Gas sensing properties of nanocomposites with ZnO nanowires

To cite this article: A A Bobkov and V I Gorshanov 2018 J. Phys.: Conf. Ser. 1038 012047

View the article online for updates and enhancements.

Related content
- Laser emission of low-threshold excitation from ZnO nanowires
  Li Cao, Bingsuo Zou, Chaorong Li et al.
- Effect of Oxidation Temperature on the Morphology of ZnO Nanowires Fabricated by Directed Melt Oxidation of Al-Zn Alloy
  Ssang-Jo Kim, Won-Jae Lee, Byoung-Chul Shin et al.
- Density-Controlled Growth of ZnO Nanowires Via Nanoparticle-Assisted Pulsed-Laser Deposition and Their Optical Properties
  Ruiqian Guo, Jun Nishimura, Masato Matsumoto et al.
Gas sensing properties of nanocomposites with ZnO nanowires

A A Bobkov, V I Gorshanov

Micro- and nanoelectronics department, Saint Petersburg State Electrotechnical University, 5 Prof. Popova Street, Saint Petersburg, Russia

Abstract. In this work gas sensitivity of zinc oxide nanostructures to reducing gases (acetone and isopropyl alcohol) was investigated; impedance spectroscopy method was used for resistance measurements in a wide range of frequencies. Special attention is payed to the idea that increasing surface area of the samples leads to a corresponding increase in sensitivity. In order to check it, gas sensitivity of ZnO – SiO$_2$ nanocomposites was measured first; after that the samples were used to form ZnO nanowires on their surface, and the comparison of gas sensitivity of samples with and without nanowires is presented.

1. Introduction

Zinc oxide is a II-VI compound semiconductor with a direct bandgap of 3.4 eV at room temperature, which has found various applications in microelectronics and optoelectronics [1]. It has also been widely investigated as a gas sensing material; although a few metal oxides change their resistance after being subjected to gas, ZnO is one of the prominent ones [2].

When zinc oxide sample is in the atmosphere, oxygen species get adsorbed by the surface of the semiconductor. In such case oxygen acts as a trap for electrons, thus the surface conductivity gets lower than the bulk conductivity. However, when the sample is exposed to a reducing or oxidizing gas, the oxygen species start interacting with the gas species; after the interaction the concentration of oxygen on the semiconductor surface changes, which leads to changes in surface conductivity. In general, when a n-type metal oxide semiconductor (like ZnO or SnO$_2$) is exposed to a reducing gas, its surface conductivity increases; when it is exposed to an oxidizing gas, its conductivity decreases. The situation is opposite with p-type metal oxides [3].

As long as all the interactions responsible for gas sensing properties happen on the surface of semiconductor, using nanostructured materials which have bigger surface area has often [4,5] been considered an option for increasing gas sensitivity of metal oxides. This work compares gas sensing properties of ZnO – SiO$_2$ nanocomposite samples before and after ZnO nanowires were grown on the nanocomposite surface.

2. Experimental methods

2.1. Samples synthesis

ZnO – SiO$_2$ nanocomposite films were obtained using sol-gel synthesis; the method had been shown in [5] and [6]. Inorganic salt Zn(NO$_3$)$_2$•6H$_2$O was used as the ZnO precursor; in order to improve the adhesion TEOS was used. The resulting sol was kept at room temperature for several days. After that
the solution was spin-coated on silicon substrates (3000 RPM during 15 seconds); the spin-coating was followed by 30 minutes annealing of the samples carried out at a temperature of 500 °C. Monocrystalline silicon plates, which had been previously chemically purified, were used as substrates.

The acquired layers were used to form ZnO nanowires via hydrothermal method, which had been shown in [7] and [8]. As the growth solution, an aqueous solution of zinc acetate, hexamethylenetetramine (HMTA) and cetyltrimethylammonium bromide (CTAB) was used. The samples were put into the solution and kept in it for 90 minutes at a temperature of 85°C. After the end of the process the samples were rinsed with distilled water and air dried. The resulting nanowires are shown in figure 1.

![SEM-image of nanowires obtained by hydrothermal synthesis on ZnO – SiO₂ nanocomposite film.](image)

**Figure 1.** SEM-image of nanowires obtained by hydrothermal synthesis on ZnO – SiO₂ nanocomposite film.

2.2. Measurements method

In order to measure gas sensitivity of the samples impedance spectroscopy method was used. The impedance spectroscopy implies measuring real and imaginary resistance of a sample in a wide range of frequencies (during this work the measurements were conducted between 100 Hz and 500 kHz); after that an equivalent electric circuit is often matched to the Im(Re) graph [9].

In this work, in order to compare sensitivity properties of different samples, we used a formula that is to describe the relative change of complex resistance of a sample in the air and in the gas:
\[ S(f) = \frac{\Delta Z}{Z_a} = \frac{Z_a - Z_g}{Z_a} = \frac{\sqrt{\text{Re}^2(Z_a) + \text{Im}^2(Z_a)} - \sqrt{\text{Re}^2(Z_g) + \text{Im}^2(Z_g)}}{\sqrt{\text{Re}^2(Z_a) + \text{Im}^2(Z_a)}} \]

where \( Z_a \) is the complex resistance of a sample in the air; \( Z_g \) is the complex resistance of a sample in the gas. In order to conduct the measurements, contact pads were formed using electrically conductive adhesive containing silver.

During the measurements samples’ temperature was 200 °C; the gas concentration was 3000 ppm.

After the measurements the highest sensitivity of samples and corresponding frequencies were determined.

3. Results and discussion

The results of measuring gas sensitivity of the samples are shown in table 1; the sensitivity was calculated according to the previously given formula.

| Gas              | Parameter                      | Without nanowires | With formed nanowires |
|------------------|--------------------------------|-------------------|-----------------------|
| Acetone          | Maximum sensitivity, relative units | 0.15              | 0.219                |
|                  | Frequency of max. sensitivity, kHz | 0.4               | 1.4 – 2.1            |
| Isopropyl alcohol| Maximum sensitivity, relative units | 0.045             | 0.188                |
|                  | Frequency of max. sensitivity, kHz | 0.4               | 1.3 – 2.5            |

As can be seen from the table, after the nanowires were grown on nanocomposite samples, the sensitivity improved noticeably. Sensitivity to acetone increased 1.46 times, while sensitivity to isopropanol increased more than 4.17 times.

This result corroborates the fact that the processes responsible for gas sensitivity properties of metal oxides all take place on the surface of materials and increase in surface area which happens with usage of nanostructured materials also increases gas sensitivity.

The study was performed by a grant from the Russian Science Foundation (project 17-79-20239).

References

[1] Klingshirn C, Hauschild R, Priller H, Decker M, Zeller J and Kalt H 2005 *Superlattices and Microstructures* **38** 4–6 209–22
[2] Korotcenkov G 2007 *Materials Science and Engineering B* **139** 1 1–23
[3] Fine G F, Cavanagh L M, Afonja A and Binions R 2010 *Sensors* **10** 6 5469–502
[4] Hjiri M, Mir L E and Leonardi S G 2014 *Chemosensors* **2** 2 121–30
[5] Bobkov A A 2014 *Young Scientist* 7 115–18 (in Russian)
[6] Bobkov A A and Karpov S S 2012 *Young Scientist* 9 21–5 (in Russian)
[7] Bobkov A A et al. 2015 *Physics and Technology of Semiconductors* **49** 10 (in Russian)
[8] Lashkova N A, Maksimov A I, Ryabko A A, Bobkov A A, Moshnikov V A and Terukov E I 2016 *Physics and Technology of Semiconductors* **50** 9 (in Russian)
[9] Barsoukov E and Macdonald J R 2005 *Impedance Spectroscopy: Theory, Experiment, Applications* (Hoboken: John Wiley & Sons)