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CHEMICAL PHYSICS OF NANOMATERIALS

Conductivity of Nanostructured India Oxide Films Containing Co_3O_4 or ZrO_2

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Abstract—The effect of additives of cobalt and zirconium oxides on the conductivity of nanostructured composites based on indium oxide is studied. It is shown that addition of up to 20 wt % ZrO_2 to In_2O_3 leads to a sharp decrease in the conductivity of the composite. For the Co_3O_4–In_2O_3 system, the conductivity decreases up to a Co_3O_4 content of 60 wt %, after which it increases. At a Co_3O_4 content in the Co_3O_4–In_2O_3 system of up to 60 wt %, *n*-type conduction takes place, changing to *p*-type at 80 to 100 wt % Co_3O_4. Zirconium oxide exhibits practically no *n*-type conduction, so electric current in the ZrO_2–In_2O_3 system flows through In_2O_3 nanocrystals, i.e., *n*-type conduction takes place. Possible causes of the observed effects are considered.

Keywords: nanocomposites, conductivity, indium oxide, cobalt oxide, zirconium oxide, *n*- and *p*-type semiconductors

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INTRODUCTION

Nanostructured metal oxide films are the basis of high-efficiency chemical sensors for detecting various chemical compounds [1, 2]. The conductometric sensory effect manifests itself as a change in the conductivity of a sensitive metal-oxide layer because of the chemical reaction of the analyte with active centers present on the surface of metal-oxide nanoparticles, causing a change in the potential barriers to electron transfer between nanoparticles [3, 4]. The conductivity of a metal-oxide composite, and consequently its sensory ability, depends on the nature of its constituent components, primarily on the path through which the current flows in the system. Therefore, studies of the conductivity in complex metal–oxide systems used as conductometric sensors are of considerable importance.

We have previously studied the conductivity and sensory characteristics of metal oxide composites consisting of *n*-type semiconductors, such as SnO_2–In_2O_3, ZnO–In_2O_3, and CeO_2–In_2O_3, in the detection of hydrogen and CO [5–8]. It has been established that the conductivity of mixed composite films is largely determined by their composition. For example, in the SnO_2–In_2O_3 system at an In_2O_3 content of up to 19 wt %, electric current passes through SnO_2 nanocrystals [9]. In this case, In_2O_3 additives have a significant effect on the conductivity of SnO_2 in the composite film: in the presence of In_2O_3 nanocrystals, the activation energy of electron transfer between SnO_2 nanocrystals decreases markedly. Changes in the conductivity of binary metal oxide composites are influenced by charge transfer between the components of the composite and their mutual charging and by the catalytic activity of oxides in oxygen dissociation.

The aim of the present work is to study the conductivity of binary systems consisting of *n*-type In_2O_3 semiconductor nanocrystals decorated with catalytically active Co_3O_4 and ZrO_2 nanoparticles. Mixed cobalt oxide Co_3O_4 is *p*-conductive. At temperatures of 200–500°C, ZrO_2 has practically no free electrons, and accordingly, this oxide is not *n*-conductive.

Crystals of *n*-type semiconductor metal-oxides exhibit a lower work function as compared to *p*-type crystals (hereinafter, *n*-, *p*-crystals). Therefore, for a *n*-crystal, the potential difference across the *p*–*n*-junction region leads to an increase in the potential energy of electrons in this region and, correspondingly, to a decrease in the binding energy of electrons in such a crystal. As a result, electrons are transferred from the *n*-crystal to the *p*-crystal, with a lower potential energy of electrons [10]. The inverse effect of increase in the energy of binding of electrons in *p*–*n*-junctions was

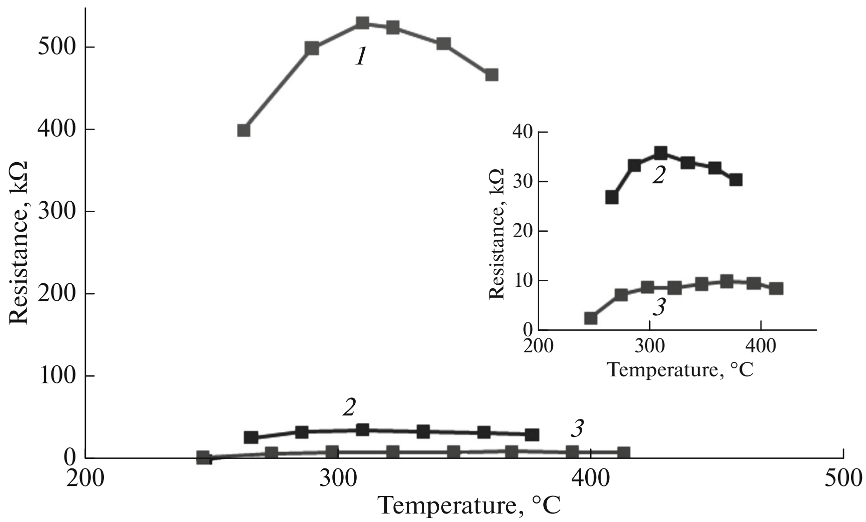

Fig. 1. Temperature dependence of the resistance of ZrO_2–In_2O_3 films in air at various ZrO_2 contents (wt %): (*1*) 20, (*2*) 10, and (*3*) 3.

observed in *p*-crystals [11, 12]. Such a change in the energy characteristics of the components of the composite should naturally influence its conductivity.

The conductivity of a nanocomposite consisting of a mixture of *n*- and *p*-type TiO_2 nanocrystals was investigated in [13]. It was shown that the redistribution of electrons and the mutual charging of contacting nanocrystals leads to a decrease in the barrier to electron transfer between contacting *p*- and *n*-nanocrystals, but to an increase in this barrier for contacts between *n*- and *p*-components. In the system under consideration, the current "bypasses" heterogeneous (*n*–*p* or *p*–*n*) junctions, characterized by a higher resistance than homogeneous ones, flowing along homogeneous pathways, through homogeneous aggregates of nanocrystals of the same type (*n*–*n* or *p*–*p*) [13].

EXPERIMENTAL

Commercial In_2O_3, Co_3O_4, and ZrO_2 nanocrystalline (30–50 nm) powders with a purity of above 99.9% were used. To prepare composite samples, a mixture of powders containing certain amounts of indium oxide and Co_3O_4 or ZrO_2, as well as a small amount of water, was carefully rubbed in an agate mortar to obtain a homogeneous slurry. The resulting aqueous pastes, containing up to 40% of solid powder, were applied onto polycor plates equipped with platinum contacts to measure the resistance of the deposited film and with a heater. After that, the plates with deposited slurry were first dried at 120°C and then annealed at 550°C until a constant resistance of the resulting metal oxide film was reached. The thickness of the films, determined from SEM microphotographs of cuts of the substrates with films was on average about 1 μm. The conductivity of the resulting composites was determined at temperatures of 250–500°C.

RESULTS AND DISCUSSION

The influence of the temperature and composition of the binary metal oxide film on the conductivity of nanostructured composites based on In_2O_3 containing various amounts of ZrO_2 or Co_3O_4 was studied.

Composites ZrO_2–In_2O_3. The resistance of ZrO_2–In_2O_3 composite films was studied at temperature from 250 to 420°C for systems containing up to 20 wt % ZrO_2, since at a higher content of the latter, the resistance becomes too high, exceeding the upper limit of reliable measurements. The temperature dependence of the resistance exhibits a maximum within 310–320°C (Fig. 1). Temperature influences the conductivity of the film due to various factors. For example, a temperature rise increases the rate of the thermally activated overcoming of intercrystalline barriers and, consequently, the conductivity of the film. In addition, the temperature affects the rate of adsorption and desorption of oxygen molecules on the surface of In_2O_3 nanoparticles, as well as their dissociation. Oxygen molecules and atoms capture electrons from the bulk of nanoparticles, which is accompanied by a decrease in the concentration of conduction electrons and, correspondingly, an increase in the resistance. The observed temperature dependence of the resistance of the film is due to a combination of these factors.

Since zirconium oxide has practically no electronic conductivity, the electric current in this composite flows through "infinite clusters," aggregates of In_2O_3 nanocrystals that permeate the entire volume of the sample [14]. In this case, the conductivity of the film depends on the concentration of conduction electrons and their mobility, which, as noted above, is determined by the barriers that prevent the transport of electrons between these nanocrystals.

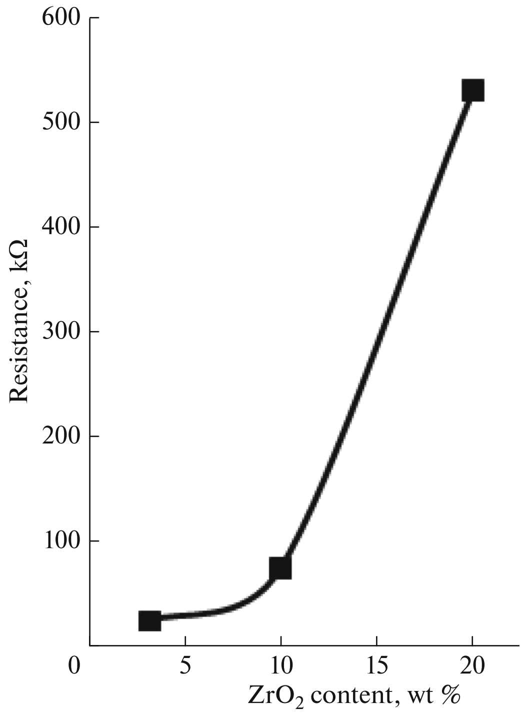

Fig. 2. Dependence of the resistance of nanostructured ZrO_2–In_2O_3 films at 320°C on the content of zirconium oxide in them.

An increase in the ZrO_2 content leads to a sharp decrease in the conductivity of the composite (Fig. 2). This effect arises because ZrO_2 additives catalyze the dissociation of O_2 [15]. Oxygen atoms formed on the surface of zirconium oxide particles, which are very efficient electron traps [16], are transferred to In_2O_3 nanocrystals because of spillover (overflow), where they trap conduction electrons, thereby decreasing their concentration in the conductive pathways of the composite and, consequently, reducing its conductivity.

Composites Co_3O_4–In_2O_3. With changing composition, the resistance of Co_3O_4–In_2O_3 composite films varies by several orders of magnitude (Figs. 3, 4). An increase in the content of cobalt oxide in the composite leads to a decrease in its conductivity, especially significantly within from 10 to 60 wt % Co_3O_4. This effect can be explained by the electronic interaction between In_2O_3 nanocrystals that make up conductivity paths for the electric current in the composite and inclusions of Co_3O_4 nanocrystals. Since the electron affinity of In_2O_3 (3.7 eV) is much lower than that of Co_3O_4 (4.7 eV), bringing in contact the composite components causes electrons to pass from In_2O_3 nanocrystals to Co_3O_4 and, consequently, decreases the concentration of conduction electrons in In_2O_3 nanocrystals. Since the content of In_2O_3 in the composite is more than 20 wt %, electric current flows through these nanocrystals, and the conductivity of *n*-type Co_3O_4–In_2O_3 composites decreases.

However, at a higher content of Co_3O_4 nanocrystals in the composite, its resistance decreases sharply, being ~100 kΩ at 260°C and only a few kΩ at 400°C at a cobalt oxide content of 80 wt %, i.e., approaches the resistance of pure nanocrystalline Co_3O_4. Our preliminary results on the sensory response to hydrogen show that, in accordance with the percolation model of the conduction of a nanocrystalline composite with a Co_3O_4 content of more than 60 wt %, *n*-type conduction through In_2O_3 nanocrystals changes to *p*-type hole conduction through nanocrystalline Co_3O_4 aggregates. In this case, exposure to a reducing gas does not lead to an increase in the conductivity of the composite, as it does in the case of *n*-type composites, but to its decrease.

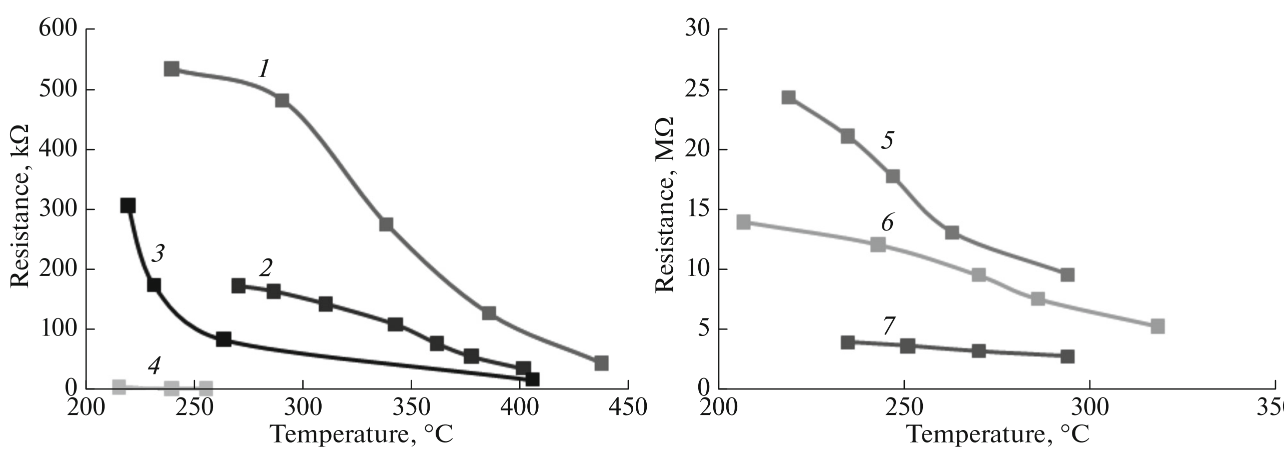

Fig. 3. Temperature dependence of the resistance of Co_3O_4–In_2O_3 films in air at various Co_3O_4 contents (wt %): (*1*) 10, (*2*) 3, (*3*) 80, (*4*) 100, (*5*) 60, (*6*) 40, and (*7*) 20.

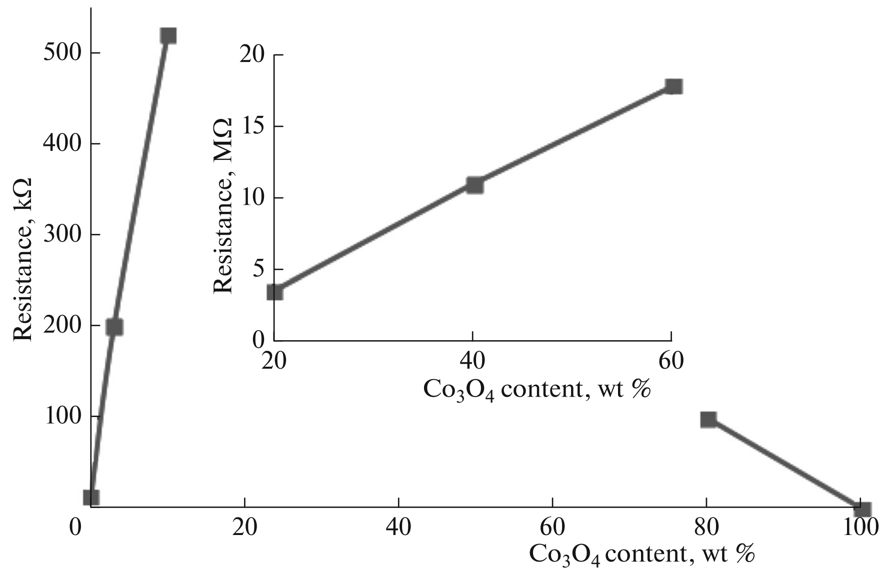

Fig. 4. Dependence of the resistance of Co_3O_4–In_2O_3 films in air on the Co_3O_4 content.

CONCLUSIONS

Thus, the results convincingly show that the addition to indium oxide of up to 20 wt % ZrO_2 leads to a decrease in the conductivity of the nanostructured composites formed. This change in conductivity takes place because of the dissociation of oxygen molecules on the surface of ZrO_2, which leads to the formation of oxygen atoms. As a result of the transport of oxygen atoms formed to indium oxide nanocrystals, over which electric current flows in the composite, the concentration of conduction electrons in In_2O_3 decreases, causing a decrease in the conductivity of the composite. The conductivity of the Co_3O_4–In_2O_3 composite decreases with increasing content of Co_3O_4 in it up to 60 wt %. This effect can be explained by the electronic interaction between In_2O_3 nanocrystals, which make up conductivity paths for electric current in the composite, and inclusions of Co_3O_4 nanocrystals. A further increase in the Co_3O_4 content in the composite leads to a sharp increase in the conductivity. In this system, at a Co_3O_4 content of up to 60 wt %, *n*-type conduction is realized, changing to *p*-type at above 80 wt % Co_3O_4.

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