

THE ELECTROCHEMICAL BEHAVIOR OF GALLIUM ARSENIDE

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Up to now there have been practically no studies made of the electrochemical properties of gallium arsenide. According to Williams [1] the GaAs stationary potential depends on the illumination. Haisty [2] has shown that etching 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 current work a method consisting of plotting polarization curves and measuring the photopotential (change in electrode potential affiliated with a pulse of light) was used in order to study gallium arsenide's electrochemical properties. We used monocrystalline n-type specimens doped with S and Te; having free electron concentrations $n = 5 \cdot 10^{15} - 10^{19} \text{ cm}^{-3}$ and specific resistance $0.46 - 0.001 \text{ ohm} \cdot \text{cm}$, and p-type GaAs doped with Zn and Mg, having hole concentrations $p = 2 \cdot 10^{18} - 10^{19} \text{ cm}^{-3}$ and specific resistance $0.02 - 0.004 \text{ ohm} \cdot \text{cm}$. The contacts were prepared by electrodeposition of copper with subsequent annealing at 300°C for 30 min. The absence of rectification or high resistance at the contact was verified by plotting the volt-ampere characteristics, for which two contacts were deposited on each specimen, one contact being subsequently removed. Before taking measurements the electrode surface was treated with a polishing etchant [4] ($\text{HF}:\text{HNO}_3:\text{H}_2\text{O} = 1:3:2$).

The method by which the photoeffect was measured has been described before [5]. The measurements were carried out in the dark in a nitrogen or hydrogen atmosphere. The solutions were prepared from "specially pure" reagents and twice distilled water.

The gallium arsenide stationary potential depends little on the gallium ion concentration in the solution and is practically independent of the conductivity type. In the dark it is about -0.4 v in N NaOH solution and about 0 v in $\text{N H}_2\text{SO}_4$ solution. Under illumination the n-type electrode potential becomes $0.3 - 0.4 \text{ v}$ more negative and the p-type electrode potential becomes slightly more positive, which agrees with [2]. In the case of p-type gallium arsenide anodic dissolution, the dependence of current on potential is described by the Tafel equation with coefficient b about 0.1 (Fig. 1, 1). It should be noted that in $\text{N H}_2\text{SO}_4$ solution the polarization curves are displaced in comparison with N NaOH solution by approximately 0.75 v in the direction of positive potential values.

A back current is observed in n-type specimens. When the electrode is illuminated the current density increases proportionally to the intensity of the light (at not very high intensities). At a certain critical potential the current begins to increase rapidly and breakdown occurs (Fig. 2). The breakdown voltage decreases with increase

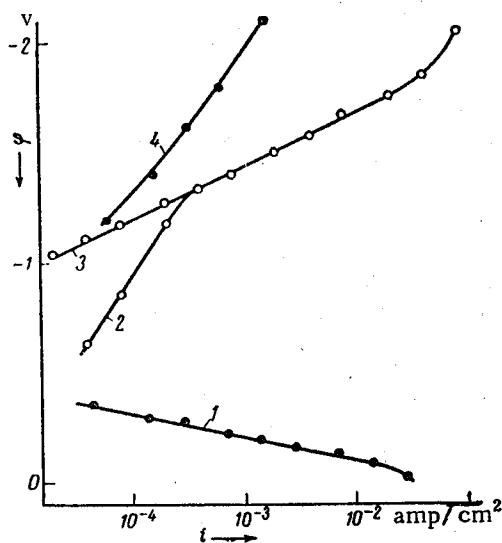


Fig. 1. Overvoltage of anodic dissolution (1) and cathodically evolved hydrogen (2, 4—increasing i , 3—decreasing i) in 0.3 N NaOH solution. 1) p-type, $p = 10^{19} \text{ cm}^{-3}$; 2), 3) n-type, $n = 10^{18} \text{ cm}^{-3}$; 4) p-type, $p = 2 \cdot 10^{18} \text{ cm}^{-3}$.

in free electron concentration in the semiconductor, and with $n \geq 10^{18} \text{ cm}^{-3}$ the n-type GaAs anodic dissolution curve (Fig. 2, 1) is practically identical to the polarization curves for p-type specimens.

* All potential values are referred to the normal hydrogen electrode.

The dependence of the potential change affiliated with a pulse of light on electrode potential is shown in Fig. 3; the ratio of the photopotential at a given potential to the photopotential at the gallium arsenide stationary potential is plotted along the axis of ordinates. It should be noted that in the case of strongly doped n- and p-type specimens the photoeffect is small. The potential change affiliated with a pulse of light is shown by the existence of a space charge in the semiconductor.* From the sign of the photopotential it is judged that when the potential is more positive than -1.6 v the space charge in n-type gallium arsenide has a positive sign (curve 1); p-type gallium arsenide carries a negative space charge when the potential is more negative than 0 v (curve 2). Comparison of the experimental dependence of the photoeffect on the n-type GaAs potential with the theoretical dependence [6] shows that the photoeffect decreases with the potential considerably more slowly than would be expected from the hypothesis that the change in potential drop in the space charge region is practically equal to the change in electrode potential. This makes us assume that at potentials more negative than the stationary potential a considerable portion of the overvoltage occurs not in the semiconductor, but in the ionic portion of the double layer.

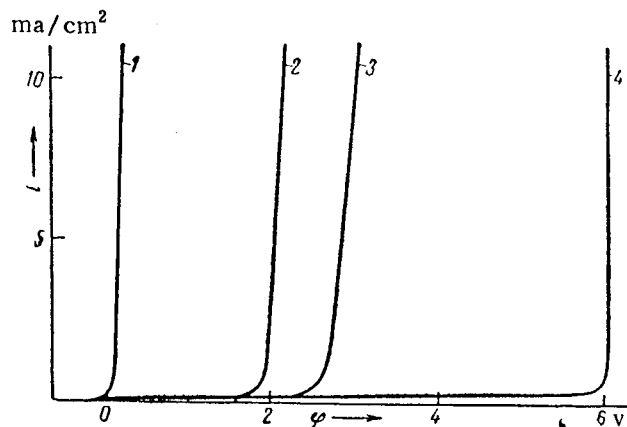


Fig. 2. Polarization curves for n-type gallium arsenide anodic dissolution in N NaOH solution. Free electron concentrations, n : 1) 10^{18} ; 2) $5 \cdot 10^{17}$; 3) $9 \cdot 10^{16}$; 4) $5 \cdot 10^{15} \text{ cm}^{-3}$.

On the other hand, the photopotential changes rapidly in the case of anodic polarization of p-type gallium arsenide (Fig. 3, 2). Evidently, when GaAs anodically dissolves, the greater part of the overvoltage is concentrated in the space charge region in the semiconductor. This confirms the fact that in n-type gallium arsenide the anodic overvoltage may be very large (up to 6 v in our experiments).

The existence of a back current during anodic polarization of n-type gallium arsenide, the increase in current with illumination, and the positive sign of the space charge allows the conclusion to be drawn that a potential barrier against holes develops at the electrolyte - n-type gallium arsenide boundary. Because of this the boundary in question behaves similarly to an electron-hole transition.

In order for the back current to pass through the barrier to the dividing boundary it is necessary to supply minority carriers (holes). The calculated hole diffusion current is many times smaller than the experimentally measured back current. This circumstance and also the absence of a clearly indicated anodic dissolution saturation current makes us assume that holes do not move to the surface by diffusion from the bulk, but result through generation in the space charge region.

In this case the theory developed for anodic dissolution of silicon [7] can be applied in order to appraise the anodic dissolution of gallium arsenide. The generated current density is calculated to be of the order of magnitude $i \approx edn_i/2\tau$, where n_i is the free electron concentration in the pure semiconductor, τ is the minority carrier life-time, d is the width

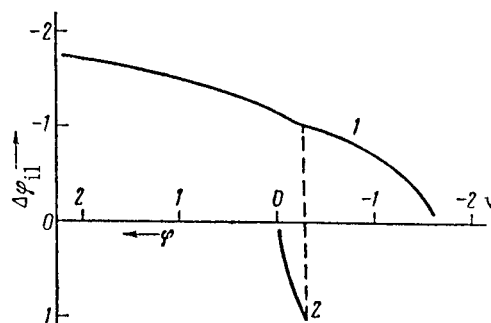


Fig. 3. Dependence of the photopotential on electrode potential in N NaOH solution. 1) n-type, $n = 5 \cdot 10^{15} \text{ cm}^{-3}$; 2) p-type, $p = 2 \cdot 10^{18} \text{ cm}^{-3}$.

* The presence of a space charge is confirmed by the low value of the electrode differential capacity. According to results obtained from capacity measurements, made by T. P. Kashcheev, the width of the space charge region increases with increase in the specific resistance of gallium arsenide and also with anodic polarization of the electrode. The author profoundly thanks T. P. Kashcheev for giving these experimental results.

of the space charge region, and e is the electron charge. Assuming $n_i = 10^8 \text{ cm}^{-3}$, $d = 10^{-5} \text{ cm}$, and $\tau = 10^{-10} \text{ sec}$ [8], we obtain 10^{-6} amp/cm^2 for the current density. A higher value (about 10^{-4} amp/cm^2 at 1v) is found experimentally.*

In the case of n-type GaAs the increase in photoeffect is more positive than -0.4 v (1, Fig. 3), which is connected, evidently, with depletion of holes in the surface layer when the anodic current passes. A similar effect was observed on germanium [9].

The field strength in the space charge region increases with increase in the potential. When a certain critical strength is attained electron - hole pairs are generated, by an avalanche process, which leads to breakdown. The wider the space charge region (i.e., the lower the free carrier concentration in the semiconductor), the higher the potential at which the field strength attains the critical value. This also explains the dependence of the breakdown voltage on donor concentration (Fig. 2). In very strongly doped n-type gallium arsenide ($n \geq 10^{18} \text{ cm}^{-3}$) the space charge layer is so thin** that electrons overcome the surface barrier by the tunnel mechanism. In this case the anodic blocking effect is not observed (1, Fig. 2).

Thus, the anodic behavior of n-type gallium arsenide depends on its semiconductor properties.

The curves of the cathodic evolution of hydrogen in alkaline solution for all n-type and strongly doped p-type specimens, studied by us, in the high current density region are practically identical. A bend is observed in the curves when the current density is 10^{-4} amp/cm^2 ; the potential is unstable in this region, and at constant current density the potential becomes more negative with passage of time. In the current density range $10^{-4} - 5 \cdot 10^{-2} \text{ amp/cm}^2$ the coefficient b in the Tafel relationship is found to be 0.14-0.25 in N NaOH solution (about 0.12 in N H_2SO_4 solution). The bend in the curves at about 0.1 amp/cm^2 current density (just as in the anodic dissolution curves at the same current density) depend, evidently, on the ohmic potential drop across the specimens. It should be noted that during the hydrogen evolution process the condition of the gallium arsenide surface changes, as is shown by the hysteresis - space curves plotted against increasing and decreasing current density (2, 3, Fig. 1). In p-type specimens having not too high hole concentrations ($2 \cdot 10^{18} \text{ cm}^{-3}$) the hydrogen overvoltage is noticeably higher, and the slope of the curve steeper, than in n-type gallium arsenide (4, Fig. 1).

The higher hydrogen overvoltage in p-type gallium arsenide, in comparison with n-type, may be connected with the semiconductor nature of the electrode. In order for this problem to be finally clarified measurements should be carried out on material having much lower acceptor concentrations than had those materials which were available to us.

Differences in the anodic dissolution rates of n- and p-type gallium arsenides can be used to explain electron-hole transitions in GaAs crystals***.

The selective etching method is based on the fact that the positive pole of the source is linked with p-type region transitions, when immersed in 10% NaOH solution, and the negative pole is linked with the n-type region or to an auxiliary electrode for polarization. The current density amounts to about 10 ma/cm^2 (calculated for the surface region with hole conductivity). There is practically no etching of n-type GaAs, but the p-type dissolves briskly, and "steps" form at the boundary between the regions.

Selective electrodeposition of copper can be used for the same ends, this occurring in 5% $\text{CuSO}_4 \cdot 5\text{H}_2\text{O} + 1\% \text{H}_2\text{SO}_4$ solution. The p-type region serves as the cathode, and a copper electrode in the same solution serves as the anode. When the current is passed in this direction the p-n transition takes place in the reverse direction, no current passes through the n-type region, and copper is electrodeposited only on the GaAs surface having hole conductivity. If this region is provided with a kovar (fernico) current conductor it is not necessary to pass current through the specimen, since electrodeposition is accomplished through operation of the kovar (anode)-gallium arsenide (cathode) pair. In order to produce a mirror-polish surface the gallium arsenide can be electropolished in 10-40% KOH or NaOH

*The p-n transition back current in GaAs monocrystals also proves to be greater than that calculated from the theory of generation in the space charge region [10].

**It is possible to appraise the width of the barrier from the differential capacity value. It is about 100A when $n = 10^{18} \text{ cm}^{-3}$.

***We made use of surface transitions, generated by zinc diffusion in n-type gallium arsenide (specific resistance about $0.5 \text{ ohm} \cdot \text{cm}$). The thickness of the n- and p-type regions were 1 and 0.1 mm respectively, and the surface areas of the crystals were 1×1 or $2 \times 2 \text{ mm}^2$.

solution, at current density 1-5 amp/cm², for 1-4 min. The best results are obtained in the case of p-type or heavily doped n-type GaAs.

We profoundly thank Professor B. N. Kabanov for his help when discussing our results.

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THE PROPERTIES OF THE V=O DOUBLE BOND IN VANADYL IONS

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It was shown earlier [1] that in aqueous vanadyl salt solutions the ratio of the proton magnetic relaxation times T_1/T_2 and time T_2 alone are very sensitive to the state of the V=O bond in VO^{2+} ions. With partial dissociation of this bond, brought about by the action of acids or by the introduction of hydroxyl into the VO^{2+} coordination sphere, time T_2 was observed to be considerably shortened, corresponding to an increase in the ratio T_1/T_2 . Thus,

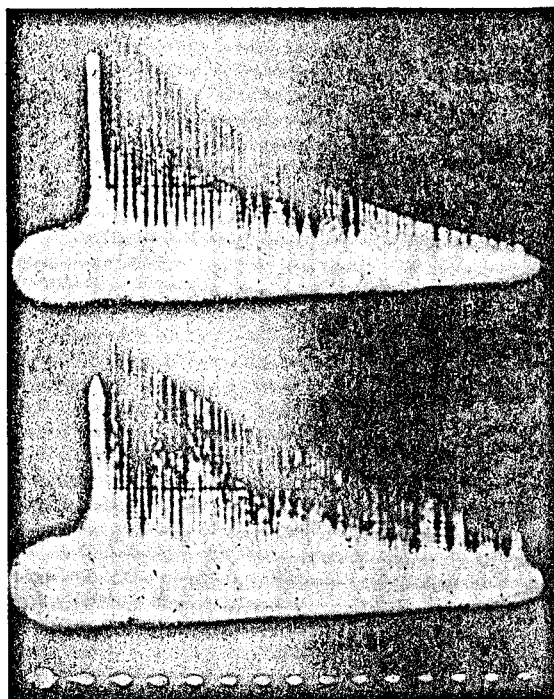


Fig. 1

carried out at 20°C. The interval between adjacent time markings equals 2 msec. It is evident (Fig. 1) that the echo signal envelopes are different in both cases. The following transverse proton relaxation time (T_2) values were found: $T_2 = 11.7$ msec for the 0.1 molar solution of $VOSO_4$ in H_2O , and $T_2 = 17.8$ msec for the 0.1 molar solution of $VOSO_4$ in 5% H_2O , 95% D_2O mixture. In proportion to the extent to which normal water is substituted by deuterium oxide in the solvent there also occurs some, but weaker, extension of the longitudinal proton relaxation time (T_1), as a result of which the ratio T_1/T_2 decreases.* The proton relaxation parameters for 0.1 molar solutions of $VOSO_4$ in H_2O and in 5% H_2O , 95% D_2O mixture are summarized in Table 1. Similar results were also obtained for 0.05 molar $VOSO_4$ solutions.

* T_1 values were measured by a "null" method [4].

a comparatively simple and practicable means was found for measuring the solvent proton relaxation characteristics, enabling the properties of complexes containing multiple bonds (for example, VO^{2+} ions) in solution to be studied. G. B. Bokii has recently reported [2] upon the importance of studying complexes with multiple bonds in their inner spheres. He observed that it was desirable to determine the states of the multiple bond by some less laborious means than this (crystals were being considered), perhaps by x-ray structural analysis. There are reasons for thinking that the method of nuclear magnetic relaxation is suitable for vanadyl solutions.

We were interested in making use of the high sensitivity of the nuclear relaxation method to study the effect of a solvent having an isotopic composition (water) on the V=O bond. With this object proton relaxation times were measured in freshly prepared equimolar solutions of $VOSO_4$ in normal water and in H_2O - D_2O mixtures. As an example, oscillograms of spin echo signals from protons, obtained with the aid of 90-180° successions of radio-frequency pulses [3], are shown in Fig. 1, on the same scale along the time axis, for 0.1 molar solutions of $VOSO_4$ in H_2O (upper) and in 5% H_2O , 95% D_2O mixture (lower). The oscillating magnetic field frequency (ν_0) was 18.1 Mc. The experiments were