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Figure 1

Figure 1: Figure 1

Abstract

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THE STATE OF THE SURFACE OF A GERMANIUM ELECTRODE DURING ANODIC DISSOLUTION

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In recent years, a number of authors (1-4) have shown, theoretically and experimentally, the connection between the mechanism and kinetics of a dissolving germanium anode and its semiconductor characteristics. However, the properties of the surface of a germanium electrode and, in particular, the change in the character of the surface conductivity with polarization and its connection with the kinetics of the process have still been insufficiently studied. In the present work, in order to elucidate this connection, the method of measuring the impedance of the phase boundary semiconductor—electrolyte was applied in combination with irradiation of the surface.

Fig. 1. *a* —state of the germanium surface during anodic polarization in the dark in 1 *N* NaOH:
1 —polarization curve of *n*-Ge (5 ohm·cm), 2 —change in the resistance of *n*-Ge (400 cps), 3 —change in the capacitance of *n*-Ge, 4 —capacitance of *p*-type (5 ohm·cm, 400 cps), 5 —resistance of *p*-type. 6 —change in R and C (5 ohm·cm) under continuous irradiation.
3′, 4′ —capacitance in the dark and in the light, 2′ —dark resistance, 5′ —under illumination, 6′ —change in $\Delta\varphi_{\text{sv}}$.

The state of the surface was studied over a wide range of polarizations and alternating-current frequencies (100 cps—200 kcps) for specimens of nearly intrinsic germanium ($\rho = 42$ ohm·cm), electron and hole types of various specific resistance, in solutions of sulfuric acid and alkali in a nitrogen atmosphere. Measurements were carried out on a specially constructed inductionless alternating-current bridge. Thick clamped specimens with an ohmic contact of large area were used. Before the experiment, the electrode surfaces were etched in a peroxide etchant or CP-4 and subjected to anodic treatment at a current density of 10^{-4}—10^{-3} A/cm^2. Pulsed irradiation was achieved by means of a diaphragm

Fig. 2. Polarization curves of different types of Ge in 1 N NaOH. 1 –hole, 5 ohm • cm; 2 –intrinsic, 42 ohm • cm; 3 –electronic, 5 ohm • cm; 4 –electronic, 0.1 ohm • cm

Figure 2: Fig. 2. Polarization curves of different types of Ge in 1 N NaOH. 1 –hole, 5 ohm • cm; 2 –intrinsic, 42 ohm • cm; 3 –electronic, 5 ohm • cm; 4 –electronic, 0.1 ohm • cm

interrupter. A hydrogen electrode in the same solution served as the reference electrode.

Figure 1 presents the general picture of the change in resistance and capacitance of *n*- and *p*-type material during anodic dissolution in the dark and under irradiation. In accordance with the course of the polarization curves, three regions of the state of the electrode surface are clearly distinguished: the kinetic, or Tafel, region, at the beginning of which the capacitance of the *p*- and *n*-types passes through a minimum (point *a*); the diffusion region of hole saturation currents for the *n*-type, where a strong increase in resistance (curve 2) and a decrease in capacitance (curve 3) are observed, corresponding to the formation of a depleted layer near the surface; and, finally, the breakdown region (*d*), when, owing to avalanche formation of pairs, a sharp drop in the resistance of the system and an increase in current occur. The ascending branch of the capacitance curve in the Tafel region is associated with consumption of current in the process of anodic dissolution. The resistance of the system in this case (curve 5) decreases. On the *n*-type, at potentials above 0.4 V, a decrease in capacitance begins, caused by diffusion limitations with respect to holes. As follows from Fig. 1b, under continuous irradiation the resistance and capacitance of electronic germanium approach the values for the *p*-type in the dark. It is characteristic that, upon irradiation of the *n*-type, a slowing of the growth of $\Delta\varphi_{\text{sv}}$ in the Tafel region (curve 6) is observed, apparently associated with an increase in the rate of surface recombination in the region of active etching. The subsequent rapid growth of $\Delta\varphi_{\text{sv}}$ in the diffusion region shows that practically the entire large (several volts) overvoltage measured is associated with a potential drop in the depleted layer.

Fig. 2. Polarization curves of different types of Ge in 1 *N* NaOH. 1 –hole, 5 Ω · cm; 2 –intrinsic, 42 Ω · cm; 3 –electronic, 5 Ω · cm; 4 –electronic, 0.1 Ω · cm.

Figures 2 and 3 give a comparison of the surface properties of intrinsic, electronic, and hole germanium anodes in 1 *N* NaOH during anodic dissolution. A relatively high frequency, 60 kHz, and a parallel equivalent electrical circuit were chosen in order, with sufficient accuracy, to relate all changes in resistance and capacitance to the space-charge region. The polarization curves and the character of the change in the photoeffect under pulsed irradiation of the electrodes are also given here.* As numerous experiments have shown, for all types of germanium in acid and alkali, with the exception of low-resistance *n*-Ge, for which diffusion limitations set in early, it is more correct to speak of a smooth change in slope

Fig. 3

Figure 3: Fig. 3

from 130 mV on the first branch to 70-80 mV at the end of the curve (Fig. 2). At least on the *p*-type curves, three sections are clearly distinguished (curve 1) with slopes of 130, 100, and 70-80 mV, respectively. The transition to the branch with the smallest slope lies in the region of potentials of 0.3 V. As will be seen below, this decrease in slope is associated with a change in the state of the surface during anodic polarization.

From Fig. 3A it follows that the capacitance of intrinsic germanium (curve 1) passes through a minimum, and the resistance through a maximum, which lies in the region of the potentials of zero photoeffect, ~ 0.3 V (curve 6, Fig. 3B). As has already been discussed in the literature ([5,6]), this point corresponds to straightened bands in the semiconductor, i.e., to the absence of a space-charge charge. The sign of the photoeffect under pulsed irradiation of intrinsic germanium at the stationary potential ($\varphi_{\text{stat}} \simeq +0.12$ V) shows that the energy bands are bent downward and, consequently, the surface is enriched with electrons as compared with the bulk. Above 0.3 V (the ascending branch of the capacitance curve) the photoeffect changes sign—the positive space charge produced by holes increases. Anodic polarization first leads to depletion of the surface in electrons, and to its gradual enrichment with holes, so that at $\varphi \sim 0.3$ V the resistance of the system is maximal.

Fig. 3. **A**—change in the resistance and capacitance of different types of Ge in 1 N NaOH at a frequency of 60 kHz: 1—intrinsic Ge, $\rho = 42$ ohm · cm; 2—*n*-type, $\rho = 5$ ohm · cm; 3—*p*-type, $\rho = 5$ ohm · cm; 4—resistance of intrinsic Ge; 8—theoretical course of the capacitance for intrinsic Ge. **B**—change in the pulsed photoeffect: 5—*p*-type; 6—intrinsic; 7—*n*-type.

Comparison of the course of the capacitance and resistance with the change in the photoeffect for electron and hole germanium shows, in agreement with the theory of space diffuse charge ([5,7]), that on the *n*-type during anodic dissolution the positive charge increases continuously—the capacitance falls, and the minimum corresponding to the potential at which the diffuse layer has the greatest thickness is shifted to the right; on the *p*-type the capacitance increases, indicating a decrease in space charge, and the capacitance minimum is shifted to the left. On hole germanium at the stationary potential the surface is of *n*-type, while the potential of zero photoeffect, corresponding to the same position of the Fermi level in the bulk and at the surface, lies at an anodic polarization of about +0.36 V (curve 5). Under these same conditions, on the *n*-type in equilibrium with the electrolyte the surface is depleted of electrons, and the flattening potential—

* The pulse duration was 5-6 $\cdot 10^{-5}$ sec.

depleted zones lies near +0.1 V (curve 7)—a small cathodic polarization. The variation of resistance and capacitance with potential thus reflects, in general, changes in the space charge under anodic polarization. However, there are very significant deviations from the theoretical course of the C–φ curves (the theoretical curve for intrinsic germanium is shown in Fig. 3 by a dotted line). These deviations must be caused, first, by the reaction proceeding at the phase boundary and, second, by the presence at the surface of levels produced by ion adsorption and dipole formation, through which the anodic-dissolution reaction proceeds. The presence, for example, of donor levels is indicated by the different sign of the photoeffect on intrinsic germanium at the stationary potential, obtained under pulsed and continuous illumination. The frequency dependence of C and R also indicates the existence of surface states and the degree of their participation in the anodic reaction.

The strong dispersion of R and C up to 0.3 V, as well as the shift of the maximum of R toward less positive potentials when the frequency is lowered, show that in this region surface states with different time constants are, in essence, being probed. Comparing the potential of the rectified zones for n- and p-types with the magnitude of the shift of the potential from equilibrium, and knowing the position of the Fermi levels for the samples in the bulk, one can estimate the fraction of the potential jump associated with the drop in the space-charge layer in the total measured overvoltage ([6,8]). Under our conditions such an estimate shows that about 80% of the measured overvoltage falls in the space charge; this overvoltage is expended on changing the concentration of electrons and holes, which are components of the anodic reaction.

Thus, the set of data presented shows that with increasing anodic polarization the germanium surface becomes depleted in electrons and enriched in holes (for the p-type, for example, the hole concentration at the surface becomes equal to the bulk concentration only at $\varphi \sim +0.36$ V). The change in the slope of the polarization curves indicates a different degree of participation of free carriers of the conduction band and the valence band in the anodic-dissolution reaction. This reaction proceeds through the stage of formation of surface dipole groups $= \mathrm{Ge(OH)O^-}$ ([2]), which are, in essence, acceptors of holes. The released electron may be transferred either to the conduction band or to the valence band. The probability of such a transition will depend on the position of this complex relative to the energy bands and on the concentration of holes at the surface. It may be assumed that this level is donor-like and lies above the middle of the forbidden band. The large slope (130 mV) in the first segment of the polarization curve is connected with the fact that, at small polarizations, the reaction proceeds mainly through the conduction band. The downward shift of the Fermi level and the increase in the hole concentration at the surface with increasing anodic voltage facilitate the transition of electrons from the reacting complex and increase the fraction of the current carried through the valence band. The decrease in the slope of the polarization curve above 0.3 V to 70–80 mV is thus caused by a decrease in the activation energy of the process when holes of the valence band participate predominantly in the reaction.

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