Electron and Phonon Tunneling Spectroscopy in Metal-Germanium Contacts*

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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 alternation of the electronic dispersion relation due to deformation-potential coupling between the holes and the LO phonons.

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 [metal-semiconductor (MS) contacts] provides a useful probe of the electronic energy spectrum of the semiconductor. In this paper 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 $1\times0.4\times0.2$ cm in a vacuum of 10^{-7} Torr. A mask with 0.018 cm diam 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[14] of dI/dV and d^2I/dV^2 were made between 2 and 10°K on a total of 10 Sb-doped units ($n=7.5\times10^{18}/\text{cm}^3$) and 11 As-doped units ($n=7.0\times10^{18}/\text{cm}^3$). Below the superconducting transition temperature, the BCS energy gap of the indium or lead contact was observed in all samples. The shape and the absolute value of the conductance versus bias curve changed little from sample to sample. Pronounced phonon structure was observed in all junctions.

The comparison of three measured conductance curves on Sb-doped samples of Ge [solid lines (a), (c), and (d)] with the model predictions of Conley *et al.*[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 of Ref. 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

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(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 versus 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 Γ_2' in the Ge Brillouin zone, and then, by the subsequent emission of a phonon,

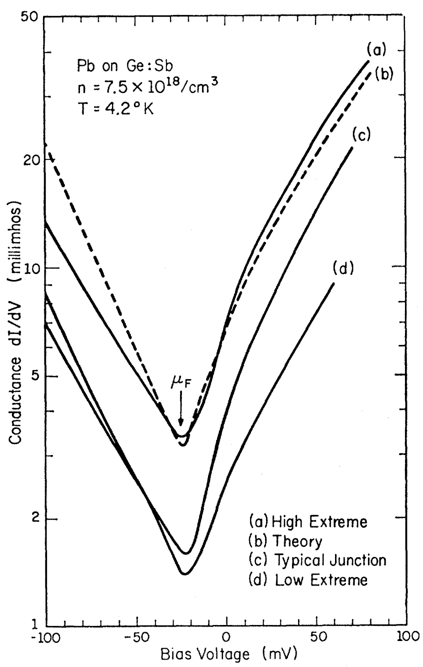

FIG. 1. Comparison between three experimentally measured conductance curves on $n=7.5\times10^{18}/cm^3$ Sb-doped Ge [solid lines (a), (c), and (d)] at 4.2°K and the calculated conductance [dashed line (b)] using the model developed in Ref. 2 for a barrier height $V_b=0.63$ eV obtained from capacitance 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 $2.5\pm0.5\times10^{-4}$ cm². Structure associated with the superconducting energy gap has been omitted. The Fermi degeneracy $\mu_F=25$ mV has been indicated.

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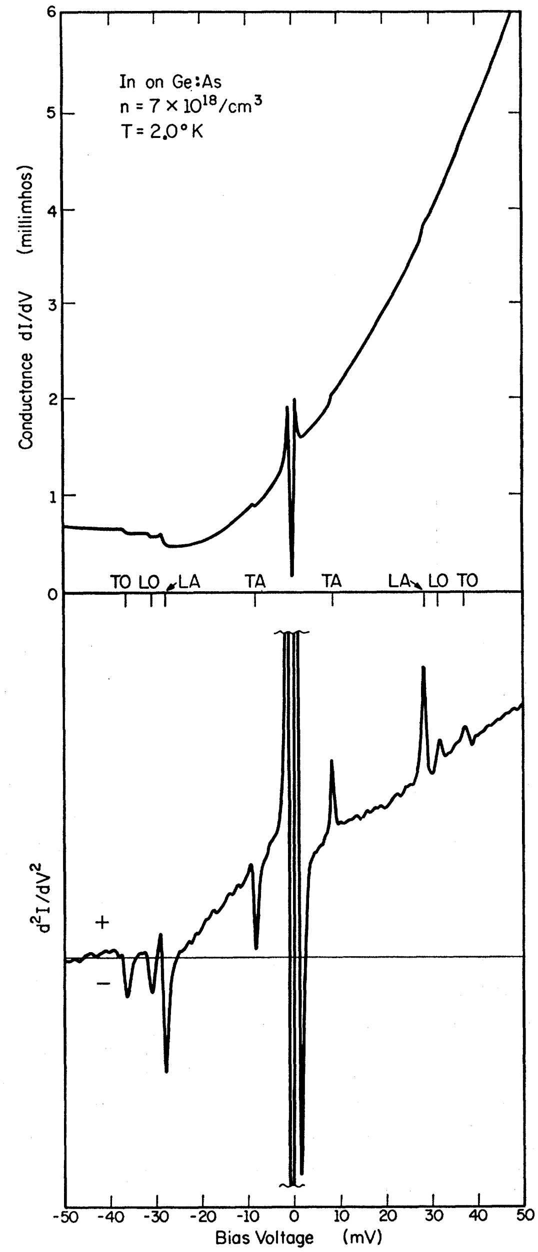

FIG. 2. Conductance and d^2I/dV^2 of an indium contact on As-doped Ge junction at 2°K. The arsenic doping is $n=7.0\times10^{18}/cm^3$. The observation of the indium superconducting gap at zero bias is shown explicitly. Its presence shifts the phonon structure to higher energies by $\Delta=0.5$ mV. Assignment of phonon energies is according to Ref. 18.

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 line shape of d^2I/dV^2 does not reflect the known phonon density of states in Ge.[16] The evidence sug-

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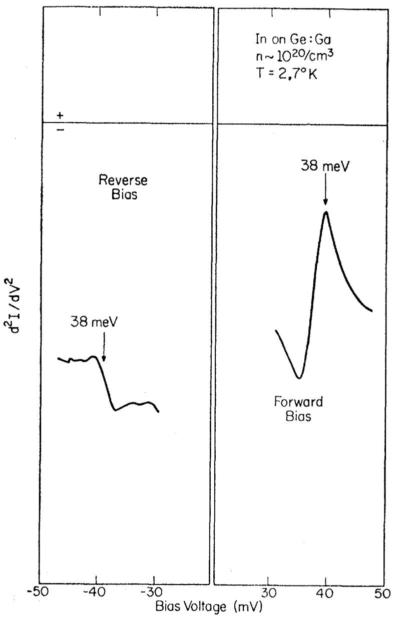

FIG. 3. Symmetrical structure in d^2I/dV^2 at $eV=\pm\hbar\omega_{LO}$ ($k=0$ optical phonon energy) observed in an air-cleaved, Ga-doped Ge junction ($n\sim10^{20}/cm^3$) at 2.7°K is shown. The contact metal is indium.

gesting identification of the mechanism as a two-step process[11,17] via evanescent states near Γ_2' is (1) the line shape 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 collective elementary excitations 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 occurring in metal-oxide-silicon 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 LO 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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