Physical Chemistry

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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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Electrochemical and Photoelectrochemical Processes on Germanium of *p*- and *n*-Type in the Region of Cathodic Polarization

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The literature contains data (^{1,2}) on the considerable influence of the state of the surface on the kinetic features of hydrogen evolution on a germanium cathode, associated with the semiconducting properties of Ge. In the present work, in studying the evolution of H_2 on Ge, along with electrochemical parameters the influence of illumination was also investigated. The experiments were carried out on *p*- and *n*-Ge of various specific resistivities ($p0.5$–$21.0\ \Omega\cdot$cm, $n1.1$ and $22.9\ \Omega\cdot$cm) in $1\,N$ solutions of KOH and H_2SO_4. The reagents used were prepared from bidistillate and chemically pure KOH and triply distilled H_2SO_4. A polyethylene apparatus was used in the work, with a thick clamped Ge electrode and a quartz window for illuminating the electrode. The surface of the electrodes (face (III)) was etched in CP-4 or in a mixture of HNO_3 with HF (Ellis etchant No. 8 (^{3})). All experiments were carried out in an atmosphere of H_2. The reference electrode was a hydrogen electrode in the solution under investigation. Illumination of the electrode was performed with a 300-W cinema lamp through a layer of water of thickness ~ 10 cm. Unseparated light was used. The light intensity at the electrode surface was $\sim 10^{-1}$ cal/cm^2 sec.

Fig. 1. Overvoltage curves in $1N$ KOH (2, 3, 5) and $1N$ H_2SO_4 (1, 4). 1, 2 – *n*-Ge ($\rho = 2\ \Omega\cdot$cm); 3, 4, 5 –*p*-Ge ($\rho = 0.5\ \Omega\cdot$cm)

The overvoltage curves were recorded by two methods: the so-called "fast" and "slow" methods, i.e., upon attainment of the stationary value of η at each current. Figure 1 shows typical stationary curves ($^{1-4}$) recorded after prolonged (10–15 h) cathodic polarization, as well as a "fast" curve (^{5}) recorded on previously unpolarized *p*-Ge.

The bend in the region of high currents on the "fast" curve and for *p*-Ge is associated with a diffusion retardation with respect to electrons (^{1,2,4}), which is absent on *n*-Ge, possessing a considerably higher, than *p*-Ge, bulk concentration of electrons in the conduction band. A number of authors ($^{5-7}$) believe that in

Figure 2

Figure 2: Figure 2

cathodic evolution of H_2 electrons of the valence band may participate, as in the case of the reduction on Ge of certain oxidizing agents ([5,8]). It should be assumed that the possibility of transfer of a valence electron to an oxidizer ion is realized only in the absence of any activation barriers at the semiconductor-solution boundary, i.e., for systems in which—

for which the electron-transfer stage is reversible. Probably, the evolution of H_2 on Ge is not such a process.

The presence on the Ge surface of hydrogen, which increases the rates of surface recombination and generation of minority carriers ([1,2,9]), leads to a smearing of the saturation-current region. Our experiments, on the one hand, confirmed the presence of a diffusion delay in p-Ge during H_2 evolution and, on the other hand, showed that its presence does not correspond to a stationary state of the surface. Figure 2a shows the course of η with time after switching on a current of 10 mA/cm^2 (curve 1). A maximum is noteworthy, the shape and height of which depend strongly on the previous history of the electrode surface. Thus, the presence of a thick ($\sim$ 1000–2000 Å) oxide film obtained by special etching ([3]) leads to an almost complete disappearance of the maximum (curve 2). It should be noted that in acid solutions, while the general character of the curves is preserved, η_{max} is considerably lower than in alkaline solutions (up to 5–6 V in 1N H_2SO_4 and up to 20–22 V in 1N KOH at $i = 10$ mA/cm^2). The descending branch of the curve is naturally associated with an increase in the rate of surface generation of electrons as hydrogen accumulates on Ge. The initial increase in overvoltage, reaching several volts, cannot be explained on the basis of the available literature data. Below we shall attempt to explain the appearance of the maximum using the results of some of our light experiments.

Fig. 2. Typical curves of the dependence of the overvoltage at 10 mA/cm^2 on time after switching on the current (in 1N KOH).
a—dark curves: 1, 2—p-Ge ($\rho = 0.5\ \Omega \cdot \text{cm}$), 3—$n$-Ge ($\rho = 1.1\ \Omega \cdot \text{cm}$).
b—effect of illumination, p-Ge ($\rho = 0.5\ \Omega \cdot \text{cm}$).

Illumination of polarized p-Ge (even in the presence of a diffusion delay) leads to a sharp decrease in overvoltage to 0.5–0.6 V (Fig. 2b). This occurs, as is known, as a result of electron generation at the surface under the action of light. The use of discontinuous illumination allowed us to observe, in addition to the photoeffect already described in the literature, irreversible phenomena associated with the course of the photoelectrochemical process.

After the illumination is switched off (Fig. 2b), the dark overvoltage η_{t} is established at a value exceeding (on the descending branch of the η_{t}—t curve) the initial value (before illumination) by an amount from several tenths of a volt to several volts. Illumination on the ascending branch of the η_{t}—t curve

Fig. 3

Figure 3: Fig. 3

and in the region of the maximum usually leads to a decrease in η_t relative to the initial value, but not below the η_t from which the rise began. Thus, illumination seems to tend to return the surface to the initial state that existed at the moment the current was switched on. Since the decrease of η_t with time in the diffusion region is associated, as was indicated, with the accumulation on the surface of hydrogen that increases electron generation, it is natural to associate the observed increase in η_t (on the descending branch) with the removal of hydrogen under the action of light. The mechanism of the observed "photodesorption" cannot be reliably established from the available data. The presence of "photodesorption" shows that the process of removal of the diffusion delay is associated with hydrogen penetrating relatively shallowly into Ge.

On the ascending branch and in the region of the maximum, "photodesorption" also occurs; however, here it is manifested not in an increase but in a decrease of η_t relative to the initial value. The course of the dark curve after illumination generally reproduces its course before illumination; therefore it may be considered that the increase of η_t at the beginning of polarization is mainly associated precisely with the accumu-

···by hydrogen evolution on the surface, and not by any other possible changes in the state of the surface (for example, reduction of oxides). Thus, it follows from our experiments that both branches of the curve η_t—t can be explained by the activity of hydrogen gradually accumulating on Ge.

To further elucidate the causes of the appearance of a maximum on the η_t—t curve, it is necessary to consider data on the influence of adsorbed hydrogen on the photoeffect in Ge in the absence of an external current.

Figure 3 shows the course of the Ge potential in the absence of an external current under illumination and in the dark (the initial Ge potential is shifted in the positive direction as a result of the presence, in these experiments, of traces of O_2 in the solution). As is seen from Fig. 3, after brief (fractions of a second) cathodic polarization the photoeffect on p-Ge almost disappears or even changes sign, while on n-Ge it increases sharply. After the same brief anodic polarization, with vigorous stirring of the solution (in the case of n-Ge under illumination), the potential returns not to its former value but to a much more cathodic one (up to −50–100 mV), which may be associated with dissolution of the oxide film; however, the photoeffects do not change substantially compared with those present before polarization.

Fig. 3. Influence of adsorbed hydrogen on the magnitude of the photoeffect at a germanium electrode. Solid lines–dark potential; dashed line–potential values obtained under brief illumination

Fig. 4

Figure 4: Fig. 4

Apparently, the observed effects are connected with the presence of hydrogen on the surface (after a cathodic pulse). It is known that adsorbed hydrogen creates on the surface of many metals, for example on Pt (^{10}), and on Si (^{11}), a dipole layer directed with the negative pole outward. However, the formation of such a layer alone cannot explain the observed phenomenon. It follows from Fig. 3 that the presence of hydrogen on the Ge surface leads to an increase in the negative charge of the surface relative to the bulk of the electrode. It may be assumed that this occurs as a result of the formation, during hydrogen adsorption, of acceptor levels located in the forbidden band, on which electrons can be localized.

It should be noted that simple bubbling of the solution with H_2 does not lead to the effect described. Molecular hydrogen is evidently an inert gas in this respect. A similar difference between the action of atomic and molecular hydrogen was also observed in the adsorption of hydrogen on Si from the gas phase (^{11}).

Fig. 4. Influence of illumination on the rate of gas evolution

The assumption concerning the acceptor properties of hydrogen makes it possible to explain the increase in η_t at the beginning of polarization (Fig. 2a, curve 1) as an increase in the concentration polarization with respect to electrons, owing to the decrease, occurring during hydrogen adsorption, of the equilibrium concentration of conduction electrons at the surface. During hydrogen adsorption, the number of centers of surface recombination also increases simultaneously; however, up to a certain moment (the maximum of the η_t—t curve), the action of hy⋯

of hydrogen as an acceptor probably prevails over its action as a center for electron generation.

As indicated above, the initial state of the surface (apparently determined by the thickness and structure of the oxide film after etching and exposure to air) strongly affects the quantitative characteristics of the η_t—t curve (the initial η_t, η_max, the rate of change of η_t); however, the presence of a maximum is a characteristic feature that always appears.

In conclusion, we shall describe one more phenomenon associated with the action of light on the semiconductor (it was observed both on p-Ge and on p-Si).

Illumination of polarized p-Ge is accompanied, at constant current density, by a change in the rate of gas evolution after the light is switched on and off (Fig. 4). This phenomenon occurs only in alkaline solutions in the presence of a considerable photoeffect (i.e., on electrodes with a still not very high rate of surface recombination). On n-Ge this phenomenon is not observed. The effect of stirring shown in Fig. 4 demonstrates that the hydrogen "disappearing" upon illumination dissolves in the electrolyte, and after the light is switched off is again evolved over a certain time, increasing the rate of gas evolution in comparison with the corresponding current flowing. Thus, slow transient processes occur here from one stationary state (dark) to another (illuminated), characterized by a lower probability of formation of gas-bubble nuclei and therefore by a higher content of hydrogen dissolved in the electrolyte. The cause of the change in the probability of nucleus formation may be a change in the surface tension of Ge, occurring as a result of charge redistribution under illumination.

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