Phonon-Assisted Tunneling in Silicon and Germanium Esaki Junctions

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Phonon cooperation in indirect tunneling transitions in narrow p-n junctions causes structure in the current voltage characteristics at low temperatures. These effects have been studied in silicon and germanium Esaki junctions using special equipment which plots continuously on an X–Y recorder the bias dependence of the current I, conductance $G=(dI/dV)$, and $(d^2I/dV^2)G^{-2}$. Twelve phonon and phonon-combination energies have been definitely revealed on the Si junctions and seven in the Ge junctions. Assignments of these energies are given; those for the Si junctions are mostly combinations of the transverse acoustic or optic phonons with intervalley scattering phonons and optic phonons of zero wave number. In the silicon junctions, in addition to the phonon-induced structure, over certain ranges of forward bias there are prominent oscillations in the second derivative curves. The origin of these oscillations is not satisfactorily understood though they have been tentatively ascribed to the Stark splitting of the energy bands in the high electric field of the junction.

INTRODUCTION

ESAKI and Miyahara[1] and Holonyak *et al.*[2] found that the current (I)-voltage (V) characteristics of Esaki junctions at low temperatures exhibited structure indicative of phonon cooperation in indirect tunneling transitions. In silicon junctions Esaki and Miyahara observed inflections in the $I-V$ curves at biases corresponding to phonon energies observed by Brockhouse[3] in neutron scattering studies and by Haynes[4] in studies of the recombination radiation spectra. Holonyak *et al.* reported similar observations together with results of studies of germanium junctions. In the latter, structure in the $I-V$ characteristic was observed when the junctions were made by alloying gallium into antimony-doped germanium and, less prominently, in junctions made with phosphorus- or arsenic-doped Ge.

Subsequently, Hall *et al.* studied phonon-induced inflections in more detail by using an electronic differentiating technique in which (dI/dV) was displayed as a function of V. Using this technique Hall has been able to resolve the four zone boundary phonon energies in germanium[5] and in addition, has been able to detect weak phonon effects in tunnel junctions made in a wide variety of compound semiconductors.[6]

It was apparent that if the differentiating techniques were taken another step so that the second derivative, d^2I/dV^2, was displayed on an $X-Y$ recorder as a function of V, the further increases in both the resolving power and the sensitivity would yield even more accurate data on the prominent phonon effects and would reveal weak effects, corresponding to combinations of phonons, that would pass unnoticed in the first derivative plots, let alone the $I-V$ curves.

Such techniques have been used successfully in a detailed study of phonon-assisted tunneling in silicon junctions which this paper describes. These experiments have revealed many new phonon and phonon combination inflections in the $I-V$ characteristics of silicon junctions, and also have provided another demonstration of the oscillations previously attributed to the Stark splitting of the energy bands in the high electric field of the junction.[7]

EXPERIMENTAL TECHNIQUES

(a) Junction Fabrication

The silicon junctions were made by alloying boron-containing aluminum wires into n-type silicon using a fast heat cycle. The boron content ranged nominally between zero and 1%. The silicon was doped either with antimony or arsenic; the Sb concentrations ranged between 5×10^{19} and 8×10^{19} cm^{-3}, resulting in peak current densities ranging from 3 to 15 amp cm^{-2}; the As concentration ranged from 2×10^{19} to 1×10^{20} cm^{-3} and the corresponding peak current densities ranged from 0.3 to 40 amp cm^{-2}. It was found that the actual value of the dopant concentration was immaterial as far as the sharpness of the phonon inflections was concerned. The germanium junctions were formed in a similar way by alloying aluminum wires into Ge of 0.001-ohm-cm resistivity doped with either Sb or As. These junctions were backwards junctions, being not quite narrow enough to display a negative-resistance region. The ohmic contact to the n-type Si or Ge was made by alloying in a gold wire.

For the measurements, the units were mounted on the end of a thin wooden stick and immersed in liquid helium in a standard container. Current and voltage leads were soldered to both the Al and Au wires attached to the crystal so that four-terminal measurements could be made.

[1] L. Esaki and Y. Miyahara, Solid State Electronics **1**, 13 (1960).
[2] N. Holonyak *et al.*, Phys. Rev. Letters **3**, 167 (1959).
[3] R. N. Brockhouse, Phys. Rev. Letters **2**, 1256 (1959).
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[5] R. N. Hall, Proceedings of the International Conference on Semiconductors, Prague, 1960.
[6] R. N. Hall, J. H. Racette, and H. Ehrenreich, Phys. Rev. Letters **4**, 456 (1960).
[7] A. G. Chynoweth, G. H. Wannier, R. A. Logan, and D. E. Thomas, Phys. Rev. Letters **5**, 57 (1960).

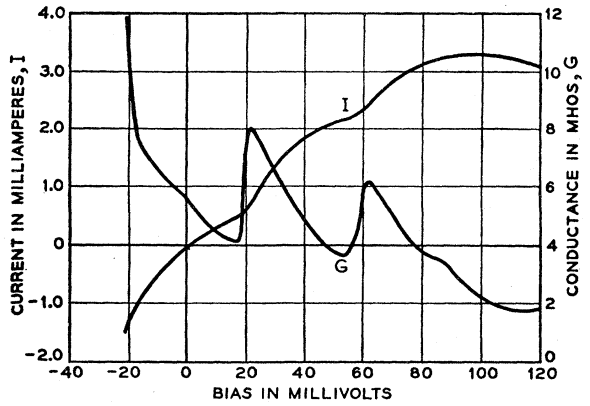

FIG. 1. Curves showing the bias dependence of the current, I, and conductance, G, of a typical silicon Esaki junction at 4.2°K.

(b) Double Differentiation Technique

The equipment used for obtaining the second derivative, d^2I/dV^2, and automatically plotting it as a function of V has been described by Thomas.[8] The low-frequency dynamic conductance, $dI/dV=G$, was determined by applying a signal with a peak-to-peak amplitude of about 1 mv to the junction as the applied bias was slowly swept through the range of interest. By means of a bridge circuit and a servo-mechanism a voltage proportional to $(d^2I/dV^2)G^{-2}$ was derived and plotted continuously as a function of V on an $X-Y$ recorder. As will become apparent, the voltages at which peaks occurred in these plots correspond to the phonon or phonon combination energies.

RESULTS

Figure 1 shows I and G as functions of V for a typical silicon junction. In the current curve of Fig. 1 there are some very prominent phonon inflections similar to those previously reported, and these give rise to rapid changes in the conductance in the G curve. For vanishingly small interrogation signals and in the absence of thermal smearing of the Fermi energies, the inflections would appear as sharp corners giving rise to an abrupt discontinuity in the conductance. Because of the smearing effects, the increase in conductance takes place over a finite voltage range and it is readily apparent that to a first approximation, the phonon energy corresponds to the bias at the mid-point in the upward swing in the conductance. This point will be approximately that at which d^2I/dV^2 is a maximum, i.e., it will be located by the corresponding peak in the second derivative curve shown in Fig. 2. [In practice, the plot showed $(d^2I/dV^2)G^{-2}$ but as the second derivative is, in general, varying much more rapidly with V than is G, it is reasonable to take the voltages at which the peaks occur in the recorder plot as indicative of the phonon energies.]

TABLE I. Phonon and phonon-combination energies observed in Ge Esaki junctions, together with their assignments.

Phonon energy in 10^{-3} ev: From neutron scattering[9]	From tunneling	Quality of inflection	Assignment
8.0	7.6	strong	TA [111]
10.1			TA [100]
26.6	27.5	strong	LA [111]
28.4			L [100]
30.5	31.6	very weak	LO [111]
34.0			TO [100]
34.6	36.0	medium	TO [111]
37.1			O [q=0]
	45.8	weak	TO [111]+ TA [100]
	56.7	very weak	LA [111]+ LA [100]
	74.4	weak	2 TO

[8] D. E. Thomas (to be published).

TABLE II. Phonon and phonon-combination energies observed in Si Esaki junctions, together with their assignments.

Phonon energy in 10^{-3} ev: From neutron scattering[3]	From tunneling	Quality of inflection	Assignment
18.2	18.4	very strong	TA
45.5	46.3	weak	LA
53.7	54.3	weak	LO
57.8	57.6	very strong	TO
64.4	65.4	weak	$TA+S_2$
76.0	78.6	medium	$(TA'+TO)$ or $(TA+TO')$
81.5	83.1	medium	$TA+O$
103.6	102	weak	$TO+S_2$
120.7	121	medium	$TO+O$
144.6	141	weak	$TA+O+O$
183.8	184	weak	$TO+O+O$
246.9	239	very weak	$TO+O+O+O$

The advantages of determining the second derivative are readily apparent from Figs. 1 and 2: in addition to locating the positions of the strong phonon peaks more precisely, several weak peaks are revealed in the second derivative curve, the counterparts of which are not noticeable in even the first derivative curve. The phonon or multiphonon energies derived from the studies of the germanium and silicon junctions are listed in Tables I and II, respectively. The precision in locating the energies is estimated as $\pm 2\%$ and only the energies that were observed in at least several junctions are listed. For the Ge junctions the *sharpness* of the phonon peaks seemed independent of dopant though they were generally more prominent in the case of Sb-doped material.[2] For the Si junctions, the choice of dopant was immaterial. In view of the very close agreement between the primary phonon energies derived from these tunneling studies and those obtained from neutron scattering studies[3,9] it is obvious that any

[9] B. N. Brockhouse and P. K. Iyengar, Phys. Rev. **111**, 747 (1958).

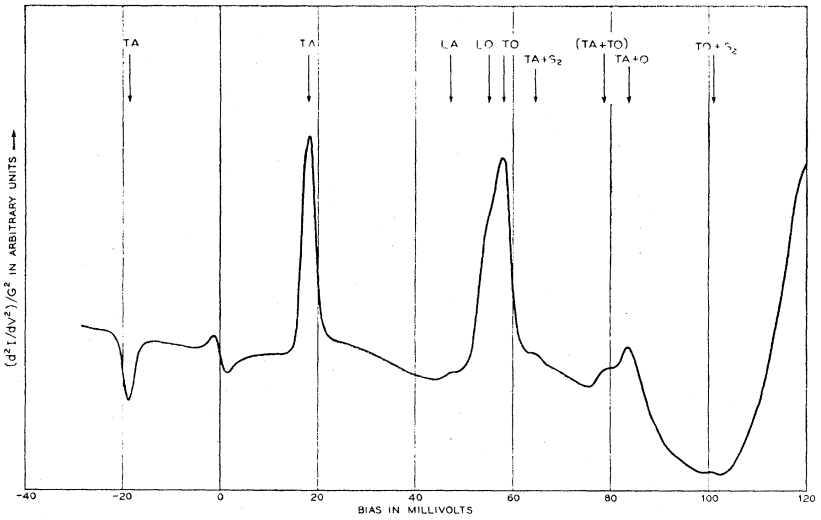

FIG. 2. Curve of $(d^2I/dV^2)G^{-2}$ against bias for the junction used for the curves of Fig. 1, showing several of the observed phonon and phonon-combination peaks together with their assignments.

effects due to series resistance in the diodes were negligible.

At forward biases generally in excess of about 0.1 volt most Si junctions exhibited an oscillatory behavior in their conductance plots and, more prominently, in their second derivative plots. A typical example is shown in Fig. 3 where the oscillatory behavior is readily apparent superimposed on more gross features caused by multi-phonon cooperation. The amplitude of these oscillations is relatively small, being about 3% of that of the peak at 121×10^{-3} ev, for example. Similar structure has been reported previously for indium antimonide junctions[7] where it was attributed to Stark splitting of the energy bands. From the estimates of the field strengths and distributions in the silicon junctions it would be consistent to ascribe the oscillations observed in these also to the Stark effect. However, the regularity of the oscillation spacing and the wide range in bias over which the oscillations occur suggest that their interpretation is not so straightforward as previously thought.

A curious feature of both Si and Ge junctions is the occurrence of a small peak in the conductance centered around zero bias. This is visible in the conductance plot, and, in differentiated form, more prominently in the second derivative plot. These conductance peaks have also been observed by Hall.[5] At present, their cause is not understood though there seems no doubt that they are fundamental and cannot be ascribed to spurious effects.

DISCUSSION

(a) Phonon Energies in Silicon Junctions

The close agreement between the lowest four phonon energies resolved in the tunnel currents and Brockhouse's values for the zone edge phonon energies in the [100] direction[3] gives us a definite identification of these phonon peaks. These are listed in the fourth column of Table II—the transverse acoustic (TA), the longitudinal acoustic (LA), the longitudinal optic (LO), and the transverse optic (TO) phonons. In the tunneling experiments indirect current contributions arising from the TA and TO phonons are very strong and are roughly comparable in magnitude. This is in contrast to the situation in optical studies where Haynes[4] has observed that recombination radiation corresponding to the emission of a TO phonon is 30 times stronger than that for the emission of a TA phonon. It may be noted, however, that the optical and electrical processes are not analogous since in the former, the scattering event occurs at a band edge whereas it occurs in the forbidden gap at the point of stationary phase in the tunneling process.[10]

There are eight phonon energies listed in Table II that must result from phonon combinations. However, simple combinations of the primary phonons are not allowed because of the necessity of satisfying the

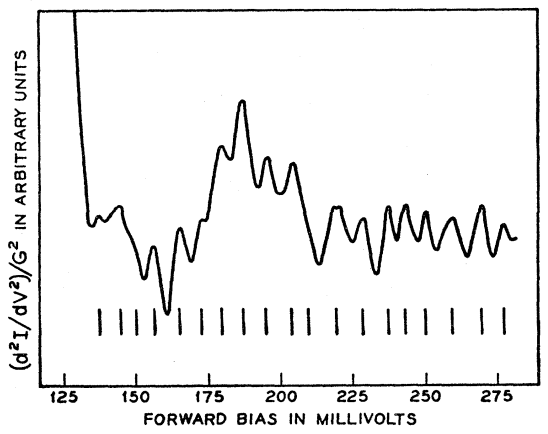

Fig. 3 Curve of $(d^2I/dV^2)G^{-2}$ against bias for a silicon Esaki junction over the bias ratge where Stark effect oscillations are revealed.

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

condition that the sum of the phonon wave numbers, q, must equal the wave number at the zone boundary, q_M. Furthermore, simple combinations of the primary phonons will account for only 4 of the observed combinations and at that, some unlikely combinations such as $(LA+LO)$ have to be used. However, a satisfactory assignment of the phonon energies can be made if the primary phonons are combined with optical phonons of zero wave number, or with phonons arising from intervalley scattering in the conduction band. The $q=0$ phonon, O, according to Brockhouse,[3] has an energy of 63.1×10^{-3} ev. Dumke[11] has deduced from Hayne's optical data the longitudinal acoustic phonon energies corresponding to scattering between valleys on the same axis (S_1) and valleys on different axes (S_2). He finds $S_1=23\times10^{-3}$ ev and $S_2=46\times10^{-3}$ ev.

As is evident from Table II, a very close agreement is obtained between the observed energies and those energies obtained by combining the TA and TO phonons with the O and S_2 phonons. The assignments are particularly satisfying for a number of reasons. With the exception of the peak at 78.6×10^{-3} ev, there is a symmetry about the system and an obviously logical sequence of assignments; completely parallel sets of combinations are used for both the TA and TO phonons and there are no missing terms in the series involving O phonons. Furthermore, no combinations involving LA or LO phonons are needed, and this is agreeable in view of the weakness of the peaks corresponding to these primary phonons.

Two of the combination energies are accounted for by invoking S_2 phonons though there is no evidence of peaks corresponding to $(TA+S_1)$ and $(TO+S_1)$ combinations. It is not immediately obvious why only the S_2 phonons should be important. [It is conceivable that one of the peaks near 80×10^{-3} ev arises from a $(TO+S_1)$ combination but then one would expect a fairly well-defined peak at about 41×10^{-3} ev corresponding to the $(TA+S_1)$ combination, and there was no evidence of such a peak.]

There remains the combination energy of 78.6×10^{-3} ev. The fact that this is so close to $(TA+TO)$ suggests that it may be a combination of a primary TA or TO phonon with a TO or a TA intervalley phonon, respectively. In Table II, the intervalley phonon is represented by a prime.

In view of the assignments shown in Table II it is of interest to make some estimates of relative strengths of the combination peaks. In particular, we would expect that (taking the phonon symbols to represent strengths):

$$TA:(TA+S_2)=TO:(TO+S_2), \tag{1}$$

and

$$TA:(TA+O):(TA+2O)[:(TA+3O)] =TO:(TO+O):(TO+2O):(TO+3O). \tag{2}$$

In addition, the ratios from term to term on each side of the second equation should be constant. Very rough estimates of the strengths of the various phonon combinations were made simply by taking the heights of the peaks in the second derivative curves relative to judicially chosen backgrounds, making no allowance for the variation of G^2. Neglecting the effect of the conductance was likely to be of serious consequence only for the $(TO+O)$ combination which happened to occur in a region where the conductance was changing rapidly with bias, i.e., near the peak current. The numbers corresponding to relations (1) and (2) were

$$100:42 \quad \text{and} \quad 100:32, \tag{1'}$$

and

$$100:23:2.8 \quad \text{and} \quad 100:<38:5.8:1.2, \tag{2'}$$

respectively, the strengths being in arbitrary units with the amplitudes of the TA and TO phonon peaks being normalized to 100. The amplitudes of the TA and TO phonon peaks were equal to within 5%. The term with the $<$ sign on the right-hand side of (2') corresponds to the $(TO+O)$ combination and this was judged to be abnormally high because of the conductance effect described above. It is apparent that the various ratios are consistent to within a factor of 2 and this is felt to be very reasonable in view of the wide limits of experimental error. Furthermore, it can be seen that in both the TA and TO series involving O phonons, the average ratio between a term containing n phonons and that with $(n+1)$ phonons is about 5 (again, to within a factor of 2).

It was found that the amplitudes of the peaks due to the TA and TO primary phonons which could be observed in reverse bias were always much smaller in amplitude than their forward bias counterparts. This is understandable since phonon emission increases the barrier transparency in forward bias and reduces it in reverse bias.

(b) Phonon Energies in Germanium Junctions

The lowest four-phonon peaks observed in the Ge junctions correlate well with the four primary phonon energies given by Brockhouse and Iyengar for the [111] direction. (By charting the positions of the phonon peaks it is readily established that this is the best fit and it is satisfying that this fit does not involve any of the [100] phonons.) However, the three phonon combination peaks resolved do not seem to fit any scheme as simple and logical as in the case of Si. It can be shown that scattering between valleys on different axes is equivalent to a [100] phonon but logical pairs made up from [111] and [100] phonons do not correspond to any of the combination energies except in the case of the peak at 56.7×10^{-3} ev, which is close to LA [100]+LA [111]. It is probably the generally small dispersion in the optical branches that relaxes the selection rules, making the assignment of

[11] W. P. Dumke, Phys. Rev. 118, 938 (1960).

the combination energies less than straightforward. With this low dispersion it is perhaps conceivable that the 45.8×10^{-3}-ev and 74.4×10^{-3}-ev peaks could be ascribed to TO [111]+TO [100] and $2TO$ combinations, respectively.

CONCLUSIONS

It is clear that the technique of double differentiation of the current-voltage characteristics of Esaki junctions resolves considerably more structure than can be observed even in conductance plots. In the present paper attention has been focused on multiphonon tunneling process in silicon and germanium junctions. In silicon in particular, the double differentiation has revealed several new multiphonon-tunneling processes all of which can be fitted into a very simple and satisfying assignment scheme. This scheme involves the transverse acoustic and optical phonons in combinations with intervalley scattering phonons, or in combinations with one or more zone-center optical phonons.

Only three multiphonon combinations have been resolved in germanium junctions and these do not seem to have such a simple assignment as is possible in silicon.

Further work, both theoretical and experimental, will be required before the origin of the peak in the conductance at zero bias is understood.

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Vacancies and Complexes in the Noble Metals*

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In part I, the changes in resistivity of a noble metal on the introduction of vacancies into the lattice are calculated, taking into account the relaxation of the lattice around the defect site. The agreement between calculated and experimental resistivities is satisfactory for a particular model of the scattering power of the vacancy. Using this same model, it is then shown how the calculations of Fumi and Brooks concerning vacancy formation energies can be modified in the light of known surface energy data to yield quite reasonable predictions of formation energies of relaxed vacancies in noble metal lattices. The agreement between calculated and experimental resistivity data implies that the phase shift of electron waves at the Fermi surface are accurate and this in turn permits the prediction of the electron density in the neighborhood of the vacancy. In part II, this electron density is used in a treatment of the interaction energy between vacancies and substitutional impurities in the noble metals. The binding energies deduced in this way from scattering theory exhibit a strong dependence on the valence of the solute atom and are invariably positive for positive valence solutes at nearest neighboring lattice sites to a vacancy. The computed binding energies are quantitatively compatible with the available experimental data.

The long-range characteristics of interaction between vacancies and both point and extended defects are also investigated in part II. Particular attention is drawn (a) to the oscillatory nature of the interaction as a function of the separation of the defects, and (b) to the different dependence on this separation for interactions concerning the different types of defect. Thus, in every case, the interaction energy oscillates with period k_F/π, k_F being the Fermi energy, while the decay of amplitude with separation takes the form r^{-3}, $r^{-\frac{5}{2}}$, or r^{-2} contingent upon the vacancy interacting with a second point defect, a dislocation, or a crystal boundary, respectively.

Part I: Vacancies in the Noble Metals

I. INTRODUCTION

EXPERIMENTS performed on silver and gold have revealed that defects, trapped in the lattice by quenching, produce changes in the volume, electrical resistivity, and the energy stored in the lattice. The interpretation of these facts is that vacancies, together with a much smaller number of divacancies, cause the observed effects.

In gold, it has been shown that the increase in volume of the lattice is proportional to the increase in resistivity,[1] with the constant $K=\partial R/\partial V=340\pm50$ μohm cm.[2] Here V is the lattice volume and R the resistivity. By means of resistivity, x-ray, and microcalorimetric techniques, the energy increase of the lattice on formation of a vacancy has been found to be about 0.97 ev in gold,[1,3] and 1.10 ev in silver.[4,5] No

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[1] J. E. Bauerle and J. S. Koehler, Phys. Rev. **107**, 1493 (1957).
[2] The author is indebted to Professor J. S. Koehler for providing this value of K as the best interpretation of the experimental evidence.
[3] W. DeSorbo, Phys. Rev. **117**, 444 (1960).
[4] M. Doyama and J. S. Koehler, Phys. Rev. **119**, 939 (1960).
[5] R. O. Simmons and R. W. Balluffi, Phys. Rev. **119**, 600 (1960).