4. D.Hadzi and N.Sheppard, Proc.Roy.Soc., 216A, 247 (1953).
5. M.S.C.Flett, Trans.Faraday Soc., 44, 767 (1948).
6. W.J.Potts and W.Wright, Analyt.Chem., 28, 1255 (1956).
7. L.J.Bellamy, "The Infrared Spectra of Complex Molecules" (Translated into Russian), Moscow, 1957, p.196.
8. R.C.Gore, R.B.Barnes, and E.Petersen, Analyt.Chem., 21, 382 (1949).
9. G.F.Svatos, C.Curran, and J.V.Quagliano, J.Amer.Chem. Soc., 77, 6159 (1955).
10. D.Segnini, C.Curran, and J.V.Quagliano, Spectrochim.Acta, 16, 540 (1960).
11. J.Lecomte, T.Poberguin, and J.Wyart, J.Phys.(U.S.S.R.), 6, 22 (1945).
12. Y.Kuroda and M.Kubo, J.Phys.Chem., 64, 759 (1960).
13. M.J.Schmelz, T.Miyazawa, S.Mizuschima, T.J.Lane, and J.V.Quagliano, Spectrochim.Acta, 9, 51 (1957).
14. S.Fronæus and R.Larsson, Acta Chem.Scand., 14, 1364 (1960).
15. E.Childers and G.W.Struthers, Analyt.Chem., 27, 737 (1955).
16. F.Cappelina, V.Carossiti, and G.Fabbri, Ann.Chim.(Italy), 50, 615 (1960).
17. J.M.Hunt, M.P.Wisherd, and L.C.Bonham, Analyt.Chem., 22, 1478 (1950).
18. T.Shimanoushi, M.Tsuboi, T.Takenischi, and N.Iwata, Spectrochim.Acta, 16, 1328 (1960).
19. A.A.Glagoleva and A.A.Ferkhmin, Zhur.Obshch.Khim., 29, 1715 (1959).
20. W.H.T.Davison, Chem.and Ind., 408 (1953).
21. J.L.Hales, J.I.Jones, and A.S.Lindsey, J.Chem.Soc., 3145 (1954).
22. D.T.Sawyer and P.J.Paulsen, J.Amer.Chem.Soc., 81, 816 (1959).
23. D.T.Sawyer and J.M.McKinnie, J.Amer.Chem.Soc., 82, 4191 (1960).
24. D.T.Sawyer, Ann.New York, Acad.Sci., 88, 307 (1960).
25. D.H.Busch and J.C.Bailar, J.Amer Chem.Soc., 75, 4574 (1953).
26. J.V.Quagliano, G.F.Svatos, and B.C.Curran, Analyt. Chem., 26, 429 (1954).
27. B.C.Curran, D.N.Sen, S.Mizuschima, and J.V.Quagliano, Analyt.Chem., 26, 429 (1954).
28. C.Duval and J.Lecomte, Bull.Soc.chim.France, 10, 180 (1943).
29. S.Mizuschima, D.N.Sen, B.C.Curran, and J.V.Quagliano, J.Amer.Chem.Soc., 77, 211 (1955).
30. S.Kirschner, J.Amer.Chem.Soc., 78, 2372 (1956).
31. R.H.Gillette, J.Amer.Chem.Soc., 58, 1143 (1936).
32. N.Fuson, M.L.Josien, E.A.Jones, and J.R.Lowson, J.Chem.Phys., 20, 1627 (1952).
33. J.Bellanato and J.R.Barceló, Spectrochim.Acta, 16, 1333 (1960).
34. D.T.Sawyer and P.J.Paulsen, J.Amer.Chem.Soc., 80, 1597 (1958).
35. H.A.Weakliem and J.L.Hoard, J.Amer.Chem.Soc., 81, 549 (1959).
36. M.L.Morris and D.H.Buseh, J.Amer.Chem.Soc., 78, 5178 (1956).
37. D.H.Busch and J.C.Bailar, J.Amer.Chem.Soc., 78, 716 (1956).
38. E.J.Kyuno, J.Chem.Soc.Japan, Pure Chem.Sec., 81, 232 (1960).
39. D.Mücke, G.Geppert, and L.Kipke, J.prakt.Chem., 12, 161 (1961).
40. D.M.Sweeny, C.Curran, and J.V.Quagliano, J.Amer. Chem.Soc., 77, 5508 (1955).
41. A.J.Saraceno, J.Nakagawa, S.Mizuschima, C.Curran, and J.V.Quagliano, J.Amer.Chem.Soc., 80, 5018 (1958).
42. V.Moreno, K.Dimetter, and J.V.Quagliano, Spectrochim. Acta, 16, 1368 (1960).
43. R.Neeb, Z.analyt.Chem., 161, 161 (1958).
44. D.Mücke, G.Geppert, and L.Kipke, J.prakt.Chem., 9, 16 (1959).
45. S.Kirschner and R.Kisling, J.Amer.Chem.Soc., 82, 4171 (1960).
46. M.P.Bernard, Compt.rend., 250, 1830 (1960).
47. W.R.Jencks and J.Carrinolo, Nature, 182, 598 (1958).
48. D.A.Long and W.O.George, Proc.Chem.Soc., 242 (1960).
49. D.A.Long and W.O.George, Trans.Faraday Soc., 56, 1570 (1960).
50. J.D.S.Goulden, Spectrochim.Acta, 15, 657 (1959).
51. J.D.S.Goulden, Spectrochim.Acta, 16, 715 (1960).
52. J.D.S.Goulden, Chem.and Ind., 721 (1960).
53. F.S.Parker, Appl.Spectroscopy, 12, 163 (1958).
54. A.E.Martin, Nature, 166, 474 (1950).
55. J.M.Hunsberger, J.Amer.Chem.Soc., 72, 5626 (1950).
56. R.S.Rassmussen and R.R.Brattain, J.Amer.Chem.Soc., 71, 1053 (1949).
57. R.S.Rassmussen, D.D.Tuncliff, and R.R.Brattain, J.Amer.Chem.Soc., 71, 1068 (1949).
58. H.Yamada, Bull.Chem.Soc.Japan, 32, 1051 (1959).
59. A.Yamamoto and Sh.Kambara, J.Chem.Soc.Japan, Pure Chem.Sec., 80, 97A, 1239 (1959).
60. L.J.Bellamy and R.F.Branch, J.Chem.Soc., 4491 (1954).
61. B.E.Bryant, J.Pariaud, and W.C.Fernelius, J.Org.Chem., 19, 1889 (1954).
62. O.E.Ayers and J.E.Land, J.Phys.Chem., 65, 145 (1961).
63. R.Cardinaud, Bull.Soc.chim.France, 634 (1960).
64. B.L.Shaw and T.H.Simpson, J.Chem.Soc., 5027 (1952); 655 (1955).

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THE ELECTROCHEMISTRY OF SEMICONDUCTORS

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I. INTRODUCTION

Recent advances in semiconductor physics, and the wide application of semiconductor devices in radio circuits have created a new branch of electrochemistry: the electrochemistry of semiconductors. Over 200 papers primarily concerned with the electrochemical properties of silicon and germanium have been published since 1955. In more recent years, electrochemists have become interested in new semiconducting materials, such as intermetallic compounds, silicon carbide, and various oxides and sulphides.

The development of semiconductor electrochemistry owes its origin to the experiments of Brattain and Garrett. In the Soviet Union, Efimov and Erusalimchik were the first to study semiconductor electrochemistry, but it was not long before the researches of workers at the Institute of Electrochemistry and the Institute of Physical Chemistry of the Academy of Sciences of the USSR, and at the Karpov Physicochemical Institute began to show an awareness of semiconductor problems. Theoretical studies of semiconductor electrochemistry in the USSR were started under the initiative of V.G.Levich.

Gerischer, Green, and Dewald are among those who have made significant contribution to the development of basic ideas in semiconductor electrochemistry.

II. THE SEMICONDUCTOR-ELECTROLYTE SYSTEM AT EQUILIBRIUM

1. Potential Distribution at the Phase Boundary

The equilibrium potential of a semiconductor is the potential difference† in the equilibrium system:

metal M | semiconductor | electrolyte | metal M.

This potential does not depend on the position of the Fermi level in the semiconductor [1,2].

The Galvani potential which appears at the phase boundary between semiconductor and electrolyte is distributed over three separate regions: the diffuse part of the double layer in the electrolyte, the Helmholtz double layer, and the semiconductor‡. Its magnitude is a function of the position of the Fermi level in the semiconductor [1,2,6]. It can be shown (see below) that in the absence of surface states§ the potential drop across the first two regions can be made negligibly small in comparison with the change in potential within the semiconductor. We shall also calculate the thickness of the space-charge layer in the semiconductor.

Consider first Poisson's equation in the form

$$\frac{d^2\varphi(x)}{dx^2} = -\frac{4\pi}{\epsilon}\rho(x), \qquad (1)$$

where $\varphi(x)$ is the potential at the point x, $\rho(x)$ is the space-charge density at the same point, and ϵ is the dielectric permittivity of the medium. The x axis is chosen normal to the phase boundary. Let the semiconductor occupy the region $x > 0$, and the electrolyte occupy the region $x < -d_0$, where d_0 is the thickness of the Helmholtz layer (of the order of 10^{-8} cm).

In an n-type semiconductor with fully ionised donor levels the space-charge density is given by the expression

$$\rho(x) = e[-n(x) + p(x) + N_D],$$

where n, p, and N_D are the concentrations of electrons, positive holes, and donors respectively, and e is the absolute value of the electronic charge. At equilibrium, the concentrations of free current carriers in the presence of an electric field in the semiconductor are given by Boltzmann expressions:

$$n(x) = n_\infty e^{\frac{e[\varphi(x)-\varphi_B]}{kT}} \qquad p(x) = p_\infty e^{-\frac{e[\varphi(x)-\varphi_B]}{kT}}. \qquad (2)$$

The symbols n_∞, p_∞, and φ_B refer to the electron concentration, the hole concentration, and the potential at a point far removed from the space-charge region ($x \to \infty$). An adequate, though qualitative, description of the system can be obtained by considering only small changes in potential. We shall assume, in other words, that $e\varphi/kT$ is much less than unity everywhere in the semiconductor. This enables us to neglect higher terms in the series expansions of the exponentials of Eqn. (2), and to express the space-charge density in the form

$$\rho(x) = \left\{-n_\infty\left[1 + \frac{e(\varphi_{(x)} - \varphi_B)}{kT}\right] + p_\infty\left[1 - \frac{e(\varphi_{(x)} - \varphi_B)}{kT}\right] + N_D\right\}e. \qquad (3)$$

At a point well inside the semiconductor there is no space charge, and $-n_\infty + p_\infty + N_D = 0$. In an n-type semiconductor $n_\infty \gg p_\infty$. Under these conditions Eqn. (3) takes the form

$$\rho(x) = -e^2\frac{[\varphi(x) - \varphi_B]}{kT}n_\infty.$$

Poisson's equation [Eqn. (1)] can now be written in the form

$$\frac{d^2\varphi}{dx^2} = \frac{4\pi e^2[\varphi(x) - \varphi_B]n_\infty}{\epsilon_1 kT}, \qquad (4)$$

where ϵ_1 is the dielectric constant of the semiconductor.

Integration of Eqn. (4) gives

$$\left(\frac{d\varphi}{dx}\right)^2 = \frac{4\pi e^2 n_\infty}{\epsilon_1 kT}[\varphi(x) - \varphi_B]^2.$$

The electric field intensity E is related to $d\varphi/dx$ by the expression $E = -d\varphi/dx$. The field at the semiconductor surface ($x = 0$) is therefore given by

$$E_1 = \frac{\varphi_1}{d_1}, \text{ where } d_1 = \sqrt{\frac{\epsilon_1 kT}{4\pi e^2 n_\infty}}. \qquad (5)$$

The quantity d_1 has the dimension of length and is called the Debye length. Expression (5) can be interpreted as

† Equilibrium potentials for reactions at germanium and silicon electrodes in aqueous solutions have been calculated [3-5]. [More recent values can be found in Holmes [160] [Ed. of Translation).]

‡ Contributions to the Galvani potential arising from adsorption of polar molecules of the solvent (or solute) on the electrode will not be considered.

§ The term surface state [7,8] refers to an electronic energy level localised at the semiconductor surface. These levels appear when the crystal lattice is cleaved to generate a surface (Tamm states), when impurities are adsorbed on the surface, and so on.

follows: the potential drop φ_1 in the semiconductor is concentrated in a region of thickness d_1 (the Debye length) such that the ratio of φ_1 to d_1 measures the intensity of the electric field at the surface of the semiconductor, E_1¶.

As stated above, the value of the Galvani potential can be considered as the sum of three terms: $\varphi = \varphi_0 + \varphi_1 + \psi'$, where φ_0, φ_1, and ψ' denote the potential drop in the Helmholtz layer, in the semiconductor, and in the diffuse part of the electrolyte double layer respectively.

The charge density in a uni-univalent electrolyte is given by

$$\rho = (c_+ + c_-)e, \tag{6}$$

where c_+ and c_- denote the number of cations and of anions per cm^3. By simultaneously solving Poisson's equation (1) and Eqn. (6) for the electrolyte we obtain an expression of the same form as Eqn. (5) for the ψ'-potential[10]. Hence we conclude that the diffuse charge distributions in the semiconductor and in the electrolyte are very similar.

Since the electric field in the Helmholtz double layer is assumed to be constant, *i.e.*

$$\varphi_0 = E_0 d_0,$$

we can express the Galvani potential in the form

$$\varphi = E_1 d_1 + E_0 d_0 + E_2 d_2, \tag{7}$$

where E_2 is the electric field in the solution at $x = -d_0$. If we now assume that the semiconductor surface is free from surface states we can use Gauss' theorem and state that the electrostatic induction does not show a discontinuity at the interface:

$$\varepsilon_0 E_0 = \varepsilon_1 E_1 = \varepsilon_2 E_2, \tag{8}$$

where ϵ_0, ϵ_1, and ϵ_2 denote the permittivities of the Helmholtz layer, the semiconductor, and the electrolyte respectively. The ratio of the potential drops can now be found from Eqns. (5) and (8):

$$\frac{\varphi_1}{\psi'} = \frac{d_1 \varepsilon_2}{d_2 \varepsilon_1}, \quad \frac{\varphi_0}{\psi'} = \frac{d_0 \varepsilon_2}{d_2 \varepsilon_0}. \tag{9}$$

Thus we see that, provided a correction for the difference in permittivity of the two media is made, the ratio of the potential drop in the semiconductor to that in the electrolyte is equal to the ratio of the corresponding Debye lengths. The Debye length of a semiconductor of not too high carrier density usually differs from the thickness of the diffuse layer in an electrolyte by several powers of ten. Thus, in a semiconductor of the germanium type with a density of donor levels $N_D = n_\infty = 10^{14}$ cm^{-3}, $\epsilon_1 = 16$, $kT = 4 \times 10^{-14}$ erg at room temperature, and we obtain

$$d_1 \simeq 10^{-4} \text{ cm}. \tag{10}$$

The thickness of the diffuse layer in an electrolyte, d_2, decreases with increase in concentration, and becomes infinitesimally small in very concentrated solutions. In a normal solution ($c = 10^{21}$ ions cm^{-3}, $\epsilon_2 = 80$) the thickness d_2 is approximately

$$d_2 \simeq 10^{-7} \text{ cm}. \tag{11}$$

The thickness of the Helmholtz layer is approximately 10^{-8} cm. Therefore, using Eqns. (9), (10), and (11), we conclude that in sufficiently concentrated solutions the major part of the Galvani potential drop occurs in the semiconductor. Thus we are justified in considering the semiconductor–solution interface as a capacitor in which the two layers of charge have a diffuse structure. The properties of the interface are determined mainly by the distributed space charge in the semiconductor.

The importance of the assumed absence of surface states on the semiconductor needs to be stressed. In the presence of a large density of surface states the potential difference across the Helmholtz layer can account for a large fraction of the drop in Galvani potential. We shall calculate the potential drop in the Helmholtz region for the case of a density of surface states $N_S = 10^{14}$ cm^{-2}, assuming a degree of ionisation of 0.1. From the formula for a plane parallel-plate condenser, the electric field in the Helmholtz layer is given by the following expression (in which $\epsilon_0 = 3$):

$$E_0 = \frac{4\pi N_s e \, 0.1}{\varepsilon_0} \simeq 10^7 \text{ V cm}^{-1}.$$

In this case the potential drop in the Helmholtz double layer accounts for a few tenths of a volt†.

Experimentally it is found that, as in the case of metallic electrodes, the potential drop across the diffuse part of the double layer in the electrolyte (ψ') is appreciable only in extremely dilute solutions. Recent work[11,12] has shown that the ψ'-potential of a germanium electrode in dilute aqueous solutions is of the order of 20–40 mV and decreases rapidly with increase in concentration.

The difference in potential across the space-charge region of the semiconductor (φ_1) can be deduced from measurements of the surface conductivity (σ) of the semiconductor in contact with the solution. Garrett and Brattain[13] have calculated an expression relating σ to φ_1 for a "dry" semiconductor surface‡. Harten[15] concluded, from a detailed study of the experimental and theoretical curves for a silicon electrode, that a potential applied to the silicon–electrolyte interface will appear almost exclusively within the semiconductor. Krotova showed[16], by the same procedure, that some 15 to 50% of the potential of a germanium electrode close to its steady-state potential appears across the Helmholtz layer. The inference is that germanium surfaces, as normally prepared, contain an appreciable density of surface states; adsorption of traces of copper from the solution can account for some of them[17].

In the zinc oxide electrode, on the other hand, practically the whole of the charge is concentrated within the semiconductor; in other words, this material is free from surface states[18–21].

Illumination of a semiconductor electrode affects the potential drop (φ_1) within the semiconductor, and therefore also the electrode potential. Garrett and Brattain[13] point out that the photopotential (*i.e.* the change in electrode potential upon illumination) must vanish when there is no

¶ We have adopted the terminology of semiconductor physics in calling the quantity d_1 the Debye length. The charge density in a double layer was first calculated, however, by Gouy[9].

† The Helmholtz potential drop can also become appreciable if the space charge in the semiconductor is very large[2].

‡ Myamlin[14] has derived an expression for σ at the semiconductor–electrolyte boundary.

space charge in the semiconductor. The electrode potential (measured against some reference electrode) which corresponds to this state of affairs is called the "flat band potential" because there is no electric field to distort the edges of the energy bands near the semiconductor surface. Measurements of photopotential are therefore a very convenient way of obtaining the value of the flat band potential [21,22]. The influence of free electron concentration on the flat band potential of germanium provides further support for the conclusion that in this material the potential drop in the space-charge region of the semiconductor is comparable in magnitude with the potential drop in the Helmholtz layer [23]§.

The flat band potential of germanium is affected by the method of surface preparation and also by the nature of the electrolyte [23]. In germanium with intrinsic conductivity, for example, the flat band potential is 0.5 V in 1 *N* KOH and 0.13 V in 1 *N* H_2SO_4, showing that even in the absence of space charge within the semiconductor, the Helmholtz potential drop (and therefore also the surface charge) is quite appreciable.

The appearance of surface charge on germanium has been discussed [23,25] in terms of oxidation of the surface. Measurements of charging curves have shown [26-30] that germanium surfaces are normally covered with a monolayer of oxide in non-oxidising solutions. Evidently the surface oxide partly dissociates (*e.g.* by forming $GeOOH^-$ groups in an alkaline medium), the degree of dissociation depending on the pH of the solution. The surface charge thus generated is retained even when there is no space charge in the semiconductor (*i.e.* at the flat band potential) and is balanced by the charge of the ions electrostatically adsorbed from the solution. The double layer present on a germanium electrode at its flat band potential has an obvious similarity to the structure of a mercury surface at the point of zero charge under conditions of specific adsorption of, say, bromide ions¶. The flat band potential should not be confused, however, with the zero-charge potential: the latter corresponds to a situation such that both the space charge and the surface charge must vanish.

The surface recombination velocity†, an important property of semiconductor surfaces, is related to the potential drop across the Debye region of the semiconductor [7]. It has been shown that the surface recombination velocity at a semiconductor–electrolyte interface is a function of potential [39-43], solution composition [44-46], and surface preparation. A characteristic, bell-shaped curve is obtained when the surface recombination velocity is plotted against potential: the situation is therefore analogous to the semiconductor–gas interface [47]. The parameters of the curve can be used to characterise the recombination centres by evaluating the ratio of the capture cross-sections for electrons and for holes [39]. Mild anodic etching of the germanium reduces the rate of surface recombination; strong cathodic polarisation, on the other hand, sharply increases it [39,48,49]. It would appear that additional recombination centres are created, under these conditions, as a result of adsorption of the evolved hydrogen or penetration of the hydrogen into the germanium crystal lattice‡.

§ See also Refs. 16 and 24.

¶ The adsorption of various ions on germanium and silicon has been investigated [31-38].

† See p. 215.

‡ It has been suggested [50] that adsorbed hydrogen can give rise to acceptor levels as well as recombination centres.

2. Differential Capacity

We shall now calculate the capacity of a semiconductor electrode. The differential capacity is defined as $C = |dQ/d\varphi|$, where Q is the total charge and φ is the total potential drop. We can write $Q = Q_1 + Q_S$, where Q_1 is the space charge in the semiconductor and Q_S the charge in the surface states. Allowing for the charge in the donor and the acceptor levels, and making use of Eqn. (2), we write Poisson's equation [Eqn. (1)] in the form

$$\frac{d^2\varphi}{dx^2} = -\frac{4\pi}{\varepsilon_1}\rho; \quad \rho = e(N_D - N_A + p - n). \tag{12}$$

where N_A is the concentration of acceptor levels.

The potential φ_B, deep within the semiconductor and far from the space-charge region, is given by the expression

$$N_D - N_A = 2n_i \sinh\frac{e\varphi_B}{kT}, \tag{13}$$

where n_i is the free electron concentration in the pure (intrinsic) semiconductor.

The last equation is readily integrated and leads to an expression for the total charge in the semiconductor, Q_1. The final result is [51]

$$Q_1 = \pm\sqrt{2}\,\frac{\varepsilon_1}{4\pi}\left(\frac{kT}{eL_D}\right)[\sinh U_B(U_B - U_S) - (\cosh U_B - \cosh U_S)]^{1/2}, \tag{14}$$

where

$$L_D = \sqrt{\frac{\varepsilon_1 kT}{8\pi e^2 n_i}}; \quad U_B = \frac{e\varphi_B}{kT}; \quad U_S = \frac{e\varphi_S}{kT}.$$

In these expressions φ_S is the potential at the semiconductor surface, *i.e.* at $x = 0$. Eqn. (14) gives the total space charge in the semiconductor, Q_1, as a function of the potential difference $\varphi_1 = \varphi_S - \varphi_B$ within the semiconductor, and of the number of donor and acceptor levels.

The next step is to allow for the charge trapped in any surface states which may be present on the semiconductor surface. We shall consider a concrete case and assume that donor levels are present on the surface (*i.e.* levels which are positively charged when empty and neutral when occupied by an electron). Let N_S be the number of surface states per unit area. The electronic occupancy of these states is governed by the Fermi distribution:

$$n_S = \frac{N_S}{1 + \exp\frac{E_S - E_F}{kT}},$$

where E_S is the energy level of the surface states and E_F is the Fermi level. The energy difference $E_S - E_F$ is a function of the potential drop in the space-charge region of the semiconductor. The actual energy of an electron in a surface state is given by

$$E_S^0 - e(\varphi_S - \varphi_B),$$

where E_S^0 is the energy level of the surface states in the absence of space charge in the semiconductor. The charge in the surface states is given by the expression

$$Q_S = e(N_S - n_S) = \frac{eN_S}{1 + \exp\frac{E_F - E_S^0 + e(\varphi_S - \varphi_B)}{kT}}. \tag{15}$$

It is convenient to evaluate the quantity $1/C$,

$$\frac{1}{C} = \left|\frac{\partial(\varphi_1 + \varphi_0 + \psi')}{\partial Q}\right| = \left|\frac{\partial(\varphi_S - \varphi_B + \varphi_0 + \psi')}{\partial Q}\right| =$$

$$= \left|\frac{\partial(\varphi_S - \varphi_B)}{\partial Q} + \frac{\partial\varphi_0}{\partial Q} + \frac{\partial\psi'}{\partial Q}\right| = \frac{1}{C_1} + \frac{1}{C_0} + \frac{1}{C_2}, \tag{16}$$

where C_1, C_0, and C_2 are the capacities of the semiconductor (with allowance for surface states), of the Helmholtz layer, and of the diffuse part of the double layer in the electrolyte, respectively. The capacity of the semiconductor, $C_1 = |dQ/d(\varphi_S - \varphi_B)|$, can be calculated[2] by means of Eqns. (12) and (15):

$$C_1 = \frac{\varepsilon_1}{4\pi\sqrt{2}L_D}\frac{|\sinh U_B - \sinh U_S|}{[\sinh U_B(U_B - U_S) - (\cosh U_B - \cosh U_S)]^{1/2}} + \\ + \frac{N_S e^2}{kT}\frac{\exp\left[\frac{E_F - E_S^0 + e(\varphi_S - \varphi_B)}{kT}\right]}{[1 + \exp[E_F - E_S^0 + e(\varphi_S - \varphi_B)]/kT]^2}. \quad (17)$$

The electric field in the Helmholtz part of the double layer is constant, and therefore the capacity C_0 of the Helmholtz region can be calculated from the formula for a parallel-plate condenser:

$$C_0 = \frac{\varepsilon_0}{4\pi d_0} \simeq 10^7 \text{ cm}^{-1} = 10\,\mu\text{F cm}^{-2}.$$

The capacity of the diffuse layer in the electrolyte is given by[10]:

$$C_2 = \frac{\varepsilon_2}{(8\pi^2)^{1/2}}\frac{1}{d_2}\cosh\frac{e\psi'}{2kT}. \quad (18)$$

We have seen that the total capacity of the semiconductor–electrolyte system is determined by the diffuse and the surface charges in the semiconductor, by the Helmholtz layer, and by the diffuse charge in the electrolyte. We shall proceed to evaluate the various contributions to the total capacity for the specific case of an n-type semiconductor ($n_i/N_D \ll 1$) free from surface charge. Under these conditions Eqn. (17) simplifies to

$$C_1 = \frac{\varepsilon_1}{\sqrt{32\pi^2}}\frac{1}{d_1}\left|\frac{1 - e^{\frac{e\varphi_1}{kT}}}{\left[e^{\frac{e\varphi_1}{kT}} - 1 - \frac{e\varphi_1}{kT}\right]^{1/2}}\right|. \quad (19)$$

Terms proportional to n_i/N_D (*i.e.* $\ll 1$) are ignored in the above formula. Green[2] has derived expressions in which these terms are retained. At potentials of the order of $\varphi \simeq kT/e$ the capacities of the semiconductor (C_1) and of the electrolyte (C_2) are found from Eqns. (18) and (19) to be inversely proportional to the appropriate Debye length. Introducing the approximate numerical values of the Debye lengths, and using Eqn. (16), the final result is that the total capacity of the system is controlled by the capacity of the diffuse part of the semiconductor double layer.

Under conditions of appreciable surface charge on the semiconductor (*e.g.* with a density $N_S = 10^{14}$ cm^{-2} of surface states, assumed to be 10% ionised) we have $e^2N_S/kT \simeq$ $\simeq 10^7$ cm^{-1} = 10 μF cm^{-2}. Applying Eqns. (17) and (18) we now find that the capacity of the semiconductor can become comparable with the Helmholtz capacity.

Let us now compute the capacity of a semiconductor electrode without surface states at the flat band potential, *i.e.* with $\varphi_S = \varphi_B$. Applying Eqn. (17), we obtain:

$$C_1 = \frac{\varepsilon_1}{4\pi L_D} = \sqrt{\cosh U_B}\sqrt{\frac{e^2\varepsilon_1}{4\pi kT}}\sqrt[4]{4n_i^2 + (N_D - N_A)^2}. \quad (20)$$

The variation of capacity with potential is shown in Fig. 1. It can be shown[52] that for an intrinsic semiconductor the capacity minimum occurs at the flat band potential. In n-type semiconductors the capacity minimum occurs at more positive potentials, and in p-type semiconductors at more negative potentials, than the flat band potential.

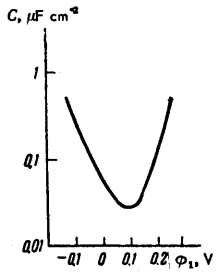


Fig. 1. Variation of differential capacity with potential drop in the space-charge region of the semiconductor, calculated for n-type germanium by Eqn. (17).

Bohnenkamp and Engell's measurements[52,53] of the capacity of the germanium electrode support the ideas outlined above. The capacity *vs.* potential curve shows a minimum, at which, in agreement with theoretical calculations, the capacity is only a few hundredths of a microfarad per cm^2, *i.e.* 2–3 orders of magnitude less than the capacity of a metal electrode. The experimentally observed relationship between capacity and electrode potential fits the theoretical expression for the effect of the potential drop in the space-charge region (φ_1) on the capacity of the electrode, see Eqn. (17)§, whence it can be concluded that changes in φ_1 account for the major part of any change in electrode potential.

The potential of minimum capacity of intrinsic germanium (*i.e.* the flat band potential) varies smoothly with the pH of the solution[52–54]. This confirms our previous conclusions as to the effect of the surface condition on the potential drop in the Helmholtz layer. The capacity minimum of intrinsic germanium lies at 0.5 V (in 1 N KOH solution) and at 0.2–0.3 V (in 1 N H_2SO_4).

Bohnenkamp and Engell's observation of the effect of frequency (between 1 and 160 kc/s) on the capacity and on the potential of minimum capacity is still unexplained¶. The effect may indicate the presence of a frequency-dependent capacity of the type associated with electrode reactions, or alternatively it may be ascribed to surface states with different relaxation times being present on germanium[55].

The capacity of the silicon electrode is somewhat lower than that of the germanium electrode. The electrode capacity is again determined by the space charge in the semiconductor[56–59]. Illumination of the electrode increases the concentration of mobile charges (as a result of the photo-excitation of hole–electron pairs), and the capacity rises towards the characteristic value of metal electrodes (~10 μF cm^{-2}).

§ Eqn. (17) takes no account of the passage of current through the semiconductor–electrolyte interface. It can, however, be applied to germanium because this electrode behaves as an ideally polarisable electrode over a certain range of potentials.

¶ The capacity of a ZnO electrode is independent of frequency[18] between 50 c/s and 100 kc/s.

Efimov and Erusalimchik found a minimum in the capacity of the germanium electrode at a quite different potential: 0.6 V in 0.1 *N* HCl. They call this potential the zero-charge potential of germanium[60]. Their high specific capacity (10–20 μF cm^{-2}), unaffected by the properties of the semiconductor, suggests that these workers were measuring the capacity of the Helmholtz layer. Before each measurement the electrodes were subjected to prolonged cathodic polarisation which, as stated above, can raise the surface recombination velocity very considerably. It would appear that this treatment also makes the semiconductor surface "metal-like". The full significance of Efimov and Erusalimchik's measurements[60], however, is far from clear. These remarks also apply to Efimov and Erusalimchik's[61] anomalously high value for the capacity of a silicon electrode.

III. KINETICS OF ELECTRODE REACTIONS

1. Rate Limitation by the Electrochemical Stage

To give a clearer understanding of the behaviour of the semiconductor–electrolyte interface we shall discuss an electrochemical redox reaction of the type

$$A^+ + e^- \rightleftarrows A. \qquad (21)$$

By analogy with the slow-discharge theory[10] we can write expressions[2,62] for the currents carried by the reduction (i_1) and the oxidation (i_2) reactions:

$$i_1 = k_1 c_{A^+} n(x=0)\, e^{-\frac{\alpha F \Delta\varphi_0}{RT}}, \qquad (22)$$

$$i_2 = k_2 e^{\frac{\beta F \Delta\varphi_0}{RT}}, \qquad (23)$$

where k_1 and k_2 are constants, c_{A^+} is the concentration of A^+ ions in the electrolyte, $n(x = 0)$ is the electron concentration at the plane separating the Helmholtz layer from the semiconductor, F is the Faraday, α and β are constants ($\alpha + \beta = 1$), $\Delta\varphi_0$ is the departure of the potential drop in the Helmholtz part of the double layer from its equilibrium value, and R is the gas constant.

Eqns. (22) and (23) are applicable to reactions, like (21), in which free electrons take part. Eqn. (22) differs from the slow-discharge equation for metallic electrodes[10] by the factor $n(x = 0)$, introduced here because the concentration of free electrons at the semiconductor–electrolyte interface is not constant. This is the fundamental difference between a metallic and a semiconducting electrode surface.

The electron concentration at the interface, $n(x = 0)$, depends on φ_1, the potential drop in the semiconductor, and obeys Boltzmann's distribution law. Applying Eqn. (2) we obtain a new expression for the current:

$$i_1 = k_1 c_{A^+} n_\infty e^{-\frac{e\varphi_1 + \alpha e \Delta\varphi_0}{kT}}. \qquad (24)$$

As we have already pointed out (see p.209) the potential drop in the Helmholtz layer is usually much smaller than the potential drop in the semiconductor. Therefore, ignoring small terms,

$$i_1 = k_1 c_{A^+} n_\infty e^{-\frac{e\varphi_1}{kT}}, \qquad (25)$$

whence

$$\left|\frac{\partial\varphi}{\partial \ln i}\right| = \frac{kT}{e} = \frac{RT}{F}. \qquad (26)$$

If the reaction at the semiconductor surface is of the second order with respect to electrons, Eqn. (22) is modified as follows:

$$i_1 = k_1 c_{A^+} [n(x=0)]^2 e^{-\frac{\alpha F \Delta\varphi_0}{RT}}, \qquad (27)$$

which leads to

$$\left|\frac{\partial\varphi}{\partial \ln i}\right| = \frac{RT}{2F}. \qquad (28)$$

Note that Eqns. (26) and (28) give values of $\partial\varphi/\partial \ln i$ similar to those obtained for metals, but for different reasons.

At high surface charges $\Delta\varphi_0$ becomes greater than φ_1, and the semiconductor electrode tends towards metallic properties. Under these conditions the kinetics of an electrochemical reaction at a semiconductor electrode will be almost indistinguishable from those at a metal electrode.

We shall consider two examples: the anodic dissolution of a semiconductor and the cathodic evolution of hydrogen, the electrochemical stage being assumed to be rate-determining in both cases. Under these conditions the evolution of hydrogen at a germanium electrode is described, irrespective of the conductivity type of the semiconductor, by a Tafel equation with a slope $RT/\alpha F$ of about 0.1–0.12, corresponding to a transfer coefficient of about 0.5.[63–67] The stoichiometric number is $\nu = 1$, the exchange current is $i_0 = 10^{-6}$–10^{-8} A cm^{-2}. Other workers[49,68–70] have reported† $RT/\alpha F = 0.16$, $\alpha = 0.3$, and $i = 10^{-7}$ A cm^{-2}.

Green[2] suggests the following mechanism for the hydrogen evolution reaction by comparing experimental results with $RT/\alpha F$ and ν values calculated for various assumed mechanisms. Hydrogen ion discharge,

$$H^+ + e^- \rightleftarrows H_{ads},$$

occurs relatively fast, and the rate-limiting stage is identified with electrochemical desorption:

$$H^+ + H_{ads} + e^- \rightarrow H_2.$$

The rate of evolution of hydrogen on an *n*-type silicon cathode also increases exponentially with electrode potential: the value of the coefficient $RT/\alpha F$ appears to vary from 0.095[73] to 0.18.[61]

Turning now to the anodic dissolution of germanium, we shall discuss a very characteristic feature of this reaction which stems from the semiconductor nature of germanium: the participation of positive holes. In other words, when a germanium atom goes into solution with a formal valency of +4‡ it gives up some of its electrons to the valence band (see p.215). Brattain and Garrett[76–78] demonstrated that the concentration of holes at the electrode surface depends on the potential§, and that the expression for the reaction overvoltage should include the term $(RT/F)\ln(p/p_0)$, where p and p_0 are the actual and the equilibrium values of the hole concentration at the surface. One method of varying p is to illuminate the electrode: in this way the authors

† The value $RT/\alpha F = 0.23$ has also been reported[71,72].

‡ At very high current densities GeO is formed as well as quadrivalent germanium compounds[74,75].

§ Other workers[79,80] later reached the same conclusion.

were able to show[78] that the current is proportional to the intensity of illumination and therefore that the slow step is kinetically of the first order with respect to holes.

The anodic oxidation of germanium in alkaline solutions consumes hydroxide ions, as shown by the appearance of a limiting current in the polarisation curves obtained in dilute NaOH solutions. The value of the limiting current is determined[81] by the rate of diffusion of OH^- ions to the electrode surface. At still higher potentials the current begins to rise again because a new reaction sets in: the dissolution of germanium, which involves water molecules. Beck and Gerischer[25] studied the effect of alkali concentration on the overvoltage (at currents well below the limiting diffusion current of OH^- ions) and concluded that the slow step in the anodic dissolution of germanium is unimolecular with respect to hydroxide ions. The current–potential relationship is described by a Tafel equation with $\beta = 0.7-0.8$¶ (Fig. 2, curve *1*).

Beck and Gerischer[25] have put forward a reaction mechanism for the anodic dissolution of germanium which accounts for these experimental facts. Germanium atoms at the electrode surface become oxidised with formation of $GeOOH^-$ groups, a process requiring one hydroxide ion and one positive hole. The slow stage is associated with the passage of the $GeOOH^-$ into solution, to give H_2GeO_3.

In the derivation of the kinetic equation (25) we used the Boltzmann distribution to give the electron concentration in the semiconductor during the passage of current. This distribution, however, is strictly applicable only to equilibrium situations, *i.e.* in the absence of external current†. We will now discuss the limitations of this procedure. Consider the expression for the current of electrons in an n-type semiconductor:

$$i = eu_- E(x)n(x) + eD_- \frac{dn(x)}{dx} \cdot \qquad (29)$$

Here u_- and D_- are the mobility and the diffusion coefficient of electrons respectively. The term eu_-En describes the drift current of electrons due to the presence of an electric field; the second term, $eD_-(dn/dx)$, is the diffusion current.

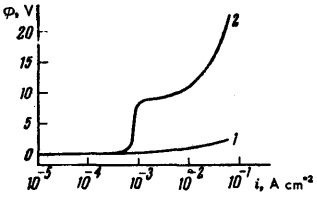


Fig. 2. Polarisation curves for the anodic dissolution of germanium: 1) p-type; 2) n-type.

For $i = 0$, integration of Eqn. (29) leads to the Boltzmann distribution. Even if $i \neq 0$, however, it is possible to have

$$i \ll eu_- En \quad i \ll eD_- \frac{dn}{dx} \cdot$$

so that in Eqn. (29) i becomes negligible in comparison with the much larger terms on the right-hand side. Under these conditions, integration of Eqn. (29) again gives the Boltzmann distribution.

It follows that we can legitimately apply Boltzmann expressions provided that the total current is much smaller than both the drift and the diffusion currents.

But what is the magnitude of expressions of the type eu_-En? Consider, for example, an anodic process at a germanium electrode. We shall assume that the presence of the electrolyte increases the steady-state concentration of holes at the surface, resulting in a Galvani potential of 0.1 V.

The electric field is of the order of φ_1/d_1. Putting $d_1 = 10^{-4}$ cm, we find $E = 10^3$ V cm^{-1}. In germanium of 1 Ω cm resistivity the concentration of free electrons, n_∞, is 2×10^{15} cm^{-3}, and the concentration of holes, p_∞, is 3×10^{11} cm^{-3}. Under these conditions the drift current of holes takes the value

$$eu_+ E p_\infty \simeq 10^{-2} \text{ A cm}^{-2}. \qquad (30)$$

Consequently, hole densities will be accurately described by Boltzmann expressions as long as the anodic current is significantly smaller than the above value†.

These results sometimes prove incorrect when applied to electrodes for which the surface density of carriers is very much less than the carrier density in the uniform bulk of the semiconductor, far from the space-charge region. The concentration of electrons at the interface is given by $n = n_\infty \exp(e\varphi_1/kT)$, and can be very small if the exponential has a low enough value. The Boltzmann distribution ceases to apply when the surface layer of the semiconductor is depleted of free carriers. Two recently published papers have dealt with the calculation of polarisation curves with allowance for a non-equilibrium distribution of carriers.

One of these[82] discusses the current–voltage characteristic of the interface between an electrolyte and an n-type semiconductor. Strong electron depletion at the equilibrium potential is assumed. This produces a surface layer with a low concentration of free carriers, of high electrical resistance, and having rectifying properties‡. When current is passed through such a contact in the forward direction, electrons are injected into it by the field and the resistance decreases. Reverse current, on the other hand, further depletes the contact of electrons and makes its resistance still higher. The donor levels are assumed[82] to be weakly ionised. The rectification at the contact is described by the ratio $\Delta V(+i)/\Delta V(-i)$, where $\Delta V(+i)$ and $\Delta V(-i)$ refer to

¶ Turner finds[26] $RT/\beta F = 0.12$, whence $\beta = 0.5$.

† We are not considering the case of very high charge on the electrode, when the Boltzmann distribution ceases to apply even under equilibrium conditions.

‡ A rectification effect is observed also at metal–solution contacts, *e.g.* when the anodic and the cathodic reaction have widely different overvoltages, or when the rate of one of these reactions is limited by concentration polarisation. We are not concerned here with this type of rectification (although it can occur at semiconducting as well as metallic electrodes), but only with rectification effects specific to the semiconductor–electrolyte interface.

the total potential drop (in the semiconductor and in the Helmholtz layer) under conditions of reverse and forward bias respectively. Its value is given by

$$\frac{\Delta V(+i)}{\Delta V(-i)} = \frac{1}{\beta}\frac{\ln\left(\frac{i}{i_0}\right)(d_1)^2}{d_0 l} \quad (31)$$

where i_0 is the exchange current of the reaction, l is the thickness of the semiconductor. Inserting $l = 10^{-3}$ cm, d_1 (the Debye length) = 10^{-4} cm, $d_0 = 10^{-8}$ cm, and $\ln(i/i_0) = 10$, we find:

$$\frac{\Delta V(+i)}{\Delta V(-i)} = 2\times10^3. \quad (32)$$

Clearly, this system has rectifying properties.

The above treatment[82] has been extended[83] to the case of an n-type semiconductor with current carriers of both types. The authors consider a reaction of type (21), involving carriers of a single type (free electrons). The equilibrium concentrations of electrons and holes in the surface layer are assumed to be much smaller than the concentration of majority carriers (free electrons) in the bulk of the semiconductor. The calculated current–voltage characteristic shows an interesting feature: rectification is present only over a limited range of potentials (of the order of the width of the energy gap) as long as the surface remains depleted of electrons and holes. As soon as the applied field raises the surface density of holes to the level of the bulk electron density a distinctive breakdown phenomenon sets in.

2. Rate Limitation by Minority Carrier Diffusion

We have so far considered systems in which the electrochemical reaction is the slowest step. This happens at low current densities (less than 10^{-4} A cm^{-2} on germanium) or when majority carriers (holes in p-type semiconductors, electrons in n-type semiconductors) are involved in the reaction. If the reaction, however, consumes minority carriers, which are present at low concentration, it is not surprising to find that the current is limited (beyond a certain potential) by the rate of arrival of minority carriers at the electrode surface. We shall discuss the kinetics of reactions of this type, taking the anodic dissolution of germanium as a concrete example[84,85].

As stated above, holes must be supplied to the interface from the bulk of the semiconductor in order that germanium shall dissolve. Part of the reaction current is carried across the phase boundary by free electrons, however, and we may write the ratio of hole to electron current in the form

$$\frac{i_+(x=0)}{i_-(x=0)} = \frac{r}{m}, \quad (33)$$

where r and m are integers. The total current of germanium dissolution is given by

$$i = i_+(x=0) + i_-(x=0) = kp^a e^{\frac{\beta F\Delta\varphi_s}{RT}}, \quad (34)$$

where a is a constant. The germanium surface at its equilibrium potential is assumed to have a high density of excess holes. The current–voltage curve for n-type germanium now takes the form

$$\frac{F\varphi}{RT} = \psi_0 + \frac{1}{\beta}\ln\frac{i}{i_0} + \ln\left(1-\frac{i}{i_{\lim}}\right), \quad (35)$$

where the term ψ_0 includes constants and functions which vary much more slowly than $\ln i$. The value of $i_{\lim}$ is given by

$$i_{\lim} = n_i^2 D_+ e^2 u_- \frac{\rho}{L}\left(1+\frac{m}{r}\right), \quad (36)$$

where n_i is the concentration of free electrons in intrinsic germanium, D_+ is the hole diffusion constant, ρ is the resistivity of the germanium, and L is the hole diffusion length.

Let us examine Eqn. (35) in detail. At currents $i \ll i_{\lim}$ the potential varies with current according to

$$\varphi \simeq \frac{RT}{\beta F}\ln\frac{i}{i_0}, \quad (37)$$

and Tafel's law is obeyed. At currents close to the limiting current the third term of Eqn. (35) becomes predominant:

$$\varphi \simeq \frac{RT}{F}\ln\left(1-\frac{i}{i_{\lim}}\right). \quad (38)$$

When the potential is raised still further a sharply defined limiting current is observed.

An analysis has been given[85] of the distribution of carriers close to the surface. Fig. 3 shows the distribution of holes for currents not very different from the limiting current. In the Debye region ($0 < x < d_1$) the hole density increases rapidly in response to the electric field. Beyond the Debye region there is no field, and the hole concentration falls below its equilibrium value (p_∞) because holes are carried away, across the boundary, by the electrochemical reaction. Under limiting current conditions the hole concentration at the edge of the Debye region effectively vanishes. At points well removed from the boundary the hole density increases, and reaches its equilibrium value (p_∞) at a depth of the order of L, the hole diffusion length. We should note that this distribution is analogous to the distribution of cations in an electrolyte undergoing discharge, at a negatively charged electrode surface under conditions of concentration polarisation: d_1 is equivalent to the thickness of the electrical double layer and L to the thickness of the diffusion layer. The limiting current can be readily evaluated by the following simple arguments. Since the whole of the region $d_1 \leq x < L$ lies beyond the space-charge layer, the supply of holes to the interface occurs mainly by diffusion. The limiting diffusion current of holes will be

$$i_{+\lim} = eD_+\left.\frac{dp}{dx}\right|_{\lim}, \quad (39)$$

where the concentration gradient $\left.\frac{dp}{dx}\right|_{\lim}$ is approximately

$$\left.\frac{dp}{dx}\right|_{\lim} = \frac{p_\infty}{L}. \quad (40)$$

Ignoring recombination in the space-charge region, and using Eqn. (33), we arrive at the total limiting current:

$$i = i_+ + i_- = \left(1+\frac{m}{r}\right)eD_+\frac{p_\infty}{L}. \quad (41)$$

Since the resistivity of the semiconductor is $\rho \simeq 1/en_\infty u_-$, and $p_\infty n_\infty = n_i^2$, Eqn. (36) follows at once. Thus the value of the limiting current is independent of the parameters of the kinetic equation (34), and is also unaffected by any assumptions as to the nature and charge of the surface states.

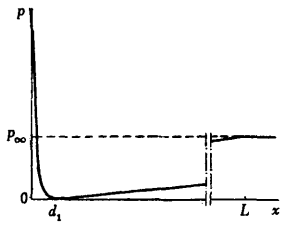


Fig. 3. Hole concentration profile near the surface of *n*-type germanium dissolving anodically under limiting current conditions.

We will now reconsider our assumption that recombination can be neglected, because the limiting dissolution current of germanium can be increased by hole generation in the Debye region. To allow for this effect we use the concept of surface recombination velocity[7], v_S. We shall not attempt to discuss the actual mechanism of hole generation at surface states or in the space-charge region. Following Shockley, we assume a hole generation current i_S proportional to the departure of the hole concentration at the edge of the space-charge region, p_1, from its equilibrium value, p_∞:

$$i_S = ev_S(p_1 - p_\infty). \tag{42}$$

Under limiting current conditions, $p_1 = 0$ and

$$|i_S| = ev_S p_\infty. \tag{43}$$

Therefore the limiting current of positive holes is given by

$$i_{+\lim} = eD_+\frac{p_\infty}{L} + ev_S p_\infty. \tag{44}$$

The hole diffusion length L and the hole lifetime τ are related by the expression $L = (D\tau)^{\frac{1}{2}}$, so that finally

$$i_{+\lim} = ep_\infty\left(\sqrt{\frac{D}{\tau}} + v_S\right). \tag{45}$$

Vdovin *et al.*[85] have discussed one particular generation mechanism, and calculated current–voltage characteristics and limiting current densities on the assumption that hole generation occurs entirely at surface states, and not within the space-charge region.

A limiting current is not observed in the anodic dissolution of *p*-type germanium, because the supply of holes to the surface cannot be diffusion-controlled when holes are the majority carriers.

Curve *2* of Fig. 2 shows an experimental polarisation curve for the anodic dissolution of *n*-type germanium. For current densities up to 10^{-4} A cm^{-2} the current–potential relationship is of the Tafel form (as in the case of *p*-type germanium). At higher potentials the current plateau appears: Flynn[86] states that the value of the limiting current is proportional to the resistivity of the germanium (ρ) and inversely proportional to the hole diffusion length (L), as required by Eqn. (36). It seems clear, therefore, that the diffusion of holes from the bulk of the specimen to its surface constitutes the slow step, and that surface recombination occurs at a negligible rate. The limiting current can be increased by providing more holes at the surface, *e.g.* by illumination of the electrode[78], by hole injection from a *p–n* junction located close to the electrode surface[87], and also by raising the temperature (which raises the bulk concentration of holes in the semiconductor)[88].

Thus in the anodic dissolution of *n*-type germanium the semiconductor–electrolyte boundary behaves very much like a reverse-biased *p–n* junction when *n*-type germanium is subjected to anodic dissolution. Current is carried across the boundary by minority carriers (holes), and the rate at which holes can diffuse from the bulk to the surface of the semiconductor determines the value of the current. The blocking current is therefore diffusional, in contrast to the type of rectification discussed on p. 213–214. Practically the whole of the potential difference applied to the electrode appears across the blocking layer of the semiconductor when limiting current is flowing: only a very small fraction of the potential is dropped across the Helmholtz layer. Since the thickness of the blocking layer is very small (of the same order as the Debye length), the field intensity within the blocking layer can exceed 10^5 V cm^{-1} for a potential of a few volts. Under these conditions hole–electron pair generation can occur by an avalanche process, which produces breakdown in this rectifier-like structure (see curve *2* of Fig. 2). The value of the breakdown voltage depends on the resistivity of the germanium, and can amount to several tens of volts in the case of high-resistivity specimens.

It should be noted that free electrons (as well as holes) can take part in the anodic dissolution of germanium, making the limiting anodic dissolution current larger than the limiting hole diffusion current [see Eqn. (36)]. The ratio $(r + m)/r = \alpha'$ is called the current multiplication coefficient by analogy with the current multiplication which takes place at a transistor collector. Brattain and Garrett[78] devised the following method of measuring α', which was adopted in more recent work[87,89]. The electrode consists of a germanium wafer which is made much thinner than the hole diffusion length (Fig. 4). An annular ohmic contact and a *p–n* junction (prepared, for example, by the indium alloy process) are placed on one side of the wafer; the opposite side is immersed in the electrolyte and acts as the anode. During polarisation of the *p–n* junction in the transmitting direction it serves as a source of holes, which diffuse through the germanium plate and reach the germanium–solution interface, where they participate in the anodic dissolution reaction. The limiting dissolution and hole diffusion currents can be measured simultaneously, and used to calculate α'. Measurements by this (and by other) methods all give[78,89] α' values of the order of 1.65, pointing to the following stoichiometric equation for the anodic dissolution of germanium in alkaline solutions:

$$Ge + 2.4e^+ + 6OH^- \rightarrow GeO_3^{2-} + 1.6e^- + 3H_2O,$$

where e^+ and e^- denote holes and electrons respectively.

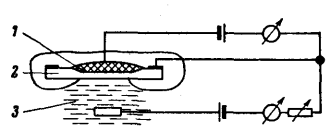


Fig. 4. Electrode for studying the role of free carriers in electrochemical reactions on germanium:
1) *p–n* junction; 2) *n*-type germanium, 3) solution.

The value of α' varies with dissolution conditions (for example, with the current of injected holes)[89-92] and cannot, therefore, be identified with any particular molecular scheme for the reaction. It would appear that when germanium goes into solution electrons have to enter both the valence band (a process which consumes holes) and the conduction band: the ratio of hole current to electron current is a statistical quantity depending on the concentration of holes at the interface, and can be altered by photo-injection of holes or by other means[89,90].

If the thickness of the electrode shown in Fig. 4 is not much greater than the thickness of the space-charge region ($\sim 20\,\mu$, say), the latter can be made to grow and "flood" the entire specimen if a sufficiently high reverse voltage is applied to the p-n junction[93,94]. Under these conditions the hole (and electron) concentrations fall much below their equilibrium values, and the germanium ceases to dissolve anodically as soon as the edge of the depletion region comes into contact with the germanium–electrolyte interface§.[93]

The limiting currents reported in the anodic dissolution of selenium[98] and of n-type cadmium sulphide[99-102] suggest that positive holes may be involved also in these reactions.

The exact mechanism whereby holes participate in the anodic dissolution of the semiconductors is still not clear. Possibly, the rupture of a covalent bond between lattice atoms becomes easier when a hole is localised at a surface atom.

The cathodic evolution of hydrogen at a p-type germanium surface also shows features indicative of minority carrier diffusion from the bulk to the surface of the semiconductor. Brattain and Garrett[78] established that free electrons take part in the reaction, which reaches a limiting rate (~ 1 mA cm^{-2}) at a definite potential. This conclusion was subsequently confirmed by Green[2], Gerischer[49], and Dewald[21]. The limiting diffusion current of electrons is usually less clearly defined than the limiting hole diffusion current: this is because the surface condition of the germanium electrode is gradually altered by the adsorption and penetration of atomic hydrogen into the germanium lattice during the evolution. These phenomena are known (see p.210) to increase the rate of surface generation and recombination of hole–electron pairs[48,86,103,104]. The exact similarity, even at very high current densities, between the polarisation curves for hydrogen evolution from n- and p-type germanium electrodes previously saturated with hydrogen[105] can be explained in the same way. Such electrodes behave like metallic electrodes and effectively lose their semiconductor properties. If the polarisation curve, on the other hand, is determined rapidly, the hydrogen overvoltage on n-type germanium is found to be smaller than on p-type[106].

The observation of Paleolog *et al.*[107] that the rate of hydrogen evolution on p-type germanium, though smaller than on n-type, decreases with increasing germanium resistivity, cannot be reconciled with the views outlined above, which require that the limiting electron current should increase with increase in resistivity — see Eqn. (36). The authors suggest[107] that valence electrons rather than free electrons are concerned in the hydrogen evolution reaction on p-type germanium.

§ A method of producing very thin germanium wafers[95,96] by this technique has been described (see also Albers and Thomas[97]).

All the instances of diffusional control so far outlined apply to electrodes of thickness many times larger than the minority carrier diffusion length, L. Calculations have also been made[108] of the voltage–current characteristic and of the limiting current value for the case of a germanium wafer of thickness $W < L$, in contact with the electrolyte on one side and provided with an ohmic metal contact (which determines the surface recombination velocity v_S) on the other side.

Under these conditions the limiting anodic dissolution current takes the value

$$i_{\lim} = \left(1 + \frac{m}{r}\right) \frac{n_i^2 D_+ e^2 u_- p}{L} \frac{D_+ \sinh \frac{W}{L} + v_S L \cosh \frac{W}{L}}{D_+ \cosh \frac{W}{L} + v_S L \sinh \frac{W}{L}}. \qquad (46)$$

Efimov and Erusalimchik[109,110] have observed, at least qualitatively, a relationship of this type between the limiting current and the resistivity and hole diffusion length of very thin germanium electrodes.

3. Generation of Minority Carriers in the Space-Charge Region

We will now discuss the anodic dissolution of n-type silicon. Eqn. (36) predicts a much smaller limiting dissolution current for silicon than for germanium of comparable resistivity if the dissolution of silicon, like that of germanium, requires holes. The quantity n_i which appears in Eqn. (36) is related to the width of the energy gap, thus:

$$n_i \simeq e^{-\frac{\Delta E}{2kT}}.$$

It follows that n_i, and therefore also the limiting diffusion current of minority carriers, must decrease very rapidly if the width of the forbidden band is increased. Experimentally, however, the dissolution of silicon is found to support currents which are comparable in magnitude to those of germanium anodes. Flynn[86] believes that generation in the space-charge region can provide the holes needed for the dissolution of silicon. One of us[111] has derived a quantitative model for the anodic dissolution of silicon in which allowance is made for generation in the Debye region. The theory of Shockley and Read[112] is used to describe the recombination process. The number of carriers recombining per unit volume and unit time works out to

$$u = \frac{pn - n_i^2}{\tau_{p_0}(n + n_1) + \tau_{n_0}(p + p_1)}, \qquad (47)$$

where

$$n_1 = n_i \exp \frac{E_t - E_i}{kT}; \quad p_1 = n_i \exp \frac{E_i - E_t}{kT}.$$

τ_{p_0} and τ_{n_0} are, respectively, the hole lifetime in a strongly n-type sample and the electron lifetime in a strongly p-type sample containing the same recombination centres as the experimental material; E_t is the energy level of the recombination centres; E_i is the Fermi level of the intrinsic semiconductor. The polarisation curve for silicon dissolution now has the form

$$\varphi = \psi_0 + \frac{RT}{2F}\left(\frac{r}{r+m}\right)^2 \left(\frac{i}{i_1}\right)^2 + \frac{RT}{\beta F} \ln \left|\frac{i}{i_0}\right|. \qquad (48)$$

where ψ_0 is a constant, i_0 is the exchange current of the silicon dissolution reaction, and the current i_1 is given by

$$i_1 = \frac{en_i^2 d_1}{\tau_{p_0} n_1 + \tau_{n_0} p_1}, \qquad (49)$$

d_1 being the Debye length of the semiconductor.

At currents $i < i_1$ the second term in Eqn. (48) varies more slowly than the third, and the current–voltage curve approximates to Tafel's law:

$$\varphi = \frac{RT}{\beta F} \ln \left| \frac{i}{i_0} \right| + \text{const.}$$

When the currents i and i_1 are of similar magnitude the parabolic relationship between current and potential becomes predominant, and the potential increases much faster than with the logarithm of the current. The current i_1 characterises the transition to a region of strongly current-dependent potential. From Eqn. (49), i_1 is proportional to the Debye length, and therefore also to the square root of the silicon resistivity:

$$i_1 \simeq \sqrt{\rho} \ . \qquad (50)$$

Eqn. (49) can be obtained by the following semiquantitative argument. We seen from Eqn. (47) that effective generation can occur where $np \ll n_i^2$; $n < n_1$; $p < p_1$. Under these conditions the rate of hole generation per unit volume will be

$$|U| = \frac{n_i^2}{\tau_{p_0} n_1 + \tau_{n_0} p_1} \ .$$

The total number of holes generated in the Debye region is found by multiplying U by the thickness of the Debye region. This product, multiplied by the electronic charge, gives the corresponding electric current in the form of Eqn. (49).

Theoretical conclusions are in qualitative agreement with experiment. Polarisation curves for the anodic dissolution of n-type silicon, taken in hydrofluoric acid or in hot alkaline solutions (when the silicon surface remains free from passivating films), show two distinct sections. At low anodic polarisations (current density up to 10^{-4} A cm^{-2}) the current–voltage curve is of the Tafel type (as in the case of p-type silicon). At more positive potentials the current increases more slowly with voltage, and approaches a limiting value ($\sim 10^{-3}$ A cm^{-2}). In this region the current density increases with silicon resistivity, as expected from Eqn. (50), and is quite independent of electrode thickness [113,114]. The slower anodic dissolution of n-type silicon as compared with p-type is conclusive proof that holes take part in this reaction.

The value of the current, and its response to changes in temperature and in illumination [115,116], support Flynn's original hypothesis [86] that the rate of anodic dissolution of n-type silicon is determined by field generation of holes in the space-charge region adjacent to the semiconductor surface, and not by the diffusional transport of holes from the bulk to the surface.

Generation of hole–electron pairs in the space-charge region also limits the rate of anodic dissolution of n-type gallium arsenide [117].

The evolution of hydrogen from p-type silicon also appears to be hindered [61,73,118]. Greger concludes [116] that the rate of this reaction is determined by the generation of free electrons in the space-charge region at the silicon–solution interface.

4. The Role of Free and Valence Electrons in Electrochemical Reactions

We have so far been concerned with reactions involving participation of free carriers of a single kind. Thus, Eqn. (22) refers to a reduction reaction in which electrons are transferred from the conduction band to the ions or molecules undergoing reduction. The kinetic equation for an oxidation reaction in which holes are consumed has a similar form. However, we have seen that even in the case of anodic dissolution of germanium free carriers of both kinds may be involved. Dewald [119], Gerischer [120–123], and also Dogonadze and Chizmadzhev [124] have examined quantitatively the relative extents to which the conduction and the valence band can be expected to contribute to the overall charge transfer between the semiconductor and the solution during an electrochemical reaction. We will summarise some of the conclusions of the most recent [124] of the above papers, dealing with the kinetics of redox reactions in which there is no adsorption of reactants and no rupture or deformation of chemical bonds.

The value of the exchange current i_0 (consisting of an electronic component i_0^e and a hole component i_0^p) was calculated by a quantum mechanical method. The ratio of the exchange currents between the solution and the conduction and the valence band is largely controlled by the factor

$$\frac{i_0^e}{i_0^p} \simeq e^{\frac{e\varphi_1}{kT}},$$

where φ_1 is the equilibrium potential drop in the semiconductor, which determines the amount of deformation of the energy bands in the surface region.

The value of φ_1 depends on the redox potential of the system. In strongly oxidising solutions the energy bands are bent upwards at equilibrium ($\varphi_1 < 0$), the surface of the semiconductor becomes richer in holes, and the hole component of the exchange current predominates. In the presence of strong reducing agents ($\varphi_1 > 0$) the conduction band plays the major part in the exchange process.

When the system departs from equilibrium, the anodic current to the conduction band (i_a^e) and the cathodic current from the valence band (i_c^p) are independent of the overvoltage, η, and equal to their respective components of the exchange current, if the potential drop in the Helmholtz layer can be neglected:

$$i_a^e = i_0^e; \quad i_c^p = i_0^p \ . \qquad (51)$$

This result is not unexpected: the overvoltage across the Helmholtz layer, which can accelerate the purely electrochemical stage of the process, is assumed negligible, whereas the concentration of charges taking part in the reaction (valency electrons in the valence band or unfilled levels in the conduction band) is large and independent of the overvoltage. The same conclusion was also reached elsewhere [125].

The anodic current to the valence band and the cathodic current from the conduction band are described by equations similar to Eqn. (25):

$$i_a^p = i_0^p e^{\frac{F\eta}{RT}}; \quad i_c^e = i_0^e e^{-\frac{F\eta}{RT}} \qquad (52)$$

Thus the components of the current at a semiconductor electrode are formally given by Tafel expressions in which

the transfer coefficients α and β are either 1 — Eqn. (51) — or 0 — Eqn. (52). The overall reaction current is the sum of these partial currents:

$$i = i_0^p(e^{\frac{F\eta}{RT}} - 1) + i_0^e(1 - e^{\frac{F\eta}{RT}}).$$

We are particularly interested in the ratio of hole current to electron current, which can be measured experimentally. At not too high overvoltages this ratio is given by:

$$\frac{i_a^p}{i_a^e} \simeq e^{\frac{F(\eta-\varphi_1)}{RT}}.$$

The quantity $\eta - \varphi_1$ is simply the potential of the electrode (except for an unknown additive constant).

The more positive the potential, therefore, the higher is the proportion of electrons from the valence band in reduction reactions and the proportion of holes in oxidation reactions.

At very high overvoltages the concentration of free carriers at the semiconductor surface becomes very large, and the surface tends towards metallic properties. In particular, the potential drop at the interface becomes concentrated mostly in the Helmholtz layer, and the above considerations cease to apply. Gerischer has discussed this system [120].

In their study [126] of the anodic dissolution of n-type germanium in solutions of oxidants (alkaline $K_3Fe(CN)_6$; $FeCl_3$), Gerischer and Beck found that the limiting germanium dissolution current increases with the concentration of the oxidising agent. They explain this phenomenon by postulating that the dissolution reaction is accompanied by some reduction of the oxidising agent, in which electrons from the valence band are involved. Thus the reduction reaction injects holes into the valence band of the semiconductor which can be used by the dissolution reaction. Hole injection has also been observed [127] in alkaline solutions of oxygen, in $KMnO_4$, and in $Ce(SO_4)_3$.

Direct experimental evidence [103], and indirect evidence based on polarisation curves [128,129], favours the hypothesis that valency electrons take part in a number of reductions. Even the formation of GeH_4 on a germanium cathode has been shown [130] to involve electrons from the valence band.

Direct measurements of the relative numbers of free and valence-band electrons taking part in reduction reactions have been carried out [131] with the electrode shown in Fig. 4. The reverse-biased p-n junction was used as a hole collector. Any reduction reaction at the germanium–solution interface which interacts preferentially with the valence band will inject holes into the semiconductor. These are able to diffuse across the thin germanium wafer, and are collected by the p-n junction. The ratio of the increase in collector current to the reduction current is effectively equal to γ, the fraction of valence-band electrons in the reduction current.

The value of γ can vary from close to unity ($KMnO_4$ 0.8–0.9, $K_3Fe(CN)_6$ 0.6–0.8) to zero ($K_2Cr_2O_7$ 0.03–0.08, H_2O_2 0). KI_3 and quinone occupy an intermediate position ($\gamma \sim 0.4$). In qualitative agreement with the theoretical calculation, the contribution of the valence band to the reduction current is found [104,132] to increase at more positive electrode potentials.

Oxidation reactions at a germanium electrode have not been studied in detail. The oxidation of bivalent vanadium ions [133], of oxalate ions, and probably also of iodide ions [134,135] does not involve positive holes. The oxidation current of $K_4Fe(CN)_6$ in acid solution [127] and of ethylide ions in a Ziegler electrolyte [136], on the other hand, passes directly into the valence band.

5. Formation of Oxide Layers on the Electrode Surface

If the products of anodic oxidation are insoluble (or sparingly soluble) the anode surface becomes covered with an adsorbed layer or with a relatively thick oxide film, which often has a very high resistance. Silicon electrodes form an oxide film in most aqueous solutions (except HF and KOH), and in some non-aqueous solutions such as methylacetamide [137–139], liquid ammonia, and sulphur dioxide [140,141].

Surface oxide can bring about passivation of the silicon anode. Electrical breakdown of the film is observed at a high enough potential (~15 V). Beyond this point the anodic current is determined by the semiconductor properties of silicon: thus, on a p-type anode the current increases exponentially with potential, whereas n-type anodes show a limiting current [73]. Under certain conditions a layer of amorphous silicon can form on the surface of a silicon single crystal [142].

Germanium oxide is readily soluble in water, but oxide layers can be produced on germanium anodes by using solutions of nitrates in methylacetamide [138,143]. When indium antimonide is oxidised in KOH solutions, the rate of formation and the properties of the oxide film depend on the crystallographic orientation of the electrode surface [144–147].

On the whole, the properties of oxide layers on silicon, germanium, and indium antimonide are relatively unaffected by the semiconducting properties of the underlying electrode material. The electrochemical behaviour of these films (rectifying properties, photo-effect, etc.) is very similar to that of anodic oxide films on aluminium, tantalum, niobium, and other metals.

IV. CHEMICAL ETCHING

Chemical etching of semiconductor surfaces is a standard operation in the radio industry and in laboratory practice (for metallographic, electronic, and other investigations). Etchants contain, as a rule, an oxidising agent, and also a complexing agent whose function is to combine with the semiconductor ions in solution [148]. The view that chemical etching involves chemical oxidation of the semiconductor followed by dissolution of the resulting oxides is widely held [149–152]. However, careful studies of the etching behaviour of germanium and silicon in solutions of the most important oxidising agents (HNO_3, H_2O_2, etc.) have demonstrated that the process is electrochemical in nature. Two complementary reactions take place on the semiconductor surface at identical rates and at a common potential: an anodic half-reaction (dissolution of the semiconductor) and a cathodic half-reaction (reduction of the oxidising agent). The parameters for these two reactions determine the steady-state potential and the corrosion rate [119,153–156].

In some cases (*e.g.* silicon in alkali solutions [73,157–159]) etching can take place by a purely chemical mechanism¶.

¶ Various aspects of chemical etching are discussed in a recent monograph [160].

A more detailed discussion of the electrochemical mechanism of corrosion seems justified. We have already stressed the fact that holes are required for the anodic dissolution of semiconductors like silicon and germanium. These holes can be generated in the bulk or at the surface of the semiconductor. It follows that the rate of corrosion of an n-type semiconductor cannot exceed the limiting rate of diffusion (or generation) of holes. By the same argument, if the cathodic reaction consumes free electrons the rate of corrosion of a p-type semiconductor is determined by the limiting rate of diffusion or generation of free electrons.

However, an additional source of supply of holes is also available to the anodic process. We have seen that many oxidising agents are reduced at a semiconductor by electrons from the valence band. Holes are thus injected into the semiconductor by the cathodic reaction, and are immediately available to the anodic reaction. Under these conditions the cathodic and the anodic reaction are no longer independent: the rate of corrosion ceases to be a function of the semiconductor properties of the sample and is limited by the diffusion of the oxidising agent in solution or by the electrochemical step. In practice the rate of corrosion of germanium in concentrated solutions of oxidising agents is found to be higher than the limiting current of holes to the electrode surface by several powers of ten. These ideas were first put forward by Gerischer and Beck [126], and were further developed by Dewald [119] and Turner [153].

In this way, many oxidising agents can play a dual role in the corrosion of semiconductors: they undergo the cathodic reaction, and they also provide holes for the anodic reaction. When holes are generated faster than the anodic dissolution can use them up, the excess holes (accompanied by an equal number of electrons) diffuse from the surface into the bulk of the corroding specimen [126,153]. This hole current has been experimentally observed by the method described on p.218. [104,132] This process can raise the bulk (as well as the surface) concentration of holes considerably, and in n-type and in weakly p-type specimens well above the equilibrium value. Since holes are involved in the potential-determining step of the reaction, the steady-state potential (but not the corrosion rate) should be a function of the initial hole concentration in the semiconductor. This effect has been observed by Gerischer and Beck [161] [dissolution of germanium in alkaline $K_3Fe(CN)_6$] and by Turner [153] and Dewald [119] (dissolution of germanium and silicon in HNO_3).

The reduction of nitric acid on germanium consumes electrons from the valence band [119,162]. In concentrated solutions of HNO_3, therefore, germanium and silicon corrode at a high rate (up to 6 A cm^{-2}), independent of the semiconductor properties of these elements. The corrosion rate is determined by the cathodic reaction, and this is found to be autocatalytic. The slow step is the formation of N_2O_4 ($HNO_3 + HNO_2 \rightarrow N_2O_4 + H_2O$), which is further reduced at the electrode. On raising the concentration of HNO_3 the rate of corrosion of germanium increases at first, reaches a maximum for a 6 N solution, and finally decreases as a result of the formation of a thick, passivating film of oxide in very concentrated solutions of HNO_3. Addition of HF destroys the passivity [163,164].

The rate of corrosion of germanium in acid solutions of hydrogen peroxide is decreased by both anodic and cathodic polarisation, suggesting that an electrochemical process is involved. Experimentally measured corrosion rates, however, are significantly higher than the values expected from polarisation curves [154,165]. It is possible that chemical oxidation of germanium by hydrogen peroxide takes place in parallel with the electrochemical corrosion process.

When finished germanium devices, containing various metallic components, are etched in H_2O_2, the anodic and the cathodic reactions become localised in different parts of the device: germanium functions as the anode, copper as the cathode. Indium and tin are usually strongly polarised and have very little effect on the rate of dissolution [166]. Under factory conditions, alkaline solutions of H_2O_2 are used for etching germanium, and the etching rate depends on the concentration of alkali [167].

Germanium is corroded by solutions of electrolytes containing dissolved oxygen, the necessary cathodic reaction being provided by the reduction of O_2. Oxygen concentrations are usually small, and the etching rate (1–10 μA cm^{-2}) is less than the limiting current of minority carriers, and unaffected by semiconductor properties. At low O_2 concentrations the etching rate is determined by the diffusion of oxygen to the reacting surface; at higher concentrations the electrochemical step (reduction of adsorbed oxygen) is rate-limiting. It is important to note that the rate of corrosion depends on the concentration of indifferent electrolyte, and reaches a maximum at a critical concentration (normally less than 0.01 N) which is characteristic of the particular electrolyte. Harvey and Gatos have suggested that the reduction of oxygen is catalysed by anions adsorbed on the germanium surface: when the adsorption of anions becomes excessive, the oxygen coverage of the surface (and therefore also the reaction rate) must decrease [168–170].

Even in the absence of oxidising agents the steady-state potential of germanium and silicon is a corrosion potential [3,171,172]. Measurements carried out under scrupulous conditions of reagent purity have shown that the cathodic process is hydrogen evolution, the anodic process is germanium oxidation to give the brown modification of GeO between pH 0 and pH 4 and the yellow modification between pH 6 and pH 12. GeO_3^{2-} ions may be involved in the potential-determining reaction at pH > 12.5. The measured steady-state potential is practically independent of the germanium conductivity type [3].

When the solution contains salts of metals more noble than silicon or germanium, the cathodic reaction takes the form of electrodeposition of these metals. The so-called "electroless" nickel plating† (followed by heat-treatment) is used to provide ohmic contacts for silicon [173].

The corrosion behaviour of $A^{III}B^{V}$ compounds is very similar to that of germanium. Thus, GaAs corrodes by an electrochemical mechanism [174] in solutions containing dissolved oxygen or $KAu(CN)_2$. In dilute solutions of oxidising agents the rate of corrosion of InSb is determined by diffusion of the oxidant [175,176]; in concentrated solutions, on the other hand, the electrochemical step is rate-determining. The compounds of the $A^{III}B^{V}$ series become passive [177] in concentrated HNO_3.

† Chemical deposition of a nickel phosphide coating by reduction of a nickel salt with hypophosphate (Ed. of Translation).

V. APPLICATION OF ELECTROCHEMICAL METHODS OF SURFACE TREATMENT IN PHYSICOCHEMICAL RESEARCH AND IN SEMICONDUCTOR TECHNOLOGY

No practical device based on a semiconductor–electrolyte system has yet been developed. The Bell Telephone Laboratories have described an internally powered transistor [178], based on the cell

Ge|KOH|Ag_2O, Ag,

and a field triode [179], in which the properties of the ZnO–electrolyte interface are utilised, but neither device has yet been put to practical use‡. Nevertheless, electrochemical methods have found wide application in semiconductor device technology.

Electrochemical (as well as chemical) etching techniques are used to remove mechanically damaged layers from semiconductor surfaces. For silicon and silicon carbide the electrolyte is a solution of hydrofluoric acid [181,182]; for germanium, solutions of sodium or potassium hydroxide have been used [183], and other compounds [184–187]. Germanium can be electropolished in aqueous alkali or in non-aqueous solutions [188–190]. Mixed melts of alkali metal halides have also been used for electropolishing germanium [191]. Silicon is electropolished in solutions of hydrofluoric acid [192–194], gallium arsenide and indium antimonide in a mixture of perchloric acid and acetic anhydride [195]. Current densities are usually between a few hundredths of an ampere and a few amperes per cm^2 of specimen surface. A very smooth surface, with a roughness of less than 50 Å, can be obtained by stirring the electrolyte [196,197].

Electrolytic polishing of germanium in KOH solutions, and also in solutions of SbOCl, produces surfaces of extremely low surface recombination velocity (of the order of 100–200 cm sec^{-1}) [198–200].

The jet-etching method [201] has been developed for the production of shallow depressions a few tens of microns in diameter on germanium wafers in the manufacture of surface-barrier transistors. A thin jet of electrolyte is directed from a glass nozzle on to the sample, which is biased anodically. The cathode is sealed in the wall of the nozzle. Under factory conditions two jets are used, one on each side of the wafer. The electrolyte consists of potassium hydroxide [202–204] or a metallic salt [173–179,182–196,198–208]. The electrolyte should have a much higher resistivity than the germanium. Etching is carried out at a current density of about 1 A cm^{-2}, and the operation is stopped when the remaining thickness of germanium (which is to form the base of the transistor) is no more than a few microns. The method is also suitable for gallium arsenide [209], but a solution of $Cd(CN)_2$ must be used as the electrolyte.

Germanium can also be jet-etched cathodically (formation of GeH_4), but very high current densities are needed (up to 160 A cm^{-2}). [210–212]

Depressions of any desired shape can be etched into germanium by the use of microcathodes situated very close to the surface [213,214]. Sharp points, with a radius of curvature of 1 μ and suitable for field emission experiments, can be prepared by etching germanium in NaOH. [215] Lastly, an electrolytic saw for germanium has been made [216] in which the cathode is a moving, fine tungsten wire.

‡ A recent communication [180] claims that the Si–H_2SO_4 system can form the basis of a radiation detector.

Thick, non-porous oxide films have been grown on germanium and silicon devices, to protect them from the effect of their ambient surroundings, by anodising the semiconductors in a solution of nitrates in methylacetamide [217].

By taking advantage of the rectifying properties of p-n junctions and of the dependence of the rate of dissolution of germanium on the type and magnitude of its conductivity, selective etching of the various parts of a transistor (emitter, base, collector) can be achieved [218–221]. Various techniques for revealing the presence of p-n junctions in germanium single crystals are based on the same principle [222,223]. If, for example, a reverse-biased p-n junction (n region connected to the positive terminal of the battery, p region connected to the negative terminal) is immersed in a dilute solution of alkali, most of the applied potential is dropped across the junction itself and the two regions are at a very different potential. The n region, being anodic, will dissolve, whereas the p region will act as a cathode. If, on the other hand, both sides of the junction are at the same (anodic) potential, and an auxiliary cathode is provided, the p region will dissolve preferentially because at a given overpotential p-type germanium anodes dissolve faster than n-type. The method can also be used to reveal boundaries between regions of the same conductivity type, but of widely different donor (or acceptor) concentration: the so-called l-h junctions [224–226].

It is also possible to delineate p-n junctions in germanium by electrodeposition of copper or gold. A reverse-biased p-n junction immersed in a solution of a copper or gold salt will be electroplated on the p side, since this region is at a cathodic potential [227–231]. If a solution of the dye Methylene Blue is used instead of the salt solution, the dye is reduced (and decolorised) on the p side of the junction [232]. Silicon junctions are not usually polarised from an external battery, but are flooded with light instead [233]: the injected hole–electron pairs are separated by the p-n junction (which behaves in this case as a photodiode), charging the n region negatively and ensuring that metal (gold, copper, or silver) is electrodeposited only on this region [234–237].

Electrodeposition is also used to prepare rectifying and ohmic contacts on silicon and germanium [238–242]. Germanium coatings on other metals can be electrodeposited from non-aqueous electrolytes [243–246]; electrolysis of molten salts gives germanium dendrites suitable for use in semiconductor devices [247].

1. H. Gerischer, in "Semiconductor Electrode Reactions", "Advances in Electrochemistry and Electrochemical Engineering, Vol. 1. Electrochemistry" (Edited by P. Delahay), Interscience, New York, 1961.
2. M. Green in "Modern Aspects of Electrochemistry. No. 2" (Edited by J. O'M. Bockris) (Translated into Russian), Inostr. Lit., 1962.
3. B. Lovreček and J. O'M. Bockris, J. Phys. Chem., 63, 1368 (1959).
4. N. de Zoubov, E. Deltombe, M. Pourbaix, Cebelcor, Rapp. Techn., No. 27, 1 (1955).
5. J. Besson and W. Kunz, Ann. Univ. Saraviensis, 7, 163 (1958).
6. M. Green, J. Chem. Phys., 31, 200 (1959).
7. W. Shockley, "Electrons and Holes in Semiconductors with Application to Transistor Electronics" (Translated into Russian), Inostr. Lit., 1953.
8. W. C. Dunlap, Jnr., "An Introduction to Semiconductors" (Translated into Russian), Inostr. Lit., 1959.
9. G. Gouy, in "The Coagulation of Colloids" (A. I. Rabinovich

and P.S. Vasil'ev, Editors), ONTI, 1936, p. 99.
10. A.N. Frumkin, V.S. Bagotskii, Z.A. Iofa, and B.N. Kabanov, "Kinetika Elektrodnykh Protsessov" (The Kinetics of Electrode Processes), Izd. Moskov. Univ., 1952.
11. W. Eriksen and R. Caines, J. Phys. and Chem. Solids, 14, 87 (1960).
12. M.J. Sparnaaij, Rec. Trav. chim., 79, 950 (1960).
13. C.G.B. Garrett and W.H. Brattain, Phys. Rev., 99, 376 (1955).
14. V.A. Myamlin, Zhur. Fiz. Khim., 35, 2166 (1961) [Russ. J. Phys. Chem., 1066 (1961)].
15. H.U. Harten, Z. Naturforsch., 16a, 459 (1961).
16. M.D. Krotova and Yu.V. Pleskov, Physica status solidi, 2, 411 (1962).
17. P.J. Boddy and W.H. Brattain, J. Electrochem. Soc., 109, 574, 812 (1962).
18. J.F. Dewald, Bell System Tech. J., 34, 615 (1960).
19. J.F. Dewald, J. Phys. and Chem. Solids, 14, 155 (1960).
20. J.F. Dewald, J. Phys. and Chem. Solids, 17, 334 (1961).
21. J.F. Dewald in "The Surface Chemistry of Metals and Semiconductors" (Edited by H.C. Gatos, J.W. Faust, Jnr., and W.J. Lafleur), Wiley, New York, 1960, p. 205.
22. W.H. Brattain, *ibid.*, p. 9.
23. Yu.V. Pleskov and V.A. Tyagai, Dokl. Akad. Nauk SSSR, 141, 1135 (1961).
24. R.M. Lazorenko-Manevich, Dokl. Akad. Nauk SSSR, 144, 1094 (1962).
25. F. Beck and H. Gerischer, Z. Elektrochem., 63, 500 (1959).
26. D.R. Turner, J. Electrochem. Soc., 103, 252 (1956).
27. E.A. Efimov and I.G. Erusalimchik, Dokl. Akad. Nauk SSSR, 134, 1387 (1960).
28. E.A. Efimov and I.G. Erusalimchik, Zhur. Fiz. Khim., 36, 98 (1962) [Russ. J. Phys. Chem., 49 (1962)].
29. W.W. Harvey, S. Sheff, H.C. Gatos, J. Electrochem. Soc., 107, 560 (1960).
30. J. Bardeleben, Z. phys. Chem., (Frankfurt), 17, 39 (1958).
31. V.S. Sotnikov and A.S. Belanovskii, Zhur. Fiz. Khim., 34, 2110 (1960) [Russ. J. Phys. Chem., 1001 (1960)].
32. V.S. Sotnikov and A.S. Belanovskii, Zhur. Fiz. Khim., 35, 509 (1961) [Russ. J. Phys. Chem., 249 (1961)].
33. V.S. Sotnikov and A.S. Belanovskii, Dokl. Akad. Nauk SSSR, 137, 1162 (1961).
34. I.M. Kuleshov and A.F. Naumova, Zhur. Fiz. Khim., 32, 62 (1958).
35. S.P. Wolsky, P.M. Rodriguez, J. Electrochem. Soc., 103, 606 (1956).
36. W.W. Harvey, W.F. LaFleur, and H.C. Gatos, J. Electrochem. Soc., 109, 155 (1962).
37. G.B. Larabee, J. Electrochem. Soc., 108, 1130 (1961).
38. V.S. Sotnikov, A.S. Belanovskii, and F.B. Nikishova, Radiokhimiya, 4, 725 (1962).
39. V.A. Tyagai and Yu.V. Pleskov, Fiz. Tverdogo Tela, 4, 343 (1962).
40. Yu.V. Pleskov, V.A. Tyagai, and M.D. Krotova, "Elektronno--dyrochnye Perekhody v Poluprovodnikakh" (*p-n* Junctions in Semiconductors), Izd. Akad. Nauk. Uzbek. SSR, Tashkent, 1962, p. 249.
41. H.U. Harten, Proc. Inst. Elect. Engineers, 106, Part B, Suppl., 906 (1959).
42. H.U. Harten, J. Phys. and Chem. Solids, 14, 220 (1960).
43. P.P. Konorov and M.N. Kolbin, Fiz. Tverdogo Tela., 3, 1553 (1961).
44. W.W. Harvey and H.C. Gatos, J. Appl. Phys., 29, 1267 (1958).
45. W.W. Harvey, J. Phys. and Chem. Solids, 14, 82 (1960).
46. W.W. Harvey, J. Phys. and Chem. Solids, 65, 1641 (1961).
47. A. Stevenson and R. Keyes, Physica, 20, 1041 (1954).
48. S.G. Ellis, J. Appl. Phys., 28, 1262 (1957).
49. H. Gerischer, Anales real Soc. españ. Fís. Quím., 56B, 535 (1960).
50. R.M. Lazorenko-Manevich, N.A. Aladzhalova, and V.I. Veselovskii, Dokl. Akad. Nauk SSSR, 133, 620 (1960).
51. R.H. Kingston and S.F. Neustadter, J. Appl. Phys., 26, 718 (1955).
52. K. Bohnenkamp and H.-J. Engell, Z. Elektrochem., 61, 1184 (1957).
53. H.-J. Engell and K. Bohnenkamp, in "The Surface Chemistry of Metals and Semiconductors" (Edited by H.C. Gatos, J.W. Faust, Jnr., and W.F. LaFleur), Wiley, New York, 1960, p. 225.
54. M. Hofmann-Perez and H. Gerischer, Z. Elektrochem., 65, 771 (1961).
55. F. Berz, J. Phys. and Chem. Solids, 23, No. 12 (1962).
56. V.I. Zvyagin and A.S. Lyutovich, Izv. Akad. Nauk Uzbek. SSR, Ser. Fiz.-Mat. Nauk, 1, 25 (1959).
57. M. Seipt, Z. Naturforsch., 14a, 926 (1959).
58. K. Böke, Z. Naturforsch., 15a, 550 (1960).
59. D. Tjapkin and S. Joksimović-Tjapkin, Tehnika, 13, Razd. Elektrotehnika, 7, E165 (1958).
60. E.A. Efimov and I.G. Erusalimchik, Zhur. Fiz. Khim., 33 441 (1959)] [Russ. J. Phys. Chem., Abs., 10 (1959)].
61. E.A. Efimov and I.G. Erusalimchik, Dokl. Akad. Nauk SSSR, 124, 609 (1959).
62. Yu.A. Vdovin, V.G. Levich, and V.A. Myamlin, "Nekotorye Voprosy Teoreticheskoi Fiziki" (Problems in Theoretical Physics), Atomizdat, 1958, p. 3.
63. S. Sheff, H.C. Gatos, and S. Zwerdling, Rev. Sci. Instr., 29, 531 (1958).
64. V.R. Erdélyi and M. Green, Nature, 182, 1592 (1958).
65. M. Green, "Solid State Physics in Electronics and Telecommunications", London, 1960, p. 619.
66. M. Green, J. Phys. and Chem. Solids, 14, 77 (1960).
67. I.V. Borovkov, Zhur. Fiz. Khim., 34, 2682 (1960) [Russ. J. Phys. Chem., 1263 (1960)].
68. J. Mieluch, Bul. Acad. polon. Sci., Ser. Sci. chim., geol., geog., 7, 1951 (1959).
69. J. Meiluch, Wiadom. Chem., 13, 679 (1959).
70. D.P. Zosimovich and N.E. Nechaeva, "Trudy 4 Soveshchaniya po Elektrokhimii" (Proceedings of the 4th Electrochemical Conference), Izd. Akad. Nauk SSSR, 1959, p. 541.
71. A.G. Pecherskaya and V.V. Stender, Zhur. Fiz. Khim., 24, 856 (1950).
72. B.N. Zuev, Metallurg. Khim. Prom. Kazakhstana, No. 6 (10), 82 (1960).
73. M. Seipt and H. Fischer, Anales real Soc. espan. Fís. Quím., 56B, 443 (1960).
74. F. Jiřsa, Z. anorg. Chem., 268, 84 (1952).
75. M.N. Platonova, Zhur. Prikl. Khim., 35, 334 (1962).
76. W.H. Brattain and C.G.B. Garrett, Physica, 20, 885 (1954).
77. W.H. Brattain and C.G.B. Garrett, Phys. Rev., 94, 750 (1954).
78. W.H. Brattain and C.G.B. Garrett, Bell. System Tech. J., 34, 129 (1955).
79. G. Déjardin, G. Mesnard, and A. Dolce, Compt. rend., 246, 1016 (1958).
80. M. Balkanski, J. Bardeleben, and A.F. Bogenschutz, J. Chim. phys., 57, 507 (1960).
81. P.F. Schmidt and M. Blomgren, J. Electrochem. Soc., 106, 694 (1959).
82. Yu.A. Vdovin, V.G. Levich, and V.A. Myamlin, Dokl. Akad. Nauk SSSR, 124, 350 (1959).
83. Yu.A. Vdovin, B.M. Grafov, and V.A. Myamlin, Dokl. Akad. Nauk SSSR, 129, 827 (1959).
84. Yu.A. Vdovin, V.G. Levich, and V.A. Myamlin, "Nekotorye Voprosy Teoreticheskoi Fiziki" (Problems in Theoretical Physics), Atomizdat, 1958, p. 10.
85. Yu.A. Vdovin, V.G. Levich, and V.A. Myamlin, Dokl. Akad. Nauk SSSR, 126, 1296 (1959).
86. J.B. Flynn, J. Electrochem. Soc., 105, 715 (1958).

87. S.G.Ellis, Phys.Rev., 100, 1140 (1955).
88. A.Uhlir, Bell System Tech.J., 35, 333 (1956).
89. Yu.V.Pleskov, Dokl.Akad.Nauk SSSR, 132, 1360 (1960).
90. H.Gerischer and F.Beck, Z.phys.Chem.(Frankfurt), 24, 378 (1960).
91. A.A.Yakovleva, T.I.Borisova, and V.I.Veselovskii, Dokl. Akad.Nauk SSSR, 133, 889 (1960).
92. W.W.Harvey, Quarterly Progress Reports, Solid State Research, Lincoln Laboratory, Massachusetts Institute of Technology, Jan., 1961.
93. E.Fröschle, Telefunken-Röhre, No.35, 63 (1958).
94. E.A.Efimov and I.G.Erusalimchik, Dokl.Akad.Nauk SSSR, 122, 632 (1958).
95. E.Fröschle, German P. 1 044 289 (1958); Chem.Zentr.I, 603 (1960).
96. R.H.Rediker and D.E.Sawyer, Proc.Inst.Radio Engineers, 45, 944 (1957).
97. W.A.Albers and J.E.Thomas, Bull.Amer.Phys.Soc., 3, 219 (1958).
98. H.Gobrecht, R.Kuhnkies, and A.Tausend, Z.Elektrochem., 63, 541 (1959).
99. R.Williams, J.Chem.Phys., 32, 1505 (1960).
100. R.Williams, Phys.Rev., 117, 1487 (1960).
101. R.Williams, Phys.Rev., 123, 1645 (1961).
102. E.Maruyama, J.Phys.Soc.Japan, 16, 2341 (1961).
103. Yu.V.Pleskov, Dokl.Akad.Nauk SSSR, 126, 111 (1959).
104. Yu.V.Pleskov, Zhur.Fiz.Khim., 35, 2576 (1961) [Russ.J. Phys.Soc., 1273 (1961)].
105. E.A.Efimov and I.G.Erusalimchik, Zhur.Fiz.Khim., 32, 1967 (1958).
106. E.A.Efimov and I.G.Erusalimchik, Zhur.Fiz.Khim., 34, 2804 (1960) [Russ.J.Phys.Chem. 1318 (1960)].
107. E.N.Paleolog, A.Z.Fedotova, and N.D.Tomashov, Dokl. Akad.Nauk SSSR, 137, 900 (1961).
108. V.A.Myamlin, Dokl.Akad.Nauk SSSR, 140, 870 (1961).
109. E.A.Efimov and I.G.Erusalimchik, Zhur.Fiz.Khim., 32, 413 (1958).
110. E.A.Efimov and I.G.Erusalimchik, Zhur.Fiz.Khim., 32, 1103 (1958).
111. V.A.Myamlin, Dokl.Akad.Nauk SSSR, 139, 1153 (1961).
112. W.Shockley and W.T.Read, Phys.Rev., 87, 835 (1952).
113. E.A.Efimov and I.G.Erusalimchik, Dokl.Akad.Nauk SSSR, 130, 353 (1960).
114. E.A.Efimov and I.G.Erusalimchik, Zhur.Fiz.Khim., 35, 384 (1961) [Russ.J.Phys.Chem., 185 (1961)].
115. P.F.Schmidt and D.A.Keiper, J.Electrochem.Soc., 106, 592 (1959).
116. G.Greger, Naturforsch., 16a, 284 (1961).
117. Yu.V.Pleskov, Dokl.Akad.Nauk SSSR, 143, 1399 (1962).
118. E.N.Paleolog, K.S.Korotkova, and N.D.Tomashov, Dokl. Akad.Nauk SSSR, 133, 170 (1960).
119. J.F.Dewald in "Semiconductors" (Edited by N.B.Hannay), (Translated into Russian), Inostr.Lit., 1962, p.619.
120. H.Gerischer in "The Surface Chemistry of Metals and Semiconductors" (Edited by H.C.Gatos), Wiley, New York, 1960, p.177.
121. H.Gerischer, Z.phys.Chem.(Frankfurt), 26, 223 (1960).
122. H.Gerischer, Z.phys.Chem.(Frankfurt), 27, 48 (1961).
123. H.Gerischer, Ann.Rev.Phys.Chem., 12, 227 (1961).
124. R.R.Dogonadze and Yu.A.Chizmadzhev, Dokl.Akad.Nauk SSSR, 150, No.2 (1963).
125. R.M.Lazorenko-Manevich and S.U.Izidinov, Dokl.Akad. Nauk SSSR, 140, 172 (1961).
126. H.Gerischer and F.Beck, Z.phys.Chem.(Frankfurt), 13, 389 (1957).
127. F.Beck and H.Gerischer, Z.Elektrochem., 63, 943 (1959).
128. Yu.V.Pleskov, Zhur.Fiz.Khim., 35, 2540 (1961) [Russ.J. Phys.Chem., 1256 (1961)].
129. E.N.Paleolog, A.Z.Fedotova, and N.D.Tomashov, Dokl. Akad.Nauk SSSR, 129, 623 (1959).
130. P.F.Schmidt and C.H.Church, J.Electrochem.Soc., 108, 296 (1961).
131. Yu.V.Pleskov, Dokl.Akad.Nauk SSSR, 130, 362 (1960).
132. Yu.V.Pleskov in "Proceedings of the Conference on Semiconductor Physics (Prague)", 1961, p.573.
133. Yu.V.Pleskov and B.N.Kabanov, Dokl.Akad.Nauk SSSR, 123, 884 (1958).
134. E.A.Efimov and I.G.Erusalimchik, Dokl.Akad.Nauk SSSR, 128, 124 (1959).
135. E.A.Efimov and I.G.Erusalimchik, Zhur.Fiz.Khim., 35, 543 (1961) [Russ.J.Phys.Chem., 266 (1961)].
136. R.J.Flannery, D.Trivich, and J.E.Thomas, J.Electrochem.Soc., 106, No.8 (1959); Paper No.66 of the October 1959 Meeting of the Electrochemical Society.
137. P.F.Schmidt, "Halbleiter und Phosphore", Braunschweig, 1958, p.570.
138. P.F.Schmidt and W.Michel, J.Electrochem.Soc., 104, 230 (1957).
139. A.Politycky and E.Fuchs, Z.Naturforsch., 14a, 271 (1959).
140. P.F.Schmidt, J.Appl.Phys., 28, 278 (1957).
141. P.F.Schmidt, F.Huber, and R.F.Schwarz, J.Phys.Chem. and Solids, 15, 270 (1960).
142. A.Gee, J.Electrochem.Soc., 107, 787 (1960).
143. S.Zwerdling and S.Sheff, J.Electrochem.Soc., 107, 338 (1960).
144. J.F.Dewald, J.Electrochem.Soc., 104, 244 (1957).
145. J.D.Venables, and R.M.Broudy, J.Appl.Phys., 30, 1110 (1959).
146. J.D.Venables and R.M.Broudy, J.Electrochem.Soc., 107, 296 (1960).
147. M.C.Lavine, A.J.Rosenberg, and H.C.Gatos, J.Appl. Phys., 29, 1131 (1958).
148. P.Wang, Sylvania Technol., 11, 50 (1958).
149. R.L.Myuller, G.P.Markova, and S.M.Repinskii, Vestnik Leningrad.Univ., Ser.Fiz.Khim., No.3, 106 (1959).
150. R.L.Myuller, A.V.Danilov, G.P.Markova, V.N.Mel'nikov, A.B.Nikol'skii, and S.M.Repinskii, Vestnik Leningrad. Univ., Zhur.Fiz.Khim., No.4, 80 (1960).
151. R.L.Myuller and N.A.Baglai, Vestnik Leningrad.Univ., No.4, 88, (1960).
152. G.S.Supin, Zhur.Prikl.Khim., 32, 478 (1959).
153. D.R.Turner, J.Electrochem.Soc., 107, 810 (1960).
154. E.N.Paleolog, N.D.Tomashov, and A.Z.Fedotova, Zhur. Fiz.Khim., 34, 1027 (1960) [Russ.J.Phys.Chem., 488 (1960)].
155. G.Feuillade, Compt.rend., 252, 1288 (1961).
156. Z.Trousil, Czech.J.Phys., 4, 238 (1954).
157. S.U.Izidinov, T.I.Borisova, and V.I.Veselovskii, Dokl. Akad.Nauk SSSR, 133, 392 (1960).
158. D.L.Klein and D.J.D.Stefan, J.Electrochem.Soc., 109, 37 (1962).
159. S.U.Izidinov, T.I.Borisova, and V.I.Veselovskii, Dokl. Akad.Nauk SSSR, 145, 598 (1962).
160. P.J.Holmes (Editor), "The Electrochemistry of Semiconductors", Academic Press, London–New York, 1962.
161. H.Gerischer and F.Beck, Z.phys.Chem.(Frankfurt), 23, 113 (1960).
162. D.R.Turner, J.Electrochem.Soc., 108, 561 (1961).
163. M.Cretella and H.C.Gatos, J.Electrochem.Soc., 105, 487 (1958).
164. H.Robbins and B.Schwarz, J.Electrochem.Soc., 106, 505 (1959); 107, 108 (1960); 108, 365 (1961).
165. N.D.Tomashov, E.N.Paleolog, and A.Z.Fedotova, Zhur. Fiz.Khim., 34, 833 (1960) [Russ.J.Phys.Chem., 396 (1960)].
166. O.G.Deryagina, E.N.Paleolog, and N.D.Tomashov, Zhur. Fiz.Khim., 34, 1952 (1960) [Russ.J.Phys.Chem., 926 (1960)].

167. R. E. Smolyanskii, V. M. Gurevich, A. M. Raikhlin, and M. I. Lukasevich, Zhur. Tekh. Fiz., 28, 2135 (1958).
168. W. W. Harvey and H. C. Gatos, J. Electrochem. Soc., 105, 654 (1958).
169. H. C. Gatos, W. W. Harvey, and M. C. Lavine, Rev. Met., 55, 1149 (1958).
170. W. W. Harvey and H. C. Gatos, J. Electrochem. Soc., 107, 65 (1960).
171. J. I. Carasso, M. M. Faktor, and H. Holloway, J. Phys. Chem., 65, 2260 (1961).
172. G. Feuillade, Compt. rend., 252, 3958 (1961).
173. M. V. Sullivan and J. H. Eigler, J. Electrochem. Soc., 104, 226 (1957).
174. R. W. Haisty, J. Electrochem. Soc., 108, 790 (1961).
175. R. L. Myuller, G. M. Orlova, and Ts'ui Chin-hua, Zhur. Obshch. Khim., 31, 2457 (1961).
176. R. L. Myuller, G. M. Orlova, and Ts'sui Chin-hua, Zhur. Obshch. Khim., 31, 2461 (1961).
177. H. C. Gatos in "The Surface Chemistry of Metals and Semiconductors" (Edited by H. C. Gatos), Wiley, New York, 1960, p. 381.
178. C. G. B. Garrett and W. H. Brattain, Phys. Rev., 95, 1091 (1954).
179. J. F. Dewald, J. Electrochem. Soc., 105, 105C (1958).
180. Electronics, No. 18, 11 (1961).
181. J. W. Faust, U. S. P. 2 861 931 (1958); Ref. Zhur. Khim., 14201 (1960).
182. J. W. Faust, "Silicon Carbide", Pergamon, Oxford, (1960), p. 403.
183. T. Gabor, J. Appl. Phys., 32, 1361 (1961).
184. A. Amaya, U. S. P. 2 890 159 (1959); Chem. Abs., 53, 16 718b (1959).
185. J. P. McKelvey and R. L Longini, J. Appl. Phys., 25, 634 (1954).
186. B. I. El'kin, "Voprosy Metallurgii i Fiziki Poluprovodnikov" (Problems in Semiconductor Metallurgy and Physics), Izd. Akad. Nauk SSSR, 1957, p. 142.
187. J. I. Carasso and E. A. Speight, B. P. 861 679 (1961).
188. I. Epelboin and M. Froment, J. Phys. Radium, Phys. Appl., Suppl. N 3, 18, 60A (1957).
189. W. Müller and A. Gaudlitz, German P. 823 763 (1951); Chem. Abs., 48, 7461h (1954).
190. B. H. Claussen, B. P. 807 297 (1959); Ref. Zhur., Metallurgiya, 24, 281 (1959).
191. P. Brouillet and I. Epelboin, Compt. rend., 237, 895 (1953).
192. D. R. Turner, J. Electrochem. Soc., 105, 402 (1958).
193. D. R. Turner, U. S. P. 2 871 174 (1959); Ref. Zhur. Khim., 14 203 (1960).
194. L. V. Maslova, O. A. Matveeva, and V. F. Afanas'ev, Fiz. Tverdogo Tela, 3, 2699 (1961).
195. D. R. Turner in "The Surface Chemistry of Metals and Semiconductors" (Edited by H. C. Gatos), Wiley, New York, 1960, p. 285.
196. M. V. Sullivan, R. M. Finne, J. Electrochem. Soc., 107, 191C (1960).
197. M. V. Sullivan, Bell Labs. Record, 39, 107 (1961).
198. G. Wallis and S. Wang, J. Electrochem. Soc., 106, 231 (1959).
199. J. R. Haynes and W. Shockley, Phys. Rev., 81, 835 (1951).
200. T. M. Buck and W. H. Brattain, J. Electrochem. Soc., 102, 636 (1955).
201. J. W. Tiley and R. A. Williams, Proc. Inst. Radio Engineers, 41, 1702 (1953).
202. V. Miles, M. V. Sullivan, and J. H. Eigler, J. Electrochem. Soc., 103, 132 (1956).
203. J. S. Lamming and G. M. Wells, B. P. 806 346 (1958); Ref. Zhur. Khim., 71 992 (1959).
204. J. J. Oberly, Acta Metallurgica, 5, 122 (1957).
205. D. D. Evers, U. S. P. 2 767 137 (1956); Ref. Zhur. Khim., 43 994 (1958).
206. W. E. Bradley, U. S. P. 2 846 346 (1958); Ref. Zhur. Metallurgiya, 266 49 (1959).
207. K. Hoselitz and T. B. Watkins, B. P. 807 042 (1959); Ref. Zhur: Metallurgiya, 26 648 (1959).
208. Z. Dragoun and E. Sipek, Bergakademie, 10, 78 (1958).
209. R. Barrie, F. A. Cunnell, J. T. Edmond, and I. M. Ross, Physica, 20, 1087 (1954).
210. M. Green and P. H. Robinson, J. Electrochem. Soc., 106, 253 (1959).
211. A. Topfer, U. S. P. 2 913 383 (1959).
212. P. F. Schmidt and D. A. Keiper, J. Electrochem. Soc., 105, 49C (1958).
213. A. Uhlir, Rev. Sci. Instr., 26, 965 (1955).
214. Z. Majewski and I. Klamka, Arch. Elektrotechnik, 4, 379 (1955).
215. N. M. Alpatova, Radiotekhnika i Elektronika, 5, 1351 (1960).
216. S. Sheff, J. Electrochem. Soc., 108, 60C (1961).
217. P. F. Schmidt, U. S. P. 2 909 470 (1959); Ref. Zhur. Khim., 1K 175 (1961).
218. I. A. Lesk and R. E. Gonzalez, J. Electrochem. Soc., 105, 469 (1958).
219. O. G. Deryagina, E. N. Paleolog, and N. D. Tomashov, Dokl. Akad. Nauk SSSR, 133, 388 (1960).
220. L. D. Armstrong and P. Kuznetzoff, U. S. P. 2 850 444 (1958); Ref. Zhur. Metallurgiya, 26 654 (1959).
221. F. W. Dehmelt, German P. 1 001 077 (1957); Chem. Abs., 53, 17 730d (1959).
222. E. Billig and J. J. Dowd, Nature, 172, 115 (1953).
223. R. W. Jackson, J. Appl. Phys., 27, 309 (1956).
224. J. I. Pankove, RCA Review, 16, 398 (1955).
225. Yu. V. Pleskov, Khim. Nauka i Prom., 3, 443 (1958).
226. P. A. Iles and P. J. Coppen, Brit. J. Appl. Phys., 11, 177 (1960).
227. G. L. Schnable, U. S. P. 2 893 929 (1959); Chem. Abs., 53, 18 697b (1959).
228. R. Glang, J. Electrochem. Soc., 107, 356 (1960).
229. R. C. Smith, J. Electrochem. Soc., 108, 238 (1961).
230. S. Ratcliffe and J. E. Hughes, Brit. J. Appl. Phys., 12, 193 (1961).
231. T. Masami, J. Phys. Soc. Japan, 15, 2254 (1960).
232. J. T. Law and P. S. Meigs, U. S. P. 2 837 471 (1958); Ref. Zhur. Metallurgiya, 22 169 (1959).
233. G. Feuillade and S. Marette, J. Chem. phys., 58, 418 (1961).
234. S. I. Silverman and D. R. Benn, J. Electrochem. Soc., 105, 107 (1958).
235. P. J. Whoriskey, J. Appl. Phys., 29, 867 (1958).
236. P. A. Iles and P. J. Coppen, J. Appl. Phys., 29, 1514 (1958).
237. D. R. Turner, J. Electrochem. Soc., 106, 701 (1959).
238. E. C. Wurst and E. H. Borneman, J. Appl. Phys., 28, 235 (1957).
239. E. H. Borneman, R. F. Schwarz, and J. J. Stickler, J. Appl. Phys., 26, 1021 (1955).
240. W. Rindner and J. M. Lavine, J. Electrochem. Soc., 108, 869 (1961).
241. D. R. Turner, J. Electrochem. Soc., 106, 786 (1959).
242. R. A. Williams, U. S. P. 2 945 789 (1960); Ref. Zhur. Khim., 16K 190 (1961).
243. G. Szekely, J. Electrochem. Soc., 98, 318 (1951).
244. B. P. 711 065 (1954); Chem. Abs., 48, 13 493i (1954).
245. A. N. Sysoev and N. N. Gavyrina, Zhur. Prikl. Khim., 33, 2001 (1961).
246. R. Sh. Nigmetova, Trudy Inst. Khim. Nauk Akad. Nauk Kazakh., SSR, 6, 178 (1960).
247. J. O'M. Bockris, J. Diaz, and M. Green, Electrochim. Acta, 4, 362 (1961).

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