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Fig. 1

Figure 1: Fig. 1

Abstract

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ELECTROCHEMICAL BEHAVIOR OF GALLIUM ARSENIDE

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The electrochemical properties of gallium arsenide have so far practically not been studied. According to Williams' data ([1]), the stationary potential of GaAs depends on illumination. Heisty ([2]) showed that the self-dissolution of GaAs in solutions containing oxidizing agents is electrochemical in nature. In the absence of oxidizing agents, GaAs is stable in aqueous solutions ([3]). In the present work, in order to investigate the electrochemical properties of gallium arsenide, methods were used involving the recording of polarization curves and measurement of the photopotential (the change in electrode potential under pulsed illumination). We used single-crystal samples of GaAs of the n-type, doped with S and Te, with a free-electron concentration n from $5 \cdot 10^{15}$ to 10^{19} cm^{-3} and a resistivity of 0.46–0.001 $\Omega \cdot$ cm, and of the p-type, doped with Zn and Mg, with a hole concentration p from $2 \cdot 10^{18}$ to 10^{19} cm^{-3} (resistivity 0.02–0.004 $\Omega \cdot$ cm). Contacts were prepared by electrodeposition of copper followed by heating at 300° for 30 min. The absence of rectification or high resistance at the contact was checked by recording the current–voltage characteristic; for this purpose, two contacts were applied to each sample, one of which was subsequently removed. Before the measurements, the electrode surface was treated with a polishing etchant ([4]) (a mixture

$$\mathrm{HF} : \mathrm{HNO_3} : \mathrm{H_2O} = 1 : 3 : 2).$$

Fig. 1. Overvoltage of anodic dissolution (1) and cathodic hydrogen evolution (2, 4 –straight-line course; 3 –reverse course) in 0.3 N NaOH solution: 1 –p-type, $p = 10^{19}$ cm^{-3}; 2, 3 –n-type, $n = 10^{18}$ cm^{-3}; 4 –p-type, $p = 2 \cdot 10^{18}$ cm^{-3}.

The method for measuring the photoeffect has been described previously ([5]). Measurements were carried out in the dark in an atmosphere of nitrogen or hydrogen. The solutions were prepared from "special purity" reagents and twice-distilled water.

Fig. 2

Figure 2: Fig. 2

The stationary potential of gallium arsenide depends little on the concentration of gallium ions in solution and is practically independent of the type of conductivity. In the dark, in 1 N NaOH solution it is about -0.4 V, and in 1 N H_2SO_4 solution about 0 V*. Under illumination, the potential of an n-type electrode becomes 0.3–0.4 V more negative, while that of a p-type electrode becomes slightly more positive, which agrees with ([2]). During anodic dissolution of p-type gallium arsenide, the dependence of current on potential is expressed by the Tafel equation with coefficient b about 0.1 (Fig. 1, 1). It should be noted that in 1 N H_2SO_4 solution the polarization

* All potential values are given relative to the normal hydrogen electrode.

the curves are shifted, in comparison with a 1 N NaOH solution, by approximately 0.75 V toward positive potential values.

For samples of the n-type a blocking current is observed. When the electrode is illuminated, the current density increases in proportion to the light intensity (at not very high intensities). When a certain critical value of the potential is reached, the current begins to increase rapidly and breakdown occurs (Fig. 2). The breakdown voltage decreases as the concentration of free electrons in the semiconductor is increased, and at $n \geq 10^{18}$ cm^{-3} the curve of anodic dissolution of n-type GaAs (Fig. 2, 1) practically coincides with the polarization curve for p-type samples.

Fig. 2. Polarization curves of anodic dissolution of n-type gallium arsenide in a 1 N NaOH solution. Concentration of free electrons n:
1—10^{18}; 2—$5 \cdot 10^{17}$, 3—$9 \cdot 10^{16}$, 4—$5 \cdot 10^{15}$ cm^{-3}

The dependence of the change in potential under pulsed illumination on the electrode potential is shown in Fig. 3; on the ordinate axis is plotted the ratio of the photopotential at a given potential to the photopotential at the stationary potential of gallium arsenide. It should be noted that in the case of heavily doped n- and p-type samples the photoeffect is small. The change in potential under pulsed illumination indicates the existence of a space charge in the semiconductor.* Judging from the sign of the photopotential, at potentials more positive than -1.6 V the space charge in electron-type gallium arsenide has a positive sign (curve 1); hole material at potentials more negative than 0 V bears a negative space charge (curve 2). Comparison of the experimentally found dependence of the photoeffect on the potential of n-type GaAs with the theoretical one [6] shows that the photoeffect changes with potential considerably more slowly than follows from the assumption that the change in the potential jump in the space-charge region is practically equal to the change in the electrode potential.

Fig. 3

Figure 3: Fig. 3

Fig. 3. Dependence of the photopotential on the electrode potential in a 1 N NaOH solution:
1 —n-type, $n = 5 \cdot 10^{15}$ cm^{-3}; 2 —p-type, $p = 2 \cdot 10^{18}$ cm^{-3}

This compels one to suppose that at potentials more negative than the stationary potential a significant part of the overvoltage falls not in the semiconductor, but in the ionic part of the double layer.

* The presence of a space charge is confirmed by the low value of the differential capacitance of the electrode. According to the results of capacitance measurements carried out by T. P. Kashcheeva, the width of the space-charge region increases as the specific resistance of gallium arsenide increases, and also upon anodic polarization of the electrode. The author expresses deep gratitude to T. P. Kashcheeva for providing the results of these experiments.

On the contrary, under anodic polarization of hole-type gallium arsenide the photopotential changes rapidly (Fig. 3, 2). Evidently, during anodic dissolution of GaAs a large part of the overvoltage is concentrated in the space-charge region in the semiconductor. This is confirmed by the fact that on electronic gallium arsenide the anodic overvoltage can be very large (up to 6 V in our experiments).

The existence of a blocking current under anodic polarization of n-type gallium arsenide, the increase in current under illumination, and the positive sign of the space charge make it possible to conclude that at the electrolyte–n-type gallium arsenide interface there arises a potential barrier for holes. As a result, the interface under consideration behaves analogously to an electron–hole junction.

For a blocking current to pass through the barrier to the interface, minority carriers (holes) must be supplied. The calculated diffusion current of holes is many orders of magnitude smaller than the experimentally measured blocking current. This circumstance, as well as the absence of a well-pronounced saturation of the anodic-dissolution current, forces one to assume that the holes are not supplied to the surface from the bulk by diffusion, but arise as a result of generation in the space-charge region.

In this case, for estimating the current of anodic dissolution of gallium arsenide one may apply the theory developed for anodic dissolution of silicon ([7]). According to the calculation, the generation current density is, in order of magnitude, $i \simeq edn_i/2\tau$, where n_i is the concentration of free electrons in the intrinsic semiconductor, τ is the lifetime of minority carriers, d is the width of the space-charge region, and e is the electron charge. Taking $n_i = 10^8$ cm^{-3}, $d = 10^{-5}$ cm, $\tau = 10^{-10}$ s ([8]), we obtain for the current density a value of 10^{-6} A/cm^2. In experiment a higher value is observed (about 10^{-4} A/cm^2 at 1 V)*.

The growth of the photoeffect under anodic polarization of n-type GaAs more positive than -0.4 V (Fig. 3, 1) is apparently connected with the depletion of holes in the surface layer during the passage of the anodic current. An analogous phenomenon was observed on germanium ([9]).

As the potential increases, the field strength in the space-charge region increases. When a certain critical value of the field strength is reached, generation of electron–hole pairs proceeds avalanche-like, leading to breakdown. The wider the space-charge region (i.e., the lower the concentration of free carriers in the semiconductor), the higher the voltage at which the field strength reaches its critical value. This explains the dependence of the breakdown voltage on donor concentration (Fig. 2). In very heavily doped n-type gallium arsenide ($n \geq 10^{18}$ cm^{-3}) the space-charge layer is so thin** that electrons overcome the surface barrier by a tunneling mechanism. In this case the anodic blocking effect is not observed (Fig. 2, 1).

Thus, the behavior of electronic gallium arsenide as an anode is determined by its semiconductor properties.

The curves of cathodic hydrogen evolution in alkaline solution for all the n-type samples used by us and for heavily doped p-type material in the region of high current densities practically coincide with one another. At a current density of 10^{-4} A/cm^2 a bend is observed on the curves; in this region the potential is unstable and, at constant current density, becomes more negative with time. In the range of current densities from 10^{-4} to $5 \cdot 10^{-2}$ A/cm^2, a Tafel dependence is observed with coefficient b in 1 N NaOH solution from 0.14 to 0.25 (in 1 N H_2SO_4 solution about 0.12). A bend in the curves at a current of about 0.1 A/cm^2 (as also on the curves of anodic dissolution—

* The blocking current of p-n junctions in GaAs single crystals also proves to be higher than that calculated from the theory of generation in the space-charge region ([10]).

** The width of the barrier can be estimated from the differential capacitance. At $n = 10^{18}$ cm^{-3} it is about 100 Å.

···at this same current density) is evidently due to the ohmic voltage drop in the specimens. It should be noted that, during the evolution of hydrogen, the state of the gallium arsenide surface changes, as indicated by hysteresis—the divergence of the "forward" and "reverse" curves (Figs. 1, 2, 3). On p-type specimens with a not very high hole concentration ($2 \cdot 10^{18}$ cm^{-3}), the hydrogen overvoltage is noticeably higher and the slope of the curve greater than on electron-conducting gallium arsenide (Figs. 1, 4).

The higher value of the hydrogen overvoltage on hole-conducting gallium arsenide, as compared with electron-conducting material, may be associated with the semiconducting character of the electrode. To clarify this question definitively, measurements should be carried out on material with a lower acceptor concentration than was available to us.

The difference in the anodic dissolution rate of n- and p-type gallium arsenide can be used to reveal electron–hole junctions in GaAs crystals.*

The method of selective etching consists in connecting the positive pole of the current source to the p-region of the junction immersed in a 10% NaOH solution, and the negative pole to the n-type region or to an auxiliary electrode for polarization. The current density is about 10 mA/cm^2 (calculated per surface area of the region with hole conductivity). n-type GaAs is practically not etched, while the p-type region dissolves intensively, and a "step" forms at the boundary between them.

Selective electrodeposition of copper may serve the same purpose; it is carried out in a solution of $CuSO_4 \cdot 5H_2O$ (5%) + H_2SO_4 (1%). The p-type region serves as the cathode, and a copper electrode in the same solution as the anode. With this direction of current, the p–n junction is biased in the blocking direction; no current passes into the n-type region, and copper electrodeposition occurs exclusively on the GaAs surface with hole conductivity. If this region is supplied with a current lead made of Kovar, then it is not necessary to pass current through the specimen, since electrodeposition is effected through the operation of the Kovar (anode)–gallium arsenide (cathode) couple. To obtain a mirror-smooth surface, gallium arsenide can be subjected to electropolishing in a 10–40% KOH or NaOH solution at a current density of 1–5 A/cm^2; the polishing time is 1–4 min. The best results are obtained in the case of p-type GaAs or heavily doped n-type material.

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* We used plane junctions formed by zinc diffusion into electron-type gallium arsenide (resistivity about 0.5 $\Omega \cdot$ cm). The thickness of the p-type region was, respectively, 1 and 0.1 mm; the area of the crystals was 1×1 or 2×2 mm^2.

Note: Figure translations are in progress. See original paper for figures.