Raman Scattering by Wave-Vector–Dependent LO-Phonon–Plasmon Modes in n-InAs†

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We elucidate the relative roles played by the accumulation space-charge region and by the skin depth in determining the magnitude of the wave vectors of the coupled LO-phonon–plasmon modes which take part in Raman scattering in n-InAs at the E_1 gap.

We have been studying the Raman scattering by optical phonons in III-V compound semiconductors and in n-InAs in particular in order to elucidate the role played by the magnitude of the scattering wave vector. Unlike the other III-V compound semiconductors, the surface of n-InAs is accumulated.[1,2] Nevertheless previous data for longitudinal modes showed a peak corresponding to unscreened LO phonons.[3,4] It was suggested[3] that the observed peak arose from scattering by LO phonons within the narrow accumulation layer ($d_{sp} \approx 50$ Å) whose wave vectors are considerably larger than the Fermi-Thomas screening wave vector, q_{FT}, and which are, therefore, unscreened.

In our work on resonance Raman scattering in n-InAs, we have observed, in "allowed" ($\hat{e}_i \perp \hat{e}_s$, where $\hat{e}_i$ and $\hat{e}_s$ are the polarization vectors of the incident and scattered radiation, respectively), longitudinal-mode scattering from chemically etched (100) surfaces of doped samples at room temperature a broad peak with its maximum between ω_L and ω_T (the frequencies of the $q \approx 0$ LO and TO phonons, respectively), as well as a sharp peak at ω_L. However, in "forbidden" ($\hat{e}_i \parallel \hat{e}_s$) scattering, we observed only a single sharp peak at ω_L. The broad structure was also seen in scattering from (111) surfaces but was absent in scattering from (110) cleaved surfaces. We note, moreover, that it was absent in scattering from mechanically polished (i.e., damaged) surfaces.

The broad structure which appears in the resonance-enhanced allowed-scattering spectra of n-InAs does not appear in the spectra of p-InAs[5] whose surface is depleted. The broad structure is associated with the presence of free carriers at the surface of n-InAs. We attribute it to scattering by coupled LO-phonon–plasmon modes having a range of wave vectors (determined by the real and the sizable imaginary parts of the scattering wave vector) which extends into the single-particle (s.p.) excitation spectrum. Similar mechanisms have been invoked in the case of scattering by coupled LO-phonon–plasmon modes in CdS[6] and EuTe.[7] The sharp peak in the allowed ($\hat{e}_i \perp \hat{e}_s$) scattering configuration at ω_L is due to deformation-potential or Fröhlich-interaction scattering by LO phonons within the narrow accumulation layer. In the forbidden ($\hat{e}_i \parallel \hat{e}_s$) configuration the sharp peak at ω_L is due to field-induced or wave-vector–dependent scattering also within the narrow accumulation layer.

The broad structure which we have observed in scattering from (100) surfaces of n-InAs has not been reported in previous investigations. We attribute this to the fact that the samples either were mechanically polished, or had (110) surfaces, or had very low carrier concentration.

Data were obtained by using the emission lines of an argon laser which lie in the vicinity of the E_1 gap of InAs (2.54 eV), a double-grating spectrometer, and standard photon-counting techniques. The samples of InAs had bulk carrier concentrations of $n = 2\times10^{16}$, 4.2×10^{17}, 1.7×10^{18}, and 3.5×10^{18} cm^{-3}. The (100) surfaces were first mechanically polished with 0.03-μm polishing compound, and then etched in a 1% solution of bromine in methanol. Polarization selection rules were used to distinguish normally allowed Raman scattering from field-induced and wave-vector–dependent scattering by LO phonons. In this connection we note that scattering by TO phonons in zinc-blende–type crystals is forbidden in backscattering from (100) surfaces, while scattering by LO phonons is forbidden in backscattering from (110) surfaces.

Figure 1(a) shows the spectra for the allowed ($\hat{e}_i \perp \hat{e}_s$) scattering configuration. In addition to the narrow peak at 240 cm^{-1}, a broad structure, dependent on sample doping, is seen. For the highly doped samples, the broad structure is peaked at a frequency between those of the TO and LO phonons and extends below the TO-phonon frequency. For the samples with lower carrier concentrations, the additional scattering appears as an extended broad shoulder on the low-frequen-

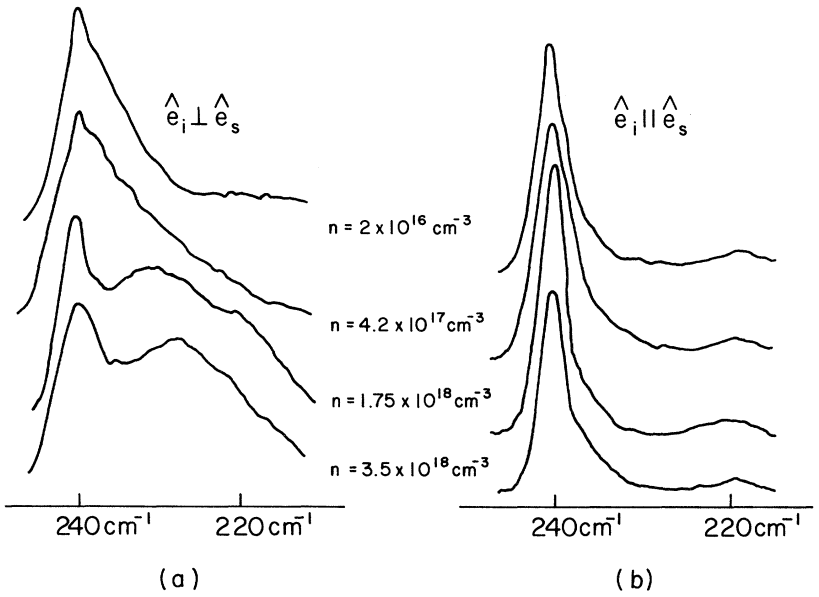

FIG. 1. Backscattering spectra from (100) polished and etched surfaces of n-InAs for different carrier densities at 4880 Å in (a) the allowed and (b) the forbidden configurations.

cy side of the LO phonon.

Figure 1(b) shows the spectra obtained in the forbidden ($e_i \| \hat{e}_s$) configuration with $\hat{e}_i$ and $\hat{e}_s$ both in the scattering plane. All the samples exhibited a sharp peak at 240 cm^{-1} corresponding to unscreened $q \approx 0$ LO phonons. The forbidden peak is due to field-induced or wave-vector–dependent scattering by unscreened LO phonons.[3,8] In addition, the spectra show a small peak at 219 cm^{-1}, the frequency of the $q \approx 0$ TO phonon, which is due to the fact that the scattering wave vector is not exactly along the normal to the surface.

The sample of n-InAs was placed in an electrolytic cell. When the sign of the applied electric field was such as to deplete the surface of carriers, the broad structure was considerably reduced. For the electric field in the opposite direction such that the carrier concentration in the accumulation layer was increased, the broad structure was enhanced, confirming the fact that the scattering involves free carriers.

Spectra obtained for samples which were only mechanically polished differed markedly from samples which were first mechanically polished and then etched. There is only a faint indication of the broad structure in the polished-sample spectrum. Not only are the unscreened LO phonon peaks considerably narrower following etching, in agreement with the data obtained by Evans and Ushioda[9] for low-carrier-density samples, but the broad structure increased dramatically following etching.

In the presence of free carriers the LO phonons and plasmons at a given wave vector are coupled via their macroscopic electric fields to form coupled LO-phonon–plasmon modes. For a given scattering wave vector ($\vec{q} = \vec{k}_i - \vec{k}_s$) one would expect to see two peaks, one corresponding to the high-frequency [$\Omega_+(q)$] modes and the other corresponding to the low-frequency [$\Omega_-(q)$] modes. However, no peaks corresponding to the $\Omega_+(q)$ modes appear in any of our spectra. The peaks corresponding to the $\Omega_-(q)$-coupled LO-phonon–plasmon modes appear as the broad structure at frequencies between ω_L and ω_T in the allowed backscattering spectra from (100) and (111) surfaces. The absence of the broad structure in the backscattering spectra from (110) surfaces indicates that the broad structure is due to longitudinal modes and, moreover, that the observed scattering by the coupled modes for (100) and (111) surfaces involves either the electro-optic or deformation-potential (atomic-displacement) mechanisms, but not the charge-density–fluctuation mechanism. The latter is further indicated by the fact that the broad structure does not appear in the forbidden ($\hat{e}_i \| \hat{e}_s$) scattering from (100) surfaces. The absence of the broad structure in the spectra of mechanically polished surfaces may be due to the possibility that, as a result of surface damage, the surface states are modified and the surface is depleted rather than accumulated.

The nature of the interaction of LO phonons and plasmons and its dependence on wave vector is now fairly well established. Detailed theoretical discussions of the wave-vector dependence of the interaction have been given by Cochran *et al.*,[10] by Lang and Pashabekova,[11] and by Cohen.[12] At high carrier densities ($\omega_p \gg \omega_L$) one can, as noted by Cowley and Dolling,[13] express the wave-vector–dependent frequency of the $\Omega_-(q)$ modes in the following convenient form:

$$\Omega_-^2(q) = \omega_T^2(q) + \Omega_0^2(q)/\epsilon(\Omega_-, q),$$

where $\epsilon(\Omega_-, q) = \epsilon_\infty(q) + \epsilon_{\text{free}}(\Omega_-, q)$; $\Omega_0^2 = 4\pi ne^2/m^*$; and $\epsilon_{\text{free}}(\Omega_-, q)$ is the wave-vector–dependent contribution of the free carriers to the longitudinal dielectric constant of the medium at $\omega = \Omega_-(q)$. For the scattering wave vectors encountered in light scattering at the E_1 gap (see below) the wave-vector dependence of $\Omega_-(q)$ is due entirely to the wave-vector dependence of $\epsilon_{\text{free}}(\Omega_-, q)$. The theory indicates that the wave-vector dependence of $\Omega_-(q)$ is essentially monotonic and that, with increasing wave vector, $\Omega_-(q)$ rises above ω_T at a point within the s.p. excitation spectrum and then approaches ω_L asymptotically.

In considering the scattering by the coupled modes, one must also take into account the fact that, when scattering takes place within the skin depth, the scattering wave vector $\vec{q} = \vec{q}' + i\vec{q}''$ has a large uncertainty determined by the imaginary parts of the incident and scattered wave vectors within the medium, whereas when scattering takes place within the accumulation layer, the uncertainty is determined by the width of the space-charge region $\Delta q_{sp} \sim 1/d_{sp}$. Additional uncertainty arises from the fact that the plasmon part of the coupled modes is Landau damped at wave vectors within the s.p. excitation spectrum. The modes which participate in the scattering within the skin depth have wave vectors in a range equal to $2q''$ centered about q'. For incident laser energies at the E_1 gap of InAs, $q' = 1\times10^6$ cm^{-1} and $q'' = 0.4\times10^6$ cm^{-1}.[14] Thus the Ω_- modes which participate in the scattering have wave vectors which range from 0.6×10^6 to 1.4×10^6 cm^{-1} and extend into the s.p. excitation spectrum.

The broad structure which results from allowed scattering by coupled modes within the skin depth corresponds to a superposition of scattering by $\Omega_-(q)$ modes whose frequencies extend from a value below ω_T to a value close to ω_L (Fig. 2).[15] The modes which lie within the s.p. excitation spectrum are Landau damped which contributes to further broadening.

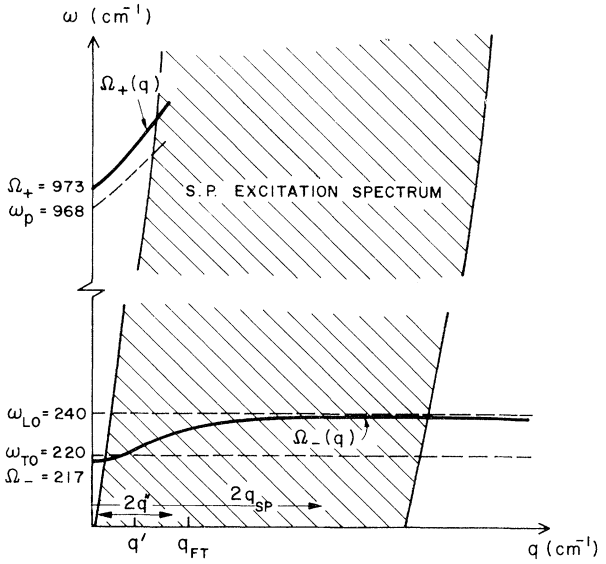

FIG. 2. Dispersion curve for the coupled LO-phonon–plasmon modes and the s.p. excitation spectrum for n-InAs. $n = 3.5\times10^{18}$ cm^{-3}, for which $m^* = 0.02m_e$, $\epsilon_\infty = 12$, $q_{FT} = 2\times10^6$ cm^{-1}, $q' = 1\times10^6$ cm^{-1}, $q'' = 0.4\times10^6$ cm^{-1}, $d_{sp} = 50$ Å, and $\Delta q_{sp} = 2/d_{sp} = 4\times10^6$ cm^{-1}.

In the case of allowed scattering by $\Omega_-(q)$ modes within the accumulation layer ($d_{sp} \approx 50$ Å), the range of wave vectors $\Delta q_{sp} = 2/d_{sp}$ is considerably larger and extends beyond the Fermi-Thomas screening wave vector $q_{FT} = 2\times10^6$ cm^{-1} for $n = 10^{18}$ carriers/cm^{-3}. As a result LO phonons at large wave vectors which are unscreened contribute to the scattering intensity, leading to a sharp peak at ω_L.

In the forbidden configuration the scattering which also takes place within the narrow accumulation layer corresponds to wave-vector–dependent and field-induced scattering. Both mechanisms depend on the macroscopic electric field of the longitudinal modes and therefore both mechanisms favor scattering by modes at large wave vectors which are unscreened. As a consequence the scattering by modes at smaller wave vectors which are only partially screened shows up as a very small shoulder on the low-frequency side of ω_L.

Finally we note that the appreciable uncertainty in the scattering wave vector, even in the case of scattering within the skin depth, is responsible for the fact that scattering by the $\Omega_+(q)$ modes which have a very large dispersion with wave vector does not appear in any of the spectra. When combined with the uncertainty in the scattering wave vector, the large dispersion would result

in a very broad peak, ~400 cm^{-1}, making it difficult to observe experimentally.

In conclusion, we have demonstrated the use of Raman scattering in determining the wave-vector dependence of the coupling between LO phonons and plasmons, and have clarified the relative roles played by the skin depth and the accumulation layer in determining the wave vectors of the modes participating in Raman scattering at the E_1 gap of n-InAs.

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[15]The ratio of the intensity of the broad peak I_b to the intensity of the narrow peak I_n is found to depend on the skin depth of the incident radiation. The latter was varied between 240 Å (at $\lambda = 4880$ Å) and 400 Å (at $\lambda = 5145$ Å). The ratio I_b/I_n was greater for large skin depths than for small skin depths. Since the narrow peak is associated with scattering by LO modes within the accumulation layer which is independent of excitation frequency, we interpret this as a further indication that the broad peak is associated with scattering by modes within the skin-depth region.

Thermodynamics of the Electron-Hole Liquid in Ge, Si, and GaAs†

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Thermodynamic properties of the electron-hole liquid are calculated for five systems: Ge, Si, and Ge under large ⟨111⟩ uniaxial stress, Si under large ⟨100⟩ uniaxial stress, and GaAs. Important effects of multiple scatterings and anisotropy are included in the correlation energy. For Ge, the ground-state energy, enhancement factor, compressibility, critical temperature, critical density, temperature dependence of Fermi energy, chemical potential, and equilibrium density are in good agreement with experiments.

In germanium and silicon at liquid helium temperatures the condensation of free excitons (FE) into "liquid" electron-hole drops (EHD) has been observed.[1] For Ge the values of the binding energy, φ, of EHD relative to FE, and the equilibrium density $n(0)$ at $T = 0$ K are reasonably well established.[1-5] Recently Thomas *et al.*,[3] McGroddy, Voos, and Christensen,[4] and Lo, Feldman, and Jeffries[5] have experimentally studied the thermodynamics of EHD in Ge and determined the ground-state energy, ϵ_g, enhancement factor, ρ, compressibility, $\chi(0)$, temperature depen-