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Anodic Dissolution of Germanium with a p-n Junction

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The study of the rate and nature of the anodic dissolution of germanium with a p–n junction is of interest in connection with the development of electrochemical methods for producing p–n junctions of specified geometric form. At present there exist several empirical methods of selective etching of p–n junctions ([1,2]), which are used in technology for the manufacture of special semiconductor devices.

The study of the kinetics and mechanism of various electrochemical reactions on a germanium electrode, carried out recently ([3–7]), makes it possible to outline ways for a rational choice of conditions for the selective etching of germanium p–n junctions. In choosing these conditions, one should take into account not only the physical properties of these junctions, as has been done up to now, but also the electrochemical characteristics of the individual components of the diode at the boundary with the solution.

We investigated the distribution of potential and current density, and consequently also the dissolution rates, on the individual components of a germanium diode under various conditions of its anodic polarization. All measurements were carried out on experimental planar p–n junctions obtained by alloying germanium with indium (DM-grade germanium was used), and also on a single crystal of germanium with a p–n junction. The germanium samples were embedded in epoxy resin (compound), ground perpendicular to the plane of the germanium-indium contact (or p-germanium–n-germanium), polished on electrocorundum powders Nos. 20 and 7, and, after etching in a hydrogen peroxide solution, subjected to anodic polarization. The latter was carried out in an unstirred solution of 0.1 N NaOH or H_2SO_4 at room temperature and in diffuse daylight. Electrical contact with the positive pole of the external current source was made from the indium side, so that the p–n junction was connected in the conducting direction. For each value of the polarizing current density, the potential distribution on different sections of the diode was determined, as well as the surface relief after dissolution. The potential was measured by means of a fine capillary probe moved over the surface ([8]), and a Linnik double microscope was used to measure the depth of dissolution (surface profile) ([9]). Knowing the

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depth of anodic dissolution of germanium and indium at different points on the surface, it was possible to calculate the true distribution of current density, i.e., to determine the fraction of current spent on dissolving one or another component of the diode (indium, *p*-germanium, or *n*-germanium). The width of the *p*-germanium zone in the samples studied was determined by depositing copper on it under cathodic polarization of the *p*–*n* junction from the indium side in a pyrophosphate solution.

Figure 1 shows the anodic polarization curves of indium, *p*-germanium, and *n*-germanium in a 0.1 *N* NaOH solution, obtained on separate samples. We see that, under the indicated conditions, the most strongly polarized anode is

is indium and *n*-type germanium. In contrast to indium, the high polarizability of *n*-germanium is in this case connected not with the onset of passivity, but with the low concentration of holes required for the reaction of its anodic dissolution (^{3}).

Figure 2a shows the distribution of potential over the surface of a planar diode at different anodic current strengths, 0.05–4.00 mA. The indicated values of the potentials do not include the ohmic potential drop at the *p*—*n* junction and represent the true value of the potential of the diode components. Figure 2b gives the surface profilograms of the diode corresponding to these currents after polarization for 60 min, and Fig. 2c gives the values of current density calculated from them. The results obtained show that under these conditions the surface of the diode proves to be unpolarized. A considerable difference in potentials exists not only between indium and germanium, which is connected with the presence of the *p*—*n* junction (equivalent to a certain ohmic resistance at the boundary of *p*- and *n*-Ge), but also between individual sections of the germanium itself. Increasing the strength of the anodic current of the external polarization leads to an increase in this difference of potentials. It should be noted that as the Ge region is moved away from the *p*—*n* junction, its potential becomes more positive. At a current strength of 4.00 mA, the change in potential on *n*-Ge reaches 300 mV, i.e., considerably exceeds the magnitude of the ohmic potential drop (70–80 mV) at this current on *n*-germanium. The magnitude of the current density on the individual components of the diode also proves to be nonuniform. As was to be expected from the anodic polarization curves presented above, the smallest dissolution current density is obtained on indium, and the largest in the region of *p*-type germanium. On *n*-germanium the value of the current density at different sections proves to be nonuniform and decreases as one moves away from the *p*—*n* junction.

Figure 2 and Figure 3

Figure 2: Figure 2 and Figure 3

Fig. 1. Anodic polarization of indium (1), *n*-germanium (2), and *p*-germanium (3) in 0.1 N NaOH solution.

It is interesting to note that the magnitude of the current density on *n*-germanium does not correspond to the limiting anodic current density for *n*-germanium at the boundary with the solution (Fig. 1) and considerably exceeds it. In our opinion, this is connected with the injection (drawing-in) of holes into the *n*-germanium region through the *p*—*n* junction, since the anodic polarization of the diode is carried out from the indium side, i.e., from the side of *p*-type germanium. If this is indeed so, then the anodic polarizability of *n*-germanium, determined by the concentration of holes, must be different at different distances from the *p*—*n* junction.

Figure 3 presents anodic polarization curves for different sections of the surface of *n*-Ge, calculated from the experimental curves of the distribution of current density and potential over the surface of the diode. Curve 5 in this diagram corresponds to the anodic polarization of this same specimen in the absence of injection, i.e., during anodic polarization of the diode from the *n*-germanium side. The results obtained confirm the assumption made above and show that, as one moves away from the region of the *p*—*n* junction, owing to the decrease in the concentration of injected holes, the anodic polarization of *n*-Ge increases. The latter leads to the fact that the values of potential and current density over the surface of *n*-Ge prove to be nonuniform. It should be noted that under our measurement conditions, owing to the high diffusion length of the minority carriers ($L = 2.6$ mm) in germanium,

of the DM grade and the relatively small thickness of the specimen, the effect of hole injection is felt throughout the entire thickness of the germanium.

The data obtained thus show that, under anodic polarization of a germanium diode from the indium side in a 0.1 *N* NaOH solution, i.e., under conditions where the anodic polarization of indium is very large, predominantly *p*-type germanium and the adjoining *n*-germanium region dissolve. By polarizing the diode anodically in the same solution from the indium side, and cathodically from the *n*-germanium side, dissolution of the latter can be completely arrested, concentrating it only in the narrow *p*-type germanium zone. Under anodic polarization of the diode in a sulfuric acid solution, in which indium is practically not polarized, we obtain preferential dissolution of the indium and the adjoining region of *p*-germanium.

Fig. 2. Distribution of potential (a), surface profile (b), and current-density distribution (c) over the surface of the diode during its anodic polarization in a 0.1 *N* NaOH solution. 1—4 mA, 2—2 mA, 3—1 mA, 4—0.4 mA, 5—0.1 mA, 6—0.05 mA

Fig. 3. Anodic polarization of n-germanium at different distances from the In/Ge boundary. 1—0.1 mm; 2—0.5 mm; 3—1.0 mm; 4—1.5 mm; 5—anodic polarization of n-Ge without injection

Fundamentally analogous results were also obtained for a single crystal of germanium with a p—n junction.

Analyzing the results obtained, we see that selective etching of different regions of a germanium diode or triode is possible as a result of the different anodic polarizability of n-germanium, p-germanium, and indium in electrolytes, and also of the presence of a p—n junction region at the boundary of germanium with electron and hole conductivity. The latter is equivalent to including in the electrode circuit an ohmic resistance variable in magnitude.

An important feature of the p—n junction is also its ability to inject minority carriers into germanium. The indicated physical properties of electron-hole junctions have a great influence on the distribution of current density over the surface of the diode. By changing the conditions of anodic polarization of the diode, i.e., by changing the magnitude of the anodic current density, the place of electrical contact, and selecting solutions with different relative

with polarity of indium and germanium of the p-type, it is possible to obtain predominant anodic dissolution either of indium or of the p- and n-regions of germanium.

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