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TUNNELING IN IV-VI COMPOUNDS

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Résumé. — Des jonctions tunnel entre métal, isolant et composé semi-conducteur IV-VI ont été réalisées pour du matériau semi-conducteur monocristallin et polycristallin.
Les caractéristiques courant-tension et les courbes de conductance ont été relevées en fonction de la température et du champ magnétique. Les résultats expérimentaux ont été interprétés par une théorie conventionnelle de l'effet tunnel et ont donné des renseignements sur les énergies de Fermi, les bandes interdites, leur variation avec la température, les travaux de sortie et les affinités électroniques.
De plus, des renseignements ont été obtenus sur des niveaux profonds avec de forts facteurs $g$ anisotropes, qui existent dans la bande interdite de certains semi-conducteurs.

Abstract. — Metal-insulator-IV-VI compound semiconductor tunnel junctions were formed for both single and polycrystalline semiconductor material. I-V and conductance characteristics were taken as a function of temperature, and magnetic field. The experimental results were interpreted in terms of a conventional tunneling theory, and yielded information on Fermi energies, band gaps, temperature dependence of band gaps, work functions and electron affinities. Also obtained was information on deep levels which have large anisotropic $g$ values and exist within the band gap of some of the semiconductors.

1. Introduction. — The development of tunneling spectroscopy in Bi [1] and Bi-Sb alloys [2] provided a powerful tool for the study of the properties of IV-VI compounds. Two techniques have been employed to fabricate tunnel junctions with the compounds. The first involves depositing the material under investigation over an oxidized metallic layer. This results in polycrystalline material. It has proved possible to deposit on $\text{Al}_2\text{O}_3$, films of SnTe and GeTe whose electrical, X-ray and optical properties are comparable to bulk properties. In general, the insulating layer used in this technique has a high dielectric breakdown strength such that sufficiently high voltages may be applied to investigate barrier heights, etc.

The second technique involves the introduction of a thin insulating layer on a single crystal and then evaporating a metal counter electrode to complete the tunnel junctions. Junctions of $\text{PbTe}$ and PbSe were fabricated by this technique by suitable evaporation of $\text{Al}_2\text{O}_3$ on epitaxially grown single crystals. Results for both techniques are illustrated in figure 1 for Bi. In order to observe certain material properties, single crystals are required, such that fine structure is often absent in polycrystalline tunnel junctions.

2. Tunneling theory for SnTe and GeTe junctions.

Although we will not discuss in great detail the theory, which was done previously, [3] we feel it is important to point out the assumptions involved and to present the predictions from the model solved. Calculations of current-voltage characteristics for the MIS (metal-insulator-semiconductor) junctions were done within the framework of the WKB approximation, assuming conservation of energy \( E \) and transverse momentum \( k_t \). Referring to figure 2,

\[ J = \left( \frac{q}{4 \pi^2 \hbar} \right) \int e^{-\lambda} \left[ f_1(E) - f_2(E) \right] dE, \]

where \( E_t \) and \( E \) are now the transverse and total kinetic energy of the electrons in the semiconductor. The limits of integration for \( E_t \) are 0 and \( E \) and for \( E \), between the two Fermi energies. By referring to the figure and recalling the definition of \( \lambda \), we can express

\[ \lambda = \left[ 2(2m)^{1/2} / h \right] \int \left[ \phi(x) - F_p + E + E_i \right]^{1/2} dx \]

for electrons in the valence band of the semiconductor, and

\[ \lambda = \left[ 2(2m)^{1/2} / h \right] \int \left[ \phi(x) - F_p - E_s - E - E_i \right]^{1/2} dx \]

for the electrons in the conduction band. The applied voltage is contained in the term \( \phi(x) \), where the Fermi level in the semiconductor is taken as \( V = 0 \).

It is possible to obtain analytical expressions for the current density by the use of the effective barrier approach. This procedure involves expanding the term in the bracket in equations 3 or 4 around its mean value [5, 6]. When the higher order terms are neglected, this procedure effectively replaces the integral by the product of its mean value and the tunneling path. This introduces an insignificant error for the case of a trapezoidal barrier [6, 7].

For voltages such that \( F_p < qV < F_p + E_g \), the electrons in the metal in the energy range \( qV - F_p \) cannot tunnel as they are opposite the forbidden gap in the semiconductor. The electrons within \( F_p \) tunnel, but with a lower probability as the barrier is increased as the voltage is raised. This gives rise to a negative resistance region [8]. It is found that the current begins to decrease at a voltage somewhat smaller than the Fermi energy \( F_p \). This voltage \( V_{\text{max}} \), when \( qV_{\text{max}} \ll \phi_1 + \phi_2 \), is given by [3]

\[ qV_{\text{max}} = F_p - 0.57(\phi_1 + \phi_2)^{1/2}/\alpha \]

where \( \alpha \) is defined by \( 2(2m)^{1/2} / h \) and \( d \) is the tunneling length. It is this voltage that is used to determine the Fermi energy from the current-voltage curves.

With the voltage further increased such that

\[ qV > F_p + E_g, \]
electrons begin to tunnel into the conduction band of the semiconductor as well as into the valence band. As the conduction band current increases very rapidly,
the observed current rise can be compared with the theoretical calculations based on eq. (3) to determine $F_p + E_g$.

When the applied voltage is greater than $\varphi_2$ in the forward direction or $\varphi_1$ in the reverse direction, the tunneling barrier is no longer trapezoidal, but triangular. The tunneling thickness is reduced by the factor $qV/\varphi$ or $qV - \varphi$ and the effective barrier becomes $\varphi/2$ or $\varphi/2$, respectively, [9] (independent of voltage). This is the well-known Fowler-Nordheim tunneling region, and such data can be used to determine the different $\varphi$'s. Theoretical current-voltage characteristics, calculated with

$$F_p = E_g = 0.5 \text{ eV}, \quad \varphi_1 = 3 \text{ eV}, \quad \varphi_2 = 2 \text{ eV}$$

and $\alpha = 18$, are shown in figure 2.

3. Results for SnTe and GeTe junctions. — The results for three SnTe junctions having various oxide thickness are shown in figure 3 where the solid and hollow circles represent the forward and reverse data points, respectively. The low-voltage negative-resistance region, the intermediate-voltage region and the high-voltage Fowler-Nordheim region are seen distinctly in comparison with the theoretical characteristics shown in figure 2.

The parameters $F_p$ and $E_g$ are determined primarily from the low-voltage reverse current, $\varphi_1$ and $\varphi_2$ from the onsets of the Fowler-Nordheim current, and then $\alpha$ is chosen to make the calculation fit the experimental data over the whole voltage range. The results are shown in figure 3 in solid and dash lines for the forward and reverse characteristics. The agreement between the data and the calculations must be considered very good considering the many assumptions made and the many effects neglected in the calculations. The parameters used are: $F_p = 0.6 \text{ eV}, E_g = 0.3 \text{ eV}, \varphi_1 = 3.1 \text{ eV}, \varphi_2 = 1.9 \text{ eV}$; and $\alpha = 16.3, 18.1, \text{ and } 20.0 \text{ eV}^{-1/2}$ for the three sets of curves. Similar calculations made for GeTe junctions are shown in figure 4 to compare with the experimental data. The parameters derived here are: $F_p = 0.45 \text{ eV}, 0.40 \text{ eV}$, and $\alpha = 14.0, 14.7 \text{ eV}^{-1/2}$ for the upper and lower curves, respectively; and $E_g = 0.2 \text{ eV}, \varphi_1 = 2.9 \text{ eV}, \varphi_2 = 2.0 \text{ eV}$. The values of $\alpha$ thus obtained are considered reasonable [10, 11, 12].

The currents at voltages higher than the barrier heights are plotted in figure 5. Samples with an extremely thick oxide were used for this purpose. The data of SnTe are seen to follow the theoretical expression over several decades. For GeTe, thick-oxide junctions are difficult to fabricate so that only a limited range can be explored. The barrier asymmetry used,

$$\varphi_0 = \varphi_1 - \varphi_2,$$

is 1.2 eV and 0.9 eV, respectively, for SnTe and GeTe.
as obtained above. Using the experimental slope in this figure and the barriers \( \varphi_1 \) and \( \varphi_2 \) determined previously, \( \alpha \) is evaluated and found to be consistent with the results shown in figure 3 and 4.

While the theoretical and experimental characteristics compare favorably in general, some discrepancies are present. It is noticed in figures 3 and 4 that the actual decrease of current in the negative-resistance region is always smaller than that predicted theoretically. In fact, in some samples, the current never decreases but merely shows a change of curvature. The assumption of the effective mass solely determined by the oxide conduction band over-estimates the negative-resistance [13], but the relatively large discrepancy here and the good agreement outside this region make it unlikely to be the primary cause.

We believe that tunneling associated with interface gap states in the semiconductor is mainly responsible for the excess current as in a semiconductor tunnel diode [14].

A study of the effect of temperature on the current-voltage data can be used as an independent means to determine the barrier heights [9, 15]. It has been shown that if the percentage change of current from zero to a finite temperature is plotted versus voltage, a peak should appear at a voltage corresponding to the barrier [9]. Figure 6 shows results plotted in this fashion. The temperature here is varied from 4.2 °K to one only slightly higher but at which an observable change of current can be recorded. The barriers are seen to agree fairly well with those found previously, although in some cases a plateau rather than a peak obscures an exact determination of the barrier.

We can combine the values of the barrier heights obtained with the Fermi level and the energy gap to calculate the work functions of the materials [16].

We see in figure 6 that the barriers are not identical for a typical Al-Al_{2}O_{3}-Al junction. However, the difference in barrier heights of 0.7 eV for counter electrodes of Au and Al is consistent with their work function differences [17]. The results for the work function for our materials, using as standard 4.2 eV for the Al work function, are 5.1 eV for SnTe and 4.8 eV for GeTe. The electron affinity is 4.2 eV for both materials.

We have also measured the temperature dependence of the energy gap below 100 °K. The experiments were performed by passing a constant current through the tunnel junction and measuring the voltage drop across it. Here \( V > F_p + E_g \), and the temperature dependence of the voltage is due to that of \( E_g \) as seen in figure 7. In these junctions, the current for \( V < F_p \) is independent of the temperature, indicating that the barrier remains unchanged. Figure 7 is a plot of the results for GeTe and two types of SnTe units. The results for all SnTe units tested, except for SnTe III, were similar to those of SnTe 89. The anomalous increase in \( E_g \) at low temperatures, seen in most of the SnTe specimens, suggests the possibility of a phase transition.

We have carried out a preliminary investigation of tunneling on a superconducting film of GeTe with a hole concentration of \( 1.2 \times 10^{21}/\text{cm}^3 \). This was the first observation of the superconducting energy gap in a semiconductor [18]. The superconducting energy gap extrapolated to \( T = 0 \) °K is 0.14 meV. It is possible to carry out a program of energy gap versus temperature for varying concentrations for a
system such as SnTe or GeTe. This has not been done in a superconducting semiconducting system previously.

4. Fine structure of PbTe and PbSe junctions: energy levels. In our study of junctions formed on epitaxially grown PbTe, a small percentage of the units exhibited negative resistance, as was observed in SnTe and GeTe. However, information about the Fermi energy and energy gap cannot be extracted simply from the data since the band bending in the semiconductor becomes important due to relatively low carrier concentrations. For PbTe, the hole concentration ranges from 4 to $8 \times 10^{18} \text{ cm}^{-3}$ and Hall mobilities range up to 150,000 cm$^2$/volt.s at 4.2 K. For the PbSe films, the hole concentrations are similar to the PbTe films but to this date we have obtained mobilities only as high as 22,000 cm$^2$/volt.s. Our analysis indicates that the PbTe surface is depleted and the Fermi level is located in the neighborhood of 50 meV above the valence band edge at zero bias, as schematically shown in figure 9.

![Figure 7](image1.png)

**Fig. 7.** - Temperature dependence of voltage $\sim E_g + E_F + 0.1 \text{ V vs. } T$. The variation is that of the energy gap $E_g$.

![Figure 8](image2.png)

**Fig. 8.** - Tunneling conductance vs. applied voltage at 1.3 K for PbTe-Al$_2$O$_3$-metal junction illustrating the general shape and the structure, S, P, and D.

![Figure 9](image3.png)

**Fig. 9.** - Schematic energy diagram of the junction at zero bias, including the energy levels of a deep center in PbTe.

![Figure 10](image4.png)

**Fig. 10.** - Conductance curves under magnetic fields a 1.3 K on an expanded scale, offset for clarity for increments of 18 kOe.
A conductance - voltage curve is plotted in figure 8 and illustrates a series of strikingly sharp peaks observed with PbTe and PbSe junctions [19]. The half-width of the sharpest peaks, 1 meV, at 1.3 °K is not temperature dependent while at 10 °K the peaks are drastically reduced due to thermal effects. The current shows a step when the Fermi level in the metal is raised by an applied voltage to an energy equal to one of the localized states in PbTe, resulting in a peak in the conductance. Successive peaks are closer together in going toward the conduction band edge. The application of a magnetic field up to 90 kOe perpendicular to the film (100) clearly splits almost all peaks with no appreciable shift of central position shown in figure 10 for PbTe. The splitting is proportional to the magnetic field and g values from 2 to 18 are obtained. The results for five such units are summarized in Table I, where the positions of peaks are measured in meV downward from the conduction band edge and observed g values are shown in the parentheses. While not all levels are always observed, there exists the repeating pattern that is seen in the table.

We correlate the data within a spectroscopic framework. The sharpest (that is the most pronounced) are identified and designated by S as in figure 8 and 10. This grouping can be done with certainty as these are not only the sharpest but also have the largest g values. If \( n = 3 \) is set for the deepest level (the closest one to the valence band), the energy values, \( E_n \), can be given by

\[
E_n = C/n^2
\]

where \( n \) is an integer and \( C \) is a constant. The energy values calculated from Equation 6 are shown in the last column of Table I, choosing a value of the constant \( C \) for the best fit.

### Table I

<table>
<thead>
<tr>
<th>Assigned Level</th>
<th>Observed energies in meV</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g values shown in the parentheses</td>
</tr>
<tr>
<td>3 S</td>
<td>167 (8.2)</td>
</tr>
<tr>
<td>3 P_{1/2}</td>
<td>117 (~ 6)</td>
</tr>
<tr>
<td>3 P_{3/2}</td>
<td>110 (~ 7)</td>
</tr>
<tr>
<td>4 S</td>
<td>100 (12.4)</td>
</tr>
<tr>
<td>4 P_{1/2}</td>
<td>86.5 (4.8)</td>
</tr>
<tr>
<td>4 P_{3/2}</td>
<td>80 (7.7)</td>
</tr>
<tr>
<td>4 D</td>
<td>72 (~ 2)</td>
</tr>
<tr>
<td>5 S</td>
<td>64 (10.5)</td>
</tr>
<tr>
<td>5 P_{1/2}</td>
<td>54 (2.0)</td>
</tr>
<tr>
<td>5 P_{3/2}</td>
<td>47 (3.8)</td>
</tr>
<tr>
<td>6 S</td>
<td>43 (~ 10)</td>
</tr>
<tr>
<td></td>
<td>41.5</td>
</tr>
<tr>
<td></td>
<td>33.5</td>
</tr>
<tr>
<td>7 S</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>25</td>
</tr>
<tr>
<td>8 S</td>
<td>23</td>
</tr>
</tbody>
</table>

Hole Density in PbTe: 5.5 × 10^{18} cm^{-3}
The principal characteristics seen between the sharpest peaks consist of doublets which are usually separated by 4 to 7 meV and are designated by \( P \) in the figures and the table. In analogy with hydrogen-like spectra, we compare the measured \( g \) values with the Landé \( g \) factors for \( S_{1/2} \) and \( P_{1/2} \) and \( P_{3/2} \) states. For unit 375-9, the ratio for the \( P \) states is \( 4.8/7.7 = 0.63 \) and the ratio for the \( S \) state to the sum for the \( P \) states is \( 12.4 (7.7 + 4.8) = 1 \), while for the Landé formula, the former is 0.5 and the latter is 1. (For different units, the former varies from 0.6 to 1, while the latter is always 1.) We designated the less prominent peaks simply as \( D \) states. We should state that the above description is a considerably simplified version of our vast experimental results. With applied magnetic fields, we occasionally see more complicated phenomena; a peak splits into three, doublets interact with each other, etc. The positions of doublets relative to the nearest \( S \) states seem to change noticeably from unit to unit. The \( D \) states are even more uncertain.

If one takes a conventional approach for shallow donors and acceptors [20], the constant \( C \) in equation 1 is given, as follows:

\[
C = E_H \frac{m^* Z^2}{m_0} \kappa^2
\]

where \( E_H \) : the hydrogenic 1\( S \) ionization energy (13.6 eV), \( m^*/m_0 \) : the ratio of the effective mass to the free electron mass, \( Z_e \) : the charge of a center and \( \kappa \) : the dielectric constant. The value of \( C \), we have obtained, is equal to 0.12 \( E_H \). It is obviously too large if one simply uses the effective mass for conduction electrons, \( m^* < 0.1 m_0 \) in PbTe, the static dielectric constant \( \kappa_0 \), 412 \( \pm \) 40, [21] (or even the optical dielectric constant, \( \kappa_{opt} \), 32.6), [22] and \( Z = 1 \).

At the present time we do not have sufficient data to analyze the energy levels for the case of PbSe junctions, although the spacing between levels also decreases as one approaches the conduction band edge. This suggests that one should be able to analyze the data within the spectroscopic framework. We have observed \( g \) values as large as 19.

5. Effects of rotation of the magnetic field in PbTe and PbSe junctions. — If the localized states are coupled to either the conduction band or the valence band states, one could expect large \( g \) values. Reported experimental \( g \) components are as large as 45 [21] and 57 [23] for electrons, and 51 [21] for holes. For PbSe the reported values are 27 and 32 for electrons and holes, respectively [21]. It is not understood at this time what type of anisotropy one should expect from whatever form of coupling is present.

The epitaxial layers of PbTe and PbSe are (100) films. We have performed rotations in two different planes (001), and (011), for PbTe and a rotation in the (001) plane for PbSe, all of which contained the normal to the film. Some experimental data are shown in figure 11 for a PbTe junction rotated in the (011) plane. This is a pseudo-three-dimensional plot of conductance vertical, angle into the paper and voltage across the junction horizontal. When rotating in the (001) plane for both PbTe and PbSe, the maxima and minima for the \( g \) value occur 90° apart and are within a few degrees from the \( <110> \) directions in the plane of rotation. However, when we rotate in the (011), in the case of PbTe, the maximum \( g \) value occurs within a few degrees from the normal to the film, and the minimum with the field parallel to the film.

![Fig. 11. — This is a pseudo-three dimensional representation of the effect of rotating the magnetic field in the (011) plane in a PbTe junction. The magnetic field was 30 kOe. Each succeeding curve taken at increments of 10° was offset by a constant amount when plotting conductance versus voltage. A glancing photograph was taken to give the effect of conductance vertical, voltage horizontal and angle into the paper.](image-url)
However, at angles midway between the maximum and minimum value, the experimental points always lie outside the solid curve. The splitting observed is proportional to the magnetic field and independent of its direction. The results for rotation in the (001) plane indicate that the observed center does not have the full symmetry of the crystal, suggesting its origin to be clusters or defects of some kind. Experiments in which the sample can be rotated in more than one plane to map out the «g surface», are in progress. If in fact we are observing a single type of center, which has a near ellipsoidal \( g \) tensor, then the results would indicate the alignment of the center is along one of the \(<111>\) directions.

The ratio of the maximum to the minimum \( g \) value in the rotation data ranges from 2 to 4 for PbTe, and 1 to 1.3 for PbSe. Although the anisotropy of the \( g \) tensor in these materials is little known, it is expected to be related to that of the mass. The larger ratio for values of \( g \) in PbTe which also has a larger mass anisotropy thus indicates the coupling of the observed levels to the bands. Deep centers, in general, have not yet been a subject of theoretical investigation even in well-known semiconductors, while extensive studies on shallow impurities have been carried out \[24\]. It has been known that PbTe (or PbSe), a rock-salt crystal, has Pb as well as Te (or Se) vacancies, providing acceptor and donors, respectively \[25\]. Therefore, it is plausible that there exist complex clusters of those centers as in the alkali halides, as was indicated by the rotation data. We are quite certain that the center is not situated in the \( Al_2O_3 \) because the structure is only seen for PbTe and PbSe. The sharpness and intensity of each peak in the conductance may depend on the average as well as the distribution in depth of the clusters from the surface.

6. Summary. — Although optical studies on SnTe had shown the existence of a small direct gap, it was necessary to show that no conduction band states were lower in energy than all valence band states to prove SnTe was a semiconductor and not a semimetal. Tunneling spectroscopy has shown that both SnTe and GeTe are semiconductors. It has been used to measure Fermi energies, semiconducting and superconducting energy gaps, temperature coefficients of energy gaps, work functions and electron affinities on heavily doped materials in which many other techniques are not applicable.

In relatively lightly doped PbTe and PbSe, tunneling has uncovered states exhibiting an atom-like spectrum deep in the energy gap with extremely high \( g \) values.

We have done preliminary work on PbTe-SnTe alloys and feel that a program of this type could lead to information on the alloy series. Effects studied but not mentioned include zero bias anomalies, phonon-assisted tunneling, etc.

I wish to express my appreciation to L. Esaki and L. L. Chang with whom I collaborated on the greatest part of this work, and also to J. F. Schooley who collaborated on the superconducting experiments, as well as numerous theoreticians here at IBM. I also want to thank M. Christie, J. Cummings, and L. Alexander for their technical assistance.

References

[11] The \( \alpha \) (for a reasonable choice of the electron mass \( m \)) would give an oxide thickness of the order of 25 Å (about half of that measured capacitively) and an effective area about 5 % of the geometric area of the junction.
DISCUSSION

ZEMEL, J. N. — A) Did you anneal the films prior to measurement? — B) Please comment on the effect of high radiant fluxes on the surface. — C) Were field effect measurements conducted with your insulating strips? — D) The surface migration effects appear to correlate with the known diffusion coefficients of PbTe, PbSe, and PbS.

STILES, P. J. — A) Yes. — B) We have not measured the effect. — C) Yes, and we found that the presence of the oxide tends to invert p-type surfaces.

CROCKER, A. J. — Do you know the concentration of these states? Are they surface states?

STILES, P. J. — No, however, from the relative magnitude of the current flowing onto these levels compared to the background current, there must be a large number.

Comment by ESASI L. — We believe that they are not just surface states in the usual sense, because of the existence of S-like states, although they seem to be located in the neighborhood of the surface.

BIRMAN, J. L. — What $T_c$ correspond to the observed gap in superconducting GeTe you measured?

STILES P. J. — $T_c = 0.4$ K.

PAPARODITIS, C. — On the mechanism of formation of the tunneling part of the Al$_2$O$_3$, on the profile of the oxide beneath the mask, on the control of the thickness of same.

STILES, P. J. — The oxide $\sim 20$ Å appears to be formed by macroscopic or microscopic transport of the oxide between a mask separated by $\sim 0.03$° from the epitaxial film, while depositing a thick oxide through the mask. — No information on the profile. — The control is related to the thickness of the thick layer.