Phonon and Polaron Interaction in Germanium-Gallium Arsenide Tunnel Heterojunctions

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The differential conductance vs voltage at 4.2°K of germanium-gallium arsenide tunnel heterojunctions exhibits structure similar to that found in tunnel diodes made in one material. In some units, a dip $V=0$, which has been attributed to polaron interaction in polar semiconductors, is observed. In addition, in these same units, bumps at voltages characteristic of phonon-assisted tunneling in germanium are found. This behavior is characteristic of neither germanium nor gallium-arsenide homojunctions alone. It shows that the units are not merely a germanium contact to a gallium-arsenide homojunction or vice versa. It is strong indication that the interface between the materials is within the space-charge region of the junction and that the interface is sharp and well ordered. The conditions for these observations are discussed.

INTRODUCTION

In recent years considerable work has been done in growth of semiconductors from the vapor phase.[1] It has been shown that it is possible to grow germanium epitaxially on a gallium arsenide substrate.[2] Since these semiconductors have almost identical lattice constants the junction between the materials might be expected to be abrupt and have a high degree of perfection. This expectation has been borne out by experiment; furthermore, the properties of the junctions have been accounted for with the assumption that there is a negligible density of interface states.[2]

p-n heterojunctions[3] can be made by vapor growth at low temperatures. It has been found[4] that diffusion in the junction region can be made sufficiently small to make possible heavily doped junctions which exhibit tunneling current[5] and negative resistance when biased in the forward direction (*p* side positive). This implies that the width of the space-charge region is of the order of 100 Å. It is difficult to eliminate completely the possibility of interdiffusion over such distances. The evidence that a tunnel heterojunction is not merely a gallium-arsenide *p-n* junction with a germanium contact, or vice versa, is somewhat indirect; e.g., the barrier voltage is intermedite between the value for germanium and gallium arsenide homojunctions. It is the purpose of this paper to report some observations of conductance vs voltage measurements of these junctions at 4.2°K. Phonon[6] and polaron[7] participation in the tunneling process has been observed. It will be shown that this is evidence not only that the junctions studied are, indeed, tunnel heterojunctions, but also that the junctions have a high degree of perfection at the interface.

EXPERIMENTAL

All junctions studied were made by depositing *n*-type germanium on *p*-type gallium arsenide. Attempts at other doping combinations failed to produce any evidence of tunneling current near $V=0$,[5] probably because the doping levels were not high enough. The gallium arsenide substrates were doped with zinc when grown from the melt, or zinc was subsequently diffused into them. The carrier concentration of grown crystals was determined by Hall effect measurements. The zinc concentration of the diffused samples was estimated from x-ray fluorescence measurements, with the use of a zinc-doped grown crystal as a standard.[8] The range of concentrations was between 8×10^{18} cm^{-3} and 6×10^{19} cm^{-3}.

The germanium was deposited on the gallium arsenide by the iodide vapor disproportionation reaction carried out in an open tube. The deposited layers were about 0.001 to 0.003 in. thick. The process for this application has been described in detail elsewhere.[3] The only difference between the present process and that previously described is that the dopant (elemental phosphorus) for the germanium was contained in a side tube, the temperature of which could be controlled independently of the main tube to which it was connected. This permitted somewhat better control over the doping level in the deposit.

The concentration of impurities in the deposited layer can be estimated in two ways: (1) from Hall effect and resistivity measurements on layers deposited on semi-insulating gallium arsenide, (2) from measurements of peak current density of a conventional alloy germanium tunnel diode made entirely in the deposited layer. Both of these methods are subject to some problems. The thickness of the deposited layer is, in general, not uniform. This will lead to error in the Hall effect measure-

[1] See J. C. Marinace, IBM J. Research Develop. 4, 248 (1960).
[2] R. L. Anderson, IBM J. Research Develop. 4, 283 (1960).
[3] We shall use the name "heterojunction" for germanium-gallium arsenide vapor grown junctions. The term "homojunctions" will be used for a *p-n* junction in one material.
[4] J. C. Marinace, IBM J. Research Develop. 4, 280 (1960).
[5] Sufficient evidence of tunneling current is considered to be a negative second derivative of current with respect to voltage for positive voltage near zero.
[6] N. Holonyak Jr., I. A. Lesk, R. N. Hall, J. J. Tiemann, and H. Ehrenreich, Phys. Rev. Letters 3, 167 (1959). L. Esaki and Y. Miyahara, Solid State Electronics 1, 13 (1960).
[7] R. N. Hall, J. H. Racette, and H. Ehrenreich, Phys. Rev. Letters 4, 456 (1960).
[8] These measurements were made by J. C. Lloyd of the IBM Research Laboratory.

ments. There is the question of the uniformity of the doping level of the layer. Indeed both types of measurements indicate that there are nonuniformities. This problem is serious for tunnel heterojunctions, since it is the first few atomic layers deposited on the substrate which determine the properties of the junction. These layers see a different atomic potential than the subsequent layers. Thus, any estimate of the impurity density in the deposited layer is subject to large uncertainty. The best estimate of the impurity density is 1 to 2×10^{19} cm^{-3}. It is felt that the actual variation of impurity density in any one deposition run was less than this uncertainty. Attempts were made to vary the impurity density in different runs by varying the temperature of the elemental dopant. This resulted in different properties of the resultant tunnel heterojunctions, but within the above uncertainties no difference could be detected in the impurity density in the deposited layers.

The temperature of the substrates during the vapor growth was approximately 375°C. The orientation of the substrate surfaces was ⟨111⟩ or ⟨110⟩. No effect due to orientation was found. During the process of making alloyed or ultrasonically soldered contacts to junctions, they were kept below this temperature. Extreme care was taken to insure that alloy contacts did not alloy through to the junctions. Some of the junctions were microsectioned and it was clearly evident that the regrown regions had not reached the heterojunction.

The electrical conductance (dI/dV) and the derivative of the conductance (d^2I/dV^2) vs voltage were measured with the diode immersed in liquid helium. The electrical circuitry for doing this was constructed in collaboration with Dr. F. Fang.

Some of the units fabricated did not show any clear evidence tunneling current[5] for $V>0$. Some of these units exhibited complicated structure in their dI/dV vs V curve which varied from unit to unit. These units sometimes occurred on the same deposition run and substrate as "good" tunnel heterojunctions. It is not certain whether the properties of these units reflect the nonuniformities in the vapor growth process or whether they result from some artifact introduced during their fabrication subsequent to the vapor growth. In either case since the nature of the current near $V=0$ is not understood, these units were excluded from consideration in this study.

Degenerate n-type germanium was also grown epitaxially onto p-type GaSb, InAs, and InSb. The doping of the substrates was not high enough for tunnel diode homojunctions, and there was no clear evidence of tunnel tunneling current[5] for $V>0$ in the heterojunctions.

RESULTS AND DISCUSSION

Figure 1 shows schematically the pertinent parts of the band structure of germanium and gallium arsenide. Germanium, on the left, has its lowest conduction band minima at the ⟨111⟩ Brillouin zone face and its valence band maximum at the zone center so that the tunneling in germanium homojunctions is indirect, i.e., it involves a change of wave vector **k**. At 4.2°K one observes bumps in the conductance vs voltage curve caused by the onset of tunneling with emission of phonons which conserve wave vector, i.e., $\mathbf{k}=\pi a^{-1}(1,1,1)$ $a=$lattice constant. There are four nondegenerate branches of the phonon spectrum at the ⟨111⟩ zone face and bumps have been observed[9] at voltages 8, 27.7, 31.3, 36.3 mV corresponding to their energies. In addition, in arsenic- and phosphorus-doped diodes an unexplained bump is observed at $V=0$.

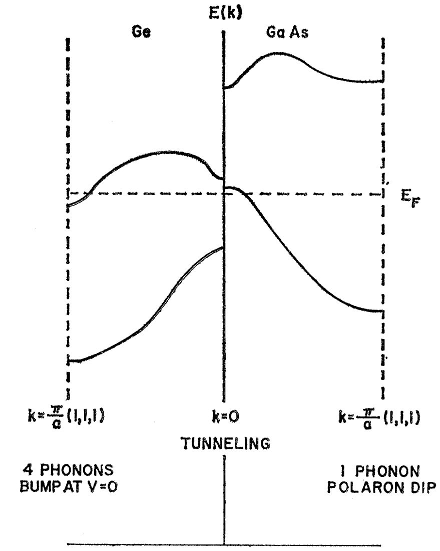

FIG. 1. A schematic diagram of the pertinent parts of the germanium and the gallium arsenide band structures. E_F is the Fermi energy. The energies in the two materials are aligned so that Fermi energy is a constant.

Gallium arsenide is a direct band gap material with both its extrema at the zone center. One phonon bump is observed[7] at $V=36.5$ mV in the tunneling current at 4.2°K caused by the emission of the longitudinal optical phonon at $k=0$. In addition, there is a dip at $V=0$, attributed by Hall, Racette, and Ehrenreich[7] to tunneling with the interaction of a polaron.

Figure 2(a) shows the dI/dV vs voltage curve for an n-germanium–p-gallium arsenide heterojunction. Figure 2(b) shows d^2I/dV^2 as a function of voltage of a similar heterojunction. The arrows indicate the voltages at which phonon bumps are observed in germanium diodes. Clearly, bumps are observed at almost precisely the same voltages in the heterojunctions. In addition, there is a dip at $V=0$ similar to the polaron dip observed in gallium arsenide homojunctions. The curve is evidently different from either a germanium or a gallium arsenide homojunction. The dip at $V=0$ is characteristic of gal-

[9] R. N. Hall, in *Proceedings of the International Conference on Semiconductors, Prague, 1960* (Czechoslovakian Academy of Sciences, Prague, 1961), p. 196.

lium arsenide but not of germanium. Four bumps are observed in germanium but only one in gallium arsenide.

If the interface of the materials is between the classical turning points for tunneling, the tunneling in the heterojunction is between the conduction band minima of germanium at $\mathbf{k}=\pi a^{-1}(1,1,1)$ and the valence band maximum of gallium arsenide at $\mathbf{k}=(0,0,0)$. If we ignore the possibility that the appropriate phonon energies in the two materials may be different, we would expect to see four bumps corresponding to the phonons with $\mathbf{k}$ at the $\langle 111\rangle$ zone face. In addition, since one side of the junction is polar, a polaron dip at the origin is expected. This is what is observed in Fig. 2.

It appears that the phonon bumps observed are in very good agreement with appropriate values for germanium. This would seem to indicate that the $\mathbf{k}=\pi a^{-1}(1,1,1)$ phonons in gallium arsenide, which contribute appreciable tunneling current, have energies very close to those in germanium. This is not unreasonable; calculations by Cochran *et al.*[10] indicate that this equality holds approximately for all the phonons at $\mathbf{k}=2\pi a^{-1}(1,0,0)$. If the dip at $V=0$ is due to tunneling with the interaction of a polaron, a value of approximately 0.5 meV for the polaron energy is obtained by the use of Hall's method[9] for evaluating the interaction energy. This is about half the value, 1.2 meV, found by Hall[9] for GaAs homojunctions, which is to be expected since only half the diode is polar, if the tunneling is between the gallium arsenide and the germanium. This agreement is probably fortuitous, however.

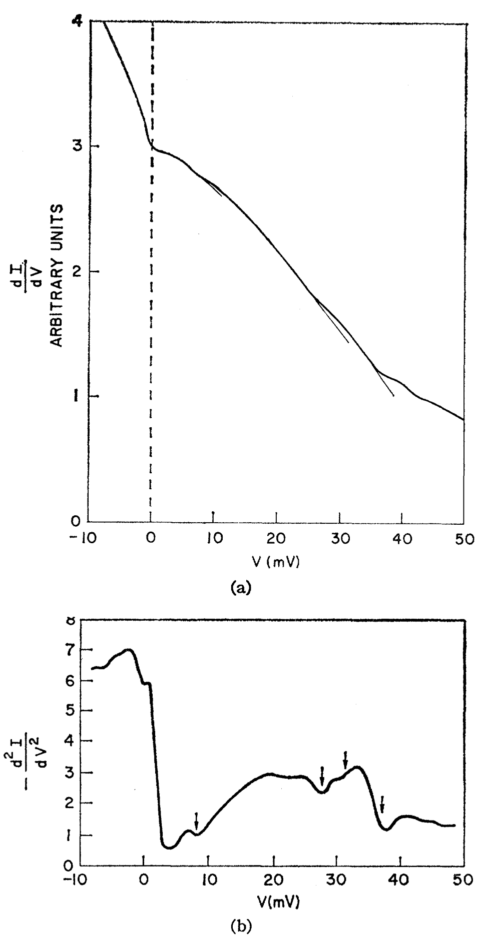

FIG. 2. (a) dI/dV vs V for a heterojunction. (b) d^2I/dV^2 vs V for a heterojunction at 4.2°K.

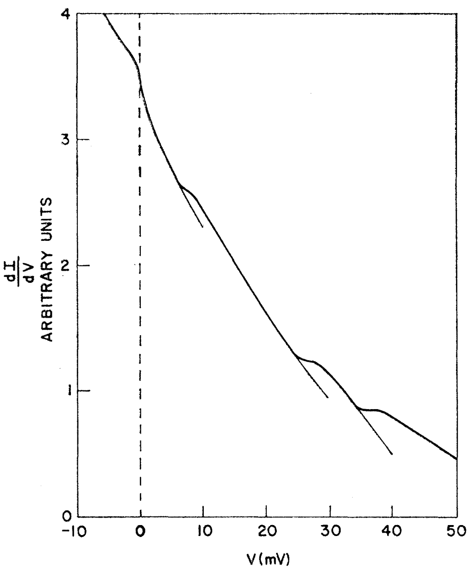

FIG. 3. dI/dV vs V for a relatively heavily doped gallium arsenide and lightly doped germanium heterojunction at 4.2°K.

Some of the early deposition runs in this work were made onto zinc-diffused gallium arsenide wafers, whose zinc concentration was not accurately known. Diodes made from these runs were not reproducible, sometimes yielding dI/dV vs V characteristics like Fig. 2 but sometimes characteristics very much like germanium homojunctions. A typical dI/dV curve is shown in Fig. 3. Rather than a dip in the curve at $V=0$ a bump is observed as in germanium homojunctions. Measurements of d^2I/dV^2 clearly show that there are four phonon bumps at the same voltages as in germanium homojunctions. The only difference in dI/dV between these junctions and germanium homojunctions is in the relative strengths of the phonon bumps. It was felt that this behavior was due to inhomogeneity of the substrate and/or the deposited layer. The possibility existed that the tunnel heterojunction was only a parallel combination of germanium and gallium arsenide homojunctions. Therefore, it was decided to investigate the impurity concentration dependence of these effects.

The results are as follows: Deposition runs with maximum possible phosphorus concentration (approx. 2×10^{19} cm^{-3}) made on a substrate with 1.6×10^{19} cm^{-3}

[10] W. Cochran, S. J. Fray, F. A. Johnson, J. E. Quarrington, and N. Williams, J. Appl. Phys. 32, 2102 (1961).

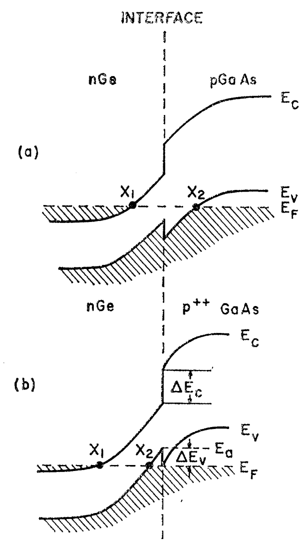

FIG. 4. Energy vs distance for heterojunctions: (a) equal dopings; (b) gallium arsenide heavily doped.

zinc impurities yielded diodes reproducibly with characteristics as shown in Fig. 2. In contrast, deposition runs made with phosphorous concentration lowered (approx. 1×10^{19} cm^{-3}) (by reducing the temperature of the elemental phosphorus) onto substrates with 6×10^{19} cm^{-3} zinc concentration yielded reproducibly characteristics similar to germanium homojunctions as shown in Fig. 3.

The mixed behavior of Fig. 2 occurs for approximately equal doping of the two sides of the junctions, and germanium-like behavior occurs for the germanium side relatively lightly doped. This is opposite to the behavior which would be expected of an inhomogeneous parallel combination of homojunctions. However, it is just what would be expected of a true heterojunction with no interface states. The situation is illustrated graphically in Fig. 4. For approximately equal dopings, the classical turning points x_1 and x_2 are on either side of the interface. For heavily doped gallium arsenide, both turning points are shifted into the germanium.

From Poisson's Equation we can calculate the condition on the relative impurity densities that both classical turning points be in the germanium. The discrete nature of the impurity charges must be neglected, i.e., the charge density must be assumed to be continuous. The impurity densities are taken to be constant in both materials right up to the interface. The transition between materials is assumed to be abrupt with no surface states. The energy band picture is assumed to hold despite the fact that there are appreciable changes in energy due to the junction field over a distance comparable to a few lattice constants. If these assumptions are made at $T=0°$K, and if the condition for both turning points being in the germanium is taken to be $E_F<E_a$ in Fig. 4 (E_F=Fermi energy), the calculation is straightforward, and the result is

$$\frac{N_n}{N_p}<\frac{\epsilon_n}{\epsilon_p}\left(\frac{E_{gp}+\Delta E_c+0.6\zeta_p}{E_{gn}+0.6\zeta_n}-1\right),$$

where the subscript n refers to n germanium and p to p gallium arsenide; E_g is the energy gap; ϵ is the dielectric constant; ΔE_c is the discontinuity in conduction band edge energy at the interface; $\zeta_n=E_F-E_{cn}$; $\zeta_p=E_{vp}-E_F$. If we neglect ζ_n and ζ_p and take $\Delta E_c=0.54$ eV, Anderson's value at room temperature for relatively pure gallium arsenide,[2] $E_{gn}=0.746$ eV, $E_{gp}=1.51$ eV, $\epsilon_n=16$, $\epsilon_p=11$, we find $N_n/N_p<2.55$. This is in reasonable agreement with experiment in view of the assumptions involved. However, since the mixed behavior of Fig. 2 does occur for approximately equal dopings, the necessary experimental ratio for germanium-like behavior appears to be somewhat smaller than this calculated value. However, the assumption that the appropriate condition is $E_F<E_a$ is somewhat arbitrary. For $E_a-\Delta E_v<E_F$ (ΔE_v=valence band discontinuity energy), there are two barriers to tunnel through as can be seen in Fig. 4. It may be that the correct conditon is $E_F<E_a-\Delta E_v$ which would bring the calculated value into closer agreement with experiment.

If ΔE_c depends upon the interface orientation or N_n and N_p, the calculated necessary value of N_n/N_p will depend on these parameters. However, unless the variation of ΔE_c is large compared to E_{gn} the qualitative conclusions will not be affected. Recent unpublished measurements by Fang and Howard[11] indicate that there is a measurable, but small, orientation effect.

In spite of attempts to make the germanium relatively heavily doped, gallium arsenide homojunction-like behavior has not been observed reproducibly. This is not surprising because solution of Poisson's equation shows that the condition for observing the behavior is that the doping in the germanium would have to be more than an order of magnitude greater than that in the gallium arsenide. This we have not been able to achieve.

The fact that the phonon and polaron structure is observed indicates that there is a high degree of order at the interface, since it implies that the transverse wave vector must be conserved in the tunneling transition. It also suggests that the phonon energies at the (111) zone face are very close to the same in germanium and gallium arsenide.

ACKNOWLEDGMENTS

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[11] F. Fang and W. Howard (to be published).