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

A. A. Yakovleva, T. I. Borisova, and V. I. Veselovskii

L. Ya. Karpov Physical Chemistry Institute

(Presented by Academician A. N. Frumkin, April 4, 1962)
Translated from Doklady Akademii Nauk SSSR, Vol. 145, No. 2,
pp. 373-376, July, 1962
Original article submitted March 30, 1962

In recent years a number of authors [1-4] have theoretically and experimentally demonstrated the connection between the dissolution mechanism and kinetics for a germanium anode and its semiconducting characteristics. However, the nature of the germanium anode surface and, in particular, the change in the character of the surface conductivity with polarization and its relationship with the process kinetics have been insufficiently studied as yet. In order to elucidate this relationship, the method of measuring the impedance at the semiconductor-electrolyte interface in conjunction with surface illumination was used in the current work.

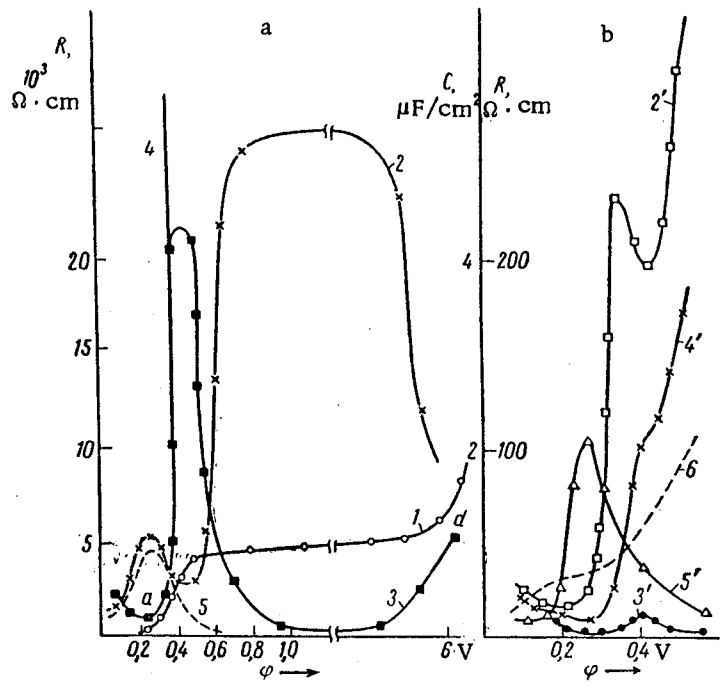

Fig. 1. a) State of the germanium surface in the case of anodic polarization in darkness in 1 N NaOH. 1) Polarization curve for n-Ge (5 Ω · cm); 2) change in resistance of n-Ge (400 Hz); 3) change in capacity of n-Ge; 4) capacity of p-Ge (5 Ω · cm, 400 Hz); 5) resistance of p-Ge. b) Change in R and C (5 Ω · cm) under continuous illumination. 3'), 4') capacity in darkness and in light; 2'), 5') resistance in darkness and in light; 6') change in $\Delta\varphi_{il}$.

The surface state was studied in a wide polarization and alternating current frequency (100 Hz-200 kHz) range for specimens of near-intrinsic germanium (ρ=42 Ω · cm), and of n- and p-types of germanium, having different specific resistances, in sulfuric acid and alkali solutions under nitrogen. The measurements were carried out in a specially designed noninductive alternating current bridge. Thick clamped samples with ohmic contacts of large

area were used. Before carrying out the experiments, the electrode surfaces were treated in a peroxide etchant or SR-4 and subjected to anodic conditioning at current density 10^{-4}-10^{-3} A/sq cm. Impulse illumination was obtained with the aid of a diaphragm breaker. A hydrogen electrode in the same solution served as a comparison electrode.

A general picture of the change in resistance and capacity of n- and p-Ge in darkness and under illumination is shown in Fig. 1. In accordance with the form of the polarization curves three electrode surface state regions are clearly distinguished: the kinetic or Tafel region, at the beginning of which the capacities of the n- and p-Ge pass through a minimum (point a), the diffusion region of saturation currents caused by holes for n-Ge, where a sharp rise in resistance (curve 2) and drop in capacity (curve 3) is observed, corresponding to the formation of an exhaustion layer close to the surface, and, finally, the rupture region (d), when the resistance falls sharply and the current rises as a consequence of avalanche formation of pairs. The ascending side of the capacity curve in the Tafel region is associated with the current consumption during the anodic dissolution process. The resistance of the system falls in this case (curve 5). For n-Ge at potentials above 0.4 V the capacity begins to decrease, this being caused by restrictions on the diffusion of holes. As follows from Fig. 1b, the resistance and capacity of n-germanium under illumination approximates to the values for p-germanium in darkness. Characteristically, a retardation in the $\Delta\varphi_{il}$ rise is observed in the Tafel region for n-Ge under illumination (curve b), connected, evidently, with increase in the attack. The subsequent rapid increase in $\Delta\varphi_{il}$ in the diffusion region indicates that practically all the measured high (several volts) overvoltage is connected with a drop in potential in the exhaustion layer.

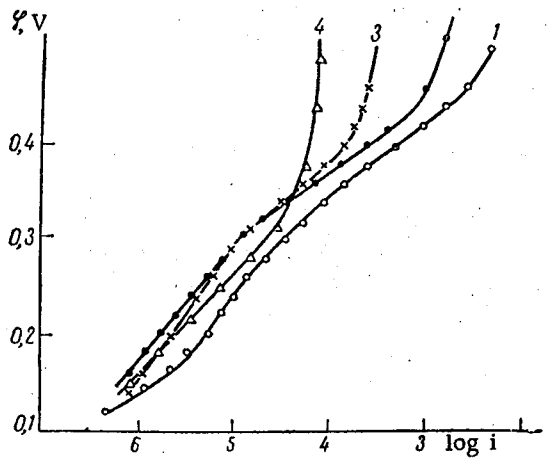

Fig. 2. Polarization curves for the different types of germanium in 1 N NaOH. 1) p-Ge, 5 Ω · cm; 2) intrinsic Ge, 42 Ω · cm; 3) n-Ge, 5 Ω · cm; 4) n-Ge, 0.1 Ω · cm.

The surface properties of intrinsic, n-type, and p-type germanium anodes in 1 N NaOH during the anodic dissolution process are compared in Figs. 2 and 3. A relatively high frequency (60 Hz) and a parallel equivalent electrical circuit were chosen in order to relate with sufficient accuracy all the change in resistance and capacity with the space charge region. Here are also shown polarization curves for, and the nature of the change in the photoeffect with impulse illumination of the electrodes*. As was shown in numerous experiments, there is a regular smooth change in the slope from 130 mV, on the initial portion of the curve, to 70-80 mV, at the end of the curve, (Fig. 2) for all types of germanium in acid and alkali, with the exception of low-resistance n-Ge, for which diffusion restrictions set in early. On the p-Ge curves, at least three portions (curve 1) having slopes 130, 100, and 70-80 mv respectively are clearly distinguished. Transition to the portion having least slope occurs in the potential region around 0.3 V. As will be evident from what follows, this decrease in slope is connected with change in the surface state during anodic polarization.

It follows from Fig. 3A that the capacity of intrinsic germanium (curve 1) passes through a minimum, and the resistance passes through a maximum, which lies in the potential region of zero photoeffect, ~0.3 V (curve 6, Fig. 3B). As has already been discussed in the literature [5, 6], this point corresponds to the rectification band in the semiconductor, i.e., the absence of a bulk space charge. The sign of the photoeffect in the case of impulse illumination of intrinsic germanium at the stationary potential ($\varphi_{stat.} = +0.12$ V) indicates that the energy band bends downwards and, consequently, the surface is enriched with electrons in comparison to the bulk. Above 0.3 V (the ascending portion of the capacity curve) the photoeffect changes sign—increases the positive space charge, generated by holes. Anodic polarization leads first of all to impoverishment of the surface in respect of electrons, and gradual enrichment of it by holes, such that when φ is ~0.3 V the resistance of the system is a maximum.

* An impulse lasted for $5\text{-}6 \cdot 10^{-5}$ sec.

Comparison of the change in capacity and resistance with change in photoeffect for n- and p-germanium indicates, in conformance with the theory of the bulk diffusion charge [5, 7], that on n-Ge during anodic dissolution the positive charge increases all the time, and the capacity decreases, its minimum, corresponding to the potential at which the diffusion layer has the greatest thickness, being displaced to the right; for p-Ge the capacity increases, indicating that the space charge decreases, and the capacity minimum is displaced to the left. The surface on p-germanium at the stationary potential is n-type, and the zero photoeffect potential, corresponding to an identical Fermi level position in the bulk and on the surface, occurs at an anodic polarization of about +0.36 V (curve B). Under the same conditions, the surface on n-germanium in equilibrium with the electrolyte is impoverished in respect of electrons, and the rectification band potential is about +0.1 V (curve 7)—the lowest cathodic polarization. The change in resistance and capacity with potential, thus, is reflected in general by the change in the space charge with anodic polarization. However, there are very substantial deviations from the theoretical form of the C-φ curves (the theoretical curve for intrinsic germanium is depicted by the broken line in Fig. 3). These deviations are probably brought about, firstly, by the occurrence of reactions at the phase boundary, and secondly, by the presence on the surface of levels brought about by ion adsorption and dipole formation, by which the anodic dissolution reaction proceeds. The presence of, for example, donor levels is indicated by the different sign of the photoeffect on intrinsic germanium at the stationary potential when produced by impulse and continuous illumination. The existence of surface states and the extent to which they participate in the anodic reaction is also indicated by the frequency dependence of C and R.

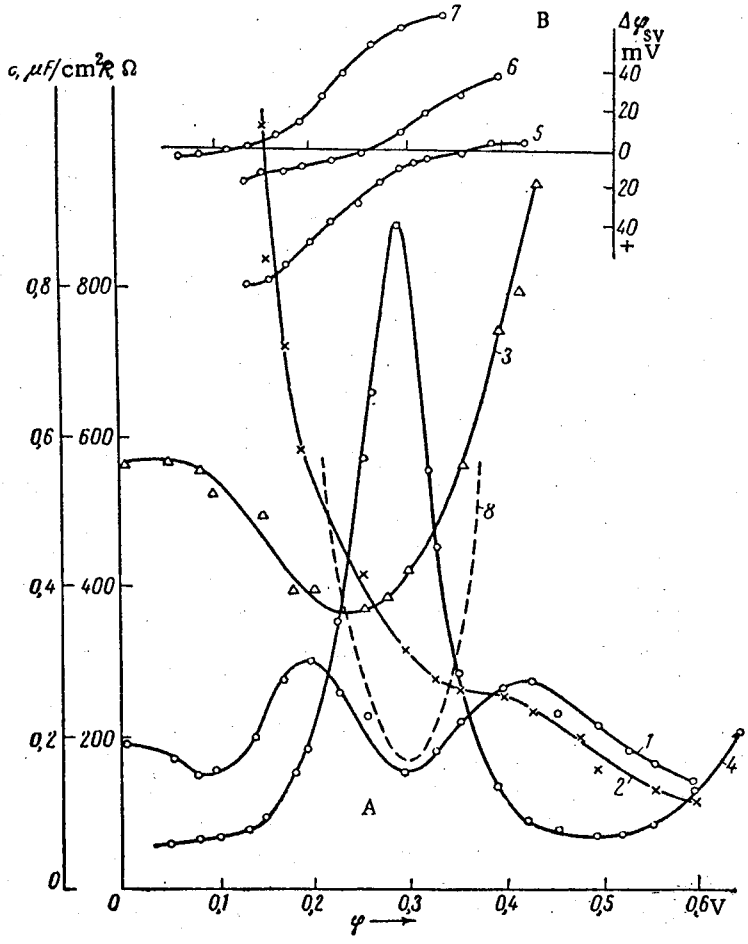

Fig. 3. A) Change in resistance and capacity of the different types of Ge in 1 N NaOH at a frequency of 60 Hz: 1) intrinsic Ge, $\rho = 42\ \Omega \cdot$ cm; 2) n-Ge, $\rho = 5\ \Omega \cdot$ cm; 3) p-Ge, $\rho = 5\ \Omega \cdot$ cm; 4) resistance of intrinsic Ge; 8) theoretical change in capacity of intrinsic Ge. B) Change in impulse- photoeffect: 5) p-Ge; 6) intrinsic Ge; 7) n-Ge.

Strong dispersion of R and C up to 0.3 V, and also displacement of the R maximum towards less positive potentials with decrease in frequency, indicate that in this region there are measured, essentially, surface states with different time constants. From a comparison of the rectification band potentials for n- and p-germanium with the size of the potential displacement from equilibrium, and from a knowledge of the Fermi level positions for samples in bulk, it is possible to evaluate the portion of the potential change connected with decrease in the space charge layer in the total overvoltage [6, 8]. Under our conditions, such evaluation indicated that approximately 80% of the overvoltage, which is expended by change in concentration of electrons and holes, appearing as components of the anodic reaction, falls in the space charge.

Thus, the adduced complex of data indicates that with increase in anodic polarization the germanium surface becomes impoverished in respect of electrons and enriched with holes (for p-Ge, for example, the hole concentration on the surface becomes equal to that in the bulk only when $\varphi \sim +0.36$ V). Change in slope of the polarization curves indicates the different extents to which the free carriers in the conductivity and valence bands participate in the anodic dissolution reaction. This reaction passes through a stage when the surface dipole group $Ge(OH)O^-$ [2] forms, this being, essentially, an acceptor of holes. Electrons can be liberated either in the conductivity band or in the valence band. The probability of such a transition will depend on the position of this complex of relatively energetic bands and on the hole concentration on the surface. It can be assumed that this is a donor level and lies above the middle of the forbidden region. The large slope (130 mV) on the initial portion of the polarization curve is connected with the fact that at low polarizations the reaction takes place in the main in the conductivity band. Downwards displacement of the Fermi level and increase in hole concentration on the surface with increase in the anode voltage facilitates transition of electrons from the complex and increases the portion of the current transmitted through the valence band. Decrease in the slope of the polarization curve above 0.3 V, down to 70-80 mv, causes, thus, decrease in the activation energy of the process with valence band holes as the main participants in the reaction.

LITERATURE CITED

1. W. H. Brattain and C. Garret, Bell Syst. Techn. J., 34, 129 (1955).
2. H. Gerischer and F. Beck, Zs. Elektrochem., 63, No. 4 (1959); H. Gerischer, Zs. Elektrochem., 65, No. 9 (1961).
3. Yu. A. Vdovin, V. G. Levich, and V. A. Myamlin, DAN, 126, 1296 (1959); V. A. Myamlin, DAN, 140, No. 4, 870 (1961).
4. E. A. Efimov and I. Erusalimchik, ZhFKh, 32, 413 (1958).
5. K. Bohnenkamp and H. Engell, Zs. Elektrochem., 61, No. 9 (1957).
6. Yu. Pleskov and V. A. Tyagai, DAN, 141, No. 5, 1137 (1961).
7. C. G. Garrett and W.H. Brattain, Phys. Rev., 99, 376 (1955).
8. R. M. Lazorenko-Manevich, DAN, 144, No. 5 (1962).
