

where α is the coefficient of linear expansion, u is the velocity of sound in the metal, and $\gamma = (1/u)(du/dT) < 0$.

SUMMARY

1. The activation energy of self-diffusion is determined by the internal pressure and the atomic structure of the metal.
2. The activation energy is approximately equal to the work of formation of two "holes" of the size of the diffusing ion.

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Mendeleev Institute of
Chemical Technology

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REDUCTION OF THE PEROXODISULPHATE ION AT A GERMANIUM CATHODE

E.A.Efimov, I.G.Erusalimchik,
and E.I.Gorgoraki

Published data on the reduction of the peroxodisulphate ion at a germanium electrode are contradictory^{1,2}. The reaction has now been studied by recording potentiostatic polarisation curves, and also by measuring the photopotential of the germanium electrode; the latter method leads to conclusions concerning the bending of the energy bands at the electrode surface.

Specimens of *n*- and *p*-germanium of resistivity 1.5 ohm cm^{-1} and diffusion length 0.7 mm were used as electrodes. A series of experiments were carried out on degenerate polycrystalline germanium possessing no semiconducting properties, and also on electrodes having a *p-n* junction. This last type consisted of circular sheets cut from a single crystal of *p*-type germanium. The *p-n* junction was produced on one side of the sheet by melting in a drop of Pb-Sb. An annular ohmic base-contact was fused into the electrode on the same side. The whole germanium sheet with the leads was insulated by means of a silicone varnish, with the exception of a portion opposite the *p-n* junction, of the same area as the latter. The thickness of the *p*-layer in the prepared electrode did not exceed 50 μm .

Fig. 1 shows polarisation curves obtained on *n*- and *p*-germanium, and also on the degenerate metal, in 0.001 *N* $\text{K}_2\text{S}_2\text{O}_8$. The curves practically coincide: *i.e.* under these conditions the reduction is independent of the type of conduction of the electrode. The limiting current of about 0.35 mA cm^{-2} is the usual limiting diffusion current of peroxodisulphate ions to the electrode surface, agreeing well in absolute magnitude with the limiting current of an amalgamated platinum electrode³.

When a curve is determined in the opposite direction (from higher to lower potentials), a hysteresis loop is produced, which indicates some acceleration of the reaction at potentials more positive than -0.9 V.

Addition of an inert electrolyte to 0.001 *N* $\text{K}_2\text{S}_2\text{O}_8$ solution somewhat diminishes the retardation of the electrode reaction (Fig. 2).

With increase in the peroxodisulphate concentration of the solution, the polarisation curves for *p*- and *n*-germanium begin to diverge. Between -0.2 and 0.1 V the rate of the reaction of the *n*-type germanium is somewhat the more rapid (Figs. 3 and 4). Fig. 5 shows the variation in photopotential of a *p*-type germanium electrode in solutions containing the peroxodisulphate ion.

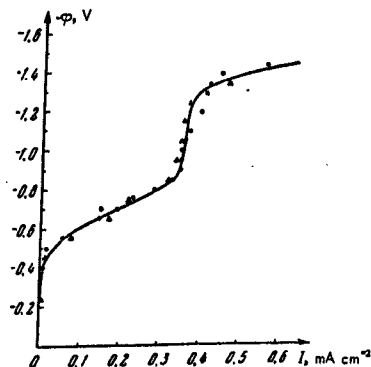


Fig. 1. Polarisation curves obtained on *n*-type, *p*-type, and degenerate germanium cathodes in 0.001 *N* $\text{K}_2\text{S}_2\text{O}_8$.

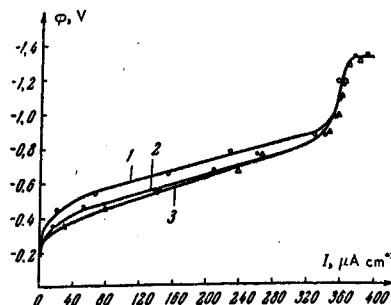


Fig. 2. Effect of inert electrolyte (Na_2SO_4) on reduction of the peroxodisulphate ion (in 0.001 *N* $\text{K}_2\text{S}_2\text{O}_8$) at an *n*-type germanium cathode. Concentration of added Na_2SO_4 : 1) 0; 2) 0.1 *N*; 3) 1.0 *N*.

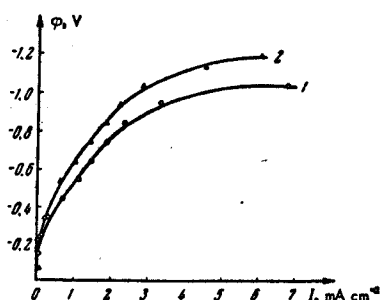


Fig. 3. Polarisation curves obtained in 0.1 N $K_2S_2O_8$ at a germanium electrode: 1) *n*-type; 2) *p*-type.

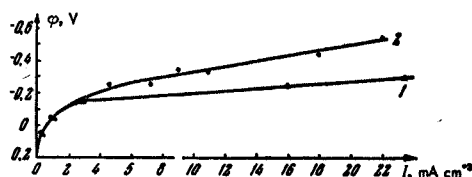


Fig. 4. Polarisation curves obtained in 2 N $K_2S_2O_8$ at a germanium cathode: 1) *n*-type; 2) *p*-type.

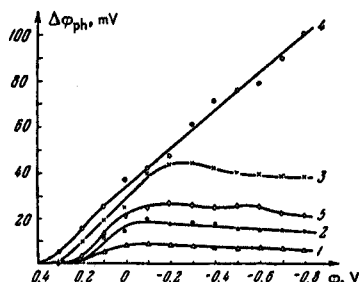


Fig. 5. Variation of photopotential of *p*-type germanium electrode with polarisation potential in solutions containing the peroxodisulphate ion. Concentration of $(NH_4)_2S_2O_8$: 1) 0.02 N; 2) 0.1 N; 3) 0.5 N; 4) 2.5 N; 5) 0.001 N $(NH_4)_2S_2O_8$ + 0.1 N Na_2SO_4 .

Since potassium peroxodisulphate is considerably less soluble than the ammonium salt, the influence of concentration on the kinetics of the process and of the distribution of the potential drop can be conveniently studied in solutions of the latter. Fig. 5 shows that, with increase in the concentration of ammonium peroxodisulphate, the photopotential increases while the potential of the planar bands becomes more positive. The latter effect is observed also with *n*-type germanium (Fig. 6).

It appears from the experimental results that the type of conduction of the germanium cathode affects reduction of the peroxodisulphate only at quite high concentrations of the $S_2O_8^{2-}$ ion in the electrolyte. The coincidence of the three curves (on *n*-type, *p*-type, and degenerate germanium) in a very dilute solution (Fig. 1) provides evidence that in such systems the potential drop occurs mainly in the electrolyte, not in the surface layer of the semiconductor. In conformity with this, the photopotential of the germanium electrode in such solutions is very low, and the bending of the bands insignificant.

The distribution of the potential drop in this system changes with increase in the electrolyte concentration. Thus in 0.1 N $K_2S_2O_8$ the curves on *p*- and *n*-type germanium begin to diverge at about -0.2 V, which corresponds sufficiently closely to the potential of the planar bands in *n*-germanium (Fig. 6). Similar agreement is found in 2.5 N $(NH_4)_2S_2O_8$.

At rather more positive potentials than -0.2 to 0.1 V the bands in the *n*-type semiconductor are bent upwards at the interface with the electrolyte, whereas those in the *p*-type semiconductor are bent downwards. If, under these conditions, the cathodic reaction involves electrons from the conduction band, it should be retarded on the *n*-type germanium by the existence of a potential barrier, and on the *p*-type because of hindrances to the diffusion of the minority current carriers. If, however, the cathodic reaction involves valency electrons, it is retarded on the *n*-type by a potential barrier to injected holes, which exists at the electrolyte interface, whereas on the *p*-type it must be quite rapid. Since the polarisation curves on the two types of germanium coincide up to potentials of -0.2 to -0.1 V, it can be concluded that the reaction is retarded in both cases. According to the above, this corresponds to the preferential participation of conduction electrons in the reduction of peroxodisulphate within this range. Below -0.1 to -0.2 V, when the bands curve downwards on both types, a barrier to electrons no longer exists at the boundary of the *n*-type. This results in some acceleration of the reaction of *n*-germanium. However, if the reaction on *p*-germanium involved only conduction electrons, the curves

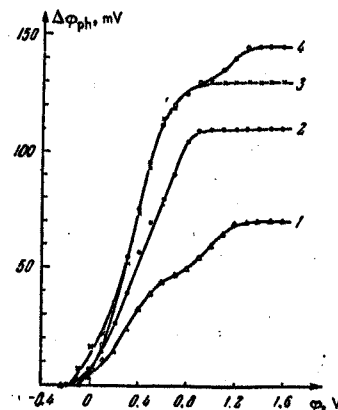


Fig. 6. Effect of concentration of peroxodisulphate ion on photopotential of *n*-type germanium electrode. Concentration of $(NH_4)_2S_2O_8$: 1) 0.02 N; 2) 0.1 N; 3) 0.5 N; 4) 2.5 N.

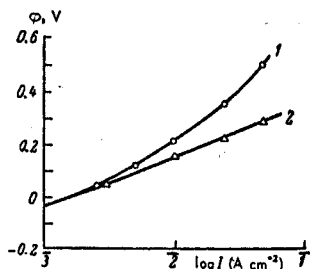


Fig. 7. Reduction of peroxodisulphate ion at a germanium electrode containing a p - n junction in 2 N $(\text{NH}_4)_2\text{S}_2\text{O}_8$ solution: 1) potential across the p -region; 2) potential across the n -region.

for this type should show a limiting electron diffusion current. Since this is not observed (Figs. 3 and 4), it must be assumed that the electrons of the valency band can also take part in the reduction, or else that the rate of surface recombination at the electrolyte interface is very high.

The shift in the potential of the planar bands to more positive values on both p - and n -type germanium can be explained on the basis of Gerischer's mechanism⁴, according to which increasing oxidant concentration in the solution must result in the bands at the boundary of the semiconductor bending downwards. Hence in this case the potential of the planar bands should be shifted to more positive potentials. The above considerations are supported by experiments on a germanium electrode having a p - n junction (Fig. 7). The injection of electrons by means of the p - n junction results in acceleration of the reaction at potentials below -0.1 V.

Frumkin and Florianovich³ showed that the reduction of peroxodisulphate ions at an amalgamated platinum electrode is appreciably accelerated by the addition of cations to the solution. The same phenomenon occurs with a germanium electrode (Fig. 2), but it is less marked. At potentials more negative than -0.1 ± 0.2 V, the surface of the germanium is negatively charged, and therefore the approach of the negative peroxodisulphate ion to the cathode is appreciably facilitated by the formation of cationic bridges and by a decrease in the potential⁵. Measurement of the photopotential of a p -type germanium electrode in a solution to which Na_2SO_4 has been added (Fig. 5) shows that the curvature of the bands is in fact increased, and a greater proportion of the potential drop occurs in the space charge layer in the semiconductor. In conformity with this, the potential drop in the Helmholtz layer diminishes, which according to Ref. 3 results in an acceleration of the reaction.

SUMMARY

1. The type of conduction of germanium appears to affect cathodic reduction of the peroxodisulphate ion only in quite concentrated solutions of the latter.
2. The possibility of both conduction and valency electrons taking part in the electrode process is examined.

3. Addition of an inert electrolyte to the solution accelerates reduction of the peroxodisulphate ion at a germanium electrode.

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NATURE OF FILM ON SURFACE OF SILICON PHOTOCELL DURING ANODIC ETCHING

M. M. Koltun

In the manufacture of nearly all semiconductor devices made of silicon the final operation is a surface treatment involving etching. In the case of silicon rectifier photocells, the mechanism of this process is extremely important, since the nature of the surface film determines to a large extent the optical and electrical characteristics of the photocell, as well as its thermal balance during operation under conditions of strong radiation heating.

As a possible method of final surface treatment of the photocell, an examination has been made of the anodic dissolution of silicon at a current density of $5\text{--}20$ mA cm⁻² in an electrolyte consisting of NH_4F (20% solution), HCl (concentrated), and H_3PO_4 (concentrated) in the proportions 20:2:1, the cathode in this system being of platinum. When the process was carried out in an electrolyte consisting of 5–10% aqueous HF , no substantial difference in the course of the anodic etching was observed compared with the process in the above electrolyte, and it may therefore be assumed that the present conditions coincide with those of experiments described in Refs. 1 and 2.

A black film remains on the surface after the anodic etching of silicon photocells. Since the process is carried out at a current density of about 10 mA cm⁻², it is occurring on the initial portion of Turner's polarisation curves, and dissolution of the silicon should be accompanied by hydrogen evolution. The gas evolved at the anode during etching has been collected and shown by chemical analysis to consist of 99.2% H_2 + 0.8% O_2 . Experiments have been made on the anodic etching of photocells at high current densities, $10\text{--}1200$ mA cm⁻². The processes occurring at the anode have been found to be very similar to those described by Turner: as the current density is increased, the film becomes thicker, acquires a brownish colour,