

THE ANODIC DISSOLUTION OF GERMANIUM IN THE PRESENCE OF REDUCING AGENTS

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It was found in previous work¹ that introduction of reducing agents of the type of $C_2O_4^{2-}$ or I^- into the electrolyte considerably accelerates the anodic dissolution of *n*-type germanium. This effect is observed at potentials more positive than 0.5 V, i.e. in the potential range in which the kinetics of the electrode process are governed by the diffusion of holes from the bulk of the semiconductor to its surface. Polarisation curves obtained in solutions of 1 N $K_2C_2O_4$ + 0.1 N HCl and of 1 N KI + 0.1 N HCl did not show the saturation current due to holes which is so characteristic of the electrochemical dissolution of *n*-type germanium.

In the present work this phenomenon has been studied in greater detail, and its mechanism elucidated, using thin plates with a *p-n* junction to which a reverse bias was applied².

EXPERIMENTAL

The electrode used was a circular plate of *n*-type germanium with a resistivity of 20 ohm cm and a diffusion length of 1 mm. The original thickness of the plate was 200 μ . On one face of the plate a *p-n* junction of total area 0.04 cm² was produced by fusing indium into it. An annular ohmic contact was fused into the same face. The whole plate, including lead was insulated with a silicone varnish and then with pure paraffin wax, apart from the portion opposite the *p-n* junction and equal to it in area. The thickness of the *n*-region of the plate was brought down to 15–17 μ by chemical etching in SR-4.

The potential of such a germanium electrode was measured against a saturated calomel half-cell at different current densities both with a back bias applied to the *p-n* junction and with the external circuit between the ohmic contact and the fused-in indium disconnected. All experiments were carried out at $20^\circ \pm 0.5^\circ$. The potentials were converted to the normal hydrogen scale.

By applying a suitable reverse bias to the *p-n* junction it proved possible to increase or to decrease the width of the band impoverished in current carriers and thereby to decrease or to increase the thickness of the layer of germanium adjacent to the electrolyte.

The above method enabled us to study the kinetics of electrochemical reactions under conditions such that the volume of semiconductor could be adjusted, and to separate phenomena associated with the generation of holes in its bulk and at the surface.

The effect observed previously¹ was explained on the hypothesis that the oxidation of reducing agents of the type of oxalate and iodide ions at a germanium anode involves not the consumption of holes but the injection of electrons into the electrode. Therefore the actual oxidation of the reducing agents cannot be controlled by the diffusion of holes from the interior of the electrode. The injection of electrons and the resulting increase in their concentration at the electrode surface produce a strong electric field,

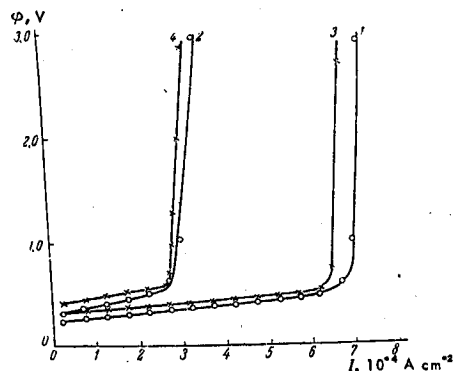


Fig. 1. Effect of potassium oxalate on the anodic dissolution potential of germanium: 1) 0.1 N HCl + 1 N $K_2C_2O_4$, *p-n* junction on open circuit; 2) 0.1 N HCl + 1 N $K_2C_2O_4$, reverse bias applied to *p-n* junction; 3) 0.1 N HCl, *p-n* junction on open circuit; 4) 0.1 N HCl, reverse bias applied to *p-n* junction.

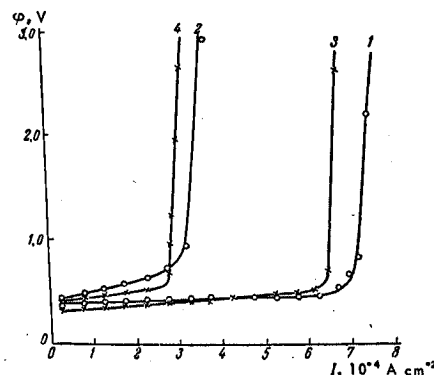


Fig. 2. Effect of potassium iodide on the anodic dissolution potential of germanium: 1) 0.1 N HCl + 1 N KI, *p-n* junction on open circuit; 2) 0.1 N HCl + 1 N KI, reverse bias applied to *p-n* junction; 3) 0.1 N HCl, *p-n* junction on open circuit; 4) 0.1 N HCl, reverse bias applied to *p-n* junction.

which in turn contributes to the appearance at the surface of a larger number of holes mainly as a result of drift. This also leads to an acceleration of the anodic dissolution of *n*-type germanium, the rate of which is limited by the concentration of holes at the germanium-electrolyte interface.

When iodide ions are used as the reducing agent, extra holes may appear in the surface layer of germanium also owing to the reverse process, the reduction of molecular iodine by Gerischer and Beck's mechanism³.

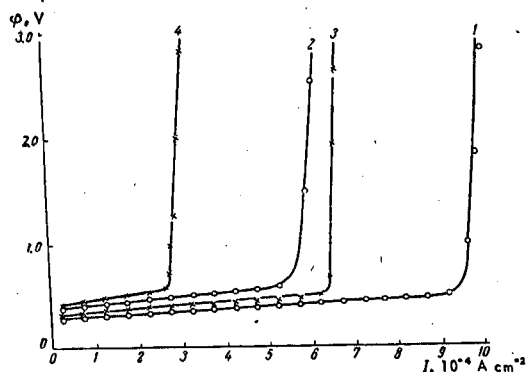


Fig. 3. Effect of potassium ferricyanide on the anodic dissolution potential of germanium: 1) 0.1 N HCl + 0.05 N $K_3Fe(CN)_6$, $p-n$ junction on open circuit; 2) 0.1 N HCl + 0.05 N $K_3Fe(CN)_6$, reverse bias applied to $p-n$ junction; 3) 0.1 N HCl, $p-n$ junction on open circuit; 4) 0.1 N HCl, reverse bias applied to $p-n$ junction.

In order to test this hypothesis as to the mechanism of the process, polarisation measurements were made on thin plates of n -type germanium with and without application of a reverse voltage to the $p-n$ junction.

As in the previous work¹, the reducing agents used were potassium oxalate and potassium iodide. Similar measurements were also carried out in the presence of potassium ferricyanide, which can be reduced at a germanium electrode by the capture of electrons from the valence band, and thus can facilitate the anodic dissolution of germanium³.

The polarisation curves obtained are shown in Figs. 1-3. In all cases in which measurements were carried out with a reverse bias on the $p-n$ junction (curves 2 and 4) a voltage of 5 V was applied to it, corresponding to an expansion of the space charge by $\sim 10 \mu$ and a diminution in the thickness of the germanium layer adjacent to the electrolyte, and not impoverished in current carriers, to 5-7 μ .

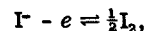
In contrast to the earlier results¹, all polarisation curves obtained on thin plates have a well defined limiting current at potentials more positive than 0.5 V. This represents a saturation current of the holes consumed in the dissolution of the germanium. Its magnitude is comparatively little changed by the introduction of reducing agents of the type of $C_2O_4^{2-}$ or I^- into 0.1 N HCl solution, but depends markedly on the presence of $K_3Fe(CN)_6$.

The application of a reverse bias to the $p-n$ junction increases the width of the band impoverished in current carriers, and, as it were, diminishes the geometrical size of the electrode. Therefore the number of holes generated in the bulk of the semiconductor will be lower in this case. This is in fact the cause of the decrease in the hole saturation current on the $\phi-I$ curves with the application of a reverse voltage to the $p-n$ junction².

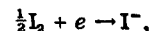
These experimental results indicate unambiguously the sources of the holes which appear at a germanium surface when reducing agents are present in the solution.

When data obtained with thick plates¹ are compared with the results of the present work, carried out on plates whose thickness is far less than the diffusion length, it is found that the increase in the rate of anodic dissolution of germanium is incomparably greater in the former case. With thick plates no hole saturation current is observed even at current densities below $10^{-2} A cm^{-2}$. With thin plates, as already noted above, the difference in saturation currents in the presence and in the absence of reducing agents is comparatively slight. This fact alone compels us to assume that the extra quantity of holes appearing at the germanium surface as a result of $C_2O_4^{2-}$ and I^- ions taking part in the electrochemical reaction is not formed directly at the electrode surface, but is mainly supplied from the interior of the semiconductor. This proposition is particularly well confirmed in experiments in which a reverse voltage is applied to the $p-n$ junction of a germanium electrode.

Actually, if the increase in current on introducing $C_2O_4^{2-}$ or I^- ions into the electrolyte were caused solely by a sharp increase in the exchange current, e.g. because of the reaction



the holes appearing by the Gerischer and Beck mechanism³ in the reaction



should be formed directly at the electrode surface. The increase in saturation current would then be the same whether the $p-n$ junction was on open circuit or whether a reverse voltage was applied to it. This is in fact the case when potassium ferricyanide is added to the electrolyte (Fig. 3).

Oxalate and iodide have practically no effect on the saturation current with the reverse bias applied to the $p-n$ junction. Consequently the holes which then appear at the surface are not formed directly on it, but arrive from the semiconductor electrode. When a reverse voltage (5 V) is applied to the $p-n$ junction, the impoverished layer occupies a large proportion of the volume of the electrode. It is hardly possible any longer for the holes formed in this layer to move to the electrode surface. Therefore the electric field produced by the injection of electrons in the oxidation of $C_2O_4^{2-}$ and I^- ions will attract to the surface only those holes which arise in a comparatively thin layer of germanium at the boundary with the electrolyte. Hence the increase in the saturation current in the presence of a reducing agent in the solution is far greater when the $p-n$ junction is on open circuit than when a back bias is applied to it.

Comparison of curves 2 and 4 in Figs. 1 and 2 shows that the increase in saturation current is somewhat greater when I^- ions are introduced into the solution than in the case of $C_2O_4^{2-}$ ions. This is due to a partial reduction of molecular iodine by the Gerischer and Beck mechanism.

SUMMARY

1. The kinetics of the anodic dissolution of n -type germanium in 0.1 N hydrochloric acid in the presence of reducing agents have been studied by means of polarisation measurements on thin germanium electrodes having a $p-n$ junction.

2. The acceleration of the dissolution of germanium when reducing agents of the type of the oxalate and iodide ions are introduced into the solution is shown to be due to an additional flow of holes from the interior of the semiconductor to its surface. This flow of holes is caused by the action of the electric field produced by the injection of electrons into germanium, associated with oxidation of the reducing agents.

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EQUILIBRIUM IN TERNARY SYSTEMS WITH PHASE SEPARATION AND SALTING-OUT

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Ternary systems with several liquid phases have received much attention because of their theoretical and practical importance. Some investigators have attempted to find the laws governing the distribution of components among the phases, others tried to give a theoretical explanation which would be applicable to practical processes of extraction and salting-out. Another group of investigators measured the vapour pressures of such systems, etc.

The distribution of a component among the phases may be described by the Nernst law if the component does not affect the miscibility of the two liquids. The Nernst distribution law may be applied to real systems if certain corrections are introduced. Various authors have proposed empirical relations¹⁻³, based in the main on accurate determinations of the composition of the conjugate solutions, from which the binodal curve was plotted. The disposition of the tie-lines gives a graphical representation of the distribution of components among the phases.

When the tie-lines in a three component liquid system, with one pair of partially miscible components, are produced, they intersect in one point, falling on the line formed by extending the side of the triangle which corresponds to the pair of the partially miscible components. This behaviour may be described by an equation derived analytically and geometrically by Tarasenkova⁴:

$$x = \frac{x_1 y_2 - x_2 y_1}{y_2 - y_1} \quad (1)$$

where x_1 and x_2 are the concentrations of one of the partially miscible components in the lower and upper layers, y_1 and y_2 are the concentrations of the component soluble in either layer, and x is the abscissa of the intersection point of the tie-lines. The correctness of this equation has been verified in a large number of similar systems⁵, although in a few cases the tie-line intersection rule has not been confirmed⁶.

Later, theoretical consideration of the rule postulating the intersection of tie-lines in a single point was extended to ternary liquid heterogeneous systems with two pairs of partially miscible components. When there is a single common heterogeneous field, the tie-lines, when produced, should meet at the vertex of the concentration triangle formed by the two sides corresponding to the two pairs of the partially miscible components. The distribution equation in this case takes the form

$$\frac{y_1}{y_2} = \frac{x_1}{x_2} \quad (2)$$

It has been found to apply to the benzene-formic acid-bromoform system⁷.

There are few data in the literature on other types of systems - with two or three pairs of partially miscible components, and with two critical points - which would enable the tie-line intersection rule to be verified. Investigation of systems of this type is generally limited to elucidation of the general character of the system and the trend of the tie-lines.

Three-component liquid heterogeneous systems in which one of the components is a salt are of special practical and theoretical interest. The general form of the phase diagrams of such systems has been considered in some detail by Mertsin⁸. In this case, also, equations for the co-ordinates of the point in which the tie-lines intersect can be derived; the point lies outside the triangle and not on a line formed by producing one of its sides⁹. In the derivation, an oblique system of co-ordinates with a 60° angle between the axes is employed. A tie-line may be represented by an equation for a straight line passing through two points:

$$\frac{x - x_1}{x_2 - x_1} = \frac{y - y_1}{y_2 - y_1} \quad (3)$$

where x_1 and y_1 , and x_2 and y_2 are the co-ordinates (concentrations) of the conjugate solutions for the given tie-line. For another tie-line, with the co-ordinates x_3 , y_3 , and x_4 , y_4 , the equation becomes

$$\frac{x - x_3}{x_4 - x_3} = \frac{y - y_3}{y_4 - y_3} \quad (4)$$

Simultaneous solution of these two equations for x and y yields the required co-ordinates of the point of intersection:

$$x = \frac{(x_4 - x_3)(x_1 y_2 - x_2 y_1) - (x_2 - x_1)(x_3 y_4 - x_4 y_3)}{(x_4 - x_3)(y_2 - y_1) - (x_2 - x_1)(y_4 - y_3)} \quad (5)$$

$$y = \frac{(y_4 - y_3)(x_1 y_2 - x_2 y_1) - (y_2 - y_1)(x_3 y_4 - x_4 y_3)}{(y_4 - y_3)(x_2 - x_1) - (y_2 - y_1)(x_4 - x_3)} \quad (6)$$

EXPERIMENTAL

The system employed, salt-ethanol-water, was selected because fairly convenient methods are available for the quantitative determination of salts and ethanol. Equilibria were studied in a cylindrical glass vessel in a water thermostat, controlled to $\pm 0.1^\circ$. The concentration of the alcohol was found by weighing out a 40-50 g sample, diluting it with water, and distilling from a Würtz flask almost to dryness; the distillate was weighed and its density was determined by means of a dilatometer; the percentage of the alcohol in the distillate and hence in the sample was then found from Tables. When the liquid phases were in equilibrium with a solid, the latter was analysed by Schreinemakers' method of residues¹⁰.