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Yu. V. Pleskov and V. A. Tyagai

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Abstract

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Yu. V. Pleskov and V. A. Tyagai

On the Distribution of Potential at the Boundary Germanium–Electrolyte Solution

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The electric double layer at a semiconductor–solution boundary is, in the simplest case, formed by a diffuse charge in the semiconductor and by electrostatically adsorbed ions of the solution; the Galvani potential at the phase boundary is composed of potential jumps in the Helmholtz layer and in the space-charge region in the semiconductor. According to ([1,2]), in the case of a nondegenerate surface, in the absence of surface states* and dipole layers, the potential drop in the Helmholtz layer constitutes an insignificant part of the total potential jump at the semiconductor–solution boundary, both at equilibrium and upon polarization of the electrode. The distribution of potential at the surface of a semiconductor electrode can be judged from the dependence of the magnitude of the space charge on the electrode potential; for this purpose we used methods for measuring the rate of surface recombination and the photopotential (i.e., the instantaneous change in the electrode potential under pulsed illumination).

The rate of surface recombination s, which depends on the external electric field, assumes a maximum value when the concentrations of holes and electrons at the semiconductor surface are equal (provided that the capture cross sections of a hole and an electron by the recombination center are the same ([3])). In this case the surface potential φ_s, i.e., the difference divided by the electron charge q between the Fermi level E_F and the middle of the forbidden band at the surface, is equal to zero, irrespective of the electron concentration in the bulk.

The magnitude of the photoeffect is large when an inversion layer is formed at the surface and small in the case of an accumulation layer. The photoeffect disappears when the space charge in the semiconductor is equal to zero (in the absence of surface states ([4])). The electrode potential corresponding to this state of the surface has been called the flat-band potential, since in this case there is no bending of the energy bands of the semiconductor at its surface. Measurement of the surface photopotential is a convenient method for determining the flat-band potential ([5]). At the flat-band potential the energy of the middle of the forbidden band at the surface has the same value E_i as in the bulk of the semiconductor, and

$$\varphi_s = \frac{E_F - E_i}{q}.$$

Thus, by simultaneously measuring the rate of surface recombination and the photopotential as functions of the electrode potential φ, we can "tie" two characteristic values of φ_s for each specimen to definite values of φ. It is easy to see that in the case of a semiconductor with its own—

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* That is, specifically adsorbed particles on the surface that are in equilibrium with the free charges in the semiconductor.

with intrinsic conductivity ($E_F = E_i$), the surface potentials of the zero photoeffect and of the maximum surface-recombination rate are practically identical and approximately equal to zero.

According to (^{1,2}), the magnitude of the Galvani potential at the semiconductor-solution boundary depends on the concentration of free electrons in the bulk of the semiconductor in the same way as the Fermi level E_F (i.e., it changes by 59 mV when the electron concentration changes by a factor of 10). Since the potential jump in the Helmholtz layer does not depend on E_F, it is precisely the second component of the Galvani potential—the potential drop in the space-charge region V_s—that reflects the change in E_F when the electron concentration in the semiconductor changes. For flat bands $V_s = 0$. If it is assumed that the potential jump in the Helmholtz layer depends little on the polarization of the semiconductor electrode, i.e., that when the electrode potential changes it is mainly V_s that changes (which, apparently, occurs in the case of an undeveloped surface in the absence of surface states (^{1})), then the magnitude of the polarization required to make the bands flat is close to V_s. Consequently, when the electron concentration in the semiconductor changes, the flat-band potential changes in the same way as V_s, i.e., practically follows the Fermi level E_F. If, however, the concentration of surface states is large, then a considerable part of the applied voltage drops in the Helmholtz layer.

Fig. 1. Electrophysical properties of the samples

Curve Nos.	Conductivity type	Specific resistivity, ohm · cm	Diffusion length of minority carriers, mm
1	p	3	0.7
2	n	3	0.7
3	p	20	1.0
4	n	20	1.5
5	n	40	2.5

On the contrary, the surface potential

$$\varphi_s = \frac{E_F - E_i}{q} + V_s$$

practically does not depend on E_F* and is only a function of the electrode potential (1). Therefore one should expect that the potential of the maximum surface-recombination rate, which is uniquely determined by the surface potential, will not depend on E_F, i.e., on the specific resistivity of germanium.

The surface-recombination rate s at the germanium–solution boundary was measured by the method of photoconductivity decay in samples 15 × 5 mm in size and 0.2–0.5 mm thick. A small voltage (50 mV) was applied to the ends of the plate through two ohmic contacts in order to measure the conductivity. The sample was illuminated by the pulsed lamp of a PST-1 strobotachometer (flash frequency 20–40 $\sec^{-1}$, flash duration about 3 μsec). The signal, proportional to the photoconductivity, was amplified by means of a wide-band USH-2 amplifier and displayed on the screen of an IO-4 pulse oscilloscope; with the aid of a time-marker system the photoconductivity decay constant was determined, i.e., the effective lifetime of minority carriers τ_e. The photopotential $\Delta\varphi_\mathrm{sv}$ was measured with the same setup. In both cases the illumination was chosen to be so small that the polarization of the electrode under illumination changed by no more than 0.01 V.

* More precisely, its change when E_F changes is compensated by an oppositely signed change in V_s.

Before the measurements, the contacts were insulated with purified paraffin; the electrode was treated in CP-4A etchant and placed in a 1 N NaOH solution. After nitrogen had been passed through the solution for a long time, the curve of the dependence of τ_e on the potential was recorded. To determine $\Delta\varphi_\mathrm{sv}$, the germanium surface was subjected to brief anodic etching in the same solution in which the measurements were carried out, as a result of which the surface recombination rate decreased considerably. It should be noted that it is not possible to determine s and $\Delta\varphi_\mathrm{sv}$ with exactly identical surface treatment, since an accurate measurement of $\Delta\varphi_\mathrm{sv}$ is possible only in the absence of appreciable recombination.

Figure 1 shows the dependence of the effective lifetime of minority carriers τ_e on the potential for 5 germanium samples with different bulk electrophysical properties (curves 1–5), as well as the curve, calculated from experimental data for sample 4, of the surface recombination rate s as a function of the electrode potential φ (curve 6). The dependence of the instantaneous photopotential on the electrode potential in a 1 N NaOH solution is shown in Fig. 2. For each sample, at a certain value of the potential the quantity $\Delta\varphi_\mathrm{sv}$ passes through zero and changes sign. The value of the potential φ_n, at which the photopotential is equal to zero, depends on the concentration of free electrons in germanium, as can be seen from Fig. 3 (1—in a 1 N NaOH solution, 2—in a 1 N H_2SO_4 solution).

Fig. 2. Electrophysical properties of the samples

No. of curves	Type of conductivity	Resistivity, ohm · cm	No. of curves	Type of conductivity	Resistivity, ohm · cm
1	n	0.004	5	p	10
2	n	3	6	p	3
3	n	20	7	p	0.5
4	n	40			

The experimental data obtained by us confirm the applicability of the ideas set forth above to the germanium-electrolyte interface. The potential of the maximum surface recombination rate (i.e., the minimum of τ_e) practically does not depend on the resistivity of germanium (Fig. 1) and is equal to −0.63 V in a 1 N NaOH solution, while the potential of the zero photoeffect, i.e., the flat-band potential, changes regularly as a function of the concentration of free electrons in the semiconductor (Fig. 3). This gives grounds to suppose that, under the conditions of our experiments (weak anodic etching of germanium immediately before the measurements), the density of surface states is not very large.* Nevertheless, a noticeable part of the applied voltage (about 30%) falls in the Helmholtz layer, as indicated by the difference between the slope of the straight lines in Fig. 3 (0.080 V per one order of magnitude of the concentration of free electrons) and the theoretical value (0.059 V).

The values of the flat-band potential of germanium with intrinsic conductivity, determined by interpolation from Fig. 3 (−0.51 V in a 1 N NaOH solution, 0.13 V in a 1 N H_2SO_4 solution), agree well with the potentials of the minimum differential capacitance measured by Bohnenkamp and Engell (^{6}) (respectively, −0.5 and 0.3 V) and by Gerischer and Peres-Fernandes (^{7}) (−0.52 V and 0.2 V). The shift of the flat-band potential on going from an alkaline solution to an acidic one indicates that the equilibrium Helmholtz potential difference is appreciable and depends on the pH of the solution. At the flat-band potential the space charge in the semiconductor is equal to zero, but the electrode surface is apparently charged negatively as a result of oxidation, and the magnitude of the charge depends on the pH of the solution. The appearance of this charge entails electrostatic adsorption of cations from the solution. Thus, the structure of the double layer at the germanium-solution surface at the flat-band potential resembles the surface of mercury at the point of zero charge in the presence of specific adsorption of iodide ions (the absence of charge in the metal does not preclude the formation of ionic double layers) *.

Fig. 3

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* On the basis of the calculations of Garrett and Brattain (^{4}), it may be concluded that, at a considerable density of surface states, the potential of the zero photoeffect depends little on E_F.

Fig. 3

Figure 1: Fig. 3

Institute of Electrochemistry
Academy of Sciences of the USSR

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[*] In work ([8]) a minimum of the differential capacitance of a germanium electrode was found at −0.6 V (in 0.1 N HCl solution), which the authors associate with the zero point of germanium. However, before the measurements the electrodes were subjected to prolonged cathodic polarization, which apparently leads to depletion of free carriers at the surface. The question of the potential of zero charge of the ionic sheath of the double layer on germanium and of the zero point of a depleted semiconductor will be the subject of further study.

Note: Figure translations are in progress. See original paper for figures.