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Abstract

Full Text

PHYSICAL CHEMISTRY

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CHANGE IN THE WORK FUNCTION OF OXIDE SEMICONDUCTORS UPON THE INTRODUCTION OF ADDITIVES

In studying the mechanism of the action of additives on the catalytic properties of semiconductors, principal attention has been devoted to comparing these properties with electrical conductivity. Despite the large amount of experimental material (1), the nature of the connection between the electronic and chemical properties of a semiconductor remains unclear. This is probably explained in part by the difficulty of passing from bulk characteristics of a semiconductor to surface characteristics, and by the possibility of considerable differences in phase and chemical composition between the surface and the bulk.

Fig. 1. Cell for measuring contact potential difference:
1 –reference electrode, 2 –metal plate with recesses for samples, 3 –iron core, 4 –electric furnace

For powders and porous bodies there are added to this the difficulties of carrying out comparable measurements of electrical conductivity. On the basis of these considerations, as well as the results of theoretical studies indicating the great significance of surface charging relative to the bulk for surface processes (2,3), we decided to investigate the effect of modifying additives on the work function of semiconductors. Most of the experiments were carried out with oxides of divalent metals (NiO, CuO, ZnO) containing lithium ions and other alkali metals. These ions exert a very strong influence both on the electrical conductivity and on the adsorption and catalytic activity of the corresponding oxides (4), but attempts to interpret the observed relationships between electrical conductivity and activity encounter insurmountable difficulties.

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Fig. 2. Change in the electron work function of CuO (1), NiO (2), and ZnO (3) upon introduction of Li_2O (20°)

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Fig. 3. Change in the work function of zinc oxide upon introduction of Na_2O (1) and Cs_2O (2) at 20°

Figure 3: Fig. 3. Change in the work function of zinc oxide upon introduction of Na_2O (1) and Cs_2O (2) at 20°

The electron work function (φ) was determined from the contact potential difference, measured by the vibrating-condenser method (^{5}). The oxide-semiconductor preparations being compared were placed in different recesses of a metal plate (Fig. 1). With the aid of an electromagnet they could be brought in turn under the vibrating gold electrode **1**. This method of measurement reduces to a minimum the effect of fluctuations in the work function of the reference electrode on the measured quantity, while at the same time ensuring identical conditioning and measurement conditions.

The results of different experiments with the same preparations were reproduced with an accuracy of 0.05 V; the error in measuring φ did not exceed 0.01 V. All

The specimens were subjected to identical conditioning in vacuum or in a CO atmosphere in order to clean the surface of adsorbed oxygen at a temperature of 300–400°, followed by evacuation to a pressure of $1 \cdot 10^{-6}$ mm Hg. The contact potential difference measurements were carried out at room temperature.

Solid solutions of Li_2O in NiO and CuO were prepared by joint decomposition of mixtures of carbonates in air by heating at 850–900°. X-ray diffraction patterns taken by M. Ya. Kushnereva show the formation of solid solutions for the systems $Li_2O + NiO$ and $Li_2O + CuO$. Zinc oxide specimens with a Li_2O additive were prepared by decomposing lithium oxalate on zinc oxide at 450, 800, and 1200°.

Figure 2 shows the change in the work function $\Delta\varphi$ for CuO, NiO, and ZnO observed upon introduction of lithium. Dissolution of lithium in the lattice causes a considerable decrease in the work function (up to 0.6–0.8 eV).

Fig. 2. Change in the electron work function of CuO (1), NiO (2), and ZnO (3) upon introduction of Li_2O (20°)

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It should be emphasized that the state of Li_2O in ZnO has not yet been established with the same certainty as for NiO, since the X-ray diffraction patterns do not reveal changes in the lattice parameter exceeding 0.0002 Å.

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With increasing Li_2O concentration, the work function at first falls sharply, then more slowly, and for an Li_2O concentration of 8% in ZnO reaches 0.7 eV. It is interesting to note that for ZnO specimens with a Li_2O impurity calcined at different temperatures, almost the same decrease in the work function is observed.

The formation of solid solutions of Li_2O and NiO is accompanied by a sharp increase in electrical conductivity (σ) and a decrease in the activation energy of conductivity (E_σ) (^{6}). For the hole semiconductor NiO this means that the Fermi level f in the bulk shifts toward the top of the valence band and, consequently, an increase in the work function $\Delta\varphi$ should be observed. The experimental data show that in this case $\Delta\varphi$ decreases.

For the electron semiconductor ZnO, the activation energy of conductivity increases from 0.2 to 1.6-2.0 eV upon introduction of lithium (^{7}), i.e., under the influence of the Li_2O impurity the Fermi level in the bulk of the crystal also shifts toward the top of the valence band. The work function for $Li_2O + ZnO$ should have increased. However, our data show that upon introducing Li_2O into the electron semiconductor (ZnO), as into the hole semiconductor NiO, the work function changes in the same direction (φ decreases).

Within the framework of the band model, this can be explained by the opposite influence of the additive located in the bulk and on the surface on the level f, namely: the lithium cation located on the surface of the semiconductor (NiO, CuO, ZnO) may be a donor, while in the bulk it is an electron acceptor.

The observed changes in $\Delta\varphi$ agree well with the nature of the effect of Li_2O on the adsorption and catalytic activity of NiO and ZnO.

Confirmation of the conclusion that the decisive role in $\Delta\varphi$ is played by an impurity localized on the surface is provided by the change in φ upon the introduction of sodium and cesium (Fig. 3). The preparations were made by decomposing oxalates and nitrates on ZnO at 400–700°. As is evident from Fig. 3, Na and Cs decrease the work function even more sharply, which is apparently associated with their predominantly surface localization on ZnO. (It is difficult to imagine the formation of a solid solution for the Na ion, and especially Cs, in ZnO, in view of the large difference in the ionic radii.)

From other additives we studied the oxides of iron and chromium in CuO, the oxides of magnesium and iron in NiO, and thorium dioxide in ZnO (Fig. 4). Only for MgO was it possible to prove the formation of solid solutions without the formation of other phases or mixtures. The data obtained for the MgO+NiO system show that the absence of a change in E_σ for solid solutions (8) still does not imply invariance of $\Delta\varphi$ for this system.

Comparison of the action of various additives introduced into the same semiconductor (ZnO) on the change in the work function shows that φ for 2% Na_2O + ZnO decreases by 0.8 eV, whereas for 2% $ThO_2 + ZnO$ it increases by 0.4 eV. Introduction of the SO_4^{2-} group onto the surface of ZnO increases the work function by 0.5 eV. Thus, the introduction of various additives into oxide semiconductors makes it possible to vary the electron work function over wide limits. Comparison of literature data on changes in the electrical conductivity of solid solutions with data on changes in the work function for these systems indicates a complex relationship between the bulk and surface electrical properties of modified semiconductors.

Fig. 4. Change in the work function of CuO, NiO, and ZnO upon the introduction of various additives:
1 –$ZnO + ThO_2$; 2 –$ZnO + ZnSO_4$; 3 –$CuO + Fe_2O_3$; 4 –$CuO + Cr_2O_3$; 5 –$NiO + Fe_2O_3$; 6 –$NiO + MgO$.

In conclusion, the authors express their gratitude to G. M. Zhabrova for providing zinc oxide preparations with additives and to M. Ya. Kushnerev for the X-ray and electron-diffraction analysis of the samples.

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