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AN EXPERIMENTAL INVESTIGATION OF  
RADIATION EFFECTS IN SEMICONDUCTORS

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Semiconductors are particularly sensitive to irradiation with high energy particles or high energy gamma rays. This sensitivity arises from the nature of the energy levels in the forbidden gap that are introduced by the defects formed by the radiation. Many of these levels are deep in the gap and thus are effective in modifying room temperature properties. Such phenomena as the free carrier concentration, the free carrier mobility, the lifetime of minority carriers for recombination, and the recombination luminescence are all strongly affected.

In order to affect the sensitivity of the material to radiation, either to increase or decrease, it is essential to determine the microscopic nature of the defects responsible for the radiation sensitivity. It is known, for example from electron spin resonance measurements, that impurities, either intentionally added or accidentally present, are often found to be contained in the defect. The simple primary defects, vacancies and interstitials, combine or interact with each other or with the impurities to form the stable defects.

Much of the work being carried out under this grant has been devoted to providing additional information about the microscopic nature of these defects. In particular, the luminescence that arises from the recombination of electrons and holes, with one of the charges being trapped by the defect, has been shown to provide significant amounts of information about the defect -- both in terms of the location of the energy level associated with the defect and the nature of the interaction of the lattice phonon field and the trapped electron. This work formed the basis of the Ph.D thesis of Dr. Robert Spry. A portion of the material of the thesis was

presented as an invited paper at the Sante Fe Conference on Radiation Effects In Semiconductors. A copy of that paper, entitled "Recombination Luminescence of Irradiated Silicon" is attached as a portion of this report. It will appear in the forthcoming proceedings of the conference. A paper is also being prepared for publication in the scientific journals. It is expected that this will be submitted for publication within the next month.

The results obtained by Dr. Spry clearly indicate the great importance of this technique. The system developed by Spry has been utilized for further studies on both silicon and germanium.

Preliminary measurements on germanium have been primarily restricted to a search for the band-to-band luminescence of the unirradiated material. The magnitude of the signal for germanium is substantially below that of silicon. It has been possible to observe the band-to-band luminescence in germanium and to observe that it disappears with irradiation. A thorough search for new luminescence has not been made, however, there appears to be two weak luminescent peaks centered at about 2.20 and 2.32 microns. A flux of  $10^{16}$  fast electrons per  $\text{cm}^2$  were used for irradiation. Unfortunately the luminescent technique appears to be substantially less sensitive for germanium than for silicon. Nevertheless, even rather weak signals can be of great value in determining the location of energy levels that arise from radiation-induced defects.

Further measurements have been made on irradiated silicon, using

fast electrons as the radiation source rather than gamma rays or neutrons as were used by Spry. Measurements of the recombination luminescence following irradiation with  $10^{15}$  electrons/cm<sup>2</sup> indicated spectra that agreed well with those reported previously by Spry.

A new experimental arrangement with increased sensitivity and resolution has been constructed. The helium dewar system has the capability of applying uniaxial stresses at temperatures between room temperatures and 4.2°K. This equipment is essentially completed and will be utilized for extensive measurements on the symmetry properties of the defects that are involved in the luminescence.

Extensive measurements are being planned for silicon material that contains lithium as an impurity. It is anticipated that the association of lithium with the defects will modify the energy levels and the phonon coupling to the trapped electron to such an extent that it will be readily observable as a shift in the spectra. These measurements can be expected to provide new evidence on the nature of these defects.

The electronic structure of highly doped semiconductors is of great importance in the understanding of devices. Significant accomplishments have been made in the development of the tunneling technique for the measurement of some of these properties. Attached to this report is a copy of a paper entitled "Evidence of Hole-Optical Phonon Interaction in Degenerate Silicon in Tunneling Measurements" by E. L. Wolf that has been submitted for publication. A copy of an abstract of the same title as the above paper is also attached. This paper is to be presented at the American Physical Society meeting in Berkeley, California on March 18-21, 1968. These papers clearly demonstrate for the first time the modification

in the bulk semiconductor states at  $\hbar\omega_0$  above and below the Fermi energy arising from free hole-optical phonon interaction. Also of great importance is the observation that a tunneling process can involve the localized phonon associated with an impurity. The boron responsible for this are believed to be those atoms that exist in the depletion region that forms the tunneling barrier. This suggests, therefore, that the tunneling technique may be very useful as a means of studying radiation induced defects in the barrier region. This possibility will be explored during the next few months.

The above experiments on tunneling were carried out on material that was highly degenerate. A number of preliminary results have been obtained on material with lower doping. It is believed that these results can be interpreted in terms of the density of states of the impurity band and that they give direct evidence of the splitting of the impurity band. As soon as some additional experiments are completed, these results will be prepared for publication. It is believed that they represent the first direct measure of the density of states of the impurity band.

The manuscript on minority carrier lifetime in irradiated silicon, based upon the Ph.D. thesis of Dr. Ralph Hewes, has been modified and will be re-submitted for publication in the Journal of Applied Physics.

#### Personnel

Dr. E. L. Wolf, Dr. Robert Spry, Mr. Colin Jones, Mr. Eric Johnson, and Mr. Donald Cullen were employed for a portion or all of the past six

months. Dr. Wolf left the University in September, 1968, to assume a position at the Research Laboratories of the Eastman Kodak Company. Dr. Spry completed his thesis and left the University in September, 1968, to assume a position in the Air Force Materials Laboratory at the Wright-Patterson Air Force Base, Dayton, Ohio.

# Recombination Luminescence of Irradiated Silicon<sup>†</sup>

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Deep traps, be they impurities, intrinsic defects, or extrinsic defects arising from irradiation, act as recombination centers in semiconductors. The position of the energy level associated with the trap can be determined by a variety of techniques. Measurements of the temperature dependence of the minority carrier lifetimes have been particularly useful in this regard. Consider a simple case of p-type material with a recombination level near the conduction band. The lifetime of minority carriers injected into the sample is determined by several processes, the trapping of electrons by the center, the thermal ionization of these trapped electrons back into the conduction band, and the recombination of a trapped electron with a hole. For the moment, let us assume that the dominant mechanism for electron-hole recombination is via this defect, that is, that the re-establishment of the thermal equilibrium population of carrier's occurs by this mechanism.

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<sup>†</sup>Supported in part by the National Aeronautics and Space Administration through Grant NsG228-62 and by the Joint Services Electronics Program, Contract Number DAAB-07-67-C-0199.

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<sup>‡</sup>Based on a thesis submitted to the Department of Physics of the University of Illinois in partial fulfillment of requirements for the degree of Doctor of Philosophy in Physics.

Within the framework of the above assumptions, a particularly interesting question now presents itself. Does the recombination of the electron and hole result in luminescence? The answer must obviously be that there is some probability of this process being radiative. It is not easy to estimate just how probable it is without knowing the details of the recombination process. Analogies can be found, however, in other semiconductors to suggest that the radiative process may occur, for example, the extrinsic luminescence observed in copper or silver doped cadmium sulphide. Other examples can be found in materials having direct or indirect transitions at the band gap.

Recombination radiation has been seen in silicon doped with a variety of chemical impurities. Figure 1 presents some of the recent results of Pokrovskii<sup>1</sup> for silicon doped with B, Ga, Bi and In and for germanium doped with Zn. It is interesting to note that the spectra are qualitatively different for these impurities. The location of the transition that would occur without the assistance of phonons is indicated by the long vertical line. The short vertical lines are labelled to correspond to transitions involving the cooperation of a band edge phonon. Boron, gallium and indium introduce levels at 0.046eV, 0.071eV and 0.16eV above the valence band respectively in silicon. Bismuth introduces a level 0.069eV below the conduction band in silicon. The spectra with B, Ga and Bi indicate that a significant zero phonon component is found.

Haynes<sup>2</sup> has studied the recombination of electrons and holes in silicon with a variety of shallow donors and acceptors. He reports



that the energy required to free the bound electron and hole as an exciton from the impurity, whether it is a donor or an acceptor, is about 0.1 times the ionization energy of the impurity.

By analogy with the above results, luminescence resulting from the recombination of electrons and holes at deep traps introduced by irradiation could be expected to provide a great deal of information about the nature of the defects interaction with the lattice and the location of the energy level in the forbidden gap.

The recombination process yielding luminescence, in the above example of p-type material, for example, may be complementary to the absorption of light by the occupied trap in n-type material, if the Fermi level lies above the trap. Of course, if the selection rules are different in the two cases, the relative strengths of the two processes will likely be quite different.

The initial report of such luminescence was made by Ivanov and Yukhnevich<sup>3</sup> utilizing p-n junctions of both silicon and germanium. The silicon was irradiated with  $\text{Co}^{60}$  gamma rays and the germanium with fast neutrons. The luminescent spectra were observed at 80°K. For low injection currents, the luminescent spectra of the irradiated silicon junction had three peaks: A weak high energy peak corresponding to the intrinsic luminescence studied by Haynes<sup>2</sup> and two lower energy peaks at 1.3 and 1.6 microns. These authors proposed that the band at 1.3 microns results from the recombination of a hole with an electron trapped at a level  $E_c - 0.18\text{eV}$ . The longer wavelength luminescence was suggested to arise from recombination via a defect at about 0.37eV from one of the bands. At high injection levels, the intrinsic luminescence became comparable in intensity to the extrinsic luminescence.

The results of a later study by Yuhnevich<sup>4</sup> are presented in Fig. 2. Fine structure on the previously reported broad band luminescence is seen in this figure. The half width of the sharp line was reported to be less than  $2 \times 10^{-3}$  eV, a width less than  $kT$  at the measurement temperature of  $80^{\circ}\text{K}$ . The second peak was separated from the high intensity line by 0.015eV, a result that was interpreted to mean that the recombination occurred with the simultaneous emission of a transverse acoustical phonon. The extrinsic luminescence disappears at temperatures above  $120^{\circ}\text{K}$ . Similar spectra were found for n- and p-type material.

Yuhnevich and Tkachev<sup>5</sup> report a still longer wavelength luminescence consisting of two sharp peaks superimposed upon a broad luminescent band. The sharp peaks occur at 0.478 and 0.488eV and are reported to have half widths of 5 and  $2.5 \times 10^{-3}$  eV, respectively. These authors report that no change in position or half width results from a change in temperature between  $65^{\circ}\text{K}$  and  $130^{\circ}\text{K}$ .

Recombination at these relatively deep traps may result from any of several processes.<sup>6</sup>

1. Defect level near the conduction band.

- a. Recombination of a bound-electron with a free-hole. By analogy with the chemical donors (Figs. 1 and 2), a strong zero phonon line would be expected. Since the free hole is presumed to be in thermal equilibrium, the width of the zero phonon line would be expected to be temperature dependent. Lines would also be expected to result from phonon assisted emission.

- b. Recombination of an exciton bound at the defect. Zero phonon and phonon-assisted recombination would be expected with the zero phonon line having a half width independent of temperature.
2. Defect near the valence band.
- a. Recombination of a bound hole with a free electron. By analogy with the chemical impurities (Figs. 1 and 2), a weak or perhaps no zero phonon line should result. If present, the zero phonon would be expected to have a temperature dependent half width.
  - b. Same as 1.b above.

Yukhnevich and coworkers, have interpreted the results of their half-width measurements to indicate that the transition must be of types b above. They suggest that the zero phonon peak at 0.967eV arises from the recombination of an electron trapped at the Si-A center with a hole localized at some excited level of the defect. Taking the Si-A center level to be 0.17eV below the conduction band, Yukhnevich finds the excited hole state to be 0.025eV above the valence band. Theoretical calculations by Kurskii<sup>7</sup> suggest that the ground state of a hole trapped by a Si-A center plus electron is about 0.13eV above the valence band. As will be seen later in this paper, the identification of the transition giving rise to the 0.967eV corresponding to process 1.b is not completely unambiguous.

A study of the recombination luminescence in irradiated silicon has also been underway at the University of Illinois<sup>8,9</sup>. This work has concentrated on 1) determining the luminescent spectra in single crystals of float-zone material and in single crystals of Czochralski material; 2) determining the dependence of the luminescent spectra upon the type of irradiation, namely fast neutrons and gamma rays; 3) studying the details of spectra at temperatures near 4°K. A portion of the results of these measurements will be reported here.

Luminescent spectra were obtained with a Jarrell-Ash Model 82-092 grating monochromator. A cooled PbS detector was used. The luminescence was excited with a 500 watt high pressure mercury light filtered to remove all photons of wave-length greater than 7500Å<sup>0</sup>. The samples varied in thickness from 0.4 to 0.9 mm. Each sample was etched in CP 4A prior to its introduction into the vacuum dewar for measurements. The strength of the luminescent signal was particularly sensitive to the surface treatment of the sample. This made it very difficult to compare absolute luminescent intensities from one run to another. The geometry of the sample, the diffusion of free carriers throughout the bulk of the sample prior to recombination, the high index of refraction, and the low efficiency for radiative recombination contributed to a low signal level. The maximum resolution was limited by the signal-to-noise of the system.

Irradiations were made at room temperature with fast neutrons from a General Dynamics Triga reactor. Thermal neutrons were removed by enclosing the samples in cadmium foil. Gamma ray irradiations were carried out in Co<sup>60</sup> facilities at the U. S. Naval Research Laboratory and the Oak Ridge National Laboratory.

Measurements at 77°K gave results in substantial agreement with Yukhnevich and co-workers. The spectra were substantially the same for n- and p-type material and for n<sup>0</sup>- and  $\gamma$  - ray irradiations. Yukhnevich reports that the intense band occurring at 0.967eV has a half-width of less than 0.002eV. The present experiments found the half width of this line to be 0.0050eV when measured with an instrumental resolution of 0.0024eV. There appears to be a significant discrepancy between these two measurements.

Measurements taken at 4°K reveal a greatly enhanced structure in the luminescence spectra of all samples. Figure 3 presents the results for a Czochralski grown sample. One of the most striking features of this spectra is the similarity in the two portions of the spectra with principal lines at 0.971eV and 0.792eV. Although some details are not identical, there is a rather complete replication of structure in the two patterns. This is indicated by the nearly constant values of the separation between corresponding bands, as demonstrated in column 6 of the table associated with Figure 3.

Figure 4 presents the data for a float zone sample of silicon irradiated with gamma rays. The most striking feature is the absence of the low energy portion of the spectra. There is no indication, within the noise limit, of a sharp line in the vicinity of 0.79eV.

Comparison of Figs. 3 and 4 suggests strongly that recombination can occur via two independent defects. The smaller concentration of oxygen in the float zone material suggests that this defect is formed only when a substantial amount of oxygen is present in the sample. It

is by no means certain, of course, that the defect involves oxygen.

The Tables accompanying Figs. 3 and 4 present the energy locations of the principal peaks in the spectra. The location of the peaks in the high energy portion of the spectra of Fig. 4 is seen to agree with the location of the peaks in the spectra of Fig. 3 within one millielectron volt. It is concluded, therefore, that the same defect is responsible for the luminescence.

Data are presented in the tables giving the separation of the lines at lower energy from the most intense line of the group. As can be seen, these separations can be identified with the energies of various phonons. The band edge phonons are obviously the most important.

Figure 5 presents data taken with the narrowest slits that the signal-to-noise would permit. In each case, the measured half width at  $4^{\circ}\text{K}$  is greater than the spectral resolution. For example, the measured width of the  $0.791\text{eV}$  line is  $0.0008\text{eV}$  when measured with an instrumental resolution of  $0.0006\text{eV}$  and is  $0.0006\text{eV}$  when measured with an instrumental resolution of  $0.0003\text{eV}$ . Although the present measurements were not able to determine the intrinsic width of this line, comparison of the data taken at  $4^{\circ}\text{K}$  with that taken at  $77^{\circ}\text{K}$  indicated that the  $0.971\text{eV}$  line width is temperature dependent. The spectral resolution of the instrument was measured at various slit widths using the indicated half width of the sharp infrared emission lines from a low pressure mercury discharge.

On the basis of this result, it is suggested that the recombination process is described by 1.a above; i.e. a bound electron-free hole. The temperature dependence arises from the thermal energy of the free hole in the valence band. The relative intensity of the

0.971eV peak to the lower energy peaks suggest that this is a zero phonon. As pointed out above, a strong zero phonon line involving recombination of a free carrier is likely only for a level near the conduction band.

A recombination process involving excitons trapped at the neutral oxygen center, as suggested by Yuhnevich is a very attractive explanation for the data. Such processes are well known and give a large probability for recombination with no phonons being involved and for multiple phonon interactions. The binding energy of the exciton to the neutral oxygen would be expected to be at least a few millivolts. Thus, at temperatures near 4<sup>0</sup>K, it would certainly be trapped. This mechanism is only ruled out by the results of the measurements of the temperature dependence of the half width. The conclusion that this is not the process must be considered tentative, however, until it has been possible to utilize sufficient resolution to determine the intrinsic line width of the zero phonon lines.

The model of the recombination center responsible for the 0.792eV line and its associated multi-phonon pattern is unknown at this time. Stress measurements are in progress that are expected to yield the symmetry of the recombination center.

The band gap in silicon at 4<sup>0</sup>K is 1.165eV.<sup>10</sup> The energy difference between the most intense line, centered at 0.971eV, and the band gap is 0.194eV. Although this value is somewhat larger than measured by other techniques, it seems likely that this level arises from the Si-A center. The energy difference between the line centered

at 0.791eV and the band gap is 0.374eV, suggesting a recombination level 0.374eV below the conduction band.

These studies are being continued and will utilize higher instrumental resolution, uniaxial stresses, and annealing studies at elevated temperatures. The experiments are also being extended to germanium.

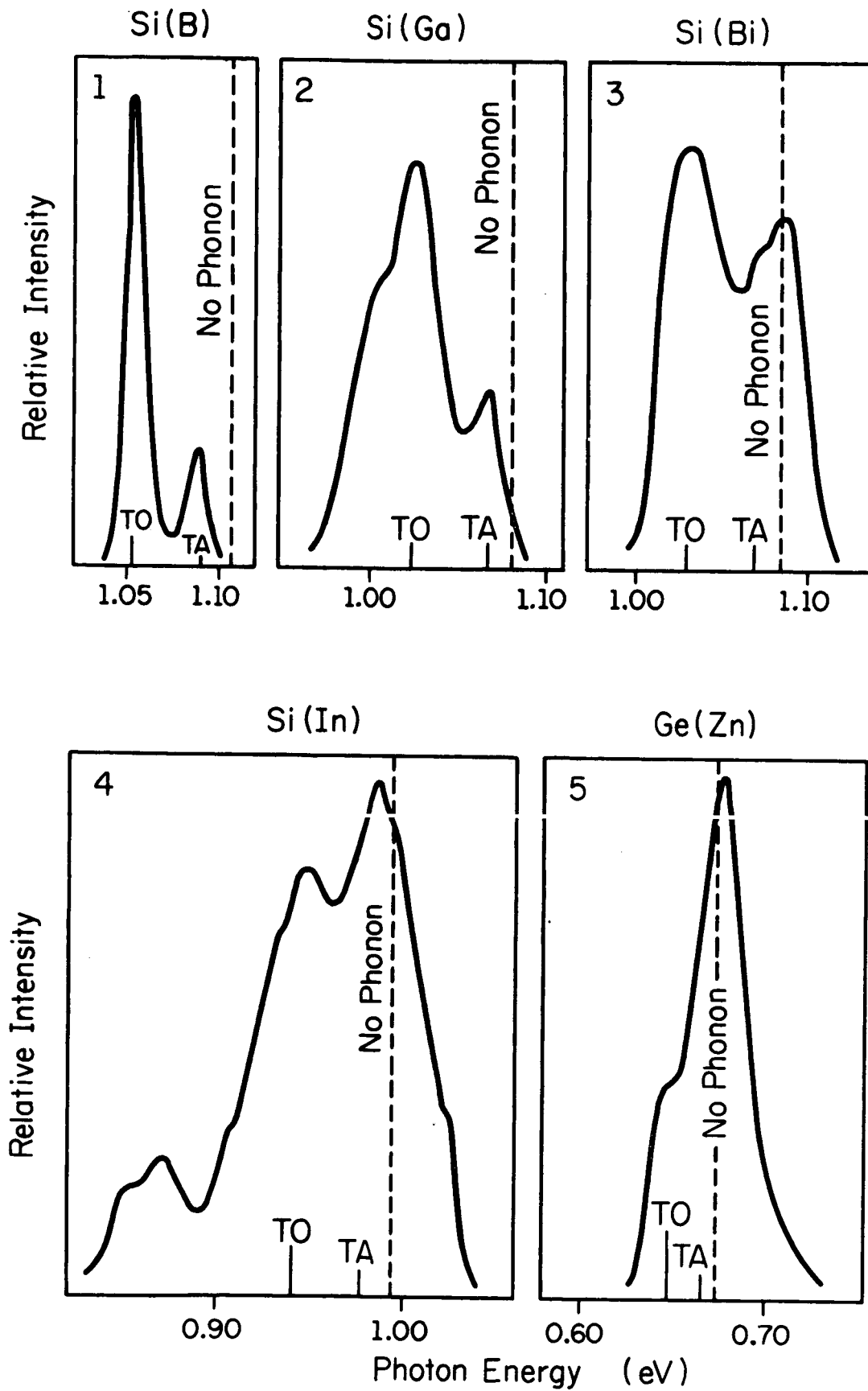


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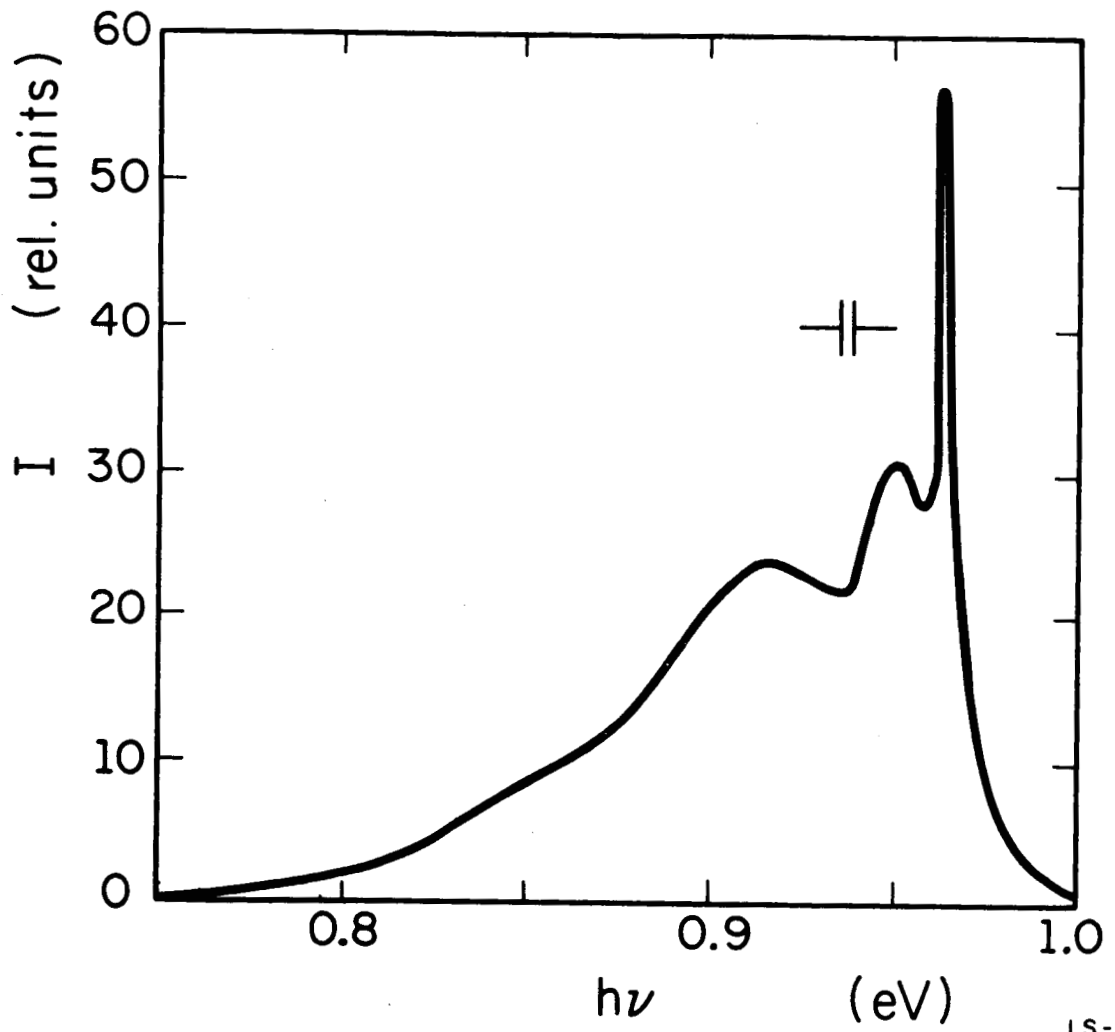
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FIGURE CAPTIONS

- Figure 1 Luminescent spectrum of deep donors and acceptors in silicon and germanium measurements taken at 20-30°K. Vertical line indicates a transition without the aid of phonons. TA and TO indicates transitions with the aid of transverse acoustic and transverse optical phonons. Donor and acceptor are indicated above each figure.
- Figure 2 Luminescent spectrum for silicon irradiated with Co<sup>60</sup> gamma rays. Measured at 80°K. After A. V. Yukhnevich, Soviet Physics- Solid State 7, 259 (1965).
- Figure 3 Luminescent spectrum for a Czochralski grown silicon sample following gamma ray irradiation. Data are presented in terms of a constant number of emitted quanta in a constant wavelength interval. Table indicates the energy location of the numbered bands.
- Figure 4 Luminescent spectrum for a float zone grown silicon sample following gamma irradiation. Data are presented in terms of constant number of quanta in a constant wavelength interval. Table indicates the energy location of the numbered bands.
- Figure 5 Luminescent spectrum of the zero-phonon line located at 0.7905 eV (line Number 6 of Fig. 3) at two different monochromator resolutions.

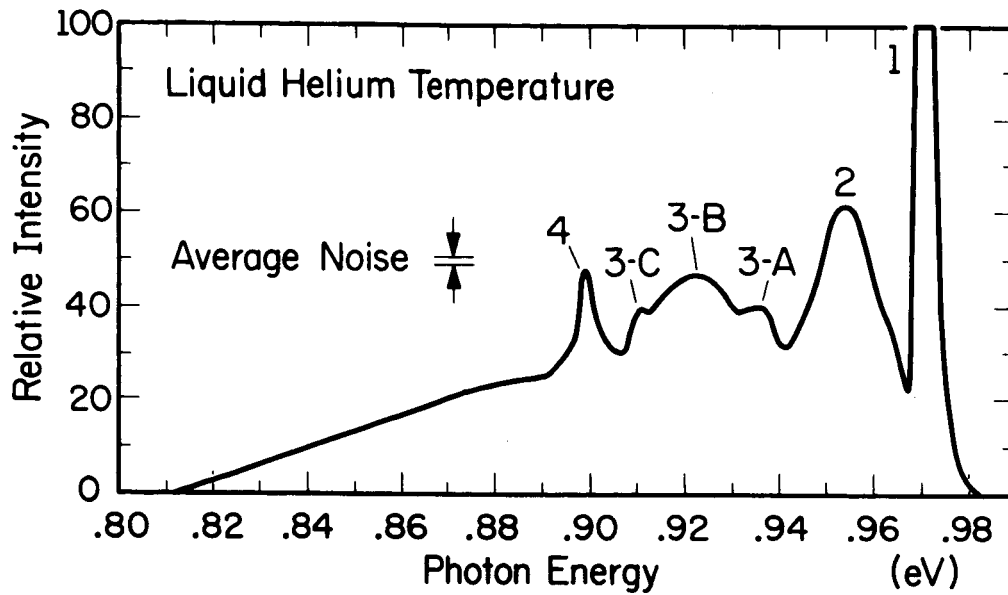


LS-159



From A.V. Yukhnevich, Soviet Physics - Solid State, 7, 259 (1965)

LS-169



Sample No.1

Silicon N-Type Float Zone  
70 ohm cm

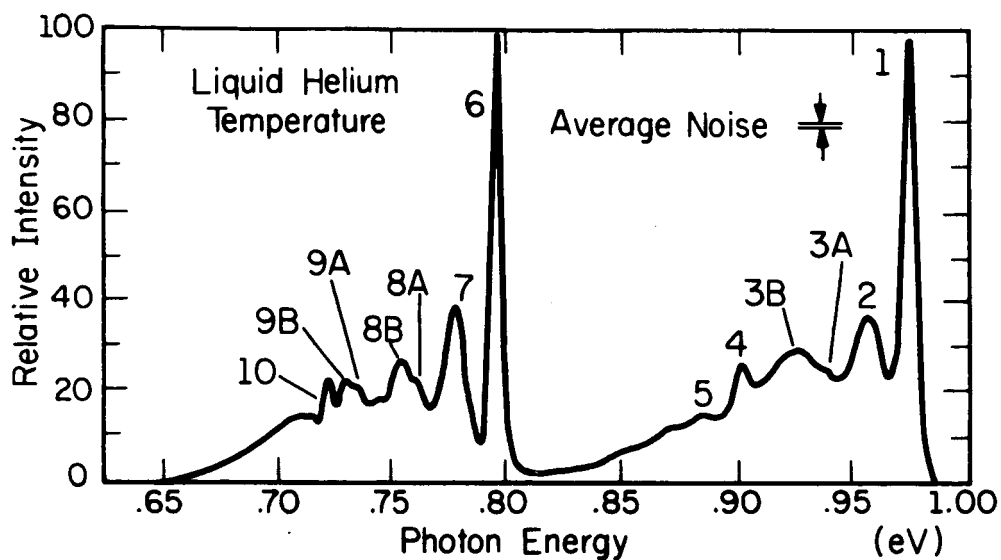
$\text{Co}^{60}$  Gamma Ray Flux:  $10^8$  R  
126 Days After Final Irradiation

LS-152

### Energy Location of Luminescence Bands

Band Number $N_i$	Peak (eV)	Band $N_j$ - Band $N_1$ (eV)	Phonon Emitted
1	0.971		zero
2	0.954	0.017	TA
3-A	0.935	0.036	2TA
3-B	0.923	0.048	L
3-C	0.911	0.060	TO
4	0.899	0.072	TO + TA
5	0.884	0.087	TO + 2TA

LS-162



Sample No.11  
Silicon N-Type Pulled  
100 ohm cm

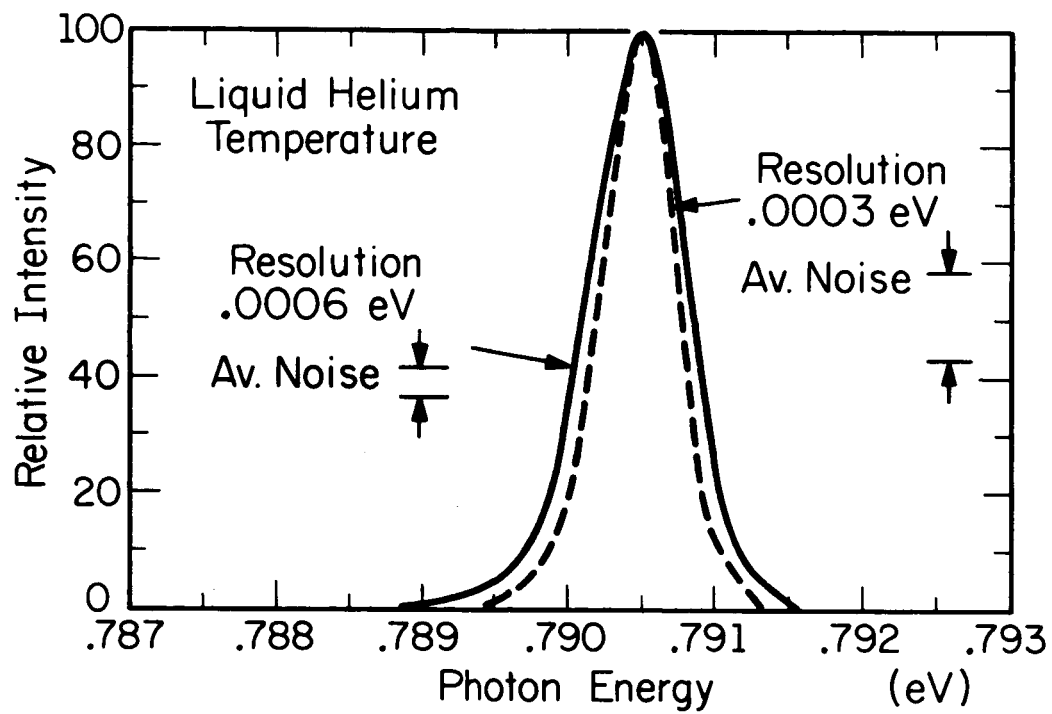
$C_{60}$  Gamma Ray Flux:  $10^8$  R  
14 Days After Irradiation

LS-180

Energy Location of Luminescence Bands

Band Number $N_i$	Peak (eV)	Band $N_1$ - Band $N_1$ (eV)	Band $N_1$ - Band $N_6$ (eV)	Corresp. Bands	Separation Between Corresponding Bands (eV)	Phonon Emitted
1	0.971			6	0.179	zero
2	0.955	0.016		7	0.180	TA
3-A	0.936	0.035		8-A	0.179	2TA
3-B	0.925	0.046				L
4	0.900	0.071		10	0.181	TO+TA
5	0.883	0.088				TO+2TA
6	0.792			1	0.179	zero
7	0.775		0.017	2	0.180	TA
8-A	0.757		0.035	3-A	0.179	2TA
8-B	0.751		0.041			L
9-A	0.730		0.062			TO
9-B	0.727		0.065			O
10	0.719		0.073	4	0.181	TO+TA

LS-167



Sample No. 12  
 Silicon N-Type Pulled  
 100 ohm cm

$C_{60}$  Gamma Ray Flux:  $10^8$  R  
 5 Days After Irradiation

EVIDENCE OF HOLE-OPTICAL PHONON INTERACTION  
IN DEGENERATE SILICON IN TUNNELING MEASUREMENTS<sup>†</sup>

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Abstract

Tunneling from a metal into degenerate p-type silicon exhibits  $d^2i/dV^2$  peaks at biases  $eV = \pm\hbar\omega_0$ , where  $\hbar\omega_0$  is the  $k = 0$  optical phonon energy of the semiconductor. It is suggested that these peaks reflect modifications in the bulk semiconductor states at energies  $\hbar\omega_0$  above and below the Fermi energy arising from hole-optical phonon interaction. An additional peak near the optical phonon frequency, but well resolved from it, is identified with vibrations of the boron acceptor impurity.

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Interaction of holes with optical phonons in the covalent group IV semiconductors was originally inferred from analysis of the temperature dependence of the hole mobility<sup>1,2</sup> and has recently been more directly verified by observations of oscillatory photoconductivity<sup>3</sup> in germanium<sup>4</sup> and silicon.<sup>5</sup> In the present measurements of  $d^2i/dV^2$  characteristics of metal-insulator-semiconductor tunnel junctions, formed using indium on degenerate p-type silicon, the interaction of holes and optical phonons at small wave-vector  $k$  is clearly indicated by peaks occurring at values of the applied bias voltage  $V$  such that  $eV = \pm \hbar\omega_0$ , where  $\hbar\omega_0$  is the optical phonon energy at  $k = 0$ . The absence of strong zone boundary phonon effects<sup>6</sup> is consistent with a direct tunneling process from the metal Fermi surface to a small Fermi surface in the semiconductor valence band at  $k \cong 0$ . The behavior at positive bias  $eV = +\hbar\omega_0$ , corresponding to a positive step in conductance, resembles that observed in direct tunneling situations in III-V semiconductors.<sup>7,8</sup> This was originally described as a threshold effect.<sup>7</sup> The companion peak in  $\frac{d^2i}{dV^2}$ , which we show in detail at negative bias  $eV = -\hbar\omega_0$ , corresponds to a decrease in conductance and thus is of the wrong sign for a threshold effect. This leads us to suggest the possibility that both peaks should be interpreted in terms of modifications in the bulk semiconductor states at  $E = \pm \hbar\omega_0$  resulting from phonon coupling.

Small area indium-silicon junctions were formed on cleaved  $\langle 111 \rangle$  faces of silicon single crystals containing  $1.3 \times 10^{20} \text{ cm}^{-3}$  boron, corresponding to a free carrier Fermi degeneracy  $\mu$  of 160 meV, assuming a density of states mass of 0.58. Small bars ( $2 \times 4 \times 10 \text{ mm}^3$ ), having  $\langle 111 \rangle$  axis, were completely nickel plated<sup>9</sup> and ohmic return contacts and leads attached. The bars were then clamped, scribed with a diamond, and fractured by application of a sharp bending force. Inspection of the silicon faces showed that portions of

each exposed the {111} cleavage plane<sup>10</sup>. Although such areas rarely exceeded 0.5 mm in diameter, this sufficed to locate the tunneling contact, 0.01 to 0.1 mm in diameter, formed by spring-loading against the cleaved face an indium wire freshly cut to a point using a cleaned razor blade mounted in a microtome. A force of 10 to 100 milligrams was applied to the point. These operations were performed in the air in about 10 minutes; absorption and/or oxidation on the surfaces are thought to produce a tunneling barrier of substantially lower transmission than the silicon depletion layer alone.<sup>11</sup> The extreme softness of the indium insures that local pressures under the contact do not appreciably exceed the average pressure of 0.1 to 1.0 Kg/mm<sup>2</sup>, and makes the assembled contact in its jig stable enough mechanically to permit mounting in an immersion dewar system and cooling to 4.2°K or lower. The absence of heating or chemical treatment of the silicon surface in this scheme insures that the boron density is constant to within a few Angstroms of the surface.

The tunneling configuration is taken such that at positive bias the metal Fermi level is raised relative to the semiconductor Fermi level. Electron energy in the semiconductor is measured from the Fermi level, so that the valence band edge occurs at  $E = \mu = 160$  meV. For positive bias  $V$ , final states for tunneling transitions from the metal lie in the valence band in the range  $0 \leq E \leq eV$ . At negative bias, the process may be regarded as tunneling of holes into occupied ( $E < 0$ ) states in the valence band.

Second derivative spectra at 4.2°K and 1.6°K are shown in Figs. 1 and 2, respectively. The main peaks occur at  $V = \pm 64.9 \pm 0.5$  mV,

which is in excellent agreement with the value 64.8 mV obtained from Raman scattering<sup>12</sup> for the  $k = 0$  optical phonon in silicon. This structure has been observed in a sequence of five samples with reproducible energies and band shapes. Within an experimental accuracy of  $0.1^{\circ}\text{K}$  of the transition temperature of indium, 3.41 deg. K, prominent superconducting structure appears in a millivolt range at  $V = 0$  (note reduced gain in Fig. 2 near  $V = 0$ ). In addition, structure clearly identifiable as (modulation broadened) indium phonon structure<sup>13</sup> appears in Fig. 2 at approximately  $V = \pm 15$  mV. These features are in reasonable agreement with published results for normal metal - superconducting indium tunneling data and their appearance is taken as strong justification for the interpretation of the spectra shown in Figs. 1 and 2 in terms of tunneling.

The 77.8 mV peak present in both spectra agrees well in energy with the localized vibrational mode of boron in silicon, as observed in infrared absorption<sup>14</sup> in samples containing up to  $1.3 \times 10^{19} \text{ cm}^{-3}$  boron. Since the strength of this peak relative to the 64.9 mV peak decreases rapidly as the boron concentration decreases, it seems clear that this peak is associated with the boron impurity. A corresponding peak at negative bias of -77.8 mV has not been seen. However, the signal-to-noise ratio was generally poorer at negative bias by virtue of a sharply rising conductance in this range. The zero bias anomaly observed at  $4.2^{\circ}\text{K}$  corresponds to a minimum in conductance with full width between points of maximum slope of 4 mV. This structure is broader than the conductance maximum reported previously<sup>15, 16</sup> in silicon p-n junctions at high doping, which we also observe at lower boron concentrations of

$5 \times 10^{19} \text{ cm}^{-3}$  and  $2 \times 10^{19} \text{ cm}^{-3}$ . The minimum shown in Fig. 1 is too narrow, on the other hand, to be explained as resulting from excitation of collective modes in the barrier.<sup>16,17</sup> Additional weak features in Fig. 1 are peaks at 19.5 mV and 128.6 mV identified as the transverse acoustic phonon at the zone boundary and twice the  $k = 0$  phonon, respectively.

The prominent  $\frac{d^2 i}{dV^2}$  peak at + 64.9 mV corresponds to an increase ( $\sim 10\%$ ) in conductance  $di/dV$  at this bias. Two possible lines of argument in explaining this are (A) 64.9 mV corresponds to the opening up, at a threshold for excitation of the barrier of an additional channel for charge transfer;<sup>18</sup> (B) at the energy  $E \approx \hbar\omega_0$ , the tunneling current is altered as a result of the interaction of holes and optical phonons in the bulk. On the basis of the  $\frac{d^2 i}{dV^2}$  peak at  $+\hbar\omega_0$  alone, the data do not offer a means of discriminating between the two possibilities. However, the barrier threshold (A) as an explanation for the  $eV = +\hbar\omega_0$  peak would imply also a threshold, and hence increase in conductance at negative bias  $eV = -\hbar\omega_0$ . This is contrary to what is observed, namely that the peak in  $\frac{d^2 i}{dV^2}$  at - 64.9 mV is observed to be a decrease in conductance.

It is suggested that this may be explained by a deformation potential type interaction<sup>1-5</sup> of holes with the  $k \approx 0$  optical phonon, resulting in a modification of the states in the bulk<sup>19,8</sup> at energies  $E \approx \pm \hbar\omega_0$ . The oscillatory photoconductivity experiments demonstrate that as soon as a hole is energetically able to emit an optical phonon, it does so very rapidly.

The tunneling probability depends strongly on the wave vector  $k$  of the final state in the semiconductor, which in the absence of the phonon interaction is given by  $E = \mu - \frac{\hbar^2 k^2}{2m}$ , with  $E$  positive in the forward

direction, negative in the reverse. The conductance of the junction increases with increasing  $|k|$  in the direction of reverse bias, and decreases as  $|k|$  decreases in the direction of forward bias.<sup>17</sup> The effect of coupling with the optical phonons is indicated qualitatively in Fig. 3. Note that  $|k|$  increases to the left. In the forward direction,  $k$  is decreased for  $E$  just below  $\hbar\omega_0$  and increases for  $E$  just above  $\hbar\omega_0$ . Thus, there is a decrease in conductance as  $eV = E$  approaches  $\hbar\omega_0$  from below, followed by an increase for  $eV > \hbar\omega_0$ . In the reverse direction, the sharp decrease of  $|k|$  for  $|E|$  just greater than  $\hbar\omega_0$  is associated with the decrease in conductance at  $eV = -\hbar\omega_0$ . Preliminary calculations by Duke and Davis<sup>20</sup> indicate that this model properly predicts the qualitative features of the data near  $E = \pm \hbar\omega_0$ .

The boron impurity peak probably results from a threshold effect associated with the barrier. The data do not rule out the possibility, however, of a bulk effect involving a phonon impurity band as has been reported for superconducting alloys.<sup>21</sup>

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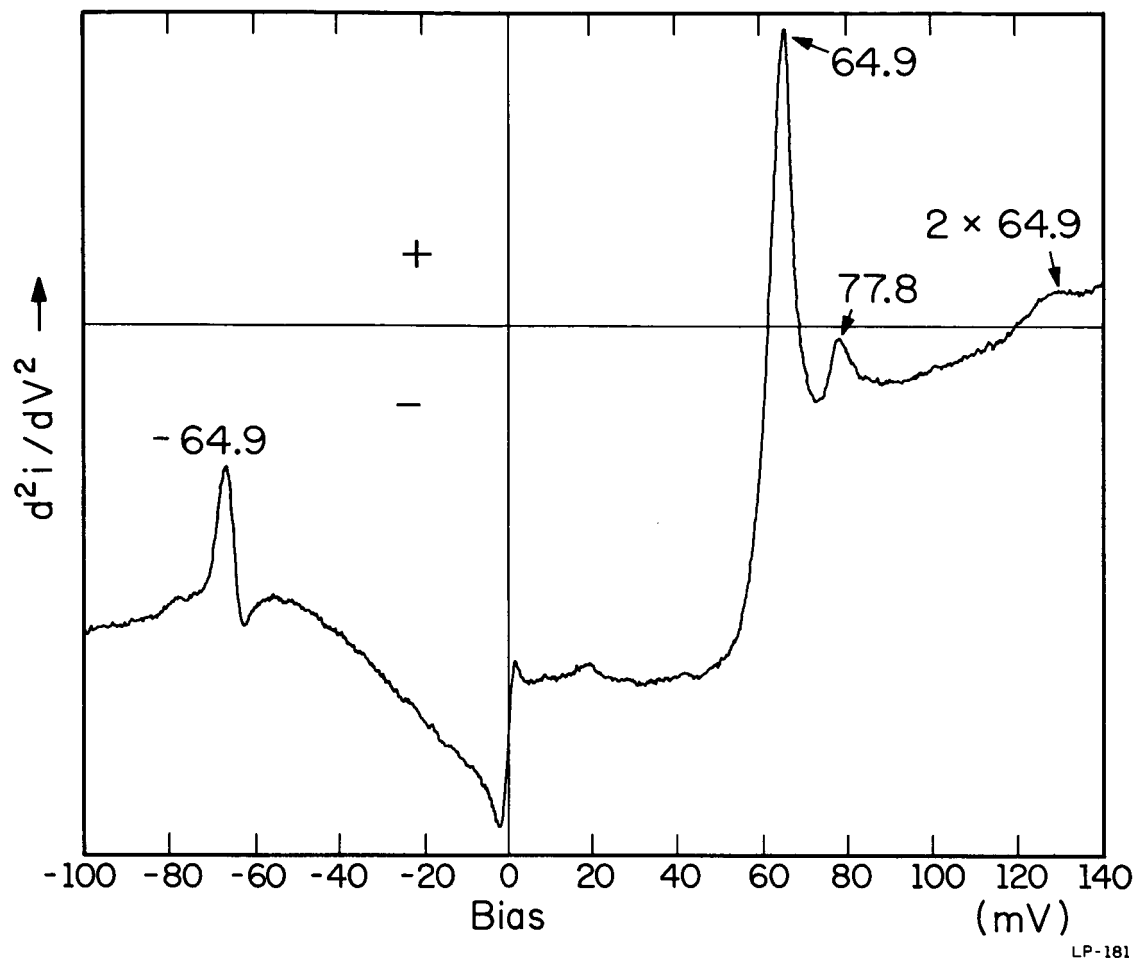
### FIGURE CAPTIONS

Figure 1.  $d^2i/dV^2$  spectrum for indium - p-type silicon ( $1.3 \times 10^{20} \text{ cm}^{-3}$  boron) tunnel junction at  $4.2^\circ \text{K}$ . Modulation level is 3 millivolts. Peaks (left to right) occur at  $-64.9(+)$ ,  $-60.7(-)$ ,  $-2(-)$ ,  $+2(+)$ ,  $+19.5(+)$ ,  $+64.9(+)$ ,  $+77.8(+)$ , and  $+129(+)$ , in millivolts.

Figure 2.  $d^2i/dV^2$  spectrum for the sample of Fig. 2 as observed at  $1.6^\circ \text{K}$ . Modulation level is 4mV peak-to-peak except in center where it is 0.3mV peak-to-peak. Differences between this curve and Fig. 2 in the range  $-20\text{mV} \leq V \leq 20\text{mV}$  are satisfactorily explained by the superconductivity of the indium, and are regarded as important justification for the techniques employed and for analysis of the spectra in terms of tunneling.

Figure 3. Schematic representation of the electron-phonon dispersion relation indicating the effect of coupling at the longitudinal optical phonon energy  $\pm \hbar\omega_0$ .





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Figure 1

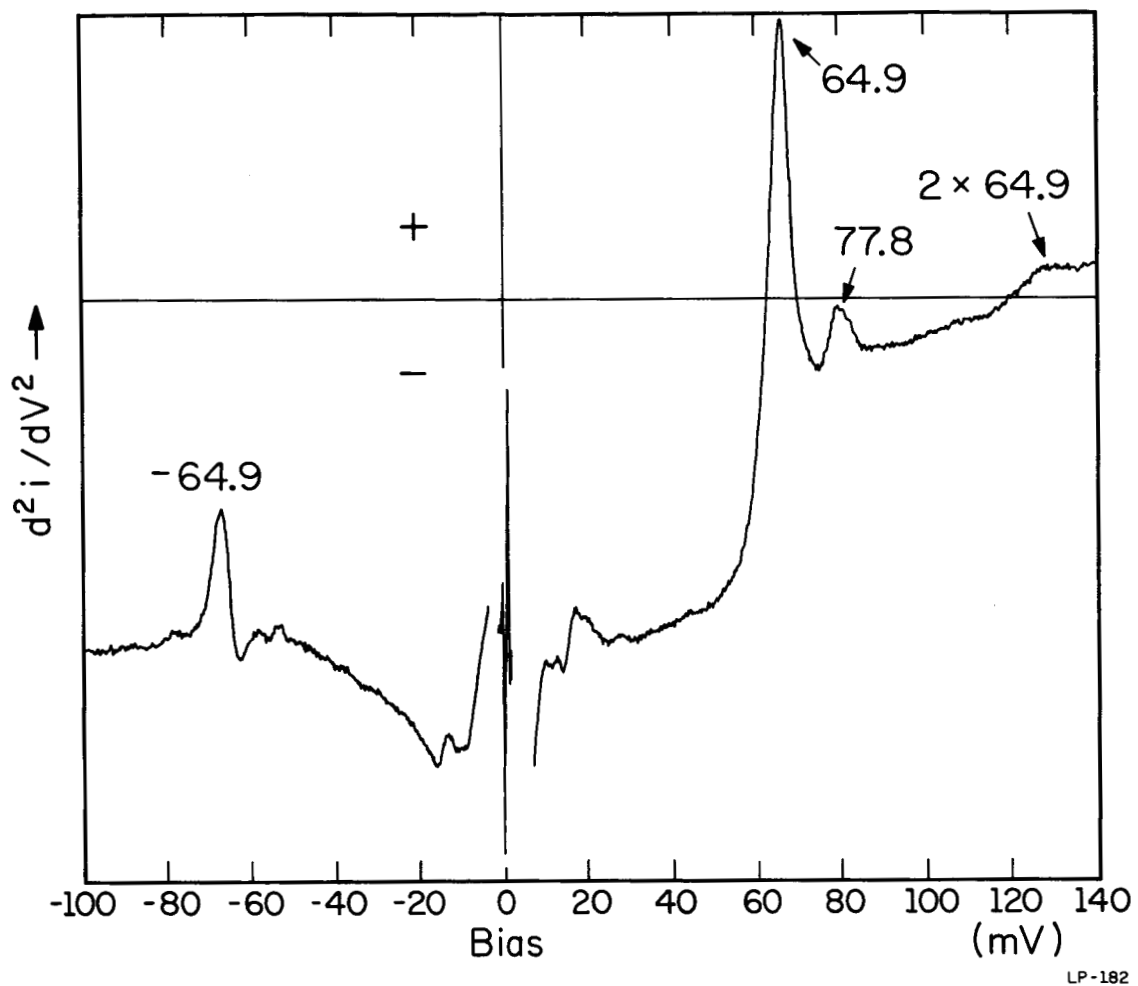


Figure 2

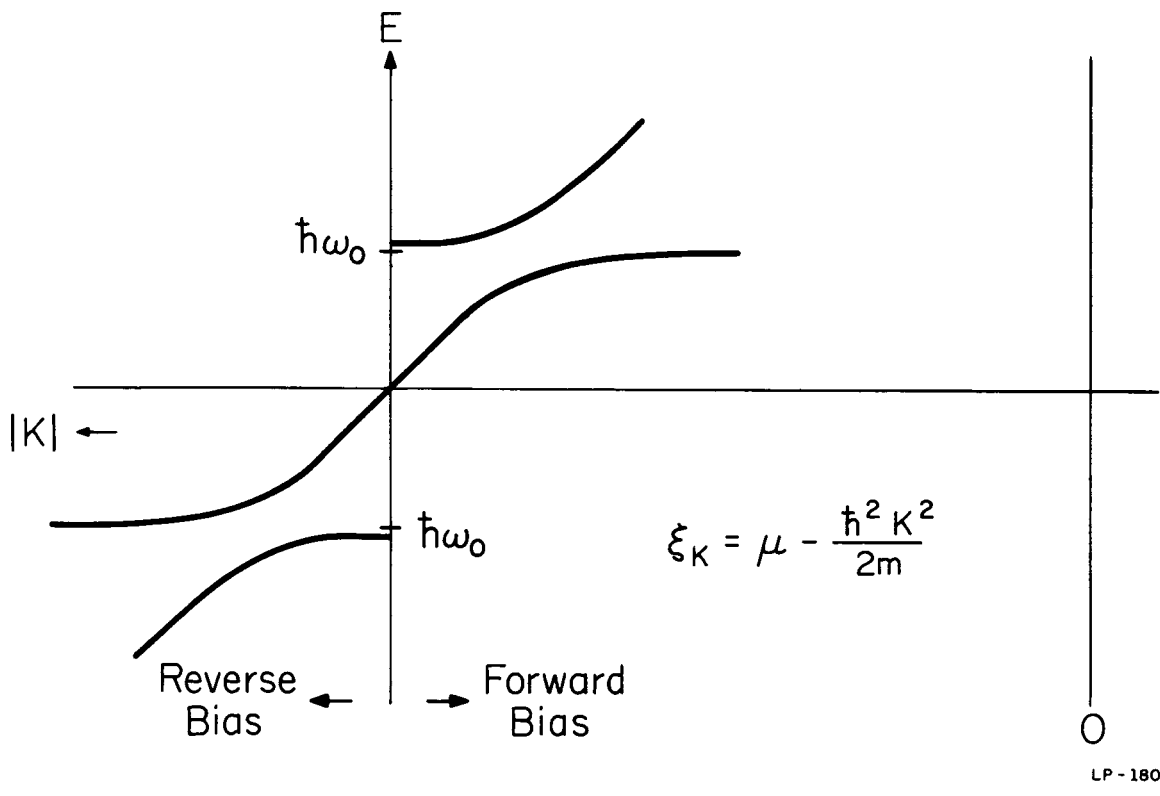


Figure 3

Evidence of Hole-Optical Phonon Interaction  
In Degenerate Silicon In Tunneling Measurements\*

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In measurements of  $d^2i/dV^2$  characteristics of metal-insulator-semiconductor tunnel junctions, formed of indium on degenerate p-type silicon, interaction of holes and optical phonons at small wave vector  $k$  is clearly indicated by symmetric peaks at bias voltages  $V$  such that  $eV = \pm \hbar\omega_0$ , where  $\hbar\omega_0$  is the optical phonon energy at  $k = 0$ . The positive peak in  $d^2i/dV^2$  at positive bias  $eV = + \hbar\omega_0$  (metal Fermi level raised with respect to silicon Fermi level), corresponding to an increase in conductance, is consistent with the opening up at the threshold for phonon emission of an additional inelastic tunneling channel in the barrier. The peak at reverse bias,  $eV = - \hbar\omega_0$ , however, corresponds to a decrease in conductance, and is thus of the wrong sign for a threshold effect. It is suggested that both peaks should be interpreted in terms of modifications in the bulk semiconductor states at energies  $\pm \hbar\omega_0$  with respect to the Fermi level resulting from phonon coupling. A discussion of various mechanisms will be given.

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