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AN EXPERIMENTAL INVESTIGATION OF RADIATION EFFECTS IN SEMICONDUCTORS

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I. Introduction

Irradiation of semiconductors with high-energy radiation, e.g., neutrons, gamma rays, and fast electrons, introduces vacancies and interstitials that diffuse through the lattice and combine with impurities or other defects. The secondary defects that are formed from the primary displacements depend upon the oxygen content of the crystal, the concentration and type of dopant, the temperature of the irradiation, and the subsequent temperature of annealing after the irradiation. Work carried out under this grant is intended to provide information about the nature of these defects. It is particularly important to determine the microscopic nature of the defect and the nature of the interaction of the defect with the lattice, particularly the interaction of the lattice phonons with the trapped charges.

Some of these defects have energy levels in the band gap which change the electrical and optical properties of the crystals. Studies of changes in minority-carrier lifetimes have been made by Hewes.[1] Studies of the infrared luminescence of optically excited silicon at liquid-nitrogen and liquid-helium temperatures have been made by Spry.[2] The luminescence that arises from indirect electron transitions from the conduction band to the valence band decreases following irradiation with neutrons and gamma rays. Several bands of luminescence appear at lower energy than the band-to-band luminescence.

It has not been possible from the previous work to determine models for the defects responsible for the various luminescence bands. Additional experiments were needed to help characterize the defects involved in the luminescence process and to determine whether the transitions involve the recombination of free carriers or the recombination of bound carriers. Measurement of the line shape and the half-width as a function of temperature from below liquid-helium temperature to liquid-nitrogen temperature provides information that can be particularly useful in determining the nature of the transition. Measurement of the changes in polarization and the shape of the luminescence spectra under uniaxial stress can help determine the defect symmetries.

The thermal stabilities of a number of lattice defects in silicon are well known. Measurements of the influence of heat treatment upon the luminescence spectra will provide a valuable correlation between the present measurements and those of other workers.

A number of studies have been carried out of the influence of irradiation upon the conduction in highly doped semiconductors. This had led to an interpretation that requires that the width of the impurity band and the population of the band be dependent upon the concentration of defects formed by the irradiation. It is important, therefore, that a direct measure of the impurity bands be determined. This is being attempted by a technique involving the tunneling between a semiconductor and a superconductor.

II. Recombination Luminescence

a. Instrumentation

In order to measure line shapes and splittings, a more sensitive system with better resolution was needed. The previous system consisted of a 0.5-meter Jarrell-Ash Model-82 spectrometer (f/8.6 optics) with an Infrared Industries PbS detector having a detectivity D* (1.2μ,135Hz,5.5Hz) = 6.8×10^{10} $Hz^{1/2}$cm/W. The system under development utilizes a 0.75-meter Engis Spex 1700-II spectrometer (f/6.8 optics) and a Hughes Santa Barbara Research PbS detector with D* (1.2μ,90Hz,6Hz) = 4.2×10^{11} $Hz^{1/2}$cm/W. Gratings are available with dispersions of 8, 16 and 64 Å per mm slit width that are blazed at wavelengths between 5000 Å and 4 microns.

A schematic diagram of the apparatus is given in Fig. 1. A HBO 500-W Orsam mercury lamp is focused on the sample. A portion of the absorbed energy is emitted as infrared luminescence and is collected by a Perkin-Elmer off-axis ellipsoidal mirror and focused onto the entrance slits of the monochromator. The light beam is chopped at 97 Hz by a Clevite 5H piezo-electric bimorphic strip located in front of the slits. The light from the monochromator is again collected and focused by an ellipsoidal mirror onto the detector. There are two filters in the system. The first is a Jena KG-3 water-and-glass filter which passes the visible light but absorbs the infrared light coming from the mercury lamp. The second is a Corning 2540 filter which passes the infrared but cuts out the visible scattered light.

The signal from the detector goes to a Princeton Applied Research HR-8 lock-in amplifier which amplifies a narrow band of frequencies about 97 Hz. The output of the amplifier is fed to a Varian G-14A-1 chart recorder.

There are several alternate arrangements that can be used. A Hughes Argon laser Model 3040H can be used as the excitation source. The laser produces 1-W pulses of fifty-nsec length at a repetition rate between 0 and 200 pulses/sec. In this case, the detector output is amplified and sent to a Princeton Applied Research CW-1 boxcar integrator. For luminescence measurements beyond 3.5 microns, a Texas Instruments InSb detector is used. Unfortunately, the detectivity is only $D^* (5.3\mu, 1000, 1) = 9\text{X}10^{10}\text{Hz}^{1/2}\text{cm/W}$. Data can also be put on magnetic tape and then fed into the CDC-1604 computer for analysis. This is done by utilizing a Dynamics Research Corporation optical shaft encoder that is attached to the wavelength drive of the monochromator. This produces pulses every tenth of an angstrom which are sent to a counter. Depending on the resolution desired, the detector voltage and the sample temperature are read onto the tape every 100, 10, 1 or 0.1 angstroms.

A sample dewar for doing variable-temperature measurements under stress has been constructed. The sample holder is a hollow copper can isolated from the helium section of the dewar by stainless-steel tubing. Helium is drawn through a needle valve into the hollow sample holder and then to a tube going back through the helium bath and a control valve to a vacuum pump. By varying the flow through the two valves and the power input to the heaters on the sample holder, it is possible to obtain stable temperatures from about $6^{o}K$ to $40^{o}K$.

The sample is held against the sample holder by a phosphor-bronze spring and is stressed between two clamps. The lower clamp is adjustable through a gear drive from outside the dewar with adjustments being made by a stainless-steel rod passing through an O-ring on the room-temperature dewar. The rod has a screw-driver-type end which fits the gear drive on the sample holder. Except when adjustments are being made, the rod is pulled back from the sample holder leaving it thermally isolated. Preliminary measurements are under way to align the system and to evaluate its over-all sensitivity.

b. Spectral Line Widths

Preliminary data has been taken on the line widths and temperature dependence of the sharp zero-phonon lines observed at 1.28μ and 1.57μ.[1] The line at 1.278μ has been observed from $6^{o}K$

to $40^{o}K$. The data thus far has a large scatter due to changes in the background luminescence. It is possible to say that the observed half width is less than 6 Å and $6^{o}K$ and less than 10 Å at $40^{o}K$ with an instrument resolution of 3.6 Å. If the line shape is approximated by a gaussian, the actual half width is related to the observed half width by[3]

$$\left(\Delta_{1/2\ \mathrm{act}}\right)^2 = \left(\Delta_{1/2\ \mathrm{obs}}\right)^2 - \left(\Delta_{1/2\ \mathrm{instrument\ resolution}}\right)^2$$

Where $\Delta_{1/2\ \mathrm{obs}}$ is the half width of the line observed with an instrumental resolution of $\Delta_{1/2\ \mathrm{instrument\ resolution}}$, $\Delta_{1/2\ \mathrm{act}}$ is the actual half width of the line. Using this expression gives a half width of $\lesssim 5$ A^{o} at $6^{o}K$ and $\lesssim 8.5$ A^{o} at $40^{o}K$.

The data for the peak at 1.57μ is better since the intensity is stronger and the background did not vary in the vicinity of the peak. Using the above formula, the half width of the line appeared to remain constant over the region $6^{o}K$ to $30^{o}K$ at a value of 3.5 Å ± .5 Å. Preliminary attempts to observe a splitting of the lines with an applied stress have been unsuccessful to date.

c. Recombination in Germanium

The attempt to find recombination luminescence related to defects created by radiation damage in germanium has been unsuccessful. Band-to-band luminescence has been seen with non-irradiated samples at liquid-nitrogen temperature using a low-resolution monochromator. Neither band-to-band nor luminescence associated with radiation-induced defects has been seen with the higher-resolution Jarrell-Ash system at liquid-helium temperature. Since the system yields strong signals for irradiated silicon, it must be concluded that the efficiency for luminescence in germanium is either much less than in silicon or that the surface treatment being used does not give long minority-carrier lifetimes at the surface. Possible luminescence in germanium, mentioned in the previous progress report, are sample independent and are considered to be spurious. The study with germanium is being discontinued for the time being.

d. Impurity Effects (Li-drifted)

Recombination luminescence is quenched in pulled silicon by the diffusion of lithium. Neither band-to-band nor radiation induced defect luminescence has been seen in this material to date. The lithium concentration was on the order of $10^{18}/cm^3$. Luminescence has been seen in lithium drifted float zone material but is of low intensity. After irradiation with fast electrons of 10^{16} and 10^{17} e/cm^2 fluxes, the recombination luminescence consists of a broad band located between 1.00 and 0.78 eV which is essentially structureless at these low intensities. It is not clear at this time whether this luminescence has any relationship to the band at 0.97 eV reported by Spry.[2]

e. Dependence Upon Dose and Annealing Temperature

Samples of 100 Ω cm N-type pulled silicon were irradiated with 10^{15}, 10^{16} and 10^{17} fast electrons/cm^2. An intense luminescence peak is found at 0.97 eV that differs by at most a fact of two between the 10^{15} and 10^{17} irradiations. A band at 0.79 eV is barely discernible. After standing approximately two weeks at room temperature, the intensity of the 0.79 eV band grows to about one half of that of the 0.97 eV band. Upon remaining longer at room temperature, the 0.79 eV band decays until it is barely discernible after 5 weeks. This annelaing pattern appears to be the same as observed by Spry for gamma irradiated material.[3] A similar annealing behavior seems to exist in samples kept at dry ice temperatures.

The spectrum of a 100 Ω cm N-type pulled sample irradiated with 10^{16} e/cm^2 is shown after a room temperature anneal of 53 days in Fig. 2. Figure 3 presents the spectrum that exists after a 14 hr. anneal at 300°C. Spectacular changes have occurred in the spectrum. The 0.97 eV luminescence peak has disappeared completely leaving a new series commencing at 0.95 eV. The peak separation among the resolvable peaks in this family of bands is identical to that of the family commencing at 0.97 eV in freshly irradiated material. The intensity of the 0.79 eV peak and its associated family of peaks has been greatly enhanced by the anneal. The position of the peaks in this family are the same as previously observed.[2]

In the work of Spry,[2] a weak band was observed on one occasion some 0.005 eV on the high energy side of the 0.79 eV peak in unannealed material. After the 300°C anneal, a band appears in this position whose intensity is second only to the 0.79 eV line itself.

It is clear that valuable information can be obtained by studies involving the thermal treatment of irradiated samples.

Tunneling Measurements

a. Silicon

Measurements of the tunneling characteristics, dI/dV and d^2I/dV^2, of silicon MOS and MS junctions have been continued. A new technique of fabricating junctions has been investigated. Improvements in the electronic circuitry have increased the signal-to-noise ratio of the measuring apparatus making it possible to observe structure that had previously been obscured in the noise.

MOS junctions have been made from degenerate p-type silicon (1.3×10^{20} to $\sim 2.5 \times 10^{20}$ boron atoms per cm^3) by nickel plating 2 X 4 X 10 mm silicon bars cut with $\langle 111 \rangle$ axis along the long direction, ceroseal soldering a copper return wire to one end, cleaving the bar in air and evaporating dots of lead or indium, approximately 0.004 in. in diameter, onto the cleaved surface. Contact to the metal dot was made by pressing an indium wire onto the dot. A cold weld with some degree of mechanical stability was obtained in this manner.

Measurements of the conductance, $\frac{dI}{dV}$, and of d^2I/dV^2 have been made on several of these junctions at 4.2^oK and at temperatures as low as 1.5^oK. These measurements substantiate the data presented by Wolf[4] with several refinements. The $K = 0$ phonon peaks have been located more precisely and the line widths have been measured. A splitting of the structure observed by Wolf on the high-energy side of the $K = 0$ phonon peak has been observed. The principal peak, due to boron, occurs at 76.9 mev with an auxiliary weaker peak at 79.9 mev. This is demonstrated in Fig. 4. A comparison with the optical results of Balkanski[5] indicates that these two peaks arise from local phonons associated with B^{11} and B^{10}, respectively. The intensity of the two peaks is in rough agreement with the relative concentration of the two isotopes. This observation positively identifies this structure as being due to the boron impurity.

Recent measurements of $\frac{d^2I}{dV^2}$ at temperatures below 4.2^oK have revealed the presence of structure previously undetected. A weak peak, see Fig. 5, at $\sim$80mv was thought to be arising from the boron impurity. In an effort to establish the identity of this peak, a very highly doped silicon crystal containing $\sim 2.5 \times 10^{20}$ boron atoms per cm^3 has been procured. The boron content of this crystal is roughly twice that of the material previously examined. To date, however, measurements on the new crystal are inconclusive. Other weak peaks, see Fig. 5, which may be due to a two-phonon tunneling process involving the $K = 0$ optical phonon of silicon and a lead or indium phonon have been observed. Comparison of the $\frac{d^2I}{dV^2}$ data from silicon-oxide-lead and silicon-oxide-indium tunnel junctions are underway at present to establish the identity of these new peaks. The structure resulting from the superconducting energy gap in the metal and the phonons characteristic of the bulk metal was observed in every MOS junction.

Tunneling measurements have also been made on silicon-metal junctions made from boron doped silicon in the impurity band range of concentration ($\sim 5 \times 10^{18}$ to $\sim 2 \times 10^{19}$ atoms per cm^3). A discussion of the results of these measurements will appear in a paper entitled "Identification of Impurity Band Effects in the High Concentration Limit in Metal-Semiconductor Tunnel Junction" by E. Wolf, W. D. Compton and D. Cullen that will be submitted for publication within the next month. The conclusion that will be drawn in this paper is simply that the tunneling measurements have been able to directly detect the density of states of the impurity conduction band.

An attempt was made to detect phonon-assisted tunneling in n-type Si. Preliminary results with n-type Si show features in dI/dV and d^2I/dV^2 vs. bias curves similar to those observed in p-type silicon. No gap was observed for a doping level of $5 \times 10^{18}/cm^3$, in agreement with p-type data. For a doping level of $1 \times 10^{19}/cm^3$, a strong step-up in conductance was observed at 58 mV bias. No structure was observed at reverse bias. Although the structure at 58 mV is consistent with observations in Si p-n junctions[6], it is not clear by which mechanism it is caused. In analogy with phonon-assisted tunneling in Ge,(See below), we would expect peaks in d^2I/dV^2 in Si at 18, 46, 54, and 58 mV, antisymmetric with respect to zero bias. The measured absolute conductance in junctions with $1 \times 10^{19}/cm^3$ donor concentration is at least three orders of magnitude larger than that calculated from ref. 7. The theory, however, is valid only for concentration of $2 \times 10^{19}/cm^3$ or higher (degenerate material). Crystals with this high doping concentration are on order. We plan to look for phonon-assisted tunneling in Si and to verify the CDMT theory.

In an effort to make junctions that were more stable mechanically, a new type of fabrication technique was investigated. The junctions were formed by (1) cutting thin slices of silicon 0.020 X 0.160 X 0.400 inch and grinding them to a thickness of 0.010 inch, (2) nickel plating the one end of the slice and ceroseal soldering a 0.003 X 0.010 inch gold ribbon to the plated surface to serve as a back contact, (3) casting the entire sample in epoxy, (4) cleaving the epoxyed sample and depositing lead strips ($\sim$0.010 inch wide) across the cleaveage plane, (5) mounting the samples onto TO-5 transistor headers, and (6) making contact to the lead strips by means of gold ribbon and silver conducting epoxy. The gold ribbons were then soldered to the header pins. Such a junction is shown in Fig. 6. Encouraging results were obtained with some of the first few junctions. They were indeed much more stable mechanically and one junction was cycled to $4.2^{o}K$ four times with only small changes in the junction resistance. In general, however, the junction resistance of these units proved to be too small for convenient measurement and, at present, junctions made in this manner are not being used.

b. Germanium

In p-type germanium, hole-optical phonon interaction was observed similar to that reported by E. L. Wolf.[4] The doping level was $\simeq 1 \times 10^{20}/cm^3$ with gallium as dopant. The Ge data fit the theoretical lineshape calculated by Davis and Duke[8] better than the Si data. At lower levels ($2 \times 10^{19}/cm^3$ or lower), different lineshapes were observed. They are now being studied as a function of doping concentration. All contacts were made with indium tips on air cleaved material.

Tunneling into vacuum cleaved, n-type Ge was studied with Sb- and As-doped crystals. The doping range was $3.5 \times 10^{18}/cm^3$ to $1 \times 10^{19}/cm^3$. For the first time, phonon-assisted tunneling was observed in Sb- and As-doped crystals with equal strength for both dopants. For Sb-doped samples, the absolute values of conductance vs. bias fit the theory of Conley, Duke, Mahan, and Tiemann[7] quite well. The agreement of data obtained with As-doped samples is less good.

At forward bias between 100 and 250 mV, many peaks in d^2I/dV^2 were observed with As-doped crystals (none in the case of Sb-doped Ge). They were seen above and below the superconducting transition temperature of the contact material. No consistency or systematics were observed in lineshape vs. bias curves between results obtained with different contacts.

Most of these results have been submitted for publication in a Physical Review Letters. A copy of this is attached to this report.

Publications

The results of work on recombination luminescence appeared in the proceedings of the Conference on Radiation Effects in Semiconductors held at Santa Fe, New Mexico in September, 1967. Reprints of this article are attached.

Attached are reprints of the publication of E. L. Wolf entitled "Evidence of Hole-Optical-Phonon in Degenerate Silicon in Tunneling Measurements".

The manuscript of Ralph Hewes entitled "Recombination Lifetimes in Gamma-Irradiated Silicon" has been accepted for publication in Journal of Applied Physics and will appear within the next week.

A full length manuscript of the recombination luminescence by R. J. Spry and W. D. Compton has been accepted for publication in Physical Review.

Personnel

Dr. Fortunat Steinrisser, Mr. Colin Jones, Mr. Eric Johnson and Mr. Donald Cullen were employed for all of the time during the past six months. Mr. Larry Schein joined the project during the summer.

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2. "Recombination Luminescence of Irradiated Silicon" by R. J. Spry and W. D. Compton in Radiation Effects in Semiconductors, p. 421 , F. L. Vook, Ed., Plenum Press, New York (1968).

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Figure 1. Schematic diagram of the apparatus used for luminescence measurements.

Figure 2. Recombination luminescence of 100 Ω N type silicon following irradiation with 10^{16} e/cm^2. Sample remained 53 days at room temperature prior to measurement at liquid helium temperature. 1 mm slit width.

Figure 3. Recombination luminescence of 100 Ω cm N type silicon following irradiation with 10^{16} e/cm^2. Sample was annealed for 14 hours at 300^{o}C after measurement shown in Figure 2. Measured at liquid helium temperature. 1 mm slit width.

Figure 4. d^2I/dV^2 vs. bias of an indium-insulator-silicon junction at $T \sim 2^o$K for a bias range near 78 meV. The figure presents evidence for the existence of phonon-assisted tunneling involving a boron phonon in 0.001 ohm-cm sample of boron doped silicon.

Figure 5. d^2I/dV^2 vs. bias for an indium-insulator-silicon junction at $T \sim 2^o$K. Sample is boron doped with a room temperature resistivity of 0.0005 ohm cm.

Figure 6. Photograph of epoxy mounted tunneling junctions.

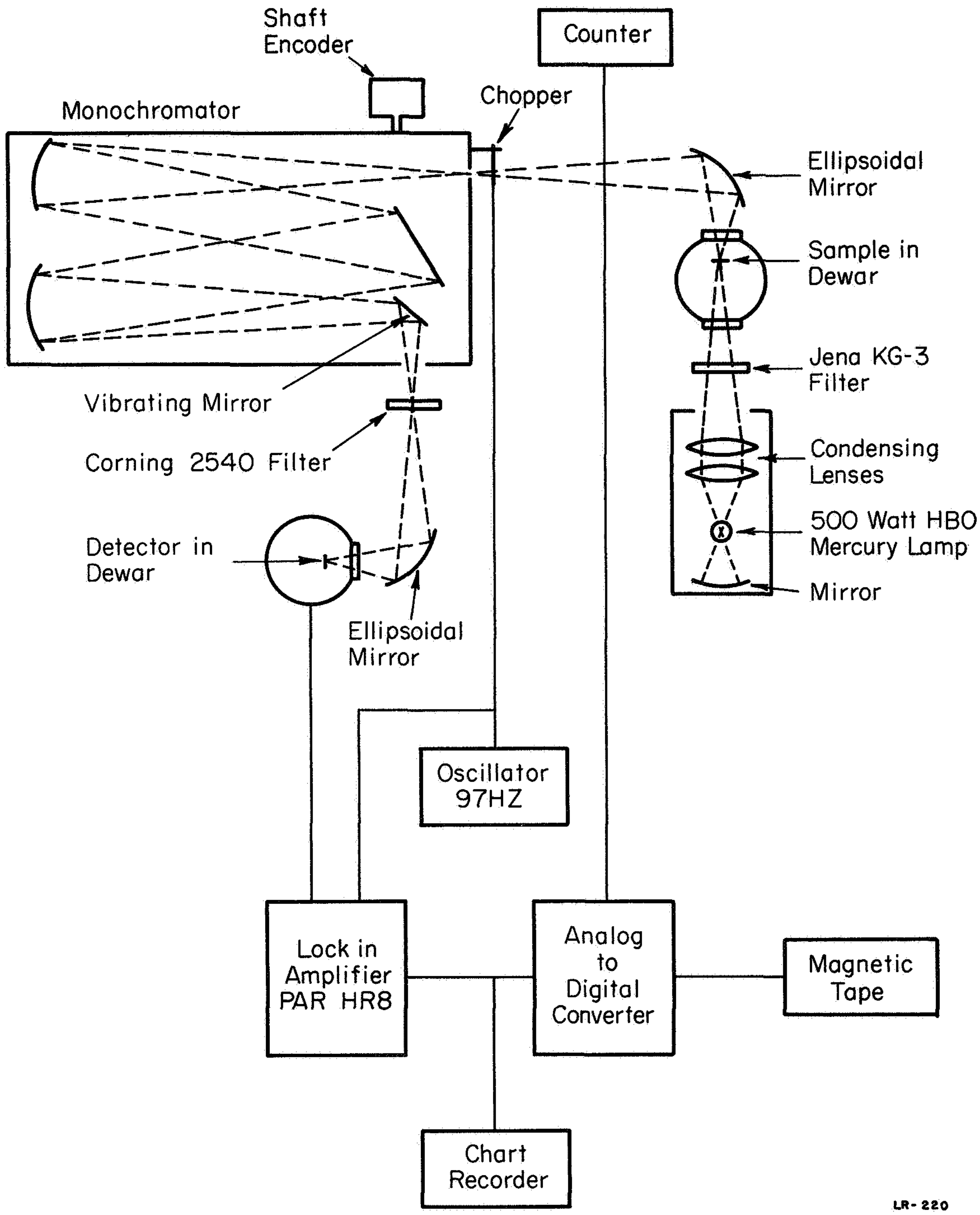
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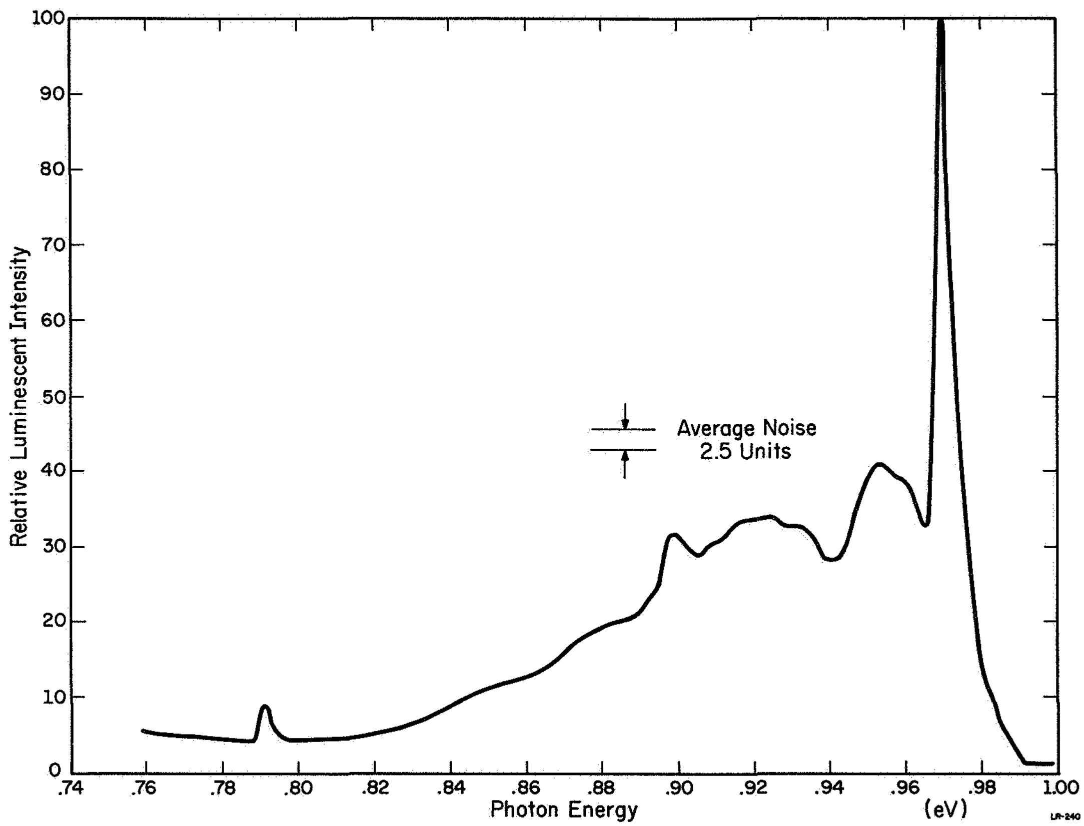
Figure 1



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Relative Luminescent Intensity
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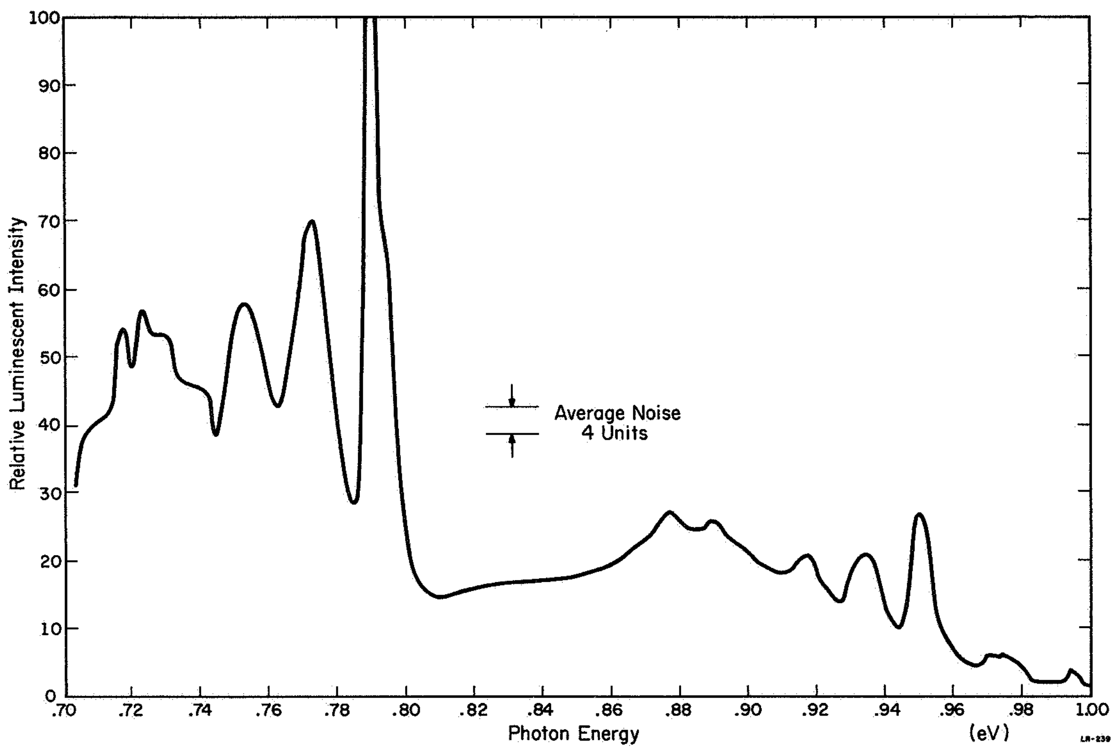
Photon Energy
(eV)
LR-240

Figure 2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Relative Luminescent Intensity
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Photon Energy
(eV)

Figure 3

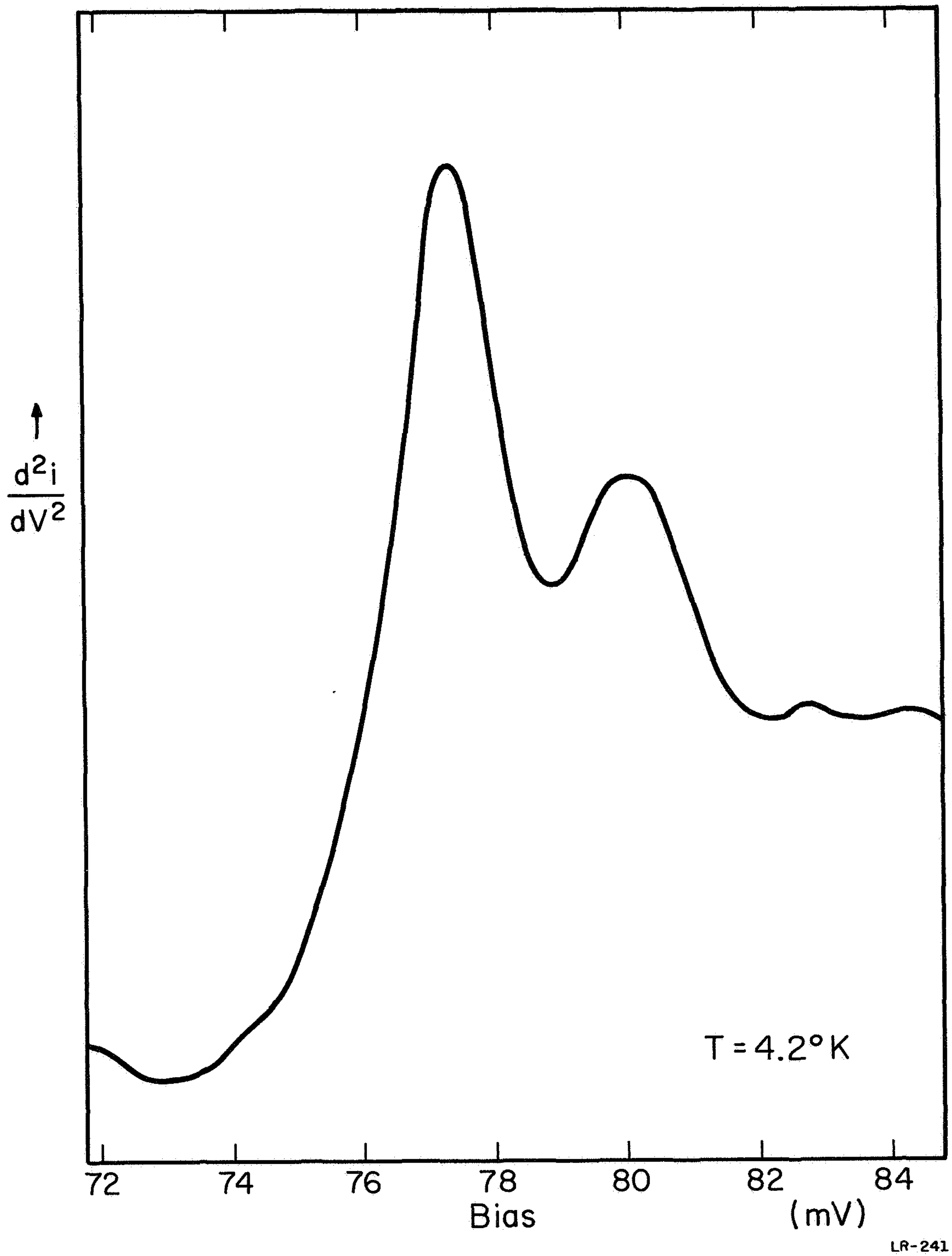

Figure 4

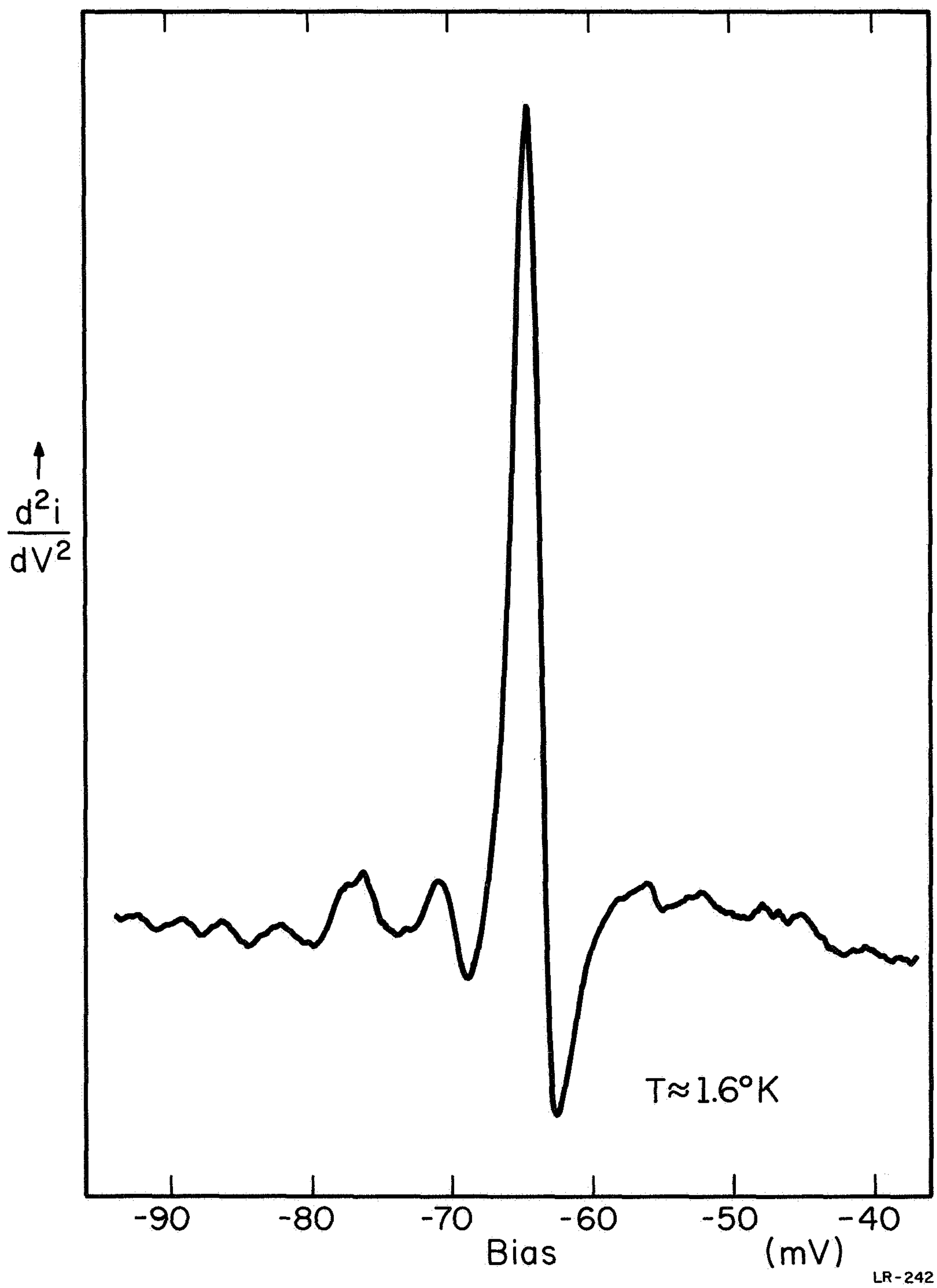

Figure 5

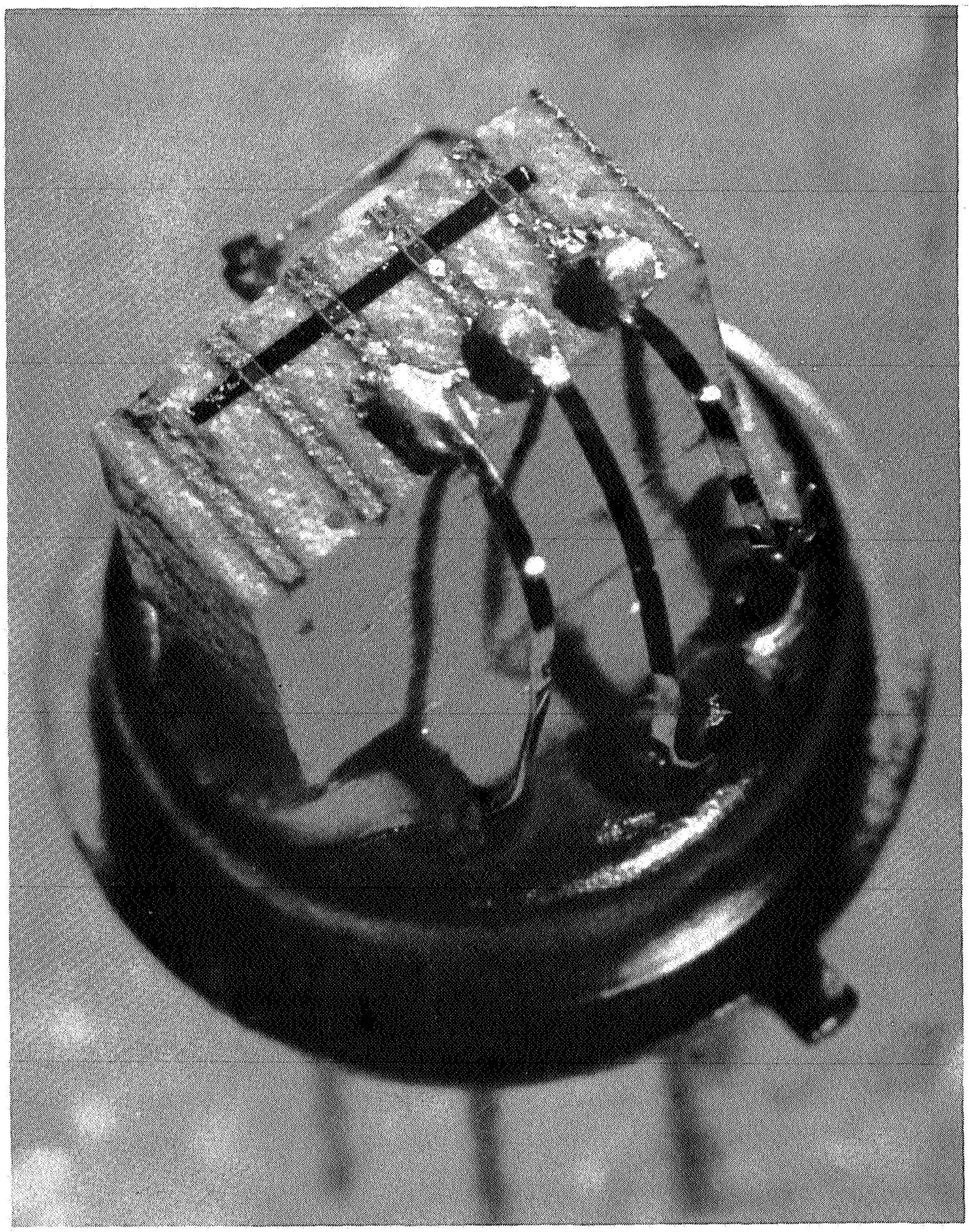

Figure 6

Reprinted from: RADIATION EFFECTS IN SEMICONDUCTORS
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RECOMBINATION LUMINESCENCE OF IRRADIATED SILICON*

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ABSTRACT

Numerous physical properties of semiconductors are affected by the point defects that are introduced by irradiation with neutrons or gamma rays. Studies of these properties have led to the establishment of the microscopic models for several of these defects. This paper reports on the luminescence that arises from the recombination of electrons and holes at these defects. The details of this luminescence give information about the energy level arising from the defect and the nature of the interaction of the defect with the lattice.

INTRODUCTION

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

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‡ 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.

electron-hole recombination is via this defect, that is, that the reestablishment of the thermal equilibrium population of carriers occurs by this mechanism.

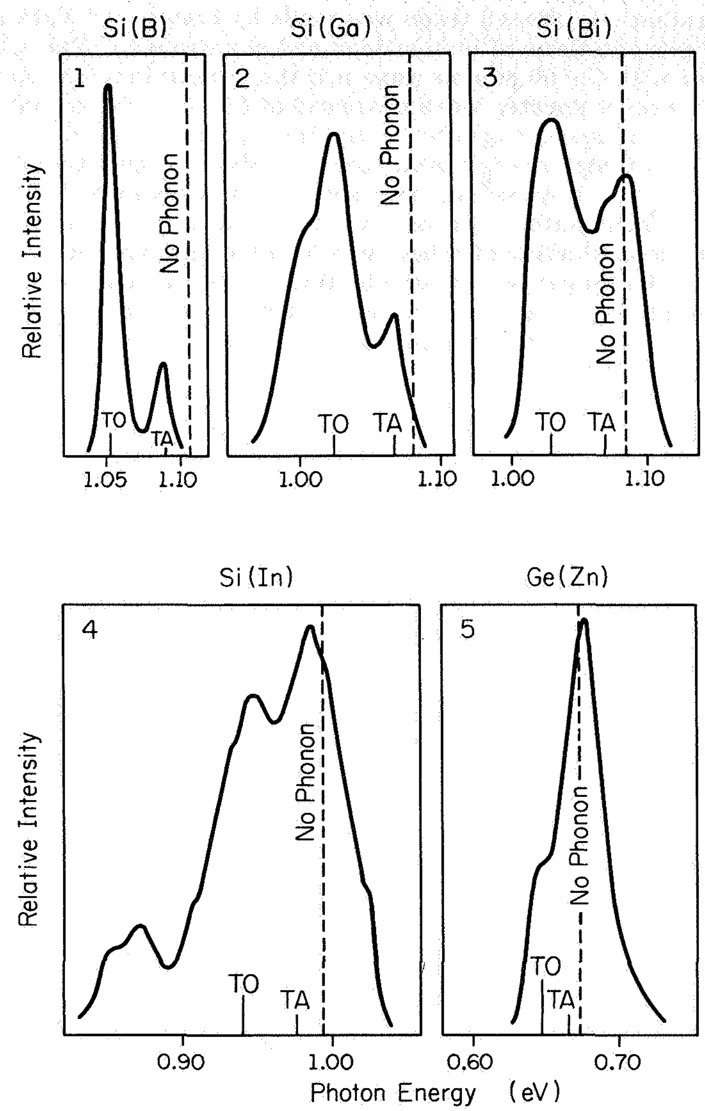
Within the framework of the above assumptions, a particularly interesting question now presents itself. Does the recombination of the electron and the hole result in luminescence? The answer must obviously be that there is some probability of this process being radiative. It is not easy to estimate just 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[1] 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 labeled to correspond to transitions involving the cooperation of a band edge phonon. Boron, gallium, and indium introduce levels at 0.046 eV, 0.071 eV and 0.16 eV, respectively, above the valence band in silicon. Bismuth introduces a level 0.069 eV below the conduction band in silicon. The spectra with B, Ga, and Bi indicate that a significant zero phonon component is seen only for the donor level. For the deeper acceptor level, arising from indium, a substantial zero phonon component is found.

Haynes[2] 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 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.



From Ya. E. Pokrovskii, "Radiative Recombination in Semiconductors", Dunod; Paris (1964)

Fig. 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 indicate transitions with the aid of transverse acoustic and transverse optical phonons. Donor and acceptor are indicated above each figure.

The initial report of luminescence from electron-hole recombination at deep radiation-induced traps was made by Ivanov and Yukhnevich[3] utilizing p-n junctions of both silicon and germanium. The silicon was irradiated with 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[2] 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 eV. The longer wavelength luminescence was suggested to arise from recombination *via* a defect at about 0.37 eV 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 Yukhnevich[4] are presented in Fig. 2. Fine structure on the previously reported broadband luminescence is seen in this figure. The half-width of the sharp line was reported to be less than 2×10^{-3} eV, a width less than kT at the measurement temperature of 80°K. The second peak was separated from the high intensity line by 0.015 eV, 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°K. Similar spectra were found for n- and p-type material.

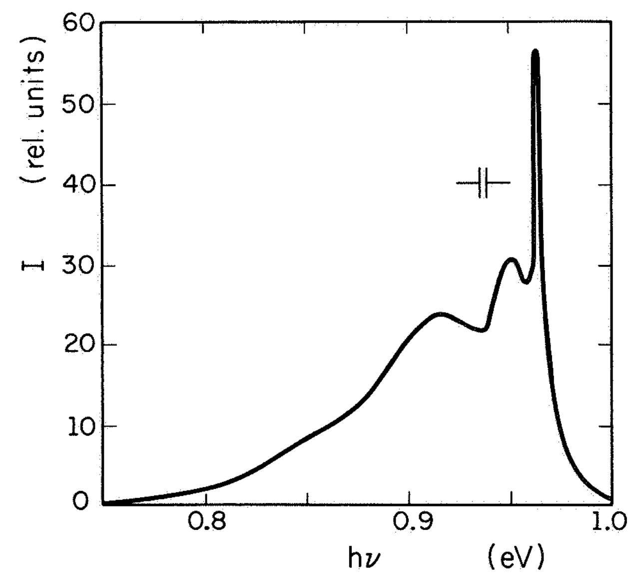


Fig. 2. Luminescent spectrum for silicon irradiated with Co-60 gamma rays. Measured at 80°K. After A. V. Yukhnevich, Ref. 4.

Yukhnevich and Tkachev[5] 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 0.488 eV and are reported to have half-widths of 5 and 2.5×10^{-3} eV, respectively. These authors report that no change in position or half-width results from a change in temperature between 65 and 130°K.

Recombination at these relatively deep traps may result from any of several processes.[†6]

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 co-workers 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 0.967 eV arises from the recombination of an electron trapped at the silicon A center with a hole localized at some excited level of the defect. Taking the silicon A center level to be 0.17 eV below the conduction band, Yukhnevich finds the excited hole state to be 0.025 eV above the valence band. Theoretical calculations by Kurskii[7] suggest that the ground state of a hole trapped by a silicon A center plus electron is about 0.13 eV above the valence band. As will be seen later in this paper, the identification of the transition giving rise to the 0.967 eV line corresponding to process 1.b is not completely unambiguous.

A study of the recombination luminescence in irradiated silicon has also been under way at the University of Illinois.[8, 9] 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, and (3) studying the details of spectra at temperatures near 4°K. A portion of the results of these measurements will be reported here.

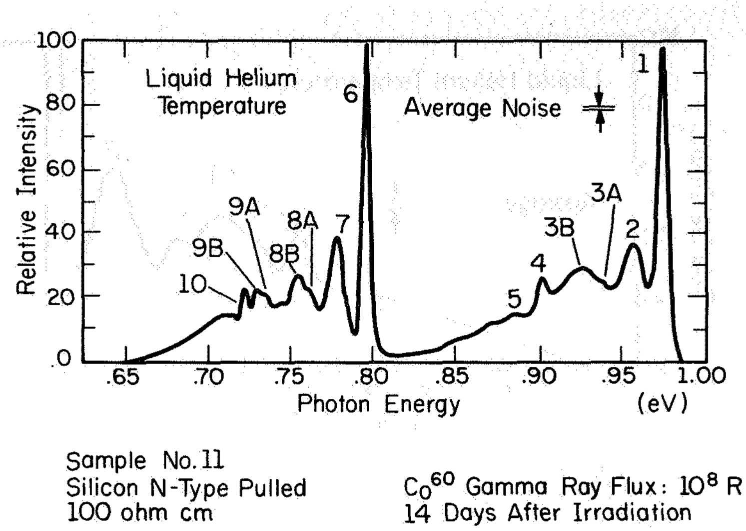
Luminescent spectra were obtained with a Jarrell-Ash Model 82-092 grating monochromator. A cooled PbS detector was used. The luminescence was excited with a 500-watt high-pressure mercury light filtered to remove all photons of wavelength greater than 7500 Å. The samples varied in thickness from 0.4 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 ratio 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-60 facilities at the U.S. Naval Research Laboratory and the Oak Ridge National Laboratory.

Measurements at 77°K gave results in substantial agreement with those of Yukhnevich and co-workers. The spectra were substantially the same for n- and p-type material and for neutron and gamma ray irradiations. Yukhnevich reports that the intense band occurring at 0.967 eV has a half-width of less than 0.002 eV. The present experiments found the half-width of this line to be 0.0050 eV when measured with an instrumental resolution of 0.0024 eV. 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 spectrum is the similarity in the two portions of the spectrum, with principal lines at 0.971 eV and 0.792 eV. 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, "Separation between corresponding bands," of the table associated with Fig. 3.

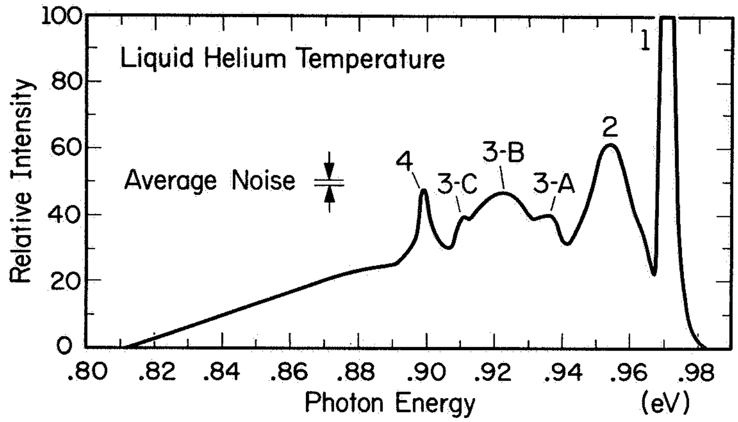
Figure 4 presents the data for a float-zone sample of silicon irradiated with gamma rays. The most striking feature is the absence of the low energy portion of the spectrum. There is no indication, within the noise limit, of a sharp line in the vicinity of 0.79 eV.



Energy Location of Luminescence Bands

Band Number N_i	Peak (eV)	Band N_i − Band N_1 (eV)	Band N_i − 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

Fig. 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.



Sample No. 1
Silicon N-Type Float Zone
70 ohm cm

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

Energy Location of Luminescence Bands

Band Number N_i	Peak (eV)	Band N_i - 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

Fig. 4. Luminescent spectrum for a float-zone 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.

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 the 0.791 eV line 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 spectrum of Fig. 4 is seen to agree with the location of the peaks in the spectrum of Fig. 3 within one milli-electron 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 ratio would permit. In each case, the measured half-width at 4°K is greater than the spectral resolution. For example, the measured width of the 0.791 eV line is 0.0008 eV when measured with an instrumental resolution of 0.0006 eV and is 0.0006 eV when measured with an instrumental resolution of 0.0003 eV. Although the present measurements were not able to determine the intrinsic width of this line, comparison of the data taken at 4°K with those taken at 77°K indicated that the 0.971 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.

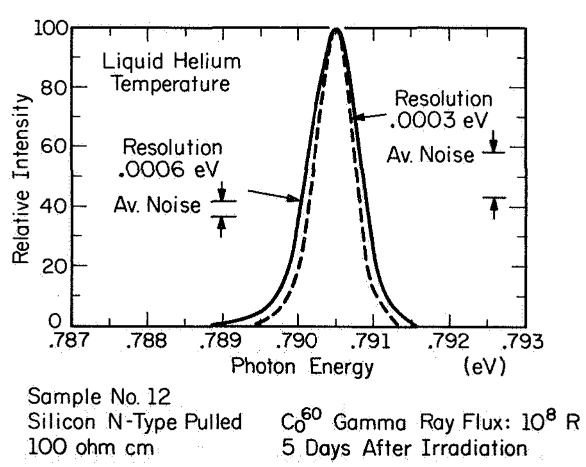


Fig. 5. Luminescent spectrum of the zero phonon line located at 0.7905 eV (line number 6 of Fig. 3) at two different monochromator resolutions.

On the basis of this result, it is suggested that the recombination process is described by 1.a above; i.e., recombination of a bound electron with a free hole. The temperature dependence arises from the thermal energy of the free hole in the valence band. The relative intensity of the 0.971 eV peak to the lower energy peaks suggests 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 Yukhnevich, is a very attractive explanation for the data. Such processes are well known and give a large probability for recombination involving no phonons 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°K, it would certainly be trapped. This mechanism is ruled out only by the results of the half-width temperature dependence measurements. 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 0.792 eV 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°K is 1.165 eV.[10] The energy difference between the most intense line, centered at 0.971 eV, and the band gap is 0.194 eV. Although this value is somewhat larger than those measured by other techniques, it seems likely that this level arises from the silicon A center. The energy difference between the line centered at 0.791 eV and the band gap is 0.374 eV, suggesting a recombination level 0.374 eV 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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DISCUSSION -- Robert J. Spry and W. Dale Compton

Comment: (G. Watkins) I would assume that the zero phonon line corresponds to a transition from the relaxed excited state of the system to the relaxed ground state, while the phonon-associated transitions represent ones in which the lattice tends not to relax during the optical transition. For the lines described in your paper, the large fraction of the luminescence in the zero phonon line and the relatively small number of phonons involved in the phonon-assisted emissions would indicate to me small changes in the relaxation for the excited and ground states. This surprises me for the A center. We have measured directly from EPR the coupling of the trapped A-center electron to lattice strain, and the value is large. Since the initial state has this electron and the final state does not, I would expect a large relaxation. Perhaps this argues against the identification of these bands with the A center.

A: (W. D. Compton) I believe that this depends upon how flat the ground state energy configuration is. If the relaxed ground and excited states are coupled to the lattice with different constants, I would agree with you. I would have suspected that the excited state and the ground state between which the transition would occur would not be very different in this case.

Q: (A. B. Lidiard) In connection with Watkins' remarks on the relation between the known Jahn-Teller distortion of the A center and the intensity of the zero phonon line, I would like to ask what is the fractional intensity of this line (= exp (-S) in terms of the Huang-Rhys factor S).

A: (W. D. Compton) We will only be able to determine the fractional intensity of the zero phonon line when we have improved the resolution of the system sufficiently to allow a direct determination of the line shape, in particular its half-width and peak intensity. It will certainly be important to determine this.

Q: (H. Y. Fan)

(1) You said that the luminescence attributed to the A center is observed in both floating-zone and crucible-grown samples. Is there a noticeable difference between the behaviors of these two types of samples?

(2) Is it possible to differentiate the bound exciton and defect-band recombination emissions by the dependence of emission on the intensity of excitation?

A: (W. D. Compton)

(1) The high energy luminescent spectrum is seen in both materials. For material of moderate to high resistivity, the A center seems to always be found by electron spin resonance measurements and by minority carrier lifetime measurements. The present results are consistent with this.

(2) The recombination mechanism can be differentiated in this way, if the trapping of carriers occurs in two distinct ways. The recombination of a bound minority carrier with a free majority carrier will certainly have a different intensity dependence than the recombination of an electron and hole that recombine from an exciton state. In this state I would suspect, however, that the exciton is not formed and then trapped at the oxygen, but that an electron is first trapped, followed by the trapping of a hole into a bound state, with the subsequent recombination of the trapped pair. This would then have the same intensity dependence, I believe, as the bound-to-free recombination.

Q: (A. H. Kalma) Yukhnevich has interpreted the higher energy spectrum as both the A center and something else. Is the A-center explanation the latest one? He seemed to move away from the A-center explanation when he found the higher energy spectrum in approximately the same intensity in both pulled and floating-zone crystals.

A: (W. D. Compton) It is my understanding that Yukhnevich still interprets the higher energy spectrum as arising from recombination at the A center. I have seen a little of a very recent publication on this topic by the Russian workers, but unfortunately I have been unable to get a copy of it.

Q: (D. K. Wilson) Have you examined the dependence of the luminescent intensity on the intensity of the exciting radiation? This dependence could be useful in distinguishing bound-to-bound and free-to-bound transitions.

A: (W. D. Compton) I agree that this measurement would provide some valuable information. We are limited, however, by the low luminescent intensity, and have generally worked only with the maximum available level of excitation.

Q: (W. L. Brown) Why are your results so surface sensitive since your recombination photons are so far from the band gap? How about using electron beam excitation? Or an IR laser?

A: (W. D. Compton) Since the exciting light is confined to wavelengths less than 7500 Å, the absorption is confined to the surface. Thus, surface conditions of the sample are quite important. Either electron beam or laser excitation would be feasible, and we have plans to use laser excitation.

Q: (C. E. Barnes)

(1) Can you obtain additional information about the nature of the recombination luminescence by studying the temperature dependence of the peak position?

(2) According to your measurements, does the ratio of the impurity-exciton binding energy to the A-center ionization energy agree with the roughly constant ratio found by Haynes?

A: (W. D. Compton)

(1) The peak position of the zero phonon line shifts to higher energy upon cooling from liquid nitrogen to liquid helium temperature. The shift is almost the same as occurs for the band gap over the same temperature range. Since levels near the band edges will shift with the band, about the same shift in peak position will likely occur for a "bound-bound" transition as for a "bound-free" transition, if the bound states are reasonably shallow.

(2) The luminescence measurement can give the binding energy of the exciton to the trap if the depth of the trap is known. If we assume that the recombination is of a bound electron and a free hole, this places the level 0.194 eV below the conduction band. This is 20 to 25 millivolts deeper than most of the thermal release measurements place it. If one assumes that the exciton is bound to the ionized silicon A center by 0.1 of the ionization energy of the center, this would give a binding of about 20 millivolts. The agreement between the thermal data and the luminescence data would be substantially improved if this is the case. I believe that it is essential to determine, unambiguously, the nature of the recombination process before one can proceed further with this argument.

Q: (L. J. Cheng)

(1) What is the irradiation fluence dependence of your luminescence intensity?

(2) What are the relative intensities between the samples irradiated with Co-60 gamma rays and neutrons in your experiments?

A: (W. D. Compton)

(1) The luminescent intensity is generally proportional to the radiation fluence. It is difficult to determine this precisely or to see if the luminescent intensity saturates with radiation fluence, since the intensity of luminescence depends quite critically upon the surface treatment of the material.

(2) The absolute intensity of the luminescence seems to depend only upon the number of defects present and not upon the nature of the irradiation. Using defect introduction rates for neutron irradiation and gamma irradiation, as determined from minority carrier lifetime measurements, one would estimate that the total damage introduced by the high neutron fluence is substantially greater than for the highest gamma fluence. Since the luminescent intensities are roughly equivalent for the irradiations, this may indicate that only the isolated defects formed by neutron irradiation are effective in generating luminescence.

Q: (D. Landis) Is any significance attached to the fact that the two spectra have similar amplitudes?

A: (W. D. Compton) The spectra that I presented had about the same intensity for the peaks at 0.971 eV and 0.791 eV. The ratio of these peaks is by no means constant, however, and depends upon the length of time that the sample has been stored at room temperature following the irradiation. The 0.791 eV peak and its associated phonon structure is very small immediately following irradiation, increases to have about the same magnitude as the 0.971 eV, and then decreases with a very long time constant.

Electron and Phonon Tunneling Spectroscopy

in Metal-Germanium Contacts*

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ABSTRACT

Measurements of the tunneling characteristics of metal electrodes on vacuum-cleaved Sb-doped Ge reveal greatly improved agreement with the one-electron model relative to chemically fabricated units. Strong phonon-assisted tunneling in both Sb- and As-doped Ge is observed, and is interpreted in terms of a two-step process via an evanescent state at Γ_2'. The tunneling characteristics at $eV \cong \pm \hbar\omega_{LO}$ in Ga-doped Ge are interpreted in terms of the alteration of the electronic dispersion relation due to deformation potential coupling between the holes and the longitudinal optical phonons.

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†National Science Foundation Post-doctoral Fellow.

It has been suggested theoretically[1-4], and verified for n-type Ge[5] and for both n- and p-type GaAs[6,7], that tunneling through Schottky-barrier contacts on a degenerate semiconductor (MS contacts) provides a useful probe of the electronic energy spectrum of the semiconductor. In this letter we show that the fabrication technique of evaporation of metal electrodes on vacuum-cleaved semiconductor surfaces not only substantially improves the agreement between the one-electron calculation of the tunnel characteristics and their measured values, but also permits accurate measurements of phonon-energies[7,8] and estimates of electron-phonon coupling constants in the semiconductor. The precision of this phonon spectroscopy is comparable to that in indirect p-n tunnel diodes. However, the MS contacts provide a far more versatile spectroscopic tool as evidenced, for example, both by our ability to distinguish between the Keldysh-Kane[9,10], Kleinman[11], and impurity-induced[12] mechanisms of phonon assisted tunneling in Ge, and by the applicability of the method to direct as well as indirect semiconductors.

The MS contacts were made by cleaving Ge bars with the dimensions 1 x 0.4 x 0.2 cm in a vacuum of 10^{-7} Torr. A mask with 0.018 cm diameter holes was brought close to the (100) surface. Indium or lead was evaporated at a rate of 50 Å/sec to a thickness of approximately 5000 Å . After removing the bars from the vacuum system, a freshly cut indium tip was pressed into a metal dot situated on a good cleavage plane. Cold welding provided fairly stable contacts.[13]

Measurements of dI/dV and d^2I/dV^2[14] were made between 2°K and 10°K on a total of 10 Sb-doped units ($n = 7.5 \times 10^{18}/cm^3$) and 11 As-doped units ($n = 7.0 \times 10^{18}/cm^3$). Below the superconducting transition temperature, the BCS energy gap in In or Pb was observed in all samples. The shape and the absolute value of the conductance vs bias curve changed little from sample to sample. Pronounced phonon structure was observed in all junctions.

The comparison of 3 measured conductance curves on Sb-doped samples of Ge [solid lines (a), (c), and (d)] with the model predictions of CDMT[2] [dashed line (b)] is shown in Fig. 1. The most commonly observed conductance curves were similar to (c), whereas (a) and (d) represent the high- and the low-conductance extremes. The structure associated with the BCS energy gap has been omitted for simplicity. The Sb-doping was selected for comparison with the experiments of Conley and Tiemann.[5] Comparison of Fig. 1 with Fig. 3 in reference 5 indicates that the vacuum-cleaved samples exhibit a much sharper minimum in conductance relative to the chemically prepared units. This fact substantially improves the agreement with the one-electron theory of Schottky-barrier tunneling, although the agreement in As-doped Ge samples is not as good as that shown in Fig. 1. Note that the absolute magnitude as well as the shape of the experimental curve is adequately described by the model. One of the consequences of the model is that, in forward bias (negative voltage in Fig. 1), it predicts a too rapid increase in conductance because the exponential character of the potential barrier for semiconductor states below μ_F (Fermi degeneracy) is ignored.[7] The barrier height V_b was taken to be the value $V_b = 0.63 \pm 0.03$ eV obtained from measurements of capacitance vs bias at 77°K.

The observation of incremental increases in the conductance of metal-n-type Ge contacts due to inelastic tunneling with phonon emission is shown in Fig. 2. Although identical structure is exhibited by Sb-doped Ge, the characteristics of an As doped unit are shown in Fig. 2 because of the well-known difficulty in observing phonon-assisted tunneling in any but Sb doped Ge p-n tunnel diodes.[15] Ours is the first observation of large, sharp phonon-assisted tunneling characteristics in As-doped Ge, and illustrates well the flexibility and potentialities of MS tunneling as a spectroscopic tool.

The results shown in Fig. 2 are attributed, for reverse bias, to the two-step process of an electron first tunneling from the metal into an evanescent state associated with the electronic spectrum at $\Gamma_2{}'$ in the Ge Brillouin zone, and then, by the subsequent emission of a phonon, being scattered into a current-carrying state at L_1. The inverse process occurs at forward bias. The evidence which weighs against phonon-assisted tunneling via an impurity channel is: (1) the phonon processes have comparable strength in Sb and As doped units; and (2) the lineshape of d^2I/dV^2 does not reflect the known phonon density of states in Ge.[16] The evidence suggesting identification of the mechanism as a two step process[11,17] via evanescent states near $\Gamma_2{}'$ is: (1) the lineshape of d^2I/dV^2 is similar to that observed in p-n junctions with sharp peaks at the zone-boundary phonon energies;[18] (2) the enhanced strength of the LA phonon peak in accordance with the selection rules for $\Gamma \rightarrow L$ transitions[17,19] and observations in Ge p-n tunnel diodes;[11,17,18] (3) the absence of pronounced phonon structure near the zone-boundary phonon energies in p-type Ge contacts; and (4) a calculation of the magnitude of the LA phonon-assisted current based upon this mechanism indicates that a 1-10% effect is to be expected. This phonon-assisted tunneling mechanism is similar to that used by Kleinman[11,20] to describe the characteristics of Ge p-n tunnel diodes. Our results provide indirect support to the junction-potential approach to phonon-assisted tunneling in homogeneous diodes.

Another advantage of MS tunneling spectroscopy of phonons is its use for separately performing phonon spectroscopy in n- and p-type materials. In air-cleaved, heavily-doped In-p-type Ge contacts, sharp structure at the zone-boundary phonon energies has not been observed, in contrast to the results on both vacuum and air-cleaved n-type Ge units. However, symmetrical structure in d^2I/dV^2 at $eV \cong \pm \hbar\omega_{LO}$ (k = 0 optical phonon energy) has been found which is analogous to that occuring in Si MOS junctions.[21] Such structure in d^2I/dV^2 is shown in Fig. 3 for an air cleaved, Ga-doped Ge junction. This structure is interpreted as due to the influence of a deformation potential interaction between the holes and the longitudinal optical phonons rather than an inelastic phonon emission process. This interaction alters the dispersion relation of the holes and, thereby, alters the tunneling characteristics for biases $eV \cong \pm \hbar\omega_{LO}$.[22]

Summarizing, we have shown that the technique of depositing metal electrodes on both vacuum and air cleaved degenerate semiconductors permits not only accurate one-electron tunneling spectroscopy, but also the gathering of information on phonon energies, electron-phonon coupling mechanisms, and electronic dispersion relations which is inaccessible by conventional indirect tunnel-diode spectroscopy.

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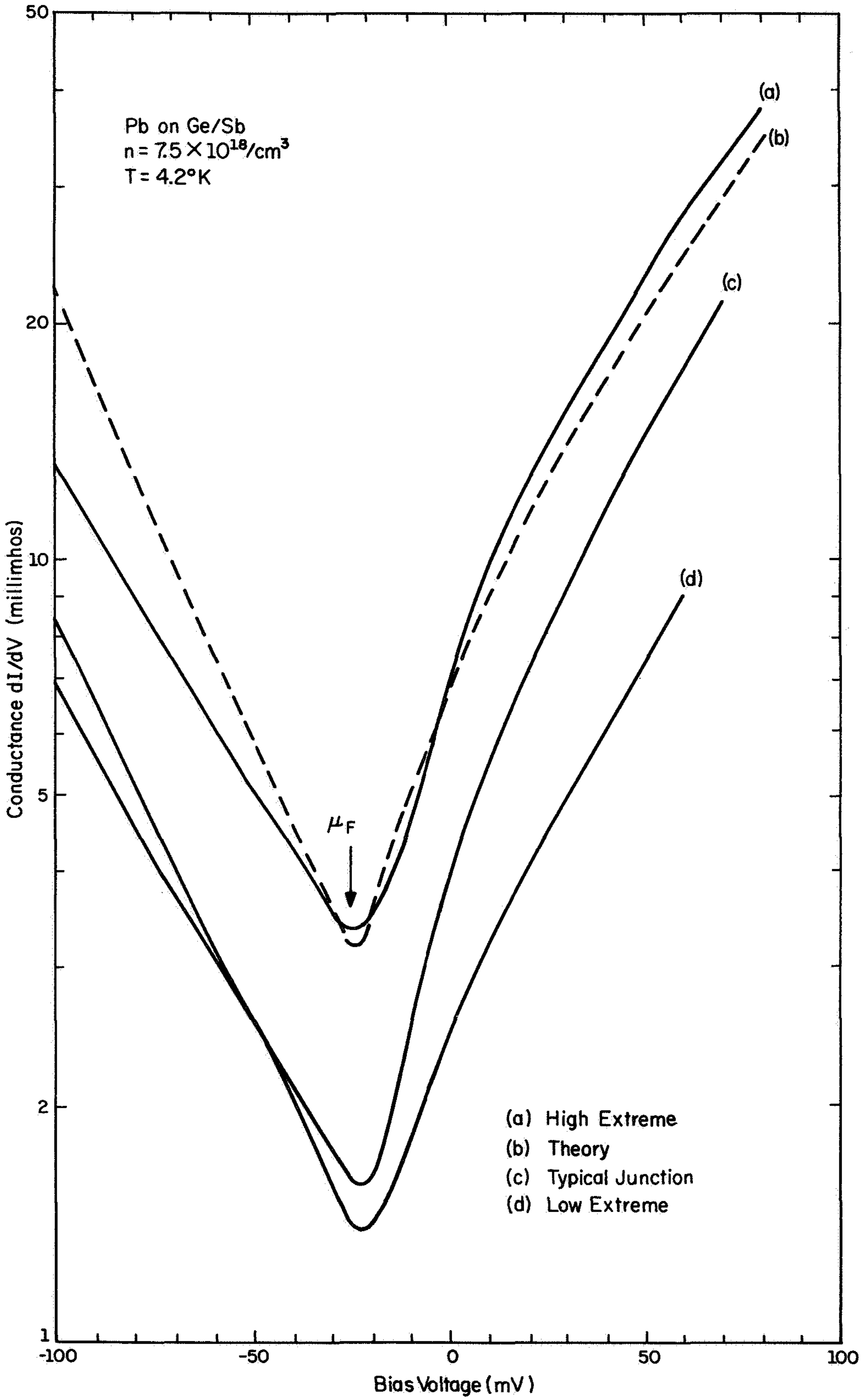
FIGURE CAPTIONS

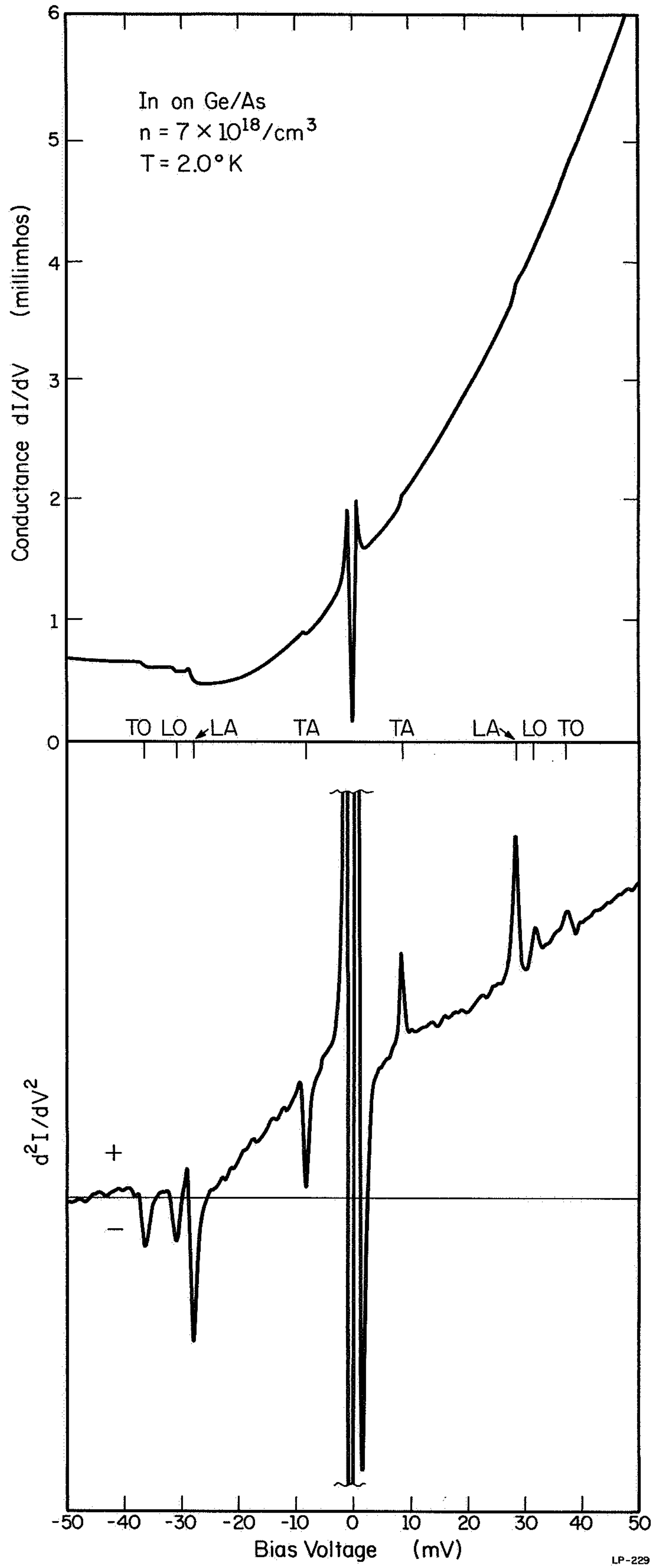
Fig. 1. Comparison between 3 experimentally measured conductance curves on $n = 7.5 \times 10^{18}/cm^3$ Sb-doped Ge [solid lines (a), (c), and (d)] at 4.2°K and the calculated conductance [dashed line (b)] using the model developed in reference 2 for a barrier height $V_b = 0.63$ eV obtained from capacitance measurements. The most commonly observed conductance curves were similar to (c), whereas (a) and (d) represent the high- and the low-conductance extremes. The contact metal is Pb and the contact area is $2.5 \pm 0.5 \times 10^{-4}$ cm^2. Structure associated with the superconducting energy gap has been omitted. The Fermi degeneracy $\mu_F = 25$ mV has been indicated.

Fig. 2. Conductance and d^2I/dV^2 of an indium contact on As-doped Ge junction at 2°K. The arsenic doping is $n = 7.0 \times 10^{18}/cm^3$. The observation of the In superconducting gap at zero bias is shown explicitly. Its presence shifts the phonon structure to higher energies by $\Delta = 0.5$ mV. Assignment of phonon energies is according to reference 18.

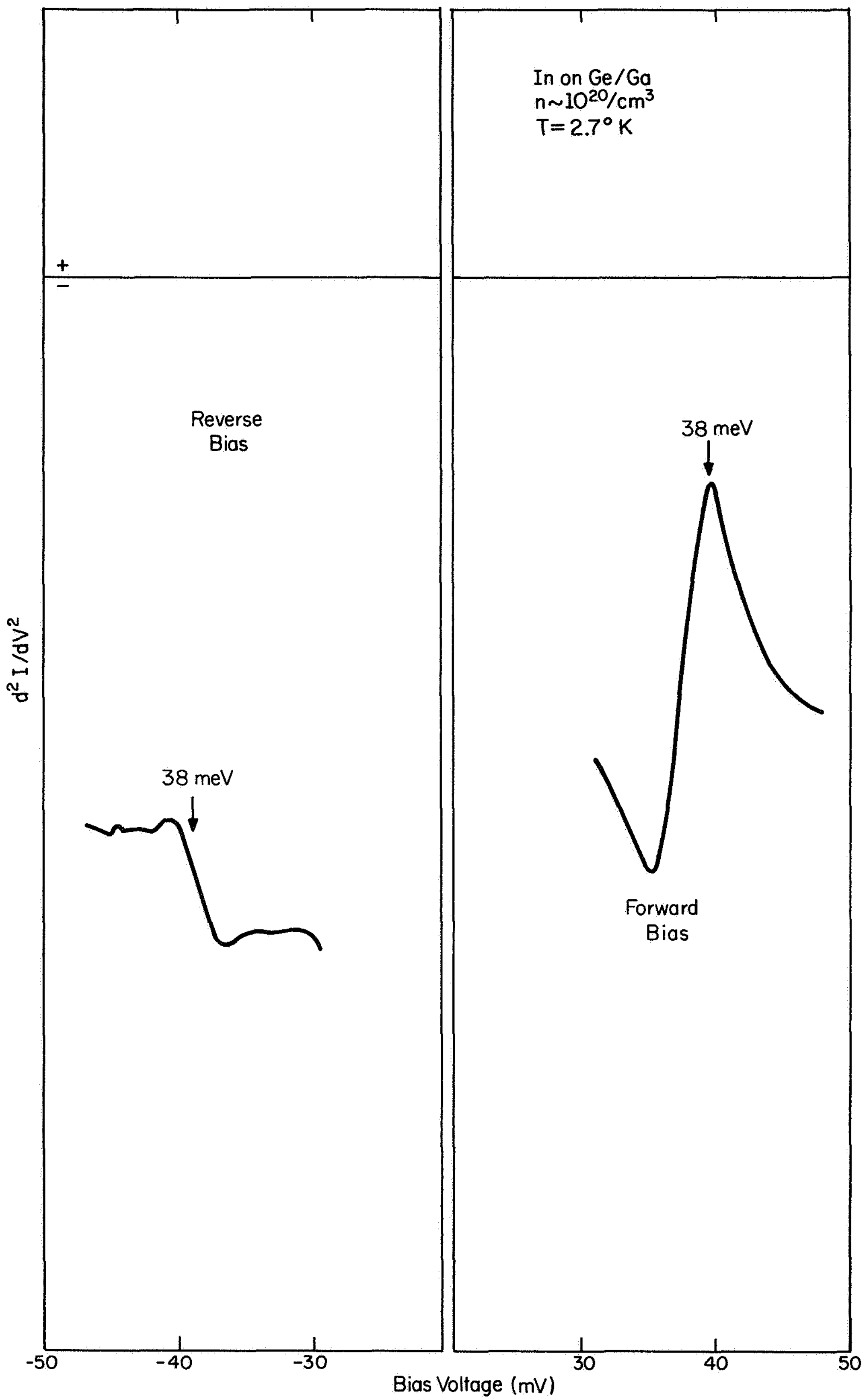
Fig. 3. Symmetrical structure in d^2I/dV^2 at $eV = \pm \hbar\omega_{LO}$ (k = 0 optical phonon energy) observed in an air-cleaved, Ga-doped Ge junction ($n \sim 10^{20}/cm^3$) at 2.7°K is shown. The contact metal is In.


Pb on Ge/Sb
n = 7.5 X 10^18/cm^3
T = 4.2°K
(a)
(b)
(c)
(d)
μF
(a) High Extreme
(b) Theory
(c) Typical Junction
(d) Low Extreme
50
20
10
5
2
1
-100
-50
0
50
100
Conductance dI/dV (millimhos)
Bias Voltage (mV)

LR-232



In on Ge/As
n = 7 × 10^18/cm^3
T = 2.0° K
Conductance dI/dV (millimhos)
TO LO LA TA TA LA LO TO
d^2I/dV^2
+
−
Bias Voltage (mV)
LP-229



In on Ge/Ga
$n \sim 10^{20}/cm^3$
$T = 2.7°$ K
+
−
Reverse
Bias
38 meV
38 meV
Forward
Bias
$d^2 I/dV^2$
-50
-40
-30
30
40
50
Bias Voltage (mV)

LR-231

EVIDENCE OF HOLE-OPTICAL-PHONON INTERACTION IN DEGENERATE SILICON IN TUNNELING MEASUREMENTS†

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Tunneling from a metal into degenerate p-type silicon exhibits peaks in d^2i/dV^2 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.

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[1,2] and has recently been more directly verified by observations of oscillatory photoconductivity[3] in germanium[4] and silicon.[5] 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[6] 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.[7,8] This was originally described as a threshold effect.[7] The companion peak in 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 ⟨111⟩ faces of silicon single crystals containing 1.3×10^{20} cm^{-3} boron, corresponding to a free-carrier Fermi degeneracy μ of 160 meV, assuming a density-of-states mass of 0.58. Small bars ($2\times4\times10$ mm^3), having ⟨111⟩ axis, were completely nickel plated[9] 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.[10] Although such areas rarely exceeded 0.5 mm diam, this sufficed to locate the tunneling contact, 0.01 to 0.1 mm diam, 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 mg was applied to the point. These operations were performed in the air in about 10 min; absorption and/or oxidation on the surfaces are thought to produce a tunneling barrier of substantially lower transmission than the silicon depletion layer alone.[11] 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^2, 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 $0<E\leq eV$. At negative bias, the

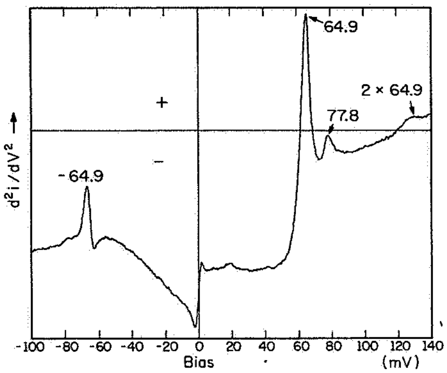

FIG. 1. d^2i/dV^2 spectrum for indium–p-type silicon (1.3×10^{20} cm^{-3} boron) tunnel junction at 4.2°K. Modulation level is 3 mV. Peaks (left to right) occur at −64.9(+), −60.7(−), −2(−), +2(+), +19.5(+), +64.9(+), +77.8(+), and +129(+), in millivolts.

process may be regarded as tunneling of holes into occupied ($E<0$) states in the valence band.

Second derivative spectra at 4.2 and 1.6°K are shown in Figs. 1 and 2, respectively. The main peaks occur at $V=\pm64.9\pm0.5$ mV, which is in excellent agreement with the value 64.8 mV obtained from Raman scattering[12] 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°K of the transition temperature of indium, 3.41°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)

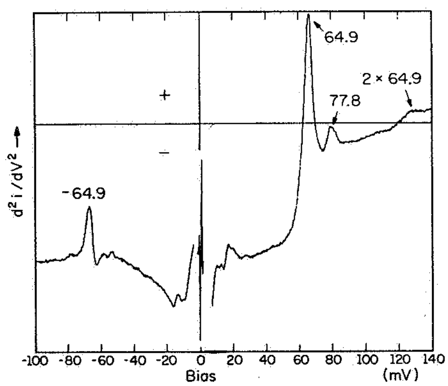

FIG. 2. d^2i/dV^2 spectrum for the sample of Fig. 1 as observed at 1.6°K. Modulation level is 4 mV peak-to-peak, except in center where it is 0.3 mV peak-to-peak. Differences between this curve and Fig. 1 in the range -20 mV $\leq V\leq 20$ mV are satisfactorily explained by the superconductivity of the indium, and are regarded as important justification for the techniques employed and for analysis of the spectra in terms of tunneling.

indium phonon structure[13] 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[14] in samples containing up to 1.3×10^{19} cm^{-3} boron. Since the strength of this peak relation 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°K corresponds to a minimum in conductance with full width of 4 mV between points of maximum slope. This structure is broader than the conductance maximum reported previously[15,16] in silicon p-n junctions at high doping, which we also observe at lower boron concentrations of 5×10^{19} cm^{-3} and 2×10^{19} 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.[16,17] Additional weak features in Fig. 1 are peaks at 19.5 and 128.6 mV identified as the transverse acoustic phonon at the zone boundary and twice the $k=0$ phonon, respectively.

The prominent peak in d^2i/dV^2 at +64.9 mV corresponds to an increase (~10 %) in conductance di/dV at this bias. Two possible lines of argument in explaining this are these: (a) 64.9 mV corresponds to the opening up, at a threshold for excitation of the barrier, of an additional channel for charge transfer.[18] (b) At the energy $E\cong\hbar\omega_0$, the tunneling current is altered as a result of the interaction of holes and optical phonons in the bulk. On the basis of the peak in d^2i/dV^2 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 d^2i/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[1-5] of holes with the $k\cong 0$ optical phonon, resulting in a modification of the states in the bulk[19,8] at energies $E\cong\pm\hbar\omega_0$. 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 $E=\mu-\hbar^2k^2/2m$, 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.[17] 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[20] 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.[21]

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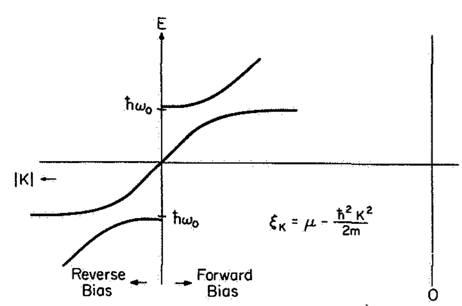

FIG. 3. Schematic representation of the electron-phonon dispersion relation indicating the effect of coupling at the longitudinal optical phonon energy $\pm\hbar\omega_0$.

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