ELECTRICAL PROPERTIES OF ELECTROSPUN ZNO NANOFIBERS

A. Stafiniak[1], B. Boratyński[1], A Baranowska-Korczyc[2], K. Fronc[2], D. Elbaum[2], R. Paszkiewicz[1], M. Tłaczała[1]

[1] Faculty of Microsystem Electronics and Photonics, Wroclaw University of Technology, Janiszewskiego 11/17, 50-372 Wroclaw, Poland, [2] Institute of Physics, Polish Academy of Sciences, al. Lotników 32/46, 02-668 Warsaw, Poland

E-mail: andrzej.stafiniak@pwr.wroc.pl

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1. Introduction

Zinc oxide shows sensing properties after exposure to various environments. The gas sensitivity is a results of chemisorption of analyzed molecules with the surface of the active layer. This interaction could generate the charge which would lead to the changes in electrical properties of semiconductor. To increase the sensitivity, the active area should have high surface-to-volume ratio [1], what can be done using highly porous material or low dimensional structures. Electrospun nanofibers combine these two properties which make them excellent candidate for sensing applications [2,3].

The electrospinning method of fabrication provides relative simplicity of their positioning on the surface of substrates [4]. Additionally, the electrospinning method is appropriate for creating long, straight and aligned nanofibers from wide range of materials (polymers, metal oxides and their composites) [5].

In the present work, we reported on dc characterization of single electrospun ZnO nanofibers. The conductivity of single fibers calcinated at 500 °C and 700 °C was estimated. The I-V dependence as a function of temperature were measured. The study was focused on relations between the activation energy and the grain size.

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2. Experiment

A polyvinyl alcohol (PVA) and zinc acetate solution was prepared from PVA powder, deionized water and zinc acetate dehydrate (Zn(CH3COO)2 • 2H2O) to obtain ZnO precursor. Such prepared solution was used in electrospinning process of ZnO fibers. As spun fibers undergo calcination process at 500 °C or 700 °C to remove organic phase of the composite. Details concerning the preparation and structural characterization of ZnO nanofibers were already published [6]. The obtained results showed that ZnO fibers have nanaocrystalline wurtzite structure.

To prepare the test structures, the ZnO nanofibers were collected on Si substrate with 300 nm layer of thermally grown oxide (SiO_2) during electrospinning process. Structures with single nanofiber were fabricated using photolithography technique to define the area of nanofibers and contacts. To apply ohmic contact, Ti/Au (5/100 nm) double layer metallization was deposited in a UHV system by thermal and electron beam evaporation. Details of the technology of test structures with ZnO nanofibers were already reported [7].

Electrical characterization of the structures with single nanofiber was carried out in air atmosphere after thermal treatment in 300 °C. For the current-voltage dependence measurements a point probe tester with heated stage and Agilent E3631A power supply and 34401A multimeters were used.

3. Results and Discussion

For characterization of electrical properties of a single ZnO nanofiber structures calcinated at 500 °C and at 700 °C. In Figure 1 (a, b) SEM images at high magnification of the fibers are presented. From these images the average grain size was estimated. The average grain diameter was 5 nm for the fibers calcinated at 500 °C and 35 nm for the fibers calcinated at 700 °C. Topography of the test structures with a single nanofiber and Ti/Au metallization is shown in Figure 1 (c, d - SEM images, e, f - AFM images). The distance between the contacts was 10 μm. AFM scans give information about the geometry of the fiber. In Figure 1 (e, f) the profile of the fiber cross-section is also presented.

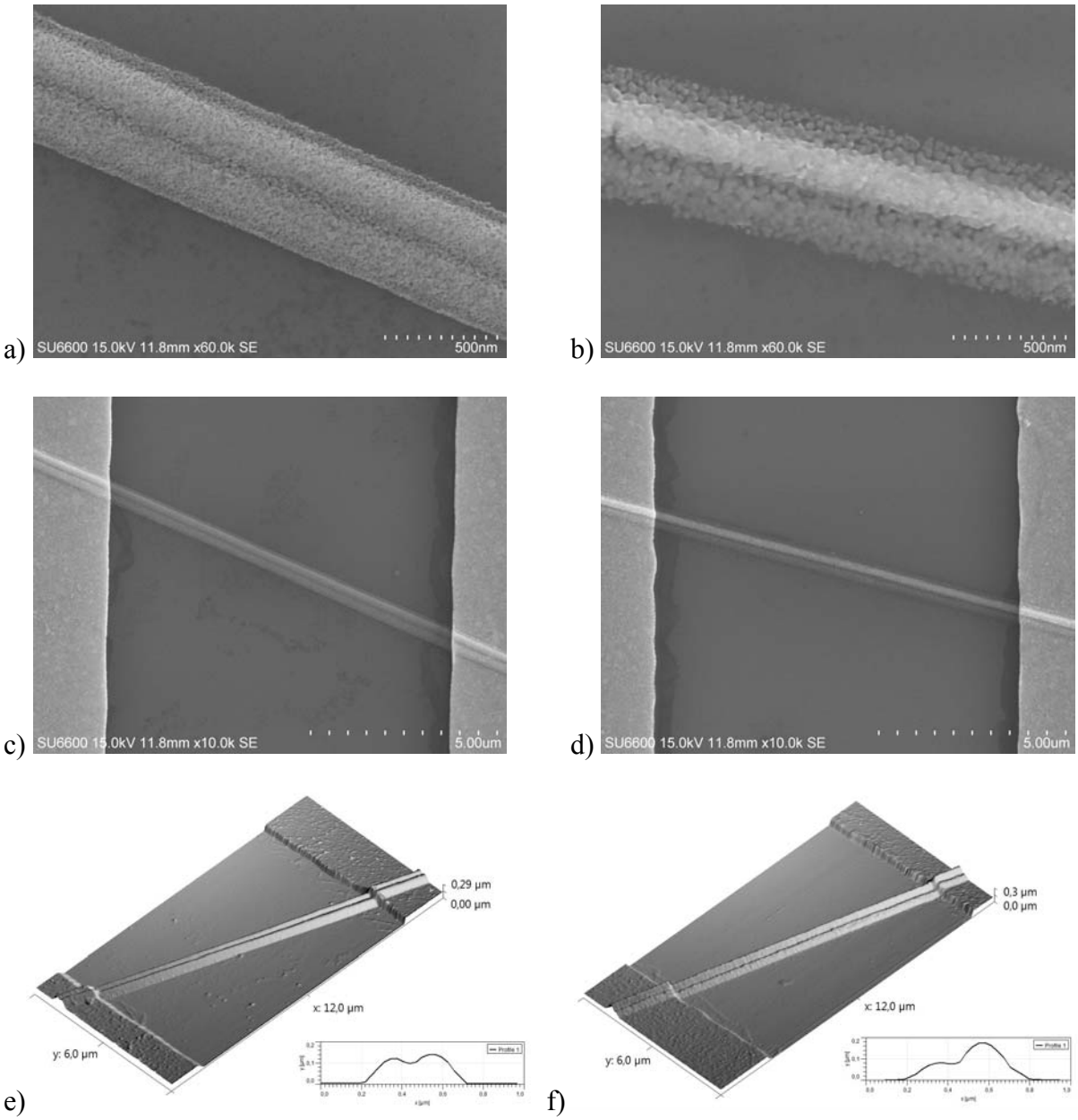

Fig.1: SEM images at high magnification of the fibers calcinated at 500 and 700 °C (a) and (b), topography of the test structures with single nanofiber and Ti/Au contact metallization: SEM images (fibers calcinated at 500 and 700 °C respectively) (c) and (d), AFM images (fibers calcinated at 500 and 700 °C respectively) (e) and (f).

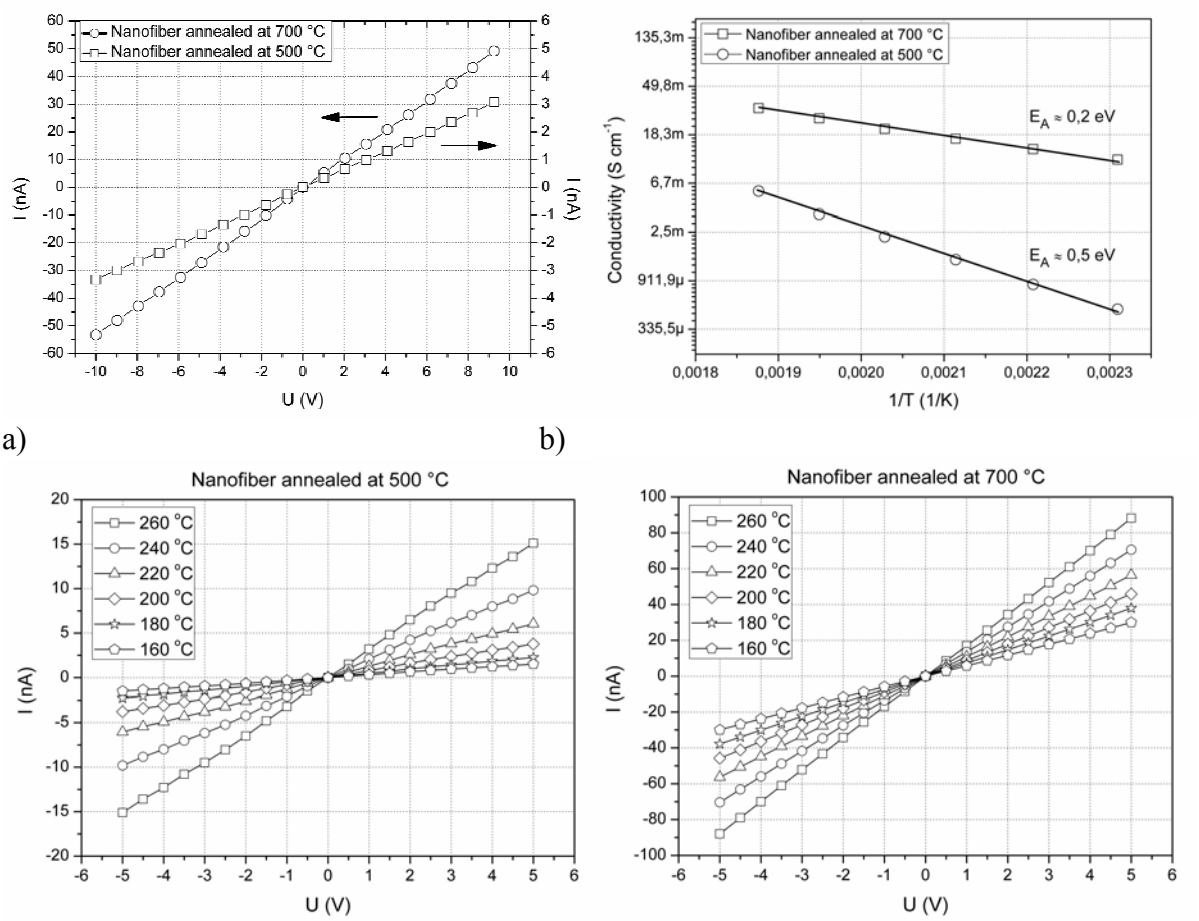

Fig.2: *The I-V characteristics of the electrospun ZnO nanofiber calcinated at 500 °C and at 700 °C at room temperature (a), Arrhenius plot of the conductivity for ZnO nanofiber (b), (c) and (d) I-V dependence measured at different* temperature *of ZnO nanofiber calcinated at 500 and at 700 °C respectively.*

Electrical characterizations of a single ZnO nanofiber were carried out by I-V measurement. The linearity of Ti/Au ohmic contacts was confirmed in a wide range of voltage values (Figure 2 a). Knowing the geometry of the fiber from AFM profile and its resistance, calculated from the curve I-V, one can calculate value of the fiber conductivity. Room temperature conductivity of fiber calcinated at 500 °C was estimated to be 0.6 $mScm^{-1}$ (resistivity - 1.7 kΩcm) and for the fiber calcinated at 700 °C is 8.3 $mScm^{-1}$ (resistivity - 120 Ωcm).

Electrical model of polycrystalline metal oxide, such as ZnO nanofibers, can be considered as two resistive elements, grain boundaries and grain interiors. Resistivity of bulk semiconducting ZnO [8] shows the level of value by several orders of magnitude lower compared to the obtained resistivity of our fibers. Therefore, in our samples the grain boundaries are the dominant factor in determining the fiber electrical properties. For nanocrystalline structures where the grain size is comparable to the charge depletion zone, the conductivity is thermally assisted and given by the Eq.(1) [9]:

$$\sigma \approx \sigma_0 \exp\left(-\frac{E_C - E_F}{k_B T}\right) \qquad (1)$$

where E_C is energy of the conduction band, E_F is the Fermi level, k_B is the Boltzmann constant ant T - absolute temperature. To investigate the thermally assisted electrical

conduction I-V dependence as a function of temperature were measured. The results are presented in Figure 2 (c) for the nanofiber calcinated at 500 °C and (d) for the nanofiber calcinated at 700 °C. Linear behaviors of the ohmic contacts to the fibers are observed in a wide temperature range. The resistance of fibers decrease with an increase of temperature.

These measurements allowed the presentation of temperature dependence on the conductivity in the Areniusa plot (Figure 2 b). From such presented characteristics the activation energy E_A was extracted according to the Eq.(1) where $E_A = E_C - E_F$. The activation energies are 0.5 eV and 0.2 eV respectively for fiber calcinated at 500 °C an at 700 °C and are comparable to the values obtained in other studies on electrospun multi- ZnO nanofibers [10]. Follow that electrical conduction of ZnO nanofiber are defined by the grain boundaries. The activation energy understood as the height of the potential barrier between the grains comes from the acceptor states on the metal oxide surface. As a result of exposure to various gas environments the barrier height is changing, what determines the sensing propertiesn of the structure. Different activation energy value of fibers annealed at different temperatures were caused by different grain sizes of the fibers. This is explained by changing the interior grain properties due to solid–gas interactions when grain size is reduced to nanometers or to the order of the thickness of the depletion zone [11]. Furthermore, this size effect leads to significant improvements in sensitivity and response time of the device [12].

4. Conclusion

In summary, we reported on DC characterization of single electrospun ZnO nanofibers calcinated at 500 and 700 °C. The conductivity at room temperature of single fiber was about 0.6 $mScm^{-1}$ (500 °C) and 8.3 $mScm^{-1}$ (700 °C). The I-V dependence as a function of temperature showed linear behaviors of fibers and contacts at a wide range of temperature and voltages. Temperature dependence of conductivity was evaluated. The activation energy was found to be dependent on the grain size which in turn depend on the fiber calcination temperature. Extracted values of activation energies were 0.5 eV for fiber with grain size 5 nm and 0.2 eV for fiber with grain size 35 nm.

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