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ON THE RELATION BETWEEN THE ELECTRICAL CONDUCTIVITY AND THE WORK FUNCTION OF MODIFIED ZINC OXIDE

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A large body of experimental material has been published in the literature on the relationship between the electrical conductivity of semiconductors and their catalytic activity ($^{1-4}$). The most widespread method for sharply changing the electrical conductivity and its activation energy, widely used by many investigators, is the introduction into oxide semiconductors of impurities that form solid solutions with them. The catalytic properties of such solid solutions changed sharply with respect to donor–acceptor reactions (CO oxidation, decomposition of N_2O, H_2/D_2), which was unambiguously associated with a change in the magnitude of the electrical conductivity and its activation energy.

According to electronic concepts, a number of investigators ($^{5-7}$) relate the activity of semiconductor catalysts to the position of the Fermi level at the surface. It should be noted that in a number of cases the experimental results obtained are in contradiction with these concepts. These discrepancies are probably due to the fact that the electrical conductivity of polycrystalline semiconductors does not reflect changes in the concentration of the electron gas at the surface. The position of the Fermi level is most correctly characterized by the value of the electron work function. A comparison of the activation energies of electrical conductivity (E_σ) and changes in the electron work function (φ) upon the introduction of impurities into ZnO is the subject of the present work.

For this purpose an apparatus was constructed that made it possible to carry out simultaneous measurements of electrical conductivity and contact potential difference on the same semiconductor specimen and under the same conditions, which excluded the possibility of any side effects. The investigation was carried out on zinc oxide specimens with additives selected in such a way that some of them increased the work function, whereas others decreased it, as had been established in a previous work (^{8}). In preparing the modified zinc oxide specimens, various methods were used that ensured the introduction of additives onto the surface and, in some cases, also into the bulk of ZnO. Luminescent-grade zinc oxide was used as the starting material.

Additives of lithium and sodium oxides were introduced by impregnating zinc oxide with oxalate salts, followed by carrying out a topochemical decomposition process at comparatively low temperatures: 450—500°. Special experiments established that, at the given temperatures and holding times, complete decomposition of the salts does in fact take place. In preparing ZnO specimens with lithium additives, the formation of solid solutions could be expected even at a temperature of 450°; for ZnO with sodium additives, the formation of solid solutions was unlikely because of the large radius of the sodium ion. Thorium additives were introduced by treating zinc oxide with solutions of thorium nitrate, leading to precipitation of thorium hydroxide on the surface. (It is known that $Th(OH)_4$ precipitates at pH 3.5—4; the pH of zinc hydroxide forming on the surfac-

of zinc oxide in aqueous solution, is 8.4). Calcination at 450° led to decomposition of the thorium hydroxide formed into the dioxide. The introduction of a zinc sulfate impurity was carried out by sorption from a solution of this electrolyte. As was established earlier (9), the sorption of zinc sulfate on zinc oxide was irreversible in character and was accompanied by the formation of basic zinc sulfates with subsequent hydrolytic destruction. Samples with additions of zinc sulfate were also calcined at 450°.

Zinc oxide with the introduced additions was subjected to X-ray and electron-diffraction examination. The samples were pressed into tablets at a pressure of 200 kg/cm^2 and placed in a special cell connected to an apparatus for the simultaneous determination of electrical conductivity and contact potential difference. The electrical conductivity was measured by the Miller method (10) at a frequency of 300 Hz. The accuracy of the resistance measurement was 15–20%. The contact potential difference between the semiconductor under study and a gold reference electrode was measured by the vibrating-capacitor method (11). The accuracy of the contact-potential-difference measurements was 0.01 V. The samples were conditioned in vacuum (10^{-5} mm Hg) at a temperature of 300–400° or in an atmosphere of carbon monoxide until a constant resistance was established. On all samples the activation energy of electrical conductivity was measured during heating and cooling of the sample, as well as the contact potential difference. The reproducibility of the measurements of the activation energy of electrical conductivity was 10%.

Table 1 gives the results of measurements of the activation energies of electrical conductivity (in eV), the contact potential difference with respect to gold, and the change in the electron work function of modified ZnO with respect to pure zinc oxide.

Table 1

No.	Zinc oxide samples	E_σ (eV)	$\Delta\varphi$ (eV)	$\Delta\varphi_{\mathrm{ZnO}} - \Delta\varphi$ (eV)
1	ZnO	0.08	−0.7	0
2	ZnO + 8% Na_2O	0.32	+0.8	−1.5
3	ZnO + 8% Li_2O	0.5	−0.1	−0.6
4	ZnO + 8% Li_2O	0.25*	−0.03	−0.67
5	ZnO + 14.5% $ZnSO_4$	0.24	−1.3	+0.6
6	ZnO + 2% ThO_2	0.17	−0.9	+0.2

* Sample calcined at 1100°.

As follows from the data presented, the activation energy of electrical conductivity of pure zinc oxide is very small, which indicates thorough purification of the preparation from sorbed oxygen. The value of the activation energy of the electrical conductivity of zinc oxide is close to published data (12).

The introduction of additions of different chemical nature leads to a decrease in electrical conductivity and an increase in its activation energy. The resistance of the samples at 350° decreases in the sequence:

$$\underset{\text{sample No. 3}}{\mathrm{ZnO} + \mathrm{Li_2O}} > \mathrm{ZnO} + \mathrm{Na_2O} > \mathrm{ZnO} + \mathrm{ZnSO_4} > \mathrm{ZnO} + \mathrm{ThO_2} > \mathrm{ZnO}.$$

Thus, on the basis of measurements of electrical conductivity alone, one could conclude that all the additions to zinc oxide used by us are acceptor additions, shifting the Fermi level downward, toward the top of the valence band.

Measurements of the work function, however, led to a different result. As follows from the data presented, additions of lithium and sodium cause a decrease—

decrease in the work function in comparison with pure zinc oxide, whereas additions of zinc sulfate and thorium dioxide lead to an increase in the work function. Consequently, on the basis of the work-function data it may be concluded that additions of both lithium and sodium are donor additions, shifting the Fermi level toward the conduction band; moreover, the effect of the sodium addition is more pronounced than that of lithium. Zinc sulfate and thorium oxide in ZnO increased the work function and the activation energy of electrical conductivity.

An increase in the calcination temperature of a sample of ZnO + 8% Li_2O did not change the character of the influence of the lithium ion on E_σ and

Δ_φ. A certain decrease in the value of E_σ should probably be explained by recrystallization of zinc oxide at 1100°.

Depending on the preparation conditions and on the chemical properties of the solid and of the impurities, the latter may be distributed in the solid in different ways. Thus, impurities may form substitutional or interstitial solid solutions, or may be adsorbed on the surface. Depending on the location of the impurity in the solid, the electrical conductivity and the work function should change in different ways.

It should be noted that all investigators studying oxide containing additions of lithium oxide believed that the lithium ions introduced into the zinc oxide lattice displace zinc ions into interstices (which should lead to an increase in the lattice parameter). However, there is practically no direct X-ray structural evidence in the literature confirming the formation of solid solutions for the ZnO + Li_2O system. Thus, for example, in work (^{13}) it was shown that for zinc oxide samples containing 0.12 and 0.32% lithium, calcined at 1000—1200°, i.e., at a temperature above the onset of sintering (the Tamman temperature is 870°), the changes in the lattice parameters are entirely insignificant. According to (^{13}), the lattice constant for pure zinc oxide is 3.2432, and for zinc oxide with an addition of 0.12% Li_2O it is 3.2431.

X-ray structural measurements of the modified zinc oxide samples were carried out by N. A. Shishakov and co-workers and by M. Ya. Kushnerev, to whom the authors express their deep gratitude. According to the data obtained, the lattice constant of zinc oxide did not change upon the introduction of additions, which gave no direct indication of the formation of solid solutions.

Apparently, on the basis of all that has been said above, it should be concluded that when oxides of lithium and sodium are introduced into zinc oxide, their content at the surface and in the bulk is different.

An impurity located on the surface and in the near-surface layer at a depth greater than the screening length affects the electrical conductivity and the work function in different ways. On the basis of a number of experimental observations it may be considered that the change in work function is due to charging of the surface, and not to the intrinsic influence of the dipole moment of the alkali ion (Na^+ or Li^+) (^{5}). An impurity located sufficiently deep and exerting no influence on the work function is an electron acceptor and increases E_σ, whereas at the grain surface this same addition is an electron donor and decreases the electron work function (φ). Lithium probably dissolves in the near-surface layer of zinc oxide, forming an interstitial solid solution, since the concentration of lithium oxide at the surface is greater than in the bulk. Therefore, a different influence of the impurity on E_σ and Δ_φ is observed. Electron diffraction patterns taken from a ZnO + 8% Li_2O sample calcined at 450° do not reveal lines of lithium oxide.

Zinc sulfate is adsorbed only on the surface of ZnO. In this case the change in the Fermi level at the surface determines both the change in electrical conductivity and the work function, which is confirmed by experiment (see Table 1). The same applies to ZnO with an addition of ThO_2.

Thus, in many cases the change in electrical conductivity cannot be used to determine unambiguously the changes in the Fermi level at the surface of modified catalysts. Therefore, the search for quantitative cor-

relationships between catalytic activity and electrical conductivity without a detailed study of the distribution of the impurity on the surface and in the bulk of the semiconductor may lead to incorrect results for modified catalysts.

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REFERENCES

1. G. M. Schwab, J. Block, *Zs. phys. Chem. N. F.*, **1**, 42 (1954); *Zs. Elektrochem.*, **58**, 756 (1954).
2. G. Parravano, *J. Am. Chem. Soc.*, **75**, 1452 (1953).
3. N. P. Keier, S. Z. Roginskii, I. S. Sazonova, *DAN*, **105**, 859 (1956).
4. A. Belyanskii, I. Deren, I. Gaber, *Bull. Polish Academy of Sciences*, sect. 3, **3**, 221 (1955); **4**, 791 (1955).
5. K. Hauffe, *Advances in Catalysis*, **7**, 213 (1955).
6. S. Z. Roginskii, *DAN*, **126**, No. 4, 817 (1959).
7. F. F. Volkenshtein, *Uspekhi khimii*, **27**, 1304 (1958).
8. E. Kh. Enikeev, L. Ya. Margolis, S. Z. Roginskii, *DAN*, **130**, No. 4 (1959).
9. G. M. Zhabrova, E. V. Egorov, *Radiokhimiya*, No. 5, 538 (1959).
10. R. N. Miller, *Rev. Sci. Instr.*, No. 7, 298 (1952).
11. V. F. Bogolyubov, *Radiotekhnika i elektronika*, No. 3, 323 (1957).
12. D. J. Bevan, J. P. Shelton, J. S. Anderson, *J. Chem. Soc.*, **1948**, 1729.
13. A. Cimino, M. Marezio, A. Santoro, *Naturwiss.*, **44**, No. 11—12, 348 (1957).