R. M. LAZORENKO-MANEVICH

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R. M. LAZORENKO-MANEVICH

INVESTIGATION OF THE DISTRIBUTION OF OVERVOLTAGE AT THE GERMANIUM–ELECTROLYTE INTERFACE

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Knowledge of the distribution of overvoltage at the interface of a semiconductor electrode with a solution is of considerable interest. Theoretically this question has already been studied (^{1}); however, up to the present time only one work is known (^{2}) in which a quantitative experimental investigation was carried out of the potential distribution at the silicon—electrolyte interface. In a number of works ($^{3-5}$), on the basis of indirect considerations, qualitative estimates have been made of individual components of the potential.* The specificity of contact with a conducting solution makes it difficult to apply a method based on determination of changes in surface conductivity (^{2}) at large currents flowing through the interface. As noted in the literature (^{1,3}), for the interface of a semiconductor with an electrolyte it may prove useful to measure the capacitance of the electrode at relatively high frequencies, when the measured capacitance should coincide with sufficient accuracy with the capacitance of the space-charge layer C_{oz} in the semiconductor.

However, in the case where there is a sufficient number of "fast" surface states at the surface, they may determine a substantial part of the measured capacitance up to the highest frequencies. Judging from the literature (^{6}), for germanium, for example, the density of "fast"states at the interface with a gas is 10^{11}—10^{12} cm^{-2}, and their time constants are of the order of 10^{-8} sec. Since the average density of space charge in Ge is $\sim 10^{11}$ cm^{-2}, it is clear that there can be no complete confidence in the correctness of interpreting the measured capacitance as C_{oz}.

Below a method is described by means of which the indicated difficulties can be avoided. In accordance with (^{1}) and the considerations set forth above, the electrode capacitance measured at a certain potential is the sum $C_{\text{oz}} + C'_{\text{ps}}$, where C'_{ps} is the capacitance of those surface states which are probed at the given frequency. If the potential φ of the electrode is shifted so that the concentration of majority carriers at the surface decreases, and the electrode is then illuminated, it is possible, by changing the light intensity, to reach a state in which the potential in the space-charge layer φ_{oz} is equal to the initial one. Under certain conditions the capacitance of the electrode will then also be equal to the initial one. Indeed, from the known formula for C_{oz} of a nondegenerate

Figure 1

Figure 1: Figure 1

semiconductor with fully ionized bulk impurities (1,7), it follows that, at not too large φ_{oz}, the capacitance in the case of a sufficiently doped semiconductor is determined only by φ_{oz} and depends almost not at all on the concentration of nonequilibrium carriers. C_{oz} passes through a minimum, on one side of which it is determined by the charge of the majority carriers and bulk impurity levels, and on the other by the charge of minority carriers. Since under illumination C_{oz} always increases, it is clear that the method under discussion can be used only in that region of φ_{oz} where, with increasing band bending, C_{oz} decreases, i.e., where C_{oz} is determined by the majority carriers. For low-resistance samples this region may be sufficiently large; for intrinsic and near-intrinsic samples it is practically absent.

* After this article was written, work (12) appeared, the results of which, obtained by another method, completely agree with ours.

On the basis of the consideration carried out in (8), it may be concluded that, in the range of applicability of the method under discussion, C_{pc} is practically independent of the excitation level (at low levels) and is determined only by φ_{oz}. Thus, in the indicated region the total capacitance of the electrode also does not depend on the excitation level, determined by the position of the quasi-Fermi levels, which makes it possible to use it as an indicator in determining $\Delta\varphi_{\text{oz}}$.

Fig. 1. Distribution of overvoltage, capacitance, and resistance at frequencies of 5 kHz $(2a, 4, 6)$ and 20 kHz $(2, 3, 5)$ during anodic dissolution of n-Ge ($\rho = 1.1\ \Omega \cdot \text{cm}$) in $1\,N$ KOH (A) and $1\,N$ H_2SO_4 (B). 1–φ; $2, 2a$–$(\varphi - \Delta\varphi_{\text{oz}})$; $3, 4$–C; $5, 6$–R; the horizontal dashed line in A marks the stationary self-dissolution potential φ_{st}; in B, $\varphi_{\text{st}} = 0$.

By the method described, $\Delta\varphi_{\text{oz}}$ was determined for anodic dissolution of n-Ge and cathodic hydrogen evolution on p-Ge. Impedance measurements were carried out with an ordinary ac bridge at frequencies from 0.4 to 20 kHz in a parallel circuit. In work at high frequencies, possible errors due to the presence of parasitic inductances in the circuit were not taken into account, since in the method used knowledge of the absolute impedance values is not required. For the same reason, it was considered possible to use, as an additional electrode for applying the ac voltage, a platinized Pt grid placed parallel to the electrode under study. Illumination was carried out through the grid; all experiments were performed in a polyethylene cell; the reference electrode was a hydrogen electrode in the solution under study. The measurements were carried out as follows: at each value of the current the bridge was balanced; then the current was changed by a small amount, and the bridge was balanced by illuminating the electrode.

Anodic dissolution of germanium has been studied rather thoroughly (4, 9) and

Fig. 2. Equivalent circuit of an n-Ge anode. R_{ss}—resistance to charging of surface states; R_{ohm}—ohmic resistance of the volumes of the solution and the electrode; C_{g}—capacitance of the Helmholtz part of the double layer; the remaining designations are in the text.

Figure 2: Fig. 2. Equivalent circuit of an n-Ge anode. R_{ss}—resistance to charging of surface states; R_{ohm}—ohmic resistance of the volumes of the solution and the electrode; C_{g}—capacitance of the Helmholtz part of the double layer; the remaining designations are in the text.

proceeds without special complications; therefore the described procedure was first used as applied to this process. The polarization curves presented in Fig. 1, as well as the dependences of the capacitance C and resistance R on potential, in general agree with those described in the literature. We shall discuss them here only in connection with the following circumstance. As shown in Fig. 1, the curves $(\varphi - \Delta\varphi_{\text{oz}}) - \lg i$, obtained by the described method, are practically independent, over almost the entire investigated range of potentials, of the frequency at which C and R are measured (this independence is retained also at lower frequencies—down to 0.4 kHz). However, at potentials more positive than 250–300 mV there is uncertainty in the values of $\Delta\varphi_{\text{oz}}$, arising from incomplete compensation of the bridge during illumination of the electrode. To determine which of the obtained curves is correct, it is necessary to examine in more detail the course of the C and R curves.

The initial increase of R at $\varphi <$ 250–300 mV apparently reflects an increase in the resistance of the space-charge layer R_{sc} when it is depleted of electrons. In any case, the measured R (as well as the measured C) in this region depends only on φ_{sc}, as is indicated by the very possibility of exact compensation of the bridge, unbalanced when the bridge current is increased, by illuminating the electrode. It can be shown (this has been done elsewhere) that with such compensation by illumination the potential changes practically only in the space-charge layer. Beginning approximately from the middle of the descending portion, R ceases to depend on illumination. This is expressed in the fact that, at a constant value of the current, the bridge can be compensated at any illumination intensity only by changing the capacitance in the compensating arm of the bridge, at constant resistance. Thus, the R measured in this region is determined mainly by the reaction resistance R_{r}, which cannot change under illumination if the current is constant. This conclusion is also supported by the noticeable decrease in this region of the dispersion of resistance with frequency. The increase of R with further increase of φ is associated with the transition to the region of diffusion current of holes.

Fig. 2. Equivalent circuit of an n-Ge anode. R_{ss}—resistance to charging of surface states; R_{ohm}—ohmic resistance of the volumes of the solution and the electrode; C_{g}—capacitance of the Helmholtz part of the double layer; the remaining designations are in the text.

The observed behavior of C and R can be described by the equivalent circuit shown in Fig. 2. This circuit is, in essence, the usual circuit describing the behavior of an ionic double layer, in which the structure of the double-layer capacitance is shown in detail for the case of a semiconductor electrode. The circuit is applicable only in the region of true kinetics. As follows from Fig. 3, with increasing φ there should come a point when the conductance of the $R_\mathrm{r}C_\mathrm{r}$ circuit becomes equal to the conductance of the $C_\mathrm{g}C_\mathrm{sc}R_\mathrm{sc}$ circuit, and then exceeds it. This point corresponds to the maximum and subsequent decline on the R–φ curve. If the reaction capacitance C_r is sufficiently large, then the resistance of the $R_\mathrm{r}C_\mathrm{r}$ section is determined mainly by R_r, which decreases more slowly with increasing frequency than the resistance of the $C_\mathrm{g}C_\mathrm{sc}R_\mathrm{sc}$ section. Thus, as the frequency increases, the maximum of the R–φ curve should shift toward larger φ, which is indeed observed. Since in the immediate vicinity of the maximum R is determined both by the space-charge resistance and by the reaction resistance, illumination cannot bring about bridge compensation. Subsequently such a possibility reappears, since R, as indicated, ceases to depend on illumination. Consequently, of all possible curves $(\varphi - \Delta\varphi_\mathrm{sc})$–$\lg i$, the most correct is the curve obtained at the highest frequency. To eliminate the uncertainty, one can also in this region construct the curve $(\varphi - \Delta\varphi_\mathrm{sc})$–$\lg i$, combining values of $\Delta\varphi_\mathrm{sc}$ obtained at different frequencies.

In the very first attempts to apply the described method to the cathodic process on p-Ge, we encountered a strong influence of preliminary cathodic polarization on the distribution of η. For electrodes subjected to preliminary cathodic polarization with a current of 10 mA/cm^2 for several hours (electrodes A), the values of C, after the current was switched off and a stationary state was reached, were, as shown in Fig. 3, much higher, and R much lower, than for the initial oxidized electrodes (electrodes B). It turned out that on electrodes B, right up to the onset of diffusion difficulties for electrons (^{10}), φ_sc practically does not change, whereas on electrodes A $\Delta\varphi_\mathrm{sc}$ constitutes a noticeable part of the total η. When polarization-

In the curves obtained, a strong nonstationarity of the process is observed, especially for electrodes A. This nonstationarity, in addition to the change in η, is expressed in a relatively slow increase of C and decrease of R after an initial decrease of C and increase of R, associated with the transition from one current value to another. With sufficiently long holding at a constant current density, C may even exceed the initial value (before the change in current), while R, correspondingly, may become smaller than the initial value. These slow changes of C and R may occur over tens of minutes after a constant value of η has been established. To stabilize the state of the surface, polarization by a current of alternating polarity was used: at certain time intervals (1-10 sec), during which bridge compensation was carried out, a short-time (0.08-0.4 sec) anodic pulse was applied, bringing the potential to the initial value (at $i = 0$). The polarization curves obtained in this way are shown in Fig. 3. These curves, of course, are not characteristics of the cathodic process; however, they make it possible to answer the question of the distribution of η on p-Ge. It is not yet easy to

Fig. 3.

Figure 3: Fig. 3.

explain the results obtained completely; nevertheless, it appears probable that the decisive role in the distribution of η in the cathodic process on p-Ge, as well as in the temporal changes of C and R, is played not so much by the change in charge in the surface states caused by the presence of an oxide layer, but by the adsorption of hydrogen, which creates acceptor levels on Ge, i.e., charges the surface negatively (^{10,11}).

Fig. 3. Distribution of the overvoltage, capacitance, and resistance at a frequency of 20 kHz during hydrogen evolution on p-Ge ($\rho = 0.54\ \Omega \cdot \mathrm{cm}$) in $1N$ KOH. $1, 1a$–φ; $2, 2a$–$(\varphi - \Delta\varphi_{03})$; $3, 3a$–C; $4, 4a$–R; 1—4–after 9 h of cathodic polarization with a current of 10 mA/cm^2 + 4.5 h without current; $1a$—$4a$–without preliminary polarization. $\varphi_{\mathrm{st}} = +132$ mV.

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Physicochemical Institute
named after L. Ya. Karpov

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