MOST URGENT PROBLEMS OF SEMICONDUCTOR ELECTROCHEMISTRY

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The modern state and most important theoretical and experimental problems of semiconductor electrochemistry are discussed.

In the ten years of existence of semiconductor electrochemistry, the basic principles determining the electrochemical behavior of semiconductor materials and their principal differences from metals have been determined, at least in qualitative form [1-5]. At the same time, a number of important problems, in part specifically "semiconductor," in part common to the electrochemistry of metals and semiconductors, still await their solution. The task of this article is a systematic exposition of the most important, in the opinion of the authors, unsolved problems of semiconductor electrochemistry.

DISTRIBUTION OF POTENTIAL AT THE SEMICONDUCTOR-ELECTROLYTE INTERFACE

A study of the distribution of the drop of galvanic potential between the region of the space charge in a semiconductor and the ionic portion of the electrical double layer (in concentrated solutions—the Helmholtz layer) is one of the most important stages in the investigation of the properties of the surface of a semiconductor in contact with an electrolyte. The value of the surface bending of the zones, determined as a result of these experiments, is the basic parameter in the statistical theory of the properties of a semiconductor surface. Considerable experimental material has now been accumulated, devoted to this question; the basic results may be combined into two groups.

1. The first group includes investigations devoted to a determination of the value of the potential drop in the ionic double layer and to the establishment of the relationship of this value to the crystallographic orientation of the surface of the semiconductor and chemical composition of the surface compounds that arise. Just as in the case of metallic electrodes, in the adsorption of ions on the surface of the semiconductor or the formation of surface compounds, the potential drop in the Helmholtz layer is substantially changed at the same summary potential drop at the interface. For example, in the case of germanium, silicon, and gallium arsenide the potential drop in the Helmholtz layer is determined chiefly by the formation of surface oxides in the interaction of the semiconductor with the solution and by a change in their composition during polarization of the electrode [6, 7]. The same evidently occurs on oxide and sulfur semiconductors [8, 9]. The basic experimental problem here is the determination of the sign and magnitude of the charge of the surface of the semiconductor electrode itself. The charge of the electrode surface is of great importance for a consideration of the kinetics of electrochemical processes that take place at the semiconductor-electrolyte interface. Since the traditional methods of semiconductor electrochemistry—measurement of the surface conductivity, differential capacitance, etc.—permit a measurement not of the surface, but of the space charge, we should use here other means, for example, adsorption measurements, measurement of the hardness of the electrodes or contact angles of gas bubbles. Attempts have been made to determine the zero charge potential of germanium in aqueous solutions according to the method of contact angles [10], but they have not proved very successful. More definite conclusions on the magnitude of the surface charge of germanium have been drawn on the basis of a comparison of the dimensions of the hydrogen bubbles in the cathodic liberation of hydrogen from acid and alkaline solutions [11]. No direct measurement of the value of the surface charge and zero points of semiconductor single crystals has yet been made.

Another important problem is the establishment of the type of bond between the surface atoms of the semiconductor and the adsorbed substance. This bond may be covalent or may be of a dipole character: as a result of adsorption, a surface dipole is formed, in which charges of one sign are situated on the surfaces of the semiconductor atoms, while charges of the opposite sign are situated in a layer of specifically adsorbed atoms (or molecules). The adsorption of substances whose molecules possess an intrinsic dipole moment leads to a similar result. In another limiting case (for example, in the chemisorption of charged particles) a charge of one sign is concentrated in the adsorption layer, while the charge of the other sign is formed by electrostatically adsorbed ions of the solution, as well as free charges in the solid.* We should indicate that an investigation of the surface oxides on germanium has permitted the conclusion that here both types of potential drops—"dipole" and "ionic"—are comparable in magnitude and may vary independently with variation of the composition of the solution or polarization of the electrode [6].

2. The second group of studies is related to a verification of the theoretical representations of the structure of the region of the space charge in a semiconductor. Direct measurement of the value of the space charge as a function of the surface potential, performed by the method of "rapid" charging curves, as well as an investigation of the surface conductivity, differential capacitance, rate of surface recombination, and photo effect have shown that, for a number of semiconductor materials in contact with an electrolyte, the existing theory is in satisfactory agreement with the experiment within a definite interval of surface potentials.

In recent years, however, data have appeared, indicating the insufficiency of their theory. Thus, Dewald [8] has found that in the case of an extremely large space charge, the capacitance of a zinc oxide electrode proves appreciably lower than that calculated. The same result has also been obtained in a measurement of the charging curves of cadmium sulfide electrodes.

This discrepancy between the theory and experiment is observed in such fields when the change in the potential energy at a distance of the order of the wave length of the heat carriers is comparable with the average thermal energy of the particles; hence, quantum effects become substantial here. One of them is tunneling of mobile particles into classically forbidden regions of space; as a result, the concentration of the particles is increased in comparison with that calculated without consideration of the tunnel effect. This phenomenon is analogous to the constriction of the forbidden zone of a semiconductor in a strong electric field for processes of optical absorption, considered by Keldysh [13]; it should lead to an increase in the differential capacitance. On the other hand, in the case of sufficiently large bendings of the zones close to the surface, the usual representation of a quasicontinuous nature of the spectrum of energy levels in the zones may be violated. This effect should be manifested in an increase in the width of the forbidden zone on the surface and in a decrease in the concentration of mobile charges; as a result, the region of the space charge proves broader, while the differential capacitance is reduced.

In a consideration of fixed charges on the surface of a semiconductor and close to it (ionized atoms of impurities, surface states, adsorbed ions), the discrete nature of their arrangement in the double layer region may be substantial.† The case in which a significant portion of the charges is concentrated on the surface levels is extremely important; evidently within a definite range of values of the charge captured by the surface states, shielding by mobile current carriers of each center individually should be taken into consideration [15].

One of the peculiarities of the semiconductor-electrolyte system lies in the fact that under certain conditions the charge of the semiconductor cloud of the double layer may vary considerably as a result of the penetration of charged particles from the electrolyte into the electrode. As a result, the properties of the region of the space charge may differ from those calculated on the basis of the volume characteristics of the electrode. Thus, it is known that protons and cations with small radii readily diffuse into oxide layers [16]. Alloying of the surface layer of the semiconductor, with the formation of interstitial compounds, is also possible. We should note, however, that effects of this type have not yet been studied on single-crystal electrodes.

SURFACE ELECTRONIC STATES AND ADSORPTION AT THE SEMICONDUCTOR-ELECTROLYTE INTERFACE

The concept of "rapid" and "slow" surface states is frequently used in semiconductor electrochemistry to explain the decelerated relaxation of the electrical double layer on semiconductor electrodes. Two basic problems related to surface states may be distinguished.

*In the electrochemistry of metals, these two limiting cases evidently are realized on the platinum and mercury electrodes in the presence of iodide ions.

†The problem of consideration of the discrete nature of the charge in a double layer also falls under the electrochemistry of metals [14].

1. The experimental determination of the physicochemical nature of the surface states remains an unsolved problem. In particular, no unambiguous relationship has been found between the process of generation of a surface charge and the process of adsorption of extraneous substances on the semiconductor surface (for example, in the case of copper on a germanium surface). We should mention that the properties of the surface states in the case of a "dry" semiconductor surface and a surface in contact with an electrolyte sometimes differ greatly, which may be due to an essential difference in the structure of the double layer in these two cases. The "natural" charge at the germanium-electrolyte interface (formed as a result of the standard etching and exposure to the electrolyte solution), as a rule, cannot be satisfactorily described by a system of discrete surface levels. Evidently at the germanium-electrode interface, the levels corresponding to "rapid" surface states are split into zones [17]. In those few cases in which discrete surface levels have been detected [18], the microscopic structure of the interface still remains unclear.

As for "slow" states, it is usually assumed that the levels on the "dry" surface of the semiconductor are arranged within the phase oxide or on its outer boundary. However, on the surface, for example, of germanium in aqueous solutions, there is no phase oxide; only adsorbed oxygen is present. Here slow relaxation may be due not to "slow" surface electronic states, but to polar germanium-oxygen bonds or to polar solvent molecules adsorbed on the electrode, the effective dipole moment of which may be a monotonic function of the electrode polarization. In a consideration of the role of oxygen in the creation of the surface charge, it should also be considered that the adsorbed oxygen may exist on the surface of the semiconductor in several forms, which are capable of interconversion [6].

2. An important problem is the statistical description of the processes of variation of the surface charge with variation of the external conditions (for example, the surface potential). The number of electrons on the surface levels is usually written in the form $N_t \cdot f$, where N_t is the concentration of the levels; and f is the Fermi distribution function:

$$f = \left[1 + \exp\left(\frac{E_t - E_i + e\varphi_s}{kT}\right)\right]^{-1}. \quad (1)$$

Here E_t is the energy of the level; E_i is the energy of the middle of the forbidden zone; φ_s is the surface potential. Such a description is insufficient in the case of surface levels arising as a result of adsorption, when the variation of the concentration of adsorbed particles during polarization of the electrode should also be taken into consideration. As a first approximation, we can describe the value of the adsorption with the aid of the corresponding adsorption isotherm, as is done in a consideration of metallic electrodes; however, the question of the selection of the type of isotherm remains open. Finally, since the concentration of surface states at the semiconductor-electrolyte interface may be extremely great, the interaction of charges captured at the surface with one another should be taken into consideration. This circumstance may have a substantial effect upon the statistics of the filling of surface levels and on the dependence of the adsorption on the electrode potential.

KINETICS OF ELECTRODE PROCESSES ON SEMICONDUCTOR ELECTRODES

In a study of the kinetics of the process of charge transfer through an interface, the most important problem is the determination of the nature of the slow step of the process. Just as for metallic electrodes, in the case of reaction on a semiconductor surface, the slow step may be the step of discharging, adsorption, diffusion of the reaction components, formation and breakdown of the solid phase, or the chemical step. Naturally, successes in the study of the kinetic laws of electrochemical processes are closely related to the development of the theoretical concepts of the reaction mechanism. We should emphasize that at present a detailed microscopic theory exists only for the simplest cases; this pertains to the theory of concentration polarization [4] and the theory of electronic transitions at the electrode-electrolyte interface [19]. The theory of concentration polarization is well confirmed experimentally for semiconductor electrodes; the diffusion-limiting currents of the free carriers in the semiconductor have been detected and measured [1, 4]. The theory of electron exchange between the semiconductor and electrolyte has been confirmed only qualitatively; the electronic and hole components have been isolated from the total current of the reaction; it has been found that the magnitude of the electronic component in the total current increases with increasing surface concentration of free electrons [20]. The quantitative verification of the theory is the problem of experimental investigation in this field measurement of the electronic and hole components of the total current (in particular, the exchange current) as a function of the value of the surface potential, width

of the forbidden zone, and other properties of the electrode. Unfortunately, most of the data already available in the literature cannot be directly used for this purpose, since in these experiments the distribution of overvoltage between the ionic double layer and the region of the space charge in the semiconductor was not investigated. Important information on the kinetics of oxidation-reduction reactions on semiconductor electrodes may be given by an investigation of Faraday rectification [21].

Electrochemical reactions accompanied by the formation and cleavage of chemical bonds are more complex for a detailed microscopic analysis. In this field, a further accumulation of experimental data, of which there are as yet very few, is needed. Only the formation of hydrogen on germanium and the anodic solution of semiconductors have been relatively well studied. The nature of the "amplification of the current" in the anodic solution of germanium in particular, the dependence of the current amplification factor on the crystallographic orientation of the surface and other properties of the electrode, remains unclear. The process of electrodeposition of metals, the kinetics of the adsorption of substances from solution, and the introduction of hydrogen and alkali metals into semiconductor cathodes have practically not been investigated.

In contrast to the metals, the surface concentration of mobile current carriers in semiconductors is small and is a function of the electrode potential. At thermal equilibrium, the relationship between the surface and volume concentrations of mobile particles is expressed by a Boltzmann distribution (for a nondegenerate electron gas in sufficiently weak fields); however, the use of this distribution for the derivation of the equations of electrochemical kinetics will require supplementary substantiation. In the simplest case, the influence of the current flowing on the distribution of the particles may be taken into consideration by solving the transport equation (with corresponding boundary conditions [22])

$$I = eD(neE/kT + \partial n/\partial x), \tag{2}$$

where I is the current; E is the electric field; n is the concentration of particles; D is the diffusion coefficient. The approach in this form is equivalent, on the one hand, to the problem of a nonequilibrium diffusion double layer in an electrolyte [23], and, on the other hand, to the approach used in the diffusion theory of rectification at a metal-semiconductor contact [24].

A definite difficulty is due to the insufficient definition of the term "surface concentration" for particles possessing a finite wavelength. The concentration of electrons (or holes) close to the geometrical boundary of separation (in a layer with a thickness of several angstroms) is usually introduced into the equations of kinetics, while the wavelength of the thermal current carriers comprises hundreds of angstroms.

PHOTOELECTROCHEMICAL PROCESSES

Photoelectric sensitivity is a characteristic feature of semiconductor electrodes. In contrast to various types of photochemical processes in solution, which occur with the participation of free radicals or excited states of the ions, here the primary event in the photo effect is the optical generation of nonequilibrium current carriers. This leads to a redistribution of the potential drop close to the interface and to a change in the concentrations of electrons and holes near the surface, which take part in the electrode reaction. A study of the contribution of these two factors to the change in the rate of the electrochemical conversion is the basic problem in this field.

In general, the picture of the photo effect may be very complex; it is determined, on the one hand, by the nature of the slow step of the reaction, and on the other, by the properties of the region of the space charge in a semiconductor (chiefly by the bending of the zones, mobility of the current carriers, and intensity of recombination). A substantial simplification of the real picture may be achieved by suitable selection of the experimental conditions. Thus, for example, when pulsed illumination is used, the processes of variation of the ionic charge are eliminated, and the change in the bending of the zones during irradiation can be measured using the existing theory, developed for the semiconductor-gas interface.

A number of interesting bits of information along this line have already been obtained for many single-crystal semiconductors. The stationary photo effect has been experimentally studied to a considerably lesser degree [25].

Of great interest is the further investigation of the processes of photopassivation and photoactivation [26], photodesorption [27], as well as the study of the photocatalytic activity of electrons, when simultaneous occurrence of different electrochemical reactions with the participation of both types of current carriers becomes possible during irradiation. A study of the photoelectrochemical phenomena may promote the clarification of the mechanism of photosynthesis, since, as has recently been revealed, the chlorophyll granule possesses semiconductor properties [28]. Finally, investigations in this field are taking on special important in connection with the problem of direct transformation of radiant energy to electrical energy.

The material cited above pertains chiefly to single-crystal semiconductor materials, which until recently were intrinsically the objects of semiconductor electrochemistry. An important problem is the extension of the theoretical concepts and experimental methods of investigation to polycrystalline semiconductors, in particular, to oxide films on the so-called valve metals, to oxide and sulfide electrodes, as well as the use of the concepts of semiconductor electrochemistry for the investigation of phenomena of passivation of metals.

Summarizing, we may conclude that the electrochemistry of semiconductor materials has embarked upon a stage of its development in which it is faced to a considerable degree with the same problems that face the electrochemistry of metals. On the other hand, semiconductor electrochemistry is characterized by a number of specific problems and possesses new methods for their solution.

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LITERATURE CITED

1. V. A. Myamlin and Yu. V. Pleskov, Semiconductor Electrochemistry [in Russian], Izd. "Nauka", Moscow (1965).
2. E. A. Efimov and I. G. Erusalimchik, Electrochemistry of Germanium and Silicon [in Russian], Goskhimizdat, Moscow (1963).
3. H. Gerischer, Advances in Electrochemistry and Electrochemical Engineering, 1, Ed. by P. Delahay, Interscience Publishers (1961).
4. J. Dewald, Semiconductors [Russian translation], Editor N. B. Henney, Izd. Inostr. Lit., Moscow (1962).
5. The Surface Chemistry of Metals and Semiconductors, ed. by H. C. Gatos. New York–London (1960).
6. Yu. V. Pleskov, Elektrokhimiya, 1, 4 (1965).
7. T. P. Birintseva and Yu. V. Pleskov, Izv. AN SSSR, Ser. Khim., 251 (1965).
8. J. F. Dewald, Bell System Techn. J., 34, 615 (1960).
9. V. A. Tyagai, Izv. AN SSSR, Ser. Khim., 34 (1964).
10. M. Spamaay, Surface Sci., 1, 213 (1964).
11. R. M. Lazorenko-Manevich, Dissertation [in Russian], Moscow (1963).
12. V. A. Tyagai, Elektrokhimiya, 1, 377 (1965).
13. L. V. Keldysh, ZhETF, 34, 1138 (1958).
14. B. V. Érshler, Zh. Fiz. Khimii, 20, 679 (1946).
15. J. Bardeen, Surface Sci., 2, 381 (1964).
16. P. D. Lukovtsev, Transactions of the Fourth Conference on Electrochemistry [in Russian], Izd. AN SSSR, Moscow (1959).
17. M. D. Krotova and Yu. V. Pleskov, Phys. status solidi, 3, 2119 (1963).
18. P. J. Boddy and W. H. Brattain, J. Electrochem. Soc., 109, 812 (1962).
19. R. R. Dogonadze and Yu. A. Chizmadzhev, Dokl. AN SSSR, 150, 333 (1963).
20. Yu. V. Pleskov, Zh. Fiz. Khimii, 35, 2576 (1961).
21. Yu. Ya. Gurevich and V. A. Myamlin, Dokl. AN SSSR, 155 1159 (1964).
22. V. A. Tyagai, Elektrokhimiya, 1, 387 (1965).
23. V. G. Levich, Dokl. AN SSSR, 67, 309 (1949); 124, 869 (1959).
24. A. I. Ansel'm, Introduction to Semiconductor Theory [in Russian], Moscow-Leningrad (1962).
25. A. M. Kuznetsov and R. R. Dogonadze, Izv. AN SSSR, Ser. Khim., 1885 (1964).
26. S. O. Izidinov, T. I. Borisova, and V. I. Veselovskii, Dokl. AN SSSR, 145, 598 (1962).
27. R. M. Lazorenko-Manevich, Electrochim. Acta, 10, 141 (1965).
28. E. K. Putseiko, Dokl. AN SSSR, 150, 343 (1963).