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Conductivity features of ZnO and NiO nanofiber composites

© *M.N. Martyshov*[1], *V.V. Smirnova*[1], *A.S. Ilin*[1,2], *V.B. Platonov*[1], *P.A. Forsh*[1,2], *P.K. Kashkarov*[1,3]

[1] Moscow State University, Moscow, Russia
[2] Lebedev Physical Institute, Russian Academy of Sciences, Moscow, Russia
[3] National Research Center „Kurchatov Institute“, Moscow, Russia
E-mail: mmartyshov@mail.ru

Received July 12, 2022
Revised December 9, 2022
Accepted December 13, 2022

In this work, composites of ZnO and NiO nanofibers with *n*- and *p*-type conductivity, respectively, were studied. It is shown that the conductivity of the studied composites strongly depends on the arrangement of ZnO and NiO nanofibers. In the case of a mixture of ZnO and NiO nanofibers (with their random arrangement relative to each other and electrical contacts), conduction can occur only along ZnO fibers, which have a higher conductivity compared to NiO. However, the presence of the ZnO/NiO $p-n$ heterojunction leads to the formation of depleted regions in ZnO, as a result, the conductivity of the mixture becomes several orders of magnitude lower than the conductivity of ZnO nanofibers. In the case of a two-layer composite, in which one layer consists of NiO nanofibers and the other layer consists of ZnO nanofibers, charge carriers move through the $p-n$ NiO/ZnO heterojunction, which leads to a rectifying current-voltage characteristic and opens up broad prospects for the use of such systems in electronic devices.

Keywords: metal oxides, zinc oxide, nickel oxide, heterostructures, conductivity.

DOI: 10.21883/TPL.2023.02.55372.19305

Composites based on nanocrystalline metal oxides are promising materials for photodetectors [1], gas sensors [2], and photocatalysts [3]. Different types of such composites ranging from simple mixtures [4,5] to complex core–shell structures [6,7] are being studied extensively at present. The best-studied metal oxides, such as SnO_2, ZnO, and TiO_2, feature *n*-type conductivity. This is attributable to the presence of oxygen vacancies, which act as electron donors. Certain metal oxides, such as NiO and Co_3O_4, feature *p*-type conductivity induced by cation vacancies [8]. Composites containing metal oxides with different conductivity types are of special interest, since $p-n$ heterojunctions may form in them. These heterojunctions exert a significant influence on the processes of carrier transport in such systems and provide an opportunity to control their transport properties. The majority of studied published to date (e.g., [9,10]) are focused on the examination of electrophysical characteristics of bilayer structures with *n*- and *p*-type metal oxide layers deposited successively onto a conducting substrate. At the same time, the area of contact of metal oxides in mixtures of their nanofibers increases considerably, thus also enhancing the effective area of $p-n$ heterojunctions. In the present study, we examine the conductivity of ZnO/NiO composites in the form of mixtures of nanofibers of *n*-type zinc oxide and *p*-type nickel oxide synthesized by electrospinning.

The method of synthesis of nanofibers by electrospinning was detailed in [11]. The material produced in the process of electrospinning was heated to 550°C within 5 h at a rate of 1°C/min to remove the polymer residue. A powder of metal-oxide fibers was obtained as a result of annealing. These powders were mixed with a binder (solution of terpineol in ethanol), and the produced paste was deposited onto a cover glass for the examination of electrophysical properties. This glass with a deposited film was dried at 30°C for 24 h and annealed at 550°C for 5 h. Films of the initial zinc and nickel oxides with a thickness of $\sim 1\,\mu$m were prepared this way. Planar gold contacts with a distance of $150\,\mu$m between them were deposited by vacuum thermal sputtering onto the surface of films.

Two types of composites were fabricated based on the synthesized metal oxides. Composite I was a 1:1 mixture of nanofibers of different conductivity types. These samples were produced by mixing solutions containing nanofibers of different metal oxides prior to the deposition onto a glass substrate. Composite II was a bilayer heterostructure (one layer consisted of NiO nanofibers, while the other contained ZnO nanofibers) on a glass substrate coated with transparent conducting FTO. Gold contacts 1.5 mm in diameter were deposited on top of this heterostructure.

The structural properties of powders of nanocrystalline metal oxides were examined with a Carl Zeiss NVision 40 scanning electron microscope (SEM) and a DRON-3 X-ray diffractometer. The X-ray diffraction technique was used to reveal the presence of nanocrystals and determine their mean size in the obtained powders. The conductivity of samples was measured using a Keithley 6487 picoammeter. Temperature dependences of the specific conductivity of samples were measured in a cryostat cell (fitted with a temperature controller) in the temperature range from 20 to 150°C.

Photomicrographs of the samples were obtained using the scanning electron microscope. Figure 1, *a* presents

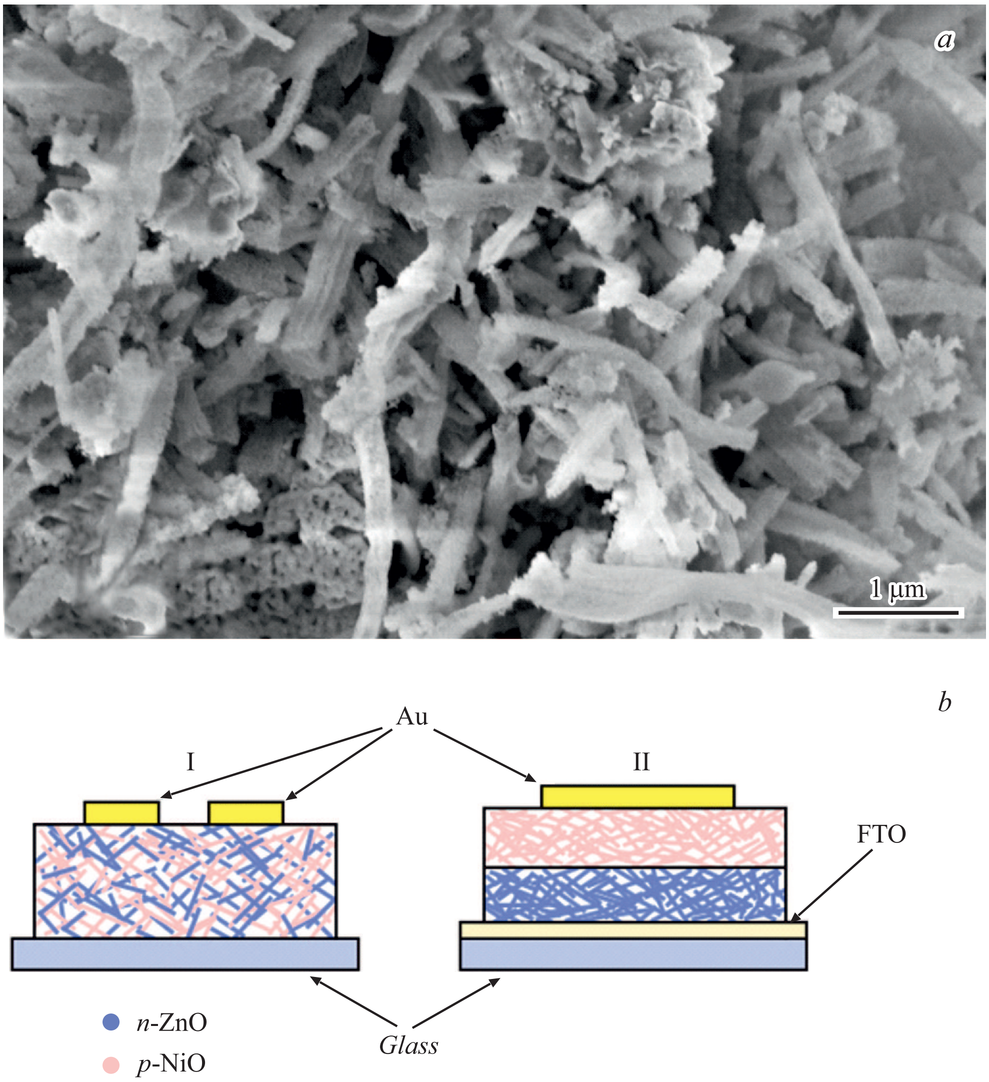

Figure 1. *a* — SEM image of composite I; *b* — schematic diagram of arrangement of composites I and II.

an example SEM image of a ZnO/NiO composite in the form of a mixture (composite I). This image reveals that the examined sample consists of long fibers 150−300 nm in diameter containing nanocrystals formed as a result of thermal annealing. The broadening of diffraction peaks was used to determine the mean size of nanocrystals for ZnO and NiO fibers, which turned out to be 33 and 8 nm, respectively. Figure 1, *b* shows the schematic diagram of two types of composites studied.

Temperature dependences of the specific conductivity for the initial ZnO and NiO samples and composite I are presented in Fig. 2, *a*. These dependences are of an activation nature and may be characterized by equation $\sigma = \sigma_0 \exp(-E_A/kT)$, where σ_0 is a pre-exponential factor that depends weakly on temperature, k is the Boltzmann coefficient, and E_A is the activation energy. The dependences were approximated by this equation; the obtained activation energies are indicated in Fig. 2, *a*. It was found that the dependence for the NiO sample remains linear in $\ln\sigma - 10^3/T$ coordinates throughout the entire range of temperature variation. The dependence for ZnO features two linear sections with different activation energies. These two sections may be associated with two donor levels in the bandgap of zinc oxide from which electrons are activated into the conduction band [12].

Figure 2, *a* also shows that the room-temperature conductivity of ZnO is more than two orders of magnitude higher than the conductivity of NiO. This may be attributed, among other factors, to the relative smallness of nanocrystals in nickel oxide (see the results of X-ray diffraction studies above). It is known that a reduction in size of nanocrystals in metal oxides may lead to a significant reduction in conductivity [13]. The conductivity of composite I, which was a 1:1 mixture of ZnO and NiO nanofibers, was also compared to the conductivity of the initial samples. With this ratio of components, carrier transport may proceed along ZnO fibers, bypassing NiO fibers with a considerably lower conductivity. Viewed through the lens

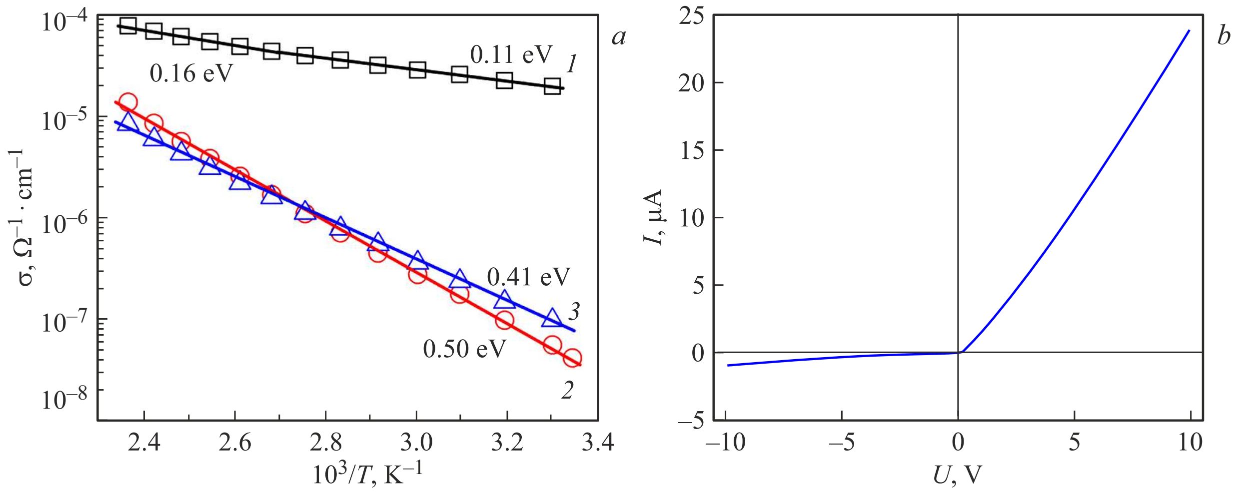

Figure 2. *a* — Temperature dependences of conductivities of ZnO (*1*), NiO (*2*), and composite I (3); *b* — current–voltage curve of composite II.

of the Bruggeman effective medium theory, composite I should be comparable in conductivity to ZnO. However, it follows from Fig. 2 that the conductivity of composite I is significantly lower than the conductivity of zinc oxide and comparable to the conductivity of nickel oxide. These data are indicative of a marked influence of heterojunctions, which are neglected in the effective medium model, on the conductivity of the studied material. The current–voltage curve (CVC) of a heterojunction (composite II; see Fig. 2, *b*) was examined in order to demonstrate that a heterojunction does indeed form between ZnO and NiO fibers. This CVC has a rectifying nature typical of semiconductor diodes. It was approximated by expression $I = I_0[\exp(q(U - IR_s)/nkT) - 1]$, where I_0 is the saturation current, R_s is the net resistance of *n*- and *p*-type regions (with the resistance of the $p{-}n$ junction itself excluded), and *n* is nonideality factor [9]. It should be noted that resistance R_s in such structures should necessarily be included into calculations, since it limits the current through the heterojunction at high voltages. The values of $R_s = 420\,\text{k}\Omega$ and $n \approx 4$ were determined as a result. It follows that heterojunctions at contacts between ZnO and NiO fibers should also form in composite I based on a mixture of nanofibers of zinc and nickel oxides.

In order to reveal the mechanism of influence of a heterojunction on the conductivity of a mixture, we examine the energy band diagram of materials. Figure 3, *a* shows the energy diagram for ZnO and NiO prior to their contact. Electronic work functions of 4.3 and 4.8 eV [9] for ZnO and NiO, respectively, were used to plot this diagram. Depletion regions with widths x_n and x_p form near the junction after contact (Fig. 3, *b*). If the size of these regions is comparable to the nanofiber diameter, a significant part of a fiber becomes depleted in carriers. The formation of depletion regions should result in a significant reduction in conductivity of the mixture (even if carrier transport is assumed to be confined to ZnO fibers), and this is what is observed experimentally.

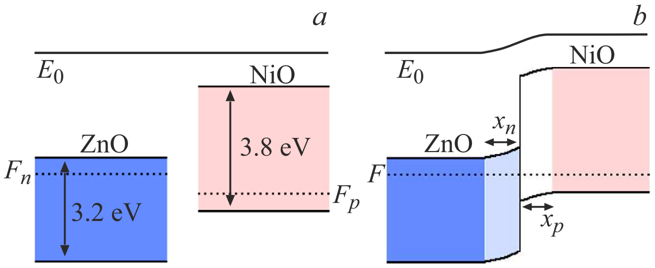

Figure 3. Energy band diagram of ZnO and NiO before (*a*) and after (*b*) contact.

Thus, it was demonstrated that the conductivity of a composite formed by ZnO and NiO nanofibers mixed in equal proportion may be supported only by ZnO fibers, which are more conductive than NiO. However, the presence of a $p{-}n$ heterojunction between ZnO and NiO nanofibers induces the emergence of depletion regions in ZnO. Therefore, the conductivity of a mixture of ZnO and NiO nanofibers becomes significantly lower than the conductivity of ZnO fibers themselves. The CVC of a bilayer $p{-}n$ heterostructure (with layers consisting exclusively of NiO and ZnO nanofibers) is rectifying in nature, since carries in this case cannot move along only one component of the mixture and are forced to go through a $p{-}n$ heterojunction. The presence of a rectifying CVC offers great opportunities for application of this material in electronics, photovoltaics, and gas sensorics.

Funding

This study was supported financially by the Russian Foundation for Basic Research and the Government of Moscow as part of scientific project No. 21-32-70038.

Conflict of interest

The authors declare that they have no conflict of interest.

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