THE DISTRIBUTION OF POTENTIAL ACROSS THE LOW-INDEX CRYSTAL PLANE OF GERMANIUM CONTACTING AN AQUEOUS SOLUTION

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The Galvani potential difference ($\Delta \phi_{\text{GeASoln}}$) between a germanium electrode and an aqueous solution may be distributed across three adjacent regions, the diffuse space charge regions in the semiconductor and the solution, separated by the Helmholtz region a few Ångströms either side of the interface. It has been shown that the PD across the space charge region of a germanium electrode ($\psi_s$) may be determined by analysis of the interfacial capacity$^1$ or photo voltaic response.$^2$

In an electrolyte solution of relatively large concentration ($\geq M/10$), the diffuse charge on the solution side of the interface (Gouy layer) is suppressed, and, with negligible error in our experiments, it can be assumed that excess charge in the solution is at the plane of closest approach of ions to the electrode surface. In this event, $\Delta \phi_{\text{GeASoln}}$ will occur only in the semiconductor space charge and the Helmholtz regions. Since a change in electrode potential is a change in $\Delta \phi_{\text{GeASoln}}$ if the other Galvani PD's in the circuit remain constant, we may write

$$\Delta V_R = \Delta V_H - \Delta \psi_s,$$

where $V_R$ is the electrode potential, becoming more positive as the electrode is more positively charged with respect to the solution. $V_H$ is the total PD across the Helmholtz region, the sign being such that a dipole with the more positive end directed towards the electrode has a positive value. $\psi_s$ was defined above and, following the sign convention current in surface physics, becomes more negative as free positive charge is added to the semiconductor. Since $\Delta V_R$ and $\psi_s$ (hence $\Delta \psi_s$) are experimentally measurable, $\Delta V_H$ may be deduced.

In this paper, the variation of $\Delta V_H$ with crystal face is examined for the case of germanium (100), (110), and (111) in contact with aqueous solutions of potassium sulfate. It will be shown that the Helmholtz PD is different for the various faces, which will be ascribed to differences in surface potential ($\chi$) arising in several ways.

The experimental arrangements, consisting of germanium electrodes in contact with purified, deoxygenated aqueous electrolytes, along with details of the preparation of electrodes, purification of materials, and experimental methods, have been described previously.$^1$ The solutions were $M/10$ K$_2$SO$_4$, buffered to pH 5.0 with phthalate, pH 7.4 and pH 10.9 with phosphate. Two kinds of electrodes were used. Type (a) were plane-parallel prisms of circular cross section (ca. 1 cm diameter × 1 cm length) with the plane ends oriented to the appropriate crystal face. Electrical contact was made to the upper face with a soldered platinum wire protected from the ambient. These electrodes were suspended with the lower face approximately coinciding with the surface of the solution but with a liquid meniscus encroaching about 1 mm up the sides. Consequently, some fraction of the exposed surface consisted of crystal planes other than that desired. Spreading resistance through the meniscus region in the solution operates to reduce the relative importance of these edges however. Type (b) electrodes were cut so that all exposed faces were of the same crystal plane. This may be achieved for (100) by a cube, (111) by a regular tetrahedron, and (110) by a rhombohedral pyramid, among other forms. The tetrahedron and the pyramid were truncated to facilitate electrical connection. The type (b) electrodes were im-

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mersed to an arbitrary depth. The solution did not contact the truncated plane. The orientation of all faces was correct to 1° determined by optical methods. The interfacial capacity was deduced by analysis of the voltage response to a square, short-duration current pulse.\textsuperscript{1} The photovoltage\textsuperscript{3} was observed in response to a triangular light pulse (35 μsec rise time, 5,700 μsec between pulses). In both cases, the response, not exceeding 10 mV, was observed on an oscilloscope. Electrode potentials were measured on a 2 × 10\textsuperscript{6} Ω impedance voltmeter versus a saturated calomel electrode. Polarization of the electrode was carried out with a constant current source. The total polarization was always anodic.

Results.—The form of the data depends on the method of polarization as illustrated in Figure 1. If changes in $V_E$ were equal to changes in $\psi_s$, the data should have the form denoted by the theoretical curves. The experimental data generally exhibit a greater swing of potential than indicated by theory. We have interpreted\textsuperscript{1, 4} this as being due to a variation in magnitude of the Helmholtz dipole with anodic current density over the range zero to ca. 10 μA cm\textsuperscript{-2}.

Rapid polarization (i.e., reading the immediately established values of $V_E$ and capacity) tends to minimize the changes in Helmholtz dipole, and data taken in this way generally fit theory over some considerable part of their extent as indicated in Figure 1 for rapid polarization superimposed on two background conditions, zero and 45 μA cm\textsuperscript{-2} anodic. The separation on the $V_E$ scale of the two theoretical curves represents the difference in Helmholtz dipole between these conditions.

When the system is allowed to come to a final steady state at each polarizing current, then at current densities greater than 10 μA cm\textsuperscript{-2} the data correspond with rapid polarization. At current densities in the range zero to 10 μA cm\textsuperscript{-2}, the
Helmholtz dipole is changing and the data show a transition between the two extreme values of the dipole. This is equivalent to a different position for the theoretical curve, between the limits indicated in Figure 1, for each current density in this range. Rapid polarization superimposed on any steady anodic current in the range zero–10 $\mu$A cm$^{-2}$ yields data which, over part of their extent, agree with a theoretical curve lying between the limits denoted in Figure 1. Both methods of polarization were used where appropriate. When it was desired to make an accurate comparison of the capacity and photovoltage under identical conditions, steady-state polarization was used. Rapid polarization data yielded information on the variation of Helmholtz dipole with crystal face and with steady polarization. Capacity data similar to that in Figure 1 were obtained for both $n$- and $p$-type samples and for all three low-index crystal planes.

The photovoltage was measured only under steady-state polarization. An example is shown in Figure 2 for the (111) surface. These data were taken simultaneously with the corresponding capacity data in Figure 1. By comparing the capacity data with theory, it is possible to deduce the quantity $(\psi_s - (kT/e)\ln\lambda)$, which is the potential across the semiconductor space charge reduced by a term which varies with the doping ($\lambda = p/n_i$), where $p$ is the bulk hole concentration and $n_i$ is the bulk electron (or hole) concentration in intrinsic germanium. In Figure 2, the measured photovoltage is plotted versus $(\psi_s - (kT/e)\ln\lambda)$ deduced from the data in Figure 1, and comparison is made with theory.\textsuperscript{3} The data indi-
cate that the simple Poisson-Boltzmann theory for the capacity and photovoltage in the semiconductor space charge applies consistently to the (111) surface, as we have previously shown for (100). Both the capacity and the photovoltage may, by comparison with theory, be used to deduce \((\psi_s - (kT/e) \ln \lambda)\) as implied by Figure 2. The result of this process is shown in Figure 3 for the three low-index planes.

![Figure 3](image)

The data for the (110) plane have been displaced downwards by 50 mV in order to separate them clearly from the (100). The (110) data are in fact between the (100) and (111). Several things are to be noted from these data. First, the estimates of \((\psi_s - (kT/e) \ln \lambda)\) versus \(V_k\), for any one crystal face, agree independently of doping or of the method of measurement, confirming the assumption that the data may be interpreted as a simple semiconductor space-charge effect. Second, the different crystal faces yield distinctly different results.

Analysis of the data in Figure 3 is complicated by the fact that since they were obtained under steady-state polarization there is a variable Helmholtz dipole over part of the range. An analysis of some rapid polarization capacity measurements is shown in Figure 4. Discussion is deferred to a later section. Similar data were taken at pH 5.0 and 10.9. The photovoltage data and some of the capacity data were taken on electrodes of type (a). The remainder of the capacity data were on electrodes of type (b). The two types of electrode agreed within the experimental error. Thus, it is evident that the edge effects on type (a) electrodes are negligible. The data will be discussed without distinction of electrode type.

**Discussion.**—The electrode potential is the sum of the Galvani PD’s across all the interfaces in the circuit

\[
M' | Ge | Soln | M^*,
\]

where \(M'\) is an ohmic metal contact to the germanium, and, for brevity, we take the same metal as a reference electrode \(M^*\). Hence,

\[
V_k = M' \Delta Ge \phi + Ge \Delta Soln \phi + Soln \Delta M^* \phi.
\]
We will consider changes in $V_E$ with moderate polarization, crystal face, and semiconductor Fermi level only. The reference electrode is unaffected by these changes; hence,

$$\Delta V_E = \Delta M' \Delta \phi + \Delta \phi^{\text{Ge}} \Delta \phi.$$  (4)

The $\phi$ across the ohmic metal-semiconductor contact will vary only with semiconductor Fermi level

$$\Delta M' \Delta \phi^{\text{Ge}} = (kT/e) \Delta \ln \lambda,$$  (5)

and hence, $\Delta V_E = (kT/e) \Delta \ln \lambda + \Delta (\phi^{\text{Soln}} - \phi^{\text{Ge}})$, and since $\phi^{\text{soln}} = \phi^{\text{soln}} + \chi^{\text{soln}}$, $\Delta V_E = (kT/e) \Delta \ln \lambda - \Delta \psi - \Delta \chi^{\text{soln}}(i\bar{j}k) + \Delta \psi^{\text{soln}} + \Delta \chi^{\text{soln}}(i\bar{j}k).$  (6)

(The conventional $\phi$ is used instead of $\phi^{\text{Ge}}$.)

The two surface potentials are considered to be orientation dependent, $\chi^{\text{soln}}$ for the obvious reason of different arrangements of atoms and bonds in each surface and $\chi^{\text{soln}}$ since the degree of orientation of solvent molecules is likely to be influenced by the geometry of the electrode surface. The term $\Delta \psi^{\text{soln}}$ will be very small compared with $\Delta \psi$, since the capacity on the solution side of the interface is some two orders of magnitude larger than that in the semiconductor space charge region. We then have

$$\Delta V_E(\phi_0 - (kT/e) \ln \lambda) = \text{constant} = \Delta V_H = -\Delta \chi^{\text{Ge}}(i\bar{j}k) + \Delta \chi^{\text{soln}}(i\bar{j}k).$$  (7)

This equation will be subsequently used in the analysis of the data.

Some general properties of Figure 4 are pertinent. We have previously derived the expression

$$\Delta V_E = \Delta V_H - \Delta \psi_s$$  (1)

and, since for a particular electrode $\lambda$ is constant, then $\Delta (\psi_s - (kT/e) \ln \lambda) = \Delta \psi_s$. A line of slope equal to minus unity implies $\Delta V_E = -\Delta \psi_s$ whence, from (1), $\Delta V_H = 0$. Consequently, the 45° slope lines in Figure 4 represent conditions of constant Helmholtz dipole. Departure of the data from these lines at increasing values of
polarization represents change in Helmholtz dipole. A line parallel with the $V_E$ axis represents $\Delta \psi_s = 0$ and, from (1), $\Delta V_E = \Delta V_H$. That is, the points of intersection on the $V_E$ scale of such a line with the data lines of Figure 4 represent changes in Helmholtz dipole only.

We may now interpret Figure 4 in terms of changes of Helmholtz dipole for the various crystal faces. There are two situations depicted; rapid polarization superimposed on steady anodic currents of zero and 45 $\mu$A cm$^{-2}$. The 45 $\mu$A cm$^{-2}$ data are identical$^1$ with any obtained in the range 10–200 $\mu$A cm$^{-2}$ and will be referred to simply as $>10$ $\mu$A cm$^{-2}$ data. The value $(\psi_s - (kT/e) \ln \lambda) = 0$ is chosen arbitrarily as a standard value, and the linear portions of the data in Figure 4 extrapolated to this value. The corresponding electrode potentials are tabulated below.

<table>
<thead>
<tr>
<th>Crystal face</th>
<th>(100)</th>
<th>(110)</th>
<th>(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>zero current</td>
<td>$-0.538$</td>
<td>$-0.497$</td>
<td>$-0.446$</td>
</tr>
<tr>
<td>$&gt;10$ $\mu$A cm$^{-2}$</td>
<td>$-0.358$</td>
<td>$-0.337$</td>
<td>$-0.297$</td>
</tr>
</tbody>
</table>

The differences between these electrode potentials must represent differences in Helmholtz dipole. Data at pH 5.0 and 10.9 which are plotted in Figure 5 show electrode potential differences of similar magnitude. The data for the three crystal faces approximate to the slope $\Delta V_H/\Delta \mathrm{pH} = RT/F$ previously demonstrated for the (100) face.$^4,^5$ At pH 5.0, the $>10$ $\mu$A cm$^{-2}$ data of the type shown in Figure 4 do not have a slope of minus unity. Both $n$- and $p$-type electrodes give a slope of $-0.7$. The reason is not known, but the data suggest that in this case the relaxation of the Helmholtz dipole on change in polarization occurs more rapidly than the data can be obtained.

We have previously interpreted the $\Delta V_H$ between zero and $>10$ $\mu$A cm$^{-2}$ as being due to adsorption of oriented water molecules on the electrode surface at the lower current densities.$^4$ This interpretation is tentative and we have no further supporting evidence to offer at the present time. In this view, the differences between
the electrode potentials for zero and >10 μa cm⁻² for any crystal face in the above table represent the additional dipole due to water molecules oriented at that face. It is assumed that at >10 μa cm⁻² the oriented layer is completely disrupted due to the removal and replenishment of adsorption sites by anodic dissolution of the electrode surface being considerably greater than the rate of adsorption of water molecules. We will then tentatively identify Δχ^Soln(ijk) from equation (7) with ΔV'_F going from zero to >10 μa cm⁻² for any crystal face on the assumption that Δχ^Ge(ijk) does not vary with polarization. Then from the above table, Δχ^Soln(100) = 0.180 V, Δχ^Soln(110) = 0.160 V, and Δχ^Soln(111) = 0.149 V. It is not necessary that we identify this quantity with the adsorbed water dipole, but this does seem the most reasonable explanation at present.

On the assumption of plane atomic surfaces with all available "dangling bonds" satisfied by hydroxyl groups, the relative densities of the groups are easily shown to be

\[ \sigma^{(100)}(1 \text{ OH}/8\text{Å}^2) > \sigma^{(110)}(1 \text{ OH}/11.3\text{Å}^2) > \sigma^{(111)}(1 \text{ OH}/13.8\text{Å}^2). \] (8)

Thus, the magnitude of Δχ^Soln(ijk) varies in the same order as σ(ijk), which is not in discord with the interpretation of the former being due to the presence of water molecules oriented by interaction with the surface hydroxyls; thus,

\[ \text{H} \quad \text{Ge-OH} \quad \text{H} \quad \text{O} \]

with densities equal to or proportional to those for hydroxyl groups shown in the inequality (8). On the assumption that χ^Soln(ijk) = 0 for currents >10 μa cm⁻², ΔV'_F for different faces under this same condition equals Δχ^Ge for these faces. (χ^Soln(ijk) is taken to be that part of the surface potential of the solution that is influenced by the presence of the electrode surface, e.g., oriented water molecules. Any remaining contribution to the total surface potential of the solution is taken to be constant with crystal face and hence disappears from ΔV'_F between crystal faces at >10 μa cm⁻².) Taking χ^Ge(100) as an arbitrary zero, we see from the table that χ^Ge(110) - χ^Ge(100) = 0.021 V and χ^Ge(111) - χ^Ge(100) = 0.061 V. The positive end of this dipole is towards the electrode since at constant (ψ^s - (kT/e) lnλ) the V_F for (111) is more positive than for the other faces (see Fig. 4).

The nature of χ^Ge(ijk) is not simple. For a surface cleaned in high vacuum, it could be interpreted simply as the dipole arising from the relative displacement of the electron cloud and the germanium nuclei by "spreading" and "smoothing." (χ^Ge(110) - χ^Ge(100) etc., would be measured as work function differences on the various faces.) In our experiment, the lattice almost certainly terminates with covalently bonded hydroxyl groups, the presence of which will considerably modify the "clean" surface potentials.

Consideration must also be given to the formation of "dissociation double layer" due to the ionization of the surface hydroxyl groups.4, 6 A pd is set up between the plane of the hydroxyl groups and the bulk of the solution due to the ionization equilibrium, e.g., for (111).

\[ \text{Ge-OH} + \text{H}_2\text{O} \rightleftharpoons \text{Ge-O}^- + \text{H}_3\text{O}^+. \] (10)
The contribution to the Helmholtz PD, if the fractional ionization is small is given by

\[ V'_H = \text{const} + \mu_{H'}^{0} + (RT/F) \text{pH}, \]

where \( \mu_{H'}^{0} \) is the standard electrochemical potential of protons in the un-ionized surface hydroxyl groups. This may not be constant with crystal face (i.e., the equilibrium constant describing equation (10) may vary with crystal face), and hence \( V'_H \) may not have the same absolute magnitude in each case. \( \Delta V'_H / \Delta \text{pH} \) should still equal \( RT/F \) for all faces as confirmed in Figure 5. With this possibility of the unknown variation of \( V'_H \) with crystal face we cannot compare \( AX_{\text{Ge}}(i_\text{u}) \) with work function differences measured on germanium surfaces in vacuum.\(^8\) The resolution of this problem might be approached by means of experiments (e.g., contact angle) which are sensitive to the surface charge density. At \( \psi_s = 0 \), in the absence of charged surface states, the surface charge is entirely due to the ionized hydroxyl groups. This will be negative, and the corresponding counter charge in the solution positive. If the point of zero charge in the solution can be detected with sufficient accuracy and the system polarized to this point, then from the change in \( \psi_s \) the change in charge in the semiconductor space-charge layer may be calculated. This will be equal to the positive counter charge that originally existed in the solution at \( \psi_s = 0 \).

**Conclusions.**—The distribution of potential across the (100), (110), and (111) planes of germanium in contact with aqueous solution has been investigated by measurement of interfacial capacity and photovoltaic response. The (110) and (111) obey the simple Poisson-Boltzmann space charge approximation\(^3\) as previously indicated for (100).\(^1\)\(^2\) The variation of Helmholtz PD with pH is approximately \( RT/F \) for all three faces. The total surface potential between the two phases is complex, but some separation has been attempted.


