Temperature Dependence of Electrical Properties of ZnO Nanorods Array

V V Petrov¹, Y N Varzarev¹ and K A Abdullin²

¹ Southern Federal University, Institute of Nanotechnologies, Electronics, and Equipment Engineering, Taganrog, 347922, Russia
² National Nanotechnology Laboratory of Open Type, al-Farabi Kazakh National University, Almaty, 050000, Republic of Kazakhstan

E-mail: vvp2005@inbox.ru

Abstract. Zinc oxide nanostructures (nanotubes, nanorods, nanowhiskers, etc.) are a promising material for various electronics devices for power system and green energy such as piezoelectric energy harvesters and solar cells. Electrical properties of ZnO nanorods grown on a glass substrate by the hydrothermal method in an aqueous solution of zinc nitrate were investigated in this work. The SEM micrograph shows that the grown nanorods are vertically oriented and the XRD pattern confirms its crystallinity with (002) preferred orientation. The temperature dependent resistivity of ZnO nanorods array measured from 300 to 523 K shows variation in resistance from \(5 \times 10^9\) Ω to \(3 \times 10^6\) Ω and temperature hysteresis and region with positive temperature coefficient of resistance at the heating that was not observed at cooling. The origin of this behavior is explained with the two competing processes - thermal generation of electrons and oxygen species adsorption on the ZnO surface. Oxygen adsorption leads to decrease in the number of oxygen vacancies that are electron donors, and consequently to a decrease in conductivity of ZnO nanorods. The values of activation energy of conductivity were calculated from the slope of linear regions on the Arrhenius plot which are 0.246, 1.466 and 0.248 eV for the heating curve and 0.650 and 0.315 eV for the cooling curve.

1. Introduction
Zinc oxide (ZnO) is a wide band-gap semiconductor and promising material for various electronics devices for power system and green energy such as piezoelectric energy harvesters and solar cells, gas sensors [1]. Recently, considerable attention has been paid to the formation and investigation of the ZnO nanostructures (nanotubes, nanorods, nanowhiskers, etc.) which are used in functional electronics devices [2, 3]. Therefore, an urgent task is to study electrical properties of such nanostructures and the effect of external influences, such as temperature, light, gas ambient on them. Temperature measurements of the electrical resistance of materials make it possible to obtain information about the mechanism of conductivity, in particular, to estimate the values of the activation energies of conductivity and to conclude that they are associated with levels of impurities or defects that are donors or acceptors of charge carriers. Previously, the temperature behavior of electrical conduction processes in ZnO have been studied by some groups [4-6]. In this works thermal activation of conductivity was observed over a wide temperature range and was associated with the influence of shallow donors - oxygen vacancies and impurities.
The study of the conductivity mechanisms in ZnO nanostructures is complicated by the fact that their developed surface adsorbs oxygen well, which has a significant effect on the conductivity mechanism. In this paper, the effect of oxygen adsorption on the temperature dependence of the resistance of an array of nanorods is shown.

2. Experimental
An array of ZnO nanorods was grown by hydrothermal technology in an aqueous solution of zinc nitrate Zn(NO$_3$)$_2$·6H$_2$O and hexamethylenetetramine C$_6$H$_12$N$_4$ on a glass substrate during 1 hour at temperature 95°C [7, 8]. The surface morphology was studied using a scanning electron microscope (SEM) Nova NanoLab 600, and X-ray diffraction (XRD) analysis to study the crystal structure was done in a MiniFlex Rigaku diffractometer with CuKα radiation. The diffractogram of polycrystal ZnO (JCPDS card no. 00-001-1136) was used to characterize the phase composition of nanorods. To measure the electrical parameters of the material, metal contacts V-Cu-Ni with a thickness of 0.2-0.3 µm were applied to the sample surface by vacuum deposition. Resistance measurements in the temperature range of 300–523 K were carried out using a Keithley 2450 source meter.

3. Results and discussion
SEM studies have shown that the formed ZnO nanorods are mainly vertical, however, a significant number of nanorods are in contact with each other. Nanorods have a length of up to 0.5-0.6 µm [5] and an average transverse size of about 30-40 nm (figure 1). XRD analysis showed that the predominant growth direction of zinc oxide during the hydrothermal synthesis of ZnO nanorods is the direction (002) (Figure 2).

![Figure 1. SEM micrograph of ZnO nanorods array](image)

![Figure 2. XRD pattern of ZnO nanorods](image)

The temperature dependence of the resistance (figure 3) shows change in resistance by three orders of magnitude - from $5 \cdot 10^9$ Ω to $3 \cdot 10^6$ Ω. A distinctive feature of this dependence is that the heating and cooling curves at temperatures above 373 K do not coincide, that is, there is a temperature hysteresis.

On this dependence, we can distinguish regions that are well approximated by the Arrhenius equation [9]:

$$\rho = \rho_0 \exp\left(\frac{E_a}{kT}\right)$$  \hspace{1cm} (1)

where $\rho_0$ is preexponential factor, $E_a$ is activation energy of conductivity and $k$ is Boltzmann constant. Three such regions can be distinguished on the heating curve – I, II and III, and two on the cooling
curve – IV and V (Figure 2). The values of the activation energy of the conductivity of a ZnO nanorods array calculated by equation (1) are given in Table 1.

![Temperature dependent resistivity of ZnO nanorods array](image)

**Figure 3.** Temperature dependent resistivity of ZnO nanorods array

**Table 1.** Activation energy of the conductivity of a ZnO nanorods array

| Region | Temperature band, K | Activation energy of conduction ($E_a$), eV |
|--------|---------------------|-----------------------------------------|
| I      | 300-373             | 0.246                                   |
| II     | 390-423             | 1.466                                   |
| III    | 450-493             | 0.248                                   |
| IV     | 523-463             | 0.650                                   |
| V      | 400-300             | 0.315                                   |

It is known that the electrical conductivity of zinc oxide is determined by oxygen vacancies, which are electron donors [2], and, accordingly, the activation energy of conductivity is determined by donor levels formed by vacancies in the forbidden zone of ZnO. During heating, in regions I and II, the decrease in the resistance of the sample with increasing temperature is determined by the thermal generation of electrons. The different activation energy of conductivity for these regions indicates that two different donor levels are sources of electrons.

Region III is a region with a positive temperature coefficient of resistance; it is observed only during heating and is absent upon cooling. A similar behavior of the electrical resistance of zinc oxide with temperature was observed in [10], where sintered ZnO was studied, in [11] on ZnO pellets prepared by uni-axial pressing and in [12] on the ZnO nanostructures grown by sol-gel method. The increase in resistance with increasing temperature in this area can be explained by the influence of adsorbed oxygen. Oxygen molecules in the atmosphere at temperatures of 373–573 K are adsorbed on
the surface of zinc oxide and become negatively charged due to the capture of electrons from near-surface ZnO layers [13]:

\[
\begin{align*}
O(\text{gas}) & \leftrightarrow O(\text{ads}) \\
O(\text{ads}) + e & \leftrightarrow O(\text{ads}) \\
O(\text{ads}) + e & \leftrightarrow 2O(\text{ads}) \\
O(\text{ads}) + e & \leftrightarrow O(\text{ads})
\end{align*}
\]

(2)  (3)  (4)  (5)

This leads to the formation of a depleted layer in the near-surface region of ZnO nanorods and a decrease in their conductivity [12]. The activation energy of conductivity on this site will correspond to the energy of oxygen adsorption. A further decrease in resistance after region III is probably caused by the predominance of thermal generation of electrons.

When the temperature decreases, extremums on the temperature dependence of the resistance is not observed, that may be due to the lack of oxygen species desorption. Sections IV and V on the cooling curve also correspond to two different values of the activation energy (Table 1).

Thus, the variations in conductivity during heating and cooling is due to two competing processes—thermal generation and recombination of electrons on one hand, and their capture by oxygen adsorbed on the surface on the other. Moreover, if in the first case, the equilibrium concentration is established almost instantly, then in the second it depends on the speed of the processes of adsorption and desorption, which is much lower and comparable with the rates of heating and cooling. Thus, the more dominant factor in the presence of hysteresis in the temperature dependence of the conductivity is oxygen species adsorption on the ZnO surface.

4. Conclusions
The temperature dependent resistivity of ZnO nanorods array obtained by hydrothermal method has been investigated. The values of activation energy of conductivity were calculated from the slope of linear regions on the Arrhenius plot. The origin of thermal hysteresis is explained with the two competing processes – thermal generation of electrons and oxygen species adsorption on the ZnO surface.

Acknowledgments
This work was financially supported by the Southern Federal University.

References
[1] Kołodzieczak-Radzimska A and Jesionowski T 2014 Mater. 7 2833–81.
[2] Wang J, Chenb R, Xiangb L, and Komarmenie S 2018 Ceram. Int. 44 7357–77.
[3] Petrov V V, Starmikova A P, Abdullin Kh A, and Makarenko D P 2018 J. Phys. Conf. Ser. 1124 022017
[4] Li X, Qi J, Zhang Q, and Zhang Y 2012 J. Appl. Phys. 112 084313
[5] Lien C C, Wu C Y, Li Z Q, and Lin J J 2011 J. Appl. Phys. 110 063706
[6] Benton B T, Greenberg B L, Aydil E, Kortshagen U R, and Campbell S A 2018 Nanotechnol. 29 415202
[7] Abdullin K A, Bakranov N B, Ismailov D V, Kalkozova J K, Kumekov S E, Podrezova L V, and Cicero G 2014 Semicond. 48 471-5.
[8] Gritsenko L V, Abdullin Kh A, Gabdullin M T, Kalkozova Zh K, Kumekov S E, Mukash Zh O, Sazonov A Y, and Terukov E I 2017 J. Cryst. Growth 457 164-70.
[9] Shalimova K V 1976 Physics of Semiconductors (Moscow: Energia)
[10] Takata M, Tsubone D, and Yanagida H 1976 J. Am. Ceram. Soc. 59 1–2, 4–8.
[11] Roy T K, Sanyal D, Bhowmick D, and Chakrabarti A 2013 Mater. Sci. Semicond. Process. 16 332-6.
[12] Santhosh Kumar A, Nagaraja K K, and Nagaraja H S 2013 AIP Conf. Proc. 1536 263–4.
[13] Rambu A P, Ilfimie N, and Rusu G I 2012 Mater. Sci. Eng. B-Adv. 177 157–63.