Δ_1 Conduction-Band Minimum of Ge from High-Pressure Studies on p-n Junctions

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The effect of hydrostatic pressure on p-n junctions of germanium has been investigated with a view to determining the energy of the Δ_1 conduction-band minimum relative to that of the L_1 minimum. The pressure-induced shift in the forward bias voltage at a constant current level, which is a measure of the energy-gap change with pressure, passes through a maximum near the pressure at which the lowest conduction band shifts from the L_1 to the Δ_1 minimum. Because of the two-band conduction in Ge at pressures above 15 kbar, the observed shift in the forward bias voltage not only represents an effective-energy-gap change determined by the density-of-state average over the two bands and their pressure coefficients, but is also modified by the change in carrier mobility with pressure. Since the junction current in the present case was dominated by electrons, the observed shifts were corrected for the electronic-mobility change with pressure, using the pressure variation of the resistivity of n-type Ge. From the effective-energy-gap change with pressure given by $\Delta E_{G\text{eff}}=\Delta(E_L-E_v)-kT\ln[1+(N_\Delta/N_L)\exp(-\Delta E/kT)]$, and using $dE_G/dV=3.7$ eV ($dE_G/dP=5.0\times10^{-3}$ eV/kbar), $N_\Delta/N_L=2.7$, and $d(\Delta E)/dV=-4.6$ eV [$d(\Delta E)/dP=-6.2\times10^{-3}$ eV/kbar], the best fit to the experimental data yields 0.18 ± 0.01 eV for the zero-pressure energy separation ΔE between the L_1 and Δ_1 minima. The observed shifts give initial pressure coefficients of $5.0\pm0.1\times10^{-3}$ and $-1.3\pm0.3\times10^{-3}$ eV/kbar for the L_1 and Δ_1 minima, respectively.

IT is well known that at atmospheric pressure, the lowest conduction-band minimum of Ge lies in the [111] directions in k space[1] (L_1 minima). Both optical[2,3] and resistivity measurements[4–7] have shown that this minimum shifts to higher energies with the application of hydrostatic pressure and a set of higher-lying minima associated with the [100] directions in k space (Δ_1 minima) become progressively important with pressure. The optical-absorption measurements of Slykhouse and Drickamer[3] have indicated a changeover in the conduction-band edge near 35 kbar. In this investigation, we have studied the current-voltage characteristics of p-n junctions of Ge as a function of hydrostatic pressure and find that the L_1 minimum crosses the Δ_1 minimum near 33 kbar. The analysis of the data yields 0.18 ± 0.01 eV for the energy separation between the two minima, at zero pressure. From our measurements the pressure coefficient of L_1 minimum is determined as $5.0\pm0.1\times10^{-3}$ eV/kbar, in excellent agreement with the previously quoted values.[6,8] Further, a pressure coefficient of $-1.3\pm0.3\times10^{-3}$ eV/kbar for the Δ_1 minimum seems consistent with our experimental findings.

Hydrostatic pressure was generated using the Teflon-cell technique which has been described previously.[9] The Ge diodes had an epitaxial structure consisting of a gallium-doped p-type substrate having a resistivity of 0.002 Ω cm and an epitaxially grown layer of boron-doped Ge, 2μ deep, having a resistivity of 0.5 Ω cm. The junction was formed by diffusing phosphorus ($n=10^{19}$) to a depth of 0.3 μ in the epitaxial p-type layer. Capacitance measurements indicated that the junctions are of the abrupt type.

Figure 1 shows a plot of the $\ln I_f$ versus applied bias voltage for different pressures at room temperature. It is seen that these curves are quite linear over the

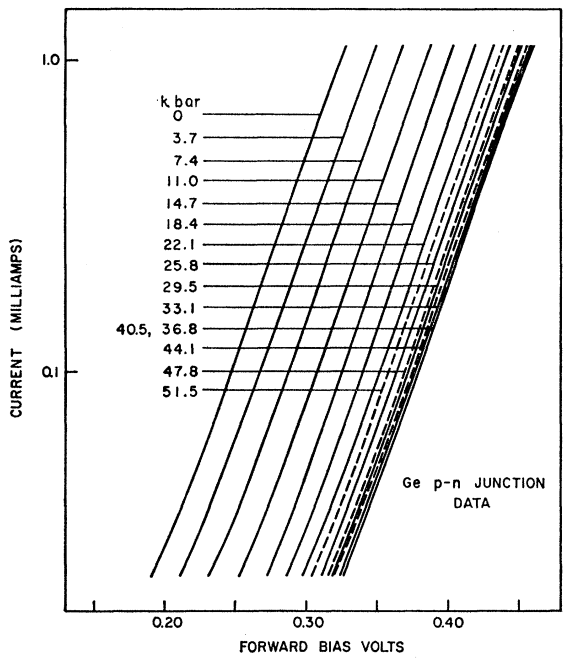

FIG. 1. Current-voltage characteristics of a forward-biased p-n junction of Ge at different pressures.

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current range used in the present study. In Fig. 2, we have plotted the shift in the applied bias voltage (as taken from Fig. 1) at a constant current of 1 mA, as a function of both the pressure and volume.

For the junctions used the forward current is dominated by the diffusion current and hence can be written as

$$I_f = I_s(\exp qV/kT - 1), \quad (1)$$

where the saturation current I_s is defined by the expression

$$I_s = (ekT)^{1/2} n_i^2 \left[\left(\frac{\mu_n}{\tau_n}\right)^{1/2} \frac{1}{P_p} + \left(\frac{\mu_p}{\tau_p}\right)^{1/2} \frac{1}{N_n} \right], \quad (2)$$

where μ_n and τ_n are the electronic mobility and lifetime on the p side, P_p is the concentration of holes on the p side, with analogous definitions for the second term in brackets. Since the intrinsic carrier concentration n_i^2 in Eq. (2) is proportional to $e^{-E_g/kT}$, it is easily seen from Eqs. (1) and (2) that the pressure-induced shift in the applied bias voltage at a constant current level is a direct measure of the change in the energy gap with pressure, when the term in brackets in Eq. (2) can be treated as pressure-independent. Such behavior was reported previously[10] in p-n junctions of Si and in GaAs junctions at pressures below 25 kbar. However, when a higher-lying conduction-band minimum becomes important, as in the case of Ge, the above method yields an effective-energy-gap variation determined by the density-of-states average of the two bands and their pressure coefficient, modified by the change in the effective electronic mobility with pressure. In the case of Ge, as electrons are transferred from the L_1 minima to the Δ_1 minima, the effective electronic mobility decreases substantially because of the different mobilities of the two minima, as well as the large interband scattering near band crossing,[6] causing the first term in Eq. (2) to vary with pressure. [Note that since our junction is heavily doped on the n side, the second term in brackets in Eq. (2) is negligible.] Therefore, in order to determine the change in the effective energy gap with pressure, we have corrected our experimental data, for the change in electronic mobility with pressure, using our resistivity-versus-pressure measurements on n-type Ge. We have assumed T_n to be pressure-independent. The corrected pressure-dependent effective energy gap is plotted in Fig. 2 (squares). The effective-energy-gap change with pressure can be expressed as[11]

$$\Delta E_{G\,\mathrm{eff}} = \Delta(E_L - E_v) - kT \ln\left[1 + \frac{N_{\Delta_1}}{N_{L_1}} \times \exp\left(\frac{-\Delta E}{kT}\right) \right], \quad (3)$$

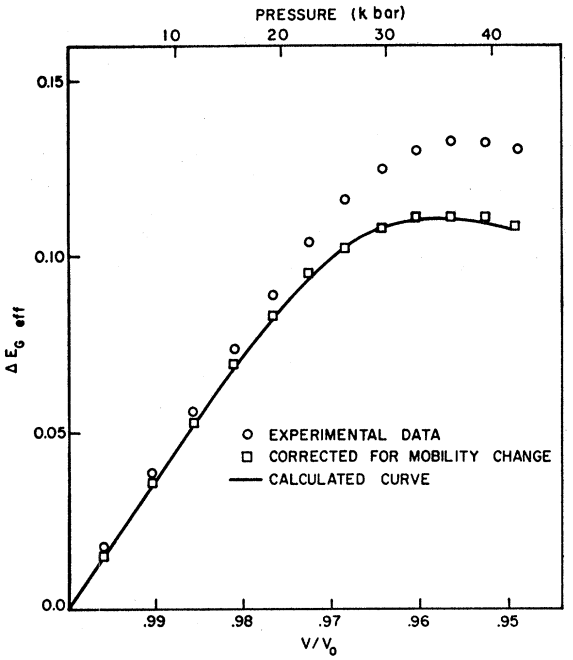

FIG. 2. Shift of the forward bias voltage (circles) at a constant current of 1 mA (representing the change in an effective energy gap) as a function of pressure and relative volume of Ge.

where $E_L - E_v$ is the gap between the valence band and the L_1 minimum, ΔE is the interband separation $E_{\Delta_1} - E_{L_1}$, and N_{Δ_1} and N_{L_1} are the effective-mass density of states for the Δ_1 and L_1 bands.

At low pressures, $\Delta E/kT$ in Eq. (3) is large and positive, and hence $\Delta E_{G\,\mathrm{eff}}$ will reflect the rate of motion of the L_1 conduction band only; from the corrected curve in Fig. 2 we determine for the initial pressure coefficient $d(E_{L_1} - E_v)/dP = 5.0 \pm 0.1 \times 10^{-3}$ eV/kbar equivalent to a volume coefficient of 3.7 eV. From Eq. (3) it is also seen that at pressures well above the crossover pressure of the L_1 and Δ_1 minima, $\Delta E_{G\,\mathrm{eff}}$ will give the rate of motion of the latter. The rate of motion of Δ_1 minimum observed in our experiment is complicated by the presence of uniaxial stress above 38 kbar due to the freezing of the n-pentane-isoamyl alcohol pressure medium, but the observed magnitude of the shift to nearly 50 kbar seems to correspond with the rate of motion of the conduction-band minimum observed with Si junctions under similar circumstances. (Slykhouse and Drickamer[3] have reported that the pressure coefficient of the shift in the absorption edge of Ge above 35 kbar became almost identical with that of Si at these higher pressures.) We therefore believe that the pressure coefficient of the Δ_1 minimum in Ge is comparable to that of Si and is not greater than -1.5×10^{-3} eV/kbar nor less than -1×10^{-3} eV/kbar. Using median values for the pressure coefficients, together with a value of

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$N_\Delta/N_L=2.7$,[12,13] which we have assumed to be pressure-independent, we have calculated $\Delta E_{G\,\mathrm{eff}}$ as a function of pressure for different values of ΔE in Eq. (3). In Fig. 2, we show the curve which best fits the corrected experimental data, calculated with $\Delta E=0.18$ eV and $d(\Delta E)/dv=-4.6$ eV $[d\Delta E/dP=-6.2\times10^{-3}$ eV/kbar] in Eq. (3). Using the limiting values of the initial pressure coefficients $[d(E_{L_1}-E_v)/dP=5.0\pm0.1\times10^{-3}$ eV/kbar and $d(E\Delta_1-E_v)/dP=-1.3\pm0.3\times10^{-3}$ eV/kbar, as given above], we are led to fix the energy separation between the L_1 and Δ_1 minima at zero pressure as 0.18 ± 0.01 eV. (Earlier estimates of this quantity ranged from 0.15 to 0.22 eV.[6])

As mentioned above, we have carried out resistivity measurements on n-type Ge as a function of pressure to 50 kbar. A maximum observed in the resistivity near 35-kbar pressure, presumably caused by interband scattering,[6] is consistent with the results described above. The details of these experiments will be published elsewhere.

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[12] The value of 2.7 for the density-of-states mass ratio N_Δ/N_L was from the effective masses calculated by Cardona and Pollak (Ref. 13) for the Δ_1 minimum of Ge and the experimental values for the L_1 minimum of Ge. The above ratio is also consistent with the ratio obtained by assuming the density-of-states mass of Si for the Δ_1 band.

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Phonon Conductivity and Acoustic Attenuation in Si

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Values of the nonlinearity constant D, which involves third-order elastic constants, are obtained for silicon from the phonon-conductivity data in the presence of point-defect scattering. The results are compared with the theoretical values obtained on the basis of Keating's theory, which has been very successful in explaining the third-order elastic constants of Si. The constant D is found to depend on temperature, and the assumption by previous workers that it is independent of temperature is not correct. Keating's theory overestimates the value of the nonlinearity constant. Its value calculated on the basis of the experimental values of the third-order elastic constants at room temperature is in much better agreement with the value obtained in the present work for the best fit between the experimental and theoretical values of phonon conductivity.

I. INTRODUCTION

OUR earlier analysis[1] of the phonon-conductivity data in Si in the framework of Callaway's formalism[2] has given information regarding different phonon-scattering processes. It was found that normal phonon processes make a negligible contribution to phonon conductivity, and point-defect scattering makes an appreciable contribution towards thermal resistance below 200°K. The phenomenological expression for the phonon-phonon scattering relaxation time $\tau_{pp}^{-1}=(B_1+B_2)\omega^2T^3$, in combination with other phonon-scattering processes, could explain very well the phonon conductivity in the entire temperature range. The value of the parameter B_1+B_2 which represents the scattering strength could not be checked in the absence of any exact theory of the phonon-phonon scattering. Recently Bateman and Mason[3] have modified Akhiezer's theory[4] and for $\omega\tau_{pp}<1$ they have shown that $\tau_{pp}^{-1}=\omega^2DE_0/3\alpha\rho V^3$, where $\omega=2\pi$ times the frequency at which acoustic attenuation α is measured, ρ is the density, V is the phonon velocity, E_0 is the total thermal energy per unit volume, and D is a nonlinearity constant which can be obtained from knowledge of the second- and third-order elastic constants. Thus if phonon-phonon scattering is responsible for the observed acoustic attenuation, one can identify τ_{pp}(acoustic) with τ_{pp}(thermal). It is then possible to obtain the values of the parameter D from the phonon-conductivity data in the temperature range where the relevant acoustic theory is valid.

The aim of the present paper is to obtain the values of the nonlinearity constant D from the phonon-conductivity data in the presence of point-defect scattering, and to compare it with the theoretical value, obtained on the basis of Keating's theory, which has been very successful in explaining the third-order elastic constants of Si. Mason and Bateman have carried out measurements of acoustic attenuation and phonon conductivity

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