Phonon Spectroscopy of Germanium-Silicon Tunnel Heterojunctions*

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The energies of the optical and acoustical phonons in germanium-silicon tunnel heterojunctions have been measured by observing the structure in the current-voltage characteristics at 4.2°K caused by the emission of such phonons. The phonon spectra are not characteristic of either germanium or silicon alone, and show that the units are not merely a germanium contact to a silicon homojunction or vice versa. Strain and interface effects give rise to a large number of weak background lines. Unusual resistance anomalies have been observed near $V=0$.

1. INTRODUCTION

IN this paper a *p-n* heterojunction is defined to be a semiconductor-semiconductor junction where the energy gap of the semiconductor on the *p* side is different from that on the *n* side. Any change in the energy gap from that of either host or bulk semiconductor is assumed to occur in the transition region (in the simplest case). In an ordinary *p-n* junction there is only one well-defined energy gap which is constant throughout the whole junction. In a heterojunction one can think of the transition region (the region in which space charge gives rise to an internal electric field) as either a continuously varying energy gap or two constant energy gaps with an abrupt discontinuity at the junction interface.

There is to date a profusion of information in the literature on heterojunctions.[1] Unfortunately, one is quickly lead to the conclusion that while rather simple theoretical models have been fully investigated, such systems are not readily realizable in practice. Practical experimental systems suffer from a variety of complex effects (primarily the result of lattice matching problems and associated interface states) and these effects have precluded the building of heterojunction devices having the many useful applications deduced from simple theoretical junction models. It is for this reason that heterojunctions are more than likely to have only academic interest, at least for the foreseeable future. Nevertheless, the junction "physics" of "physically realizable" heterojunctions is in itself interesting and must be fully understood if the variable band-gap system is ever to have any useful significance.

The majority of experimental investigations have been into the so-called abruptly discontinuous band-gap system where one semiconductor is epitaxially deposited upon another.[2] A continuously variable band-gap system would necessitate the use of either a diffusion or alloy process and has not proved to be as popular. However, it is felt that such a system offers a better chance for success, particularly if the primary semiconductors germanium and silicon are involved, and such germanium-silicon alloy heterojunctions have been reported in the literature.[3] Unfortunately, no experimental evidence has yet been presented which illustrates unambiguously in a simple fashion that any of the vast variety of experimental heterojunctions considered up until now are indeed true heterojunctions.

It is well known that germanium and silicon are indirect transition semiconductors that have a distinct phonon spectrum, and that this characterizes uniquely the current in tunneling junctions made from these materials.[4] Using such properties, Nathan and Marinace[5] have attempted to demonstrate true heterojunction action in vapor-grown Ge-GaAs junctions by examining the phonon spectrum of degenerate tunneling diodes. Unfortunately, their results are not as definitive as one is led to believe and, in fact, probably show that they have germanium homojunctions. The essential feature of their argument, that GaAs has a polaron dip at $V=0$ which is not present in Ge, is incorrect in that germanium can also have such dips and, furthermore, it is is not likely that such dips are due to polarons.[6]

This paper presents the results obtained from a study of germanium-silicon tunnel heterojunctions. The phonon spectrum of these degenerate junctions was examined using an apparatus described in a previous publication.[7] Of necessity, the interpretation of the experimental data must be highly qualitative, the theoretical aspects of the problem being insoluble at the present time. Recent results on the phonon spectra of Ge-Si alloys[8] indicate that they form an ordered diamond-type lattice. These data will be used as an aid in interpretation of the heterojunction spectra.

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[1] For example, see references given by W. G. Oldham and A. G. Milnes, Solid-State Electron. **7**, 153 (1964) or R. H. Rediker, S. Stopek, and J. H. R. Ward, *ibid.* **7**, 621 (1964).
[2] R. L. Anderson, IBM J. Res. Develop. **4**, 280 (1960).
[3] J. Shewchun and L. Y. Wei, J. Electrochem. Soc. **111**, 1145 (1964).
[4] A. G. Chynoweth, R. A. Logan, and D. E. Thomas, Phys. Rev. **125**, 877 (1962).
[5] M. I. Nathan and J. C. Marinace, Phys. Rev. **128**, 2149 (1962).
[6] R. A. Logan and J. M. Rowell, Phys. Rev. Letters **13**, 404 (1964).
[7] W. R. Patterson and J. Shewchun, Rev. Sci. Instr. **35**, 1704 (1964).
[8] R. A. Logan, J. M. Rowell, and F. A. Trumbore, Phys. Rev. **136**, A1751 (1965).

2. JUNCTION FABRICATION

Germanium-silicon heterojunction diodes were made by the alloying technique. The starting materials consisted of single-crystal silicon wafers and either single-crystal germanium wafers or alloy dots containing germanium plus a small percentage of dopant. The silicon wafer was prepared by first mechanically lapping it with suitable silicon-carbide abrasives, and then etching it to a mirror finish in *CP*4 (four parts HNO_3, three parts CH_3COOH, three parts HF). After suitable rinsing and drying, the wafer was broken or cut into small pieces suitable for the alloy process. The alloying apparatus consisted of a high-current strip heater with an electrical timer for control of the temperature cycle. The alloying is carried out by placing a silicon wafer of thickness between 10 and 20 mils on the heater with a selected spheroid of germanium on top. The area of the junction was approximately determined by the size of the germanium used. The alloy cycle consisted of an abrupt heating to a temperature between 950 and 1200°C for periods of 3 to 15 sec, followed by a similar abrupt cooling. Short alloy times were deliberately employed in an effort to form thin abrupt junctions and to minimize the diffusion of the doping elements in the germanium and the silicon. In order to obtain good wetting between the germanium and silicon, the alloying was carried out in an atmosphere of dry hydrogen.

After the junction was formed, a second alloy was carried out in which a gold wire was attached to the body of the silicon to form one of the ohmic contacts. The unit was lightly etched, washed, dried, and then mounted on a standard header and a second ohmic contact of the pressure type was made to the germanium side.

Junctions were formed using both p and n silicon wafers of 0.001 Ω-cm in which the doping agent was phosphorus for the n-type and boron for the p-type. The small single-crystal spheroids of germanium were of 0.001 Ω-cm or greater, in which the p-type doping agent was gallium and the n-type was antimony. It was found that more degenerate junctions could be formed when n-type silicon was used. Since tunneling current was more pronounced in these junctions and the spectroscopy of this current was to be studied, a decision was made to concentrate only on the n-Si–p-Ge heterojunctions. Junctions formed using a germanium-plus-dopant dot were found to exhibit greater degeneracy than the ones formed with single-crystal spheroids.

3. EXPERIMENTAL TECHNIQUES AND DATA

The n-Si–p-Ge heterojunctions that were studied were backward junctions, being not quite narrow enough to display a negative-resistance region. The measurements of first derivative dV/dI and second derivative d^2I/dV^2 were made at 4.2°K. These were plotted automatically as the applied bias was swept through the range of interest. A small sensing signal at 500 cps with a peak-to-peak amplitude less than 1 mV was used to determine the incremental resistance and second derivative.[7] Results for a typical heterojunction are shown in Figs. 1 and 2.

As can be seen from Fig. 2, the spectroscopy of the germanium-silicon heterojunctions under consideration is quite complex. Before any analysis could be performed it was necessary to catalog all the peaks, such as in Table I where only certain particular peaks are indicated. The strength of each peak was also recorded. Strength was measured relative to the strongest peak on any single unit, rather than on an absolute basis. Once such a master table was prepared, it was possible to determine that there existed a regularly repeatable pattern from unit to unit. Some 50 units were scanned in this fashion from a population of over 200 that were built.

Interest in the spectrum was restricted to the range of energies up to the maximum phonon energy that could occur. In the system under consideration this was

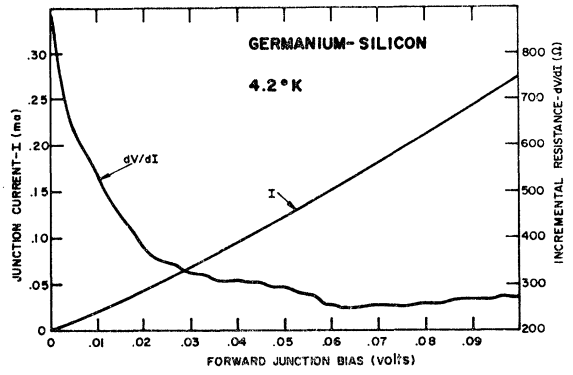

FIG. 1. Curves showing the bias dependence of the current I and incremental resistance dV/dI of a typical germanium-silicon heterojunction at 4.2°K.

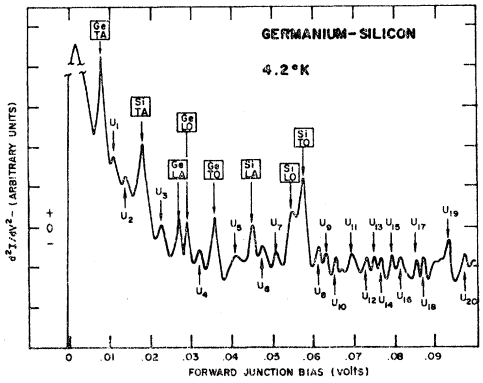

FIG. 2. Curve of d^2I/dV^2 against bias for the heterojunction used for the curves of Fig. 1, showing several identified phonon peaks and a large number of unidentified peaks marked with U's.

TABLE I. Phonon energies observed in germanium-silicon heterojunctions, together with their assignments.[a]

Diode	Energy of peak in second-derivative (meV)								Indicated composition	V_p (meV)
	TA		LA	LO	TO					
Germanium	7.805		27.49	30.55	36.04				Ge–Ge	···
Payne (Ref. 15)	S		S	W	M					
Silicon		TA				LA	LO	TO		
Logan *et al.*		18.7				47.0	56.2	59.1	Si–Si	···
(Ref. 8)		VS				W	W	S		
Ge–Si	8.50	18.5	27.5	29.5	36.0	46.1	55.0	58.1		
Mar 18–3–64									Ge–Si	113
	VS	S	W	W	M	W	M	S		
Ge–Si	9.1	19.0	29.8	33.2	39.2	46.1	55.4	58.5		
Apr 15–5–64									(96%Ge + 4%Si)–Si	190
	VS	VS	W	W	M	VW	VW	VS		
Ge–Si	9.3	18.7	30.5	33.9	40.0	46.5	55.5	58.3		
Mar 2–1–64									(94%Ge + 6%Si)–Si	135
	S	S	W	W	M	W	M	S		
Ge–Si	9.7	18.5	31.8	35.8	42.5	46.0	55.1	58.4		
Apr 15–2–64									(90%Ge + 10%Si)–Si	110
	M	VS	W	M	W	W	W	S		
Ge–Si	10.1	19.0	32.5	37.1	43.5	46.3	55.4	58.6		
Apr 15–4–64									(87%Ge + 13%Si)–Si	160
	VS	S	M	W	M	W	VW	VS		

[a] Code: VS = very strong. S = strong. M = medium. W = weak. VW = very weak. TA = transverse acoustic phonon mode. LA = longitudinal acoustic phonon mode. LO = longitudinal optic phonon mode. TO = transverse optic phonon mode.

the transverse optical (TO) mode of silicon at about 60 meV. While it has been demonstrated that combination modes can occur,[4] no attempt was made to search for such multiple modes because of the complexity of the spectra obtained. To further simplify matters, it was also decided that units having a V_{peak} in the range of interest should be eliminated. V_p is defined as the voltage at which $|dI/dV|$ has its minimum value. Since V_p is a function of the doping on both sides of the junction, it was possible for it to occur in the energy range below the highest phonon mode. In such units the phonon spectrum was already quite weak and the appearance of V_p as an additional peak served only to complicate matters. Only those units which had $V_p > 100$ meV were used in the analysis. V_p values are indicated in the last column in Table I.

4. ANALYSIS

It has already been remarked that the experimental phonon spectrum of the germanium-silicon heterojunctions under consideration is quite complex. As many as 25 peaks have been recorded in the energy range 0–100 meV on any single unit. If the situation appears formidable experimentally, it is even more so theoretically. Almost no work has been done on this subject. Price[9] has considered a simple model in calculating the transmission through an abrupt, but ordered, crystal interface, but his results do not really have any bearing on the present situation. Indeed, even simple homogeneous tunnel junctions are more complicated, in many ways, than the models on which theory has been based so far. The tunneling current characteristic for forward biases has not been accounted for. The work of Kane,[10] Price,[11] Harrison[12] and others illustrates this only too well.

Figure 3 shows the relevant parts of the band structure

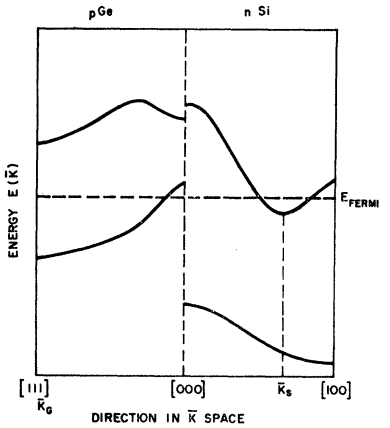

FIG. 3. A schematic diagram of the relevant parts of the germanium and silicon band structures for a n-Si–p-Ge system. E_F is the Fermi energy. The energies in the two materials are aligned so that the Fermi energy is a constant.

[9] P. J. Price, in *Proceedings of the International Conference on the Physics of Semiconductors, Exeter, 1962* (Institute of Physics and The Physical Society, London, 1962), p. 99.

[10] E. O. Kane, J. Appl. Phys. **32**, 83, (1961).

[11] P. J. Price and J. M. Radcliffe, IBM J. Res. Develop. **3**, 364 (1959).

[12] W. A. Harrison, Phys. Rev. **123**, 85 (1961).

of germanium and silicon. Germanium has its lowest conduction-band minima at the Brillouin zone edge in the [111] direction and its valence-band maximum at the zone center, whereas silicon has its lowest conduction-band minima some two-thirds of the way along the $\bar{k}$ axis in the [100] direction. Both materials are indirect, so that tunneling in homojunctions of either one involves a change of wave vector $\bar{k}$. At liquid-helium temperatures one observes inflections in the incremental resistance (or conductance) versus voltage curve which are caused by an increase in tunneling due to the participation of phonons.[4,13] There are four branches to the phonon spectrum[14] [transverse acoustic (TA), longitudinal acoustic (LA), transverse optic (TO), and longitudinal optic (LO)] so that four bumps are observed at energies corresponding to the particular value of $\bar{k}$ that is conserved. These values for germanium and silicon are given in the first two rows of Table I. The energies are resolved by looking at the second-derivative spectrum.

One can consider in a very general fashion the tunneling current as the result of transition from material "a" on one side of a thin barrier to material "b" on the other side. Provided the current is small so that the distribution functions for the "a" and "b" regions are very nearly the equilibrium Fermi distributions, then the total current density across the barrier, in a one-dimensional picture, is

$$J=J_{a\to b}-J_{b\to a}$$
$$=\frac{2\pi e}{\hbar}\sum_{k_t}\int_{-\infty}^{\infty}|M_{k_ak_b}|^2\rho_a\rho_b f_a(1-f_b)dE_k$$
$$-\frac{2\pi e}{\hbar}\sum_{k_t}\int_{-\infty}^{\infty}|M_{k_bk_a}|^2\rho_b\rho_a f_b(1-f_a)dE_k. \quad (1)$$

Here M is the matrix element for the transition from one side to the other, ρ is the density of states, and f is the distribution function. The integral over energy is taken at fixed transverse wave number $\bar{k}_t$. In a heterojunction we *cannot* take $|M_{k_ak_b}|^2=|M_{k_bk_a}|^2$, whereas in a homojunction this is the usual assumption due to symmetry. As a result, the equations governing the phonon transitions become

$$\bar{k}_a\pm\bar{q}_a=\bar{k}_b,$$
$$\bar{k}_a=\bar{k}_b\pm\bar{q}_b, \quad (2)$$

where $\bar{q}$ represents the phonon wave vector and $\bar{q}_a$ does not necessarily equal $\bar{q}_b$, as in a homojunction.

Since an evaluation of the matrix element M requires among other things a knowledge of the band structure of the system and such information is not available, then it is impossible to determine what the exact phonon transitions governed by (2) are. However, we can make a first-order estimate of what the phonon spectrum should be. Fortunately, the valence bands for germanium and silicon are quite similar so that one can envisage a substitution effect for valence bands ($\bar{q}_a\approx\bar{q}_b$). Then the $\bar{q}$ vector which must be taken up in the n-Si–p-Ge system is simply the same as in a *silicon* homojunction:

$$n\text{-Si–}p\text{-Ge} \quad |\bar{k}_b-\bar{k}_a|=\Delta\bar{k}_{\mathrm{Si}}=\bar{q}. \quad (3)$$

Referring to the band-structure diagram for a p-Si–n-Ge system in Fig. 4, we see that the $\bar{q}$ vector which must be taken up is the same as in a *germanium* homojunction:

$$p\text{-Si–}n\text{-Ge} \quad |\bar{k}_b-\bar{k}_a|=\Delta\bar{k}_{\mathrm{Ge}}=\bar{q}. \quad (4)$$

If we make the further assumption that the phonon $\bar{q}$ is taken up after the transition through the barrier, then in n-Si–p-Ge heterojunction we would epxect, in *first order*, to see silicon phonons due to the n-Si side and germanium phonons due to the p-Ge side—the particular phonon energies being determined by Eq. (3). The same situation holds for the p-Si–n-Ge heterojunction, except that the phonon energies are determined by Eq. (4). One would expect a different spectrum for a n-Si–p-Ge heterojunction from that for a p-Si–n-Ge heterojunction since $\Delta k_{\mathrm{Si}}\neq\Delta k_{\mathrm{Ge}}$. It is somewhat unfortunate that better p-Si–n-Ge heterojunctions could not be fabricated in order to verify this.

In the simple picture just advanced to get a first-order phonon spectrum, the assumption used implicitly was that tunneling occurred through an ideal barrier from a silicon bulk to a germanium bulk and vice versa. The actual n-Si–p-Ge system is much more complicated because of interface and strain effects. There can be a variety of defects which can cause a large density of interface states to occur in the tunneling barrier, and tunneling can proceed via such states rather than directly through the barrier. However, the system under consideration is an alloy one in which the band gap

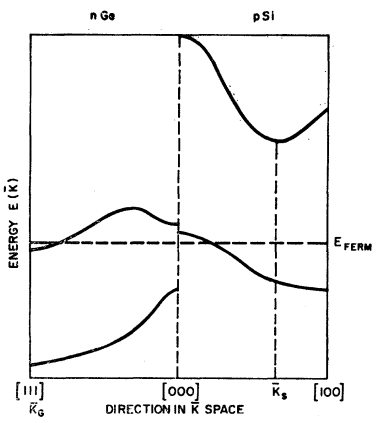

FIG. 4. A schematic diagram of the relevant parts of the germanium and silicon band structures for a p-Si–n-Ge system.

[13] R. N. Hall, in *Proceedings of the International Conference on Semiconductor Physics, Prague, 1960* (Academic Press Inc., New York, 1961), p. 193.

[14] B. N. Brockhouse, Phys. Rev. Letters **2**, 256 (1959).

changes gradually from side "a" to "b." The consequence of this is that interface states are more diffuse than in the abrupt band-gap change model considered by Nathan and Marinace,[5] where interface states are sharply confined. One would expect, then, the contribution to the phonon spectrum from tunneling via such states to consist of either a high density of very weak lines, or in the best possible case, a continuous rather than discrete spectrum. This probably accounts for the large number of lines observed experimentally in the phonon spectrum. It must be pointed out, though, that the fact that phonon structure is observed indicates that there is a reasonably high degree of order in the barrier, since this implies that the transverse wave vector is being conserved in the tunneling transition.

The lattice constant of silicon differs by about 5% from that for germanium. This causes the junction interface to be quite strained. The effect of such crystal strains is to shift the conduction-band maxima and valence-band minima. Generally, the shift is such as to produce an increase in $\Delta\bar{k}$ and hence a translation of the phonon spectrum to higher energies. Such shifts have been observed by Payne,[15] in germanium. Because the process of forming the heterojunctions is a melting of the germanium and subsequent recrystallization to form the interface, the germanium side of the junction is expected to show such effects rather than the silicon.

It has also been assumed that tunneling is occurring from a silicon side to a germanium side, i.e., the band gap of the system changes in the same width as that which defines the tunneling barrier. However, the nature of the alloy process (through time and temperature) can allow the width of the tunnel barrier to be smaller than the width in which band gap changes. This means that tunneling can occur from a silicon to a (Ge_x–Si_{1-x}) side. The time-temperature intervals used in the present experiments are such as to limit $(1-z)$ to no more than 20%.

5. DISCUSSION OF RESULTS

As remarked earlier (and seen from Fig. 2), the spectrum of a typical n-Si–p-Ge heterojunction yields a large number of lines. In the initial analysis, all were recorded in tabular form as in Table I and a search was then made for the eight phonon energies corresponding to germanium and silicon in accordance with the discussion of the previous section. Only these particular eight energies are shown for the five *typical* heterojunctions in Table I. The strengths of these eight phonon peaks are much greater than those of the unidentified lines. In general, a factor of 10 is involved. The unit in Fig. 2 is not of this type, but was chosen so as to bring out the large number of lines that can be found. In all the heterojunctions a good silicon phonon spectrum was obtained. This indicates that tunneling into the n-Si side of the junction is equally as good as that in a homojunction.

The germanium side (or Ge_x–Si_{1-x}) of the heterojunction is much more complicated. The spectrum due to that side of the junction depends on the time-temperature cycle used in the fabrication. The interpretation of the results is that tunneling is to either a germanium side or to an alloy having as much as 13% silicon, the composition of which is determined during the alloy process. In order to interpret the data, it was necessary to use the recent results of Logan *et al.*[8] on the phonon spectra of germanium-silicon alloys. The data given in Table I are for five typical heterojunctions in which the silicon composition is 0, 4, 6, 10, and 13%. As the amount of silicon is increased, the four lines in the spectrum associated with this side of the heterojunction are shifted to higher energies.

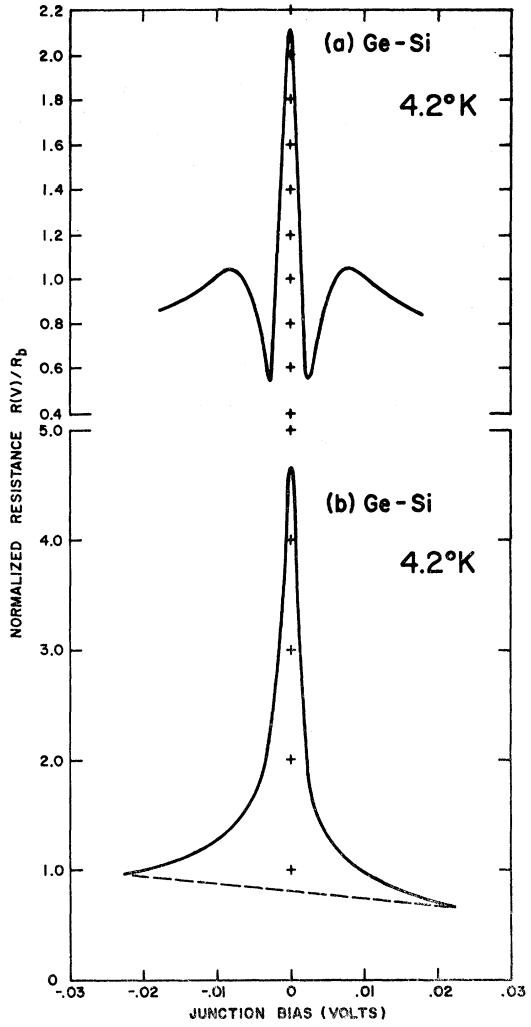

FIG. 5. The resistance $R(V)$ (normalized to the zero-bias background resistance R_b) plotted against bias for two typical Ge–Si heterojunctions at 4.2°K. The upper unit shows a W effect while the lower unit shows a Λ.

[15] R. T. Payne, Phys. Rev. Letters **13**, 53 (1964).

According to the model presented in the previous section, the spectrum due to a pure germanium side in a heterojunction should show phonon energies which are less than in a normal homojunction because $\Delta\vec{k}_{Si} \neq \Delta\vec{k}_{Ge}$. However, all the units examined did not show energies less than those quoted for unit MAR 18–3–64 in Table I. Since the phonon spectrum is rather flat (slowly changing in energy) out at the conduction-band minima of germanium and silicon, the energy translation of the four lines is not expected to be very large and considering the simplicity of the model involved it is perhaps unrealistic to see this effect. The other explanation is that crystal strains on the germanium side due to lattice mismatch have caused a shift to higher energies wiping out the expected decrease.

The general conclusion reached is that a true heterojunction has been formed and the phonon spectrum is in agreement with a simple first-order theory. The large number of additional lines (marked with U's in Fig. 2) are probably due to a large number of defect states in the tunneling barrier and on the germanium side of the junction. These unidentified peaks do not show any regularity. In any group of diodes showing the same phonon spectrum (that is, the same eight peaks), there is a random distribution of the unknown lines.

6. RESISTANCE NEAR $V=0$

The region near zero bias is quite interesting in that simple tunneling theory predicts a linear relationship between current and voltage, whereas unusual bumps and dips are observed in the incremental resistance. These observations were first made by Hall[13] in a variety of semiconductors. His interpretation of the resistance bumps in the III–V compounds was that they were due to polarons. However, it is now known that both resistance bumps and dips can be observed in *both* polar and nonpolar materials[6,16,17] and the interpretation of polarons is questionable. The strength and type of anomaly (i.e., bump or dip) depend upon dopant concentration.

Previous evidence for the existence of a heterojunction in the Ge-GaAs system as reported by Nathan and Marinace[5] is invalid since it assumes that all conductance dips (resistance bumps) are due to polarons. In fact the data suggest that homojunctions have been formed in the germanium by diffusion, with the GaAs acting as an ohmic contact.

In the Ge-Si system, large incremental resistance bumps have been seen. These are shown in Fig. 5 for two typical units. Generally, the bumps have either of the two shapes shown, a resistance "W" or a resistance "Λ." The peak resistance at zero bias is a strong function of temperature, showing a large increase with decreasing temperature. These resistance bumps are ascribed to tunneling transitions in the *p-n* heterojunction and are thought to reflect either band-edge phenomena or impurity effects. These effects are currently being studied and will be described more fully at a later date.

ACKNOWLEDGMENT

The author would like to express his indebtedness to his colleague Robert M. Williams for the many helpful suggestions concerning interpretation of the data.

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[16] R. M. Williams and J. Shewchun, Phys. Rev. Letters **14**, 824 (1965).

[17] J. Shewchun and R. M. Williams, Phys. Rev. Letters **15**, 160 (1965).