, shows good agreement with the results.

Acknowledgments

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