Luminescence and Raman scattering in periodically δ-doped GaAs

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Helium temperature Raman scattering in several periodically δ-doped GaAs with varying interlayer spacing and areal doping concentration is reported near the $E_0 + \Delta_0 = 1.861$ eV gap, with laser quantum energy in the range 1.864–2.016 eV. For the higher values of the laser energy, the spectra are dominated by nonequilibrium luminescence involving the split-off valence band. As this luminescence is proportional to the light absorption by photoexcitation of electrons from the split-off band, its intensity decreases quickly as the laser energy approaches the optical gap near and above $E_0 + \Delta_0$, whereas the Raman scattering is enhanced by resonance. Therefore, the scattering dominates the spectra at lower laser energies. A Fano interference between the quasiphonon line and a continuum of electron excitations, previously reported in those systems, was investigated in some detail. The intensity of the quasiphonon line reveals strong resonance enhancement. [S0163-1829(99)06907-6]

I. INTRODUCTION

Raman scattering has been intensively used for the investigation of the dynamics of carrier plasmas in doped semiconductors. In modulation-doped heterostructures, nearly two-dimensional electron gases are formed in which the motion perpendicular to the layers is quantized and the stationary states form subbands. The intersubband transitions can be described in terms of single-particle excitations (SPE) and the collective spin-density excitations (SDE), and charge-density excitations (CDE), and the CDE is displaced, with respect to the almost degenerate SPE and SDE, due to direct Coulomb interaction plus, in the case of polar semiconductors, the coupling with the LO lattice modes.[1,2,3] A third kind of semiconductor structure, the multi-δ modulation-doped crystals, display both the electronic properties of the homogeneously doped crystals and the modulation-doped heterostructures.[4]

Owing to the band structure of the semiconductors, the Raman cross section related to the plasma dynamics displays resonant enhancement when the laser quantum energy is close to one interband transition energy.[5] In resonance, many orders of perturbations (in perturbation theory) may contribute with similar strengths to the scattering, revealing several distinct scattering mechanisms. For a review of the involved mechanisms and their resonant behavior, see, for example, Ref. 6. Treating the response of the coupled plasma-phonon under the random-phase approximation, general formal expressions for the scattering arising from the diverse mechanisms are straightforwardly obtained, but they contain sums over the intermediate virtual states, which could not so far be performed analytically. The energy of those states is then substituted by an effective average energy and the virtual

states are eliminated using their completeness property. One consequence of this approximation is that the predicted scattering cross section is factorized as a product $R(E_g, \omega_L) S(\omega)$. The first factor, giving the resonance enhancement, is independent of the Raman shift ω, and the second, giving the scattering profile, is independent of the laser frequency ω_L. By contrast, many experiments, both in three-dimensional and quasi-two-dimensional plasmas, show a pronounced variation of the scattering profile with the laser frequency. This profile variation is manifested with special clarity in the experiments presented here owing to the broad range of the exciting laser energy.

In order to avoid the very strong luminescence that completely obscures the Raman spectra for experiments in resonance with the E_0 gap in the direct gap III-V compounds, the experiments are usually done in resonance with the $E_0 + \Delta_0$ gap. However, even at that gap the nonequilibrium luminescence (hot luminescence) has intensities that frequently compete with the intensity of the scattered light. In this paper, we demonstrate that the intensity of the luminescence is strongly dependent on the laser energy and has also some dependence with the polarization.

Resonant scattering in either single or periodically δ-doped GaAs revealed unique characteristics and a more complex behavior, as compared with the observations on both homogeneous crystals and modulation-doped heterostructures. Both the polarized ($\varepsilon_S \| \varepsilon_L$) and the depolarized ($\varepsilon_S \perp \varepsilon_L$) spectra contain broad bands, extending to some 50 meV, showing features that depend on the laser frequency, besides obviously depending on the characteristics of the sample. Abstreiter, Merlin, and Pinczuk,[7] Maciel et al.,[8] and Pusep et al.[9] interpret their data as resulting from Raman scattering originating in intersubband transitions by compar-

ing the position of the main spectral features with the calculated separation between the subbands. Wagner et al.[10] interpreted the shoulders and bumps in their depolarized spectra as originating in the intersubband transitions, by comparison with the calculated intersubband spacings, and the peaks in the polarized spectra as originating in the excitations of the coupled intersubband plasmon-phonon modes, the LO phonon and its 2LO overtone. The broad background, which appears in all spectra, was suggested to be luminescence. These authors did experiments also near resonance with the E_1 gap and for one sample observed an asymmetric feature, which was interpreted to be a Fano[11] resonance between the intrinsic LO phonon and a continuum of electronic excitations. Mestres et al.[12] interpreted their experiments on the same lines as did Wagner et al.

The polarized spectra obtained by Maciel et al.[8] show some asymmetric features near the intrinsic LO frequency, which for some laser frequencies manifested as antiresonance (scattering window). Ioriatti[13] suggested that those anomalous scattering resulted from Fano-like resonance between a continuum of electronic CDE (essentially SPE in character), and the LO mode (weakly renormalized by the interaction with the plasma dynamics) interacting via the Fröhlich Hamiltonian. Theoretical predictions were made for this interaction, valid in the near resonance condition, which were confirmed experimentally.[14]

Anjos et al. performed calculations of the Raman scattering by SDE (Ref. 15) and CDE (Ref. 16) in a periodically δ-doped crystal nominally identical to the one used by Maciel et al. The spectra were numerically calculated in the conditions of extreme resonance using second-order perturbation for the $\mathbf{p} \cdot \mathbf{A}$ Hamiltonian. As the Fröhlich mechanism contributes only in third-order perturbation theory, it was not taken into account and the phonons participate in the scattering only indirectly via the longitudinal dielectric function. The calculations generated spectra in remarkable agreement with the experiments by Maciel et al.,[8] including the antiresonance near the LO mode. On the other hand, Pusep et al.[9] observed polarized spectra for a series of samples with variable areal doping densities in which the spectral anomalies in the polarized spectra near the LO frequency could be fitted using the Fano resonance, even in the condition of extreme resonance, where the theoretical predictions by Ioriatti have no a priori reason to hold.

The available results on the resonant Raman scattering in δ-doped GaAs created a situation of considerable confusion that can be clarified only with supplementary research. We measured the resonant Raman spectra of four samples of periodically δ-doped GaAs in which both the areal doping density and the spacing between the doped layers was varied. We also made experiments on some of the samples taken from the same wafers as those used by Pusep et al.[9] These latter measurements, not shown here, are in agreement with the results that we report. Our improved signal to noise ratio and broader range of variation in the laser energy allowed considerable progress in the understanding of this subject. We conclude that some apparently contradictory observations and conclusions, previously made, resulted from the competition between distinct Raman scattering mechanisms as well as from the competition between the resonantly enhanced scattering and the fading nonequilibrium lumines-
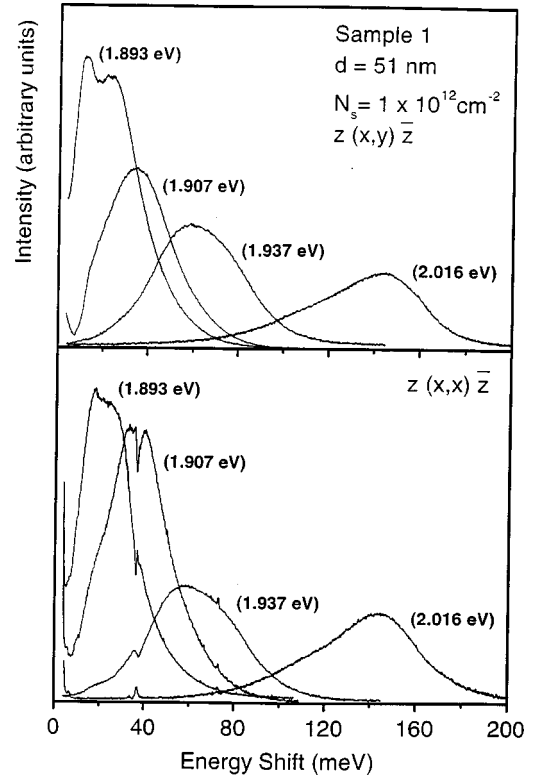

FIG. 1. Polarized and depolarized spectra of sample 1 for four laser energies. The spectra were corrected to account for the variation of the spectrometer response with the polarization and frequency of the scattered light.

cence as the laser energy decreases to approach the split-off gap.

II. EXPERIMENTS

Nearly backscattering measurements at 10 K were made in four samples of different areal doping densities N_S and interlayer spacing d. The samples contained from 10 to 20 doped layers with interlayer spacing equal to either 30 or 51 nm. The molecular-beam epitaxy growth of the samples was done at the relatively low temperature of 500 °C in order to minimize impurity diffusion. This might create a higher concentration of acceptor native defects, and consequently a slight compensation of the donor impurities. Our photoconductivity and Hall measurement tests show that this compensation is not larger than $\approx 3 \times 10^{15} \, \text{cm}^{-3}$. The excitation was done using a dye laser with power in the range 10–50 mW, focused with a spherical lens, and the spectra analyzed in a triple spectrometer were detected with a charge coupled device camera. Figures 1 and 2 show the polarized and depolarized spectra of two samples with the same interlayer spacing $d = 51$ nm and different areal doping densities for four selected laser frequencies above the $E_0 + \Delta_0$ gap at 1.861 eV. For $\hbar \omega_L$ much above the gap the depolarized spectra of both samples, which correspond to the SDE is dominated by a broad structure peaked near 1.87 eV. For sample 2, with $N_S = 3.4 \times 10^{12} \, \text{cm}^{-2}$, there appears in the structure one shoulder at the low-energy side of the peak that is absent in the spectrum of sample 1 with $N_S = 1.0 \times 10^{12} \, \text{cm}^{-2}$. For the polarized spectra, which corresponds to CDE, approximately
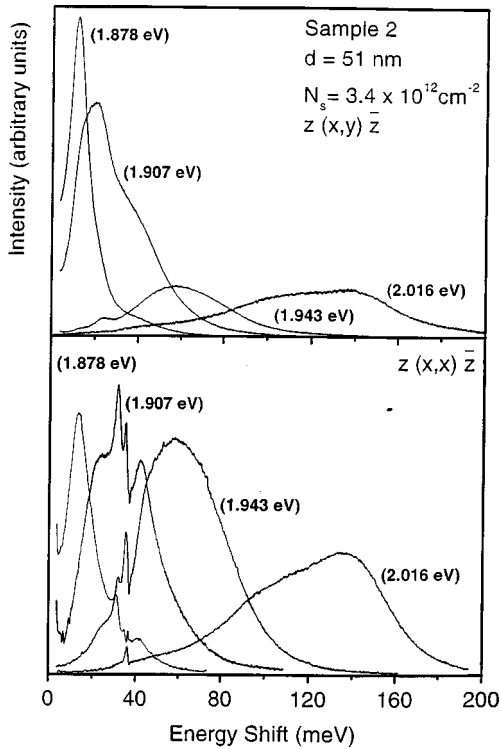
FIG. 2. Polarized and depolarized spectra of sample 2 for four laser energies. The spectra were corrected to account for the variation of the spectrometer response with the polarization and frequency of the scattered light.
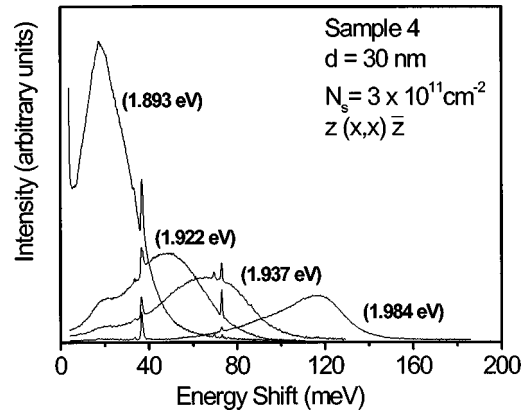

FIG. 3. Polarized spectra of sample 4 for four laser energies. The spectra were corrected to account for the variation of the spectrometer response with the frequency of the scattered light.

many laser energies. The dots show a fitting where we had to take into account the spectral complexity. The background could not be independently obtained because when the laser energy decreases toward the gap, the polarized and depolarized spectra become very different from each other. Thus, the background near the LO energy was taken into account by a third-order polynomial with free fitting parameters. Also, a Lorentzian function was used to take account of a peak at $\varepsilon_1 = 31$ meV. We interpret this peak as arising from electronic transitions between the second and third subbands in the electronic gas, but a self-consistent numerical calculation was not performed to check out this assignment. The spectra were fitted with the expression
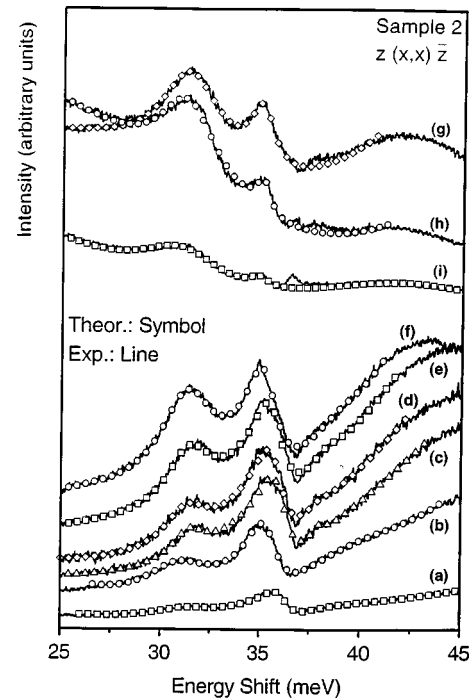
the same broad structure repeats in both samples and in addition, a sharp peak appears approximately at the energy of the LO mode. For $\hbar \omega_L \geqslant 2.00$ eV, we observed spectra similar to the ones shown in Figs. 1 and 2 for all samples. The peak of the band is at approximately 1.87 eV for all of them, varying no more than 10 meV from sample to sample. As the laser quantum energy is decreased and we approach extreme resonance, more features appear in the spectra and its peak is no longer insensitive to the laser energy. At the same time, the intensity of the "phonon" line increases, having a maximum at a sample-dependent energy about 1.9 eV, which increases with the doping concentration. Thus, the cross section for the phonon scattering is resonant. Near the resonance energy for this scattering, the phonon line shows a Fano resonance with the background. This behavior seems to be universal in the samples with interlayer spacing $d = 51$ nm, neglecting the small difference in the value of d for the samples used by Pusep *et al.*[9]

Samples 3 and 4, with $d = 30$ nm and $N_S = 1.0 \times 10^{11}$ cm^{-2}, $N_S = 3.0 \times 10^{11}$ cm^{-2}, respectively, show much less structure in the broad band. Only in sample 4 the Fano resonance can be seen with some clarity. For these two samples, there appears both the LO line and its overtone 2LO. The intensity of the 2LO line resonates very strongly at $\hbar \omega_L \cong 1.93$ eV, where, for sample 4, it becomes stronger than the LO line. Figure 3 shows the polarized spectrum of sample 4 for four selected laser quantum energies.

We return our attention to sample 2, which has the more complex behavior of the four samples. Figure 4 shows the polarized spectra in the region near the quasi-LO phonon for

FIG. 4. Line shapes fitting of the part of the polarized spectra of sample 2 around the Fano resonance The fitting was done using Eq. (2) and the procedure described in the text. The laser energies in eV are (a) 1.968, (b) 1.959, (c) 1.943, (d) 1.937, (e) 1.931, (f) 1.922, (g) 1.907, (h) 1.893, (i) 1.878.
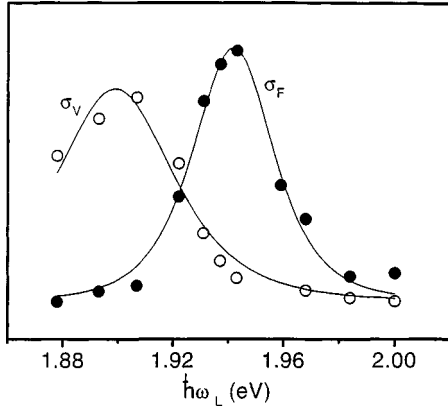
FIG. 5. Resonant enhancement of the Fano-like resonance (dots) and the line at 31 meV (open circles) for sample 2. The solid lines are fittings with Eq. (3).

$$R(E) = b(E) + \sigma_L \frac{\Gamma_L}{(E-E_L)^2 + \Gamma_L^2} + \sigma_F \frac{q^2 - 1 + 2q\varepsilon}{1 + \varepsilon^2},$$
(1)

where $\varepsilon = (E - \widetilde{E}_{LO})/\Gamma_F$. The last term in the right side of the equation represents the Fano interference between the quasiphonon excitation and the continuum of electronic excitations in the conduction band. This interference can appear in the Raman scattering due to the Fröhlich scattering mechanism.[13,14] Notice that we have used a real Fano interference parameter q. The introduction of an imaginary component was not required in practice and would make the fitting unstable. Good fittings were obtained for all spectra. The obtained quasiphonon energy was $\widetilde{E}_{LO} = (36.1 \pm 0.1)$ meV for the spectra at high laser energies but for decreasing laser energies it decreased to attain values as low as 35.1 meV. The linewidth Γ_F was also not fixed. It increased by a factor of nearly two when the Fano cross section attained maximum intensity. We cannot discard the possibility that those two anomalies are merely a consequence of neglecting the imaginary part in the Fano interference parameter. The linewidth Γ_L increases continuously for decreasing laser energies, varying by a factor of 2. This constitutes an additional evidence that the scattering profile is rather sensitive to the laser energy. The two cross sections σ_L and σ_F revealed strong resonance enhancement, as shown in Fig. 5. The solid lines in the figure are fittings with the formula

$$\sigma(\hbar\omega_L) = \frac{A}{[(\hbar\omega_L - E_R)^2 + \Gamma_R^2]^\beta},$$
(2)

for $\beta = 2$. The best fitting parameters were $E_R = 1.942$ eV, $\Gamma_R = 27$ meV for the quasiphonon line, and $E_R = 1.899$ eV, $\Gamma_R = 39$ meV for the peak at 31 meV. The data for the resonance of σ_F were good enough to exclude possibility of another exponent β in Eq. (2). Leaving this as a free parameter, its best fitting value is $\beta = 2.08$. In the case of σ_L, we cannot be certain about the value of β. The different values of E_R and Γ_R indicate that the Fano resonance and the peak at lower energy originate in two distinct scattering mechanisms.
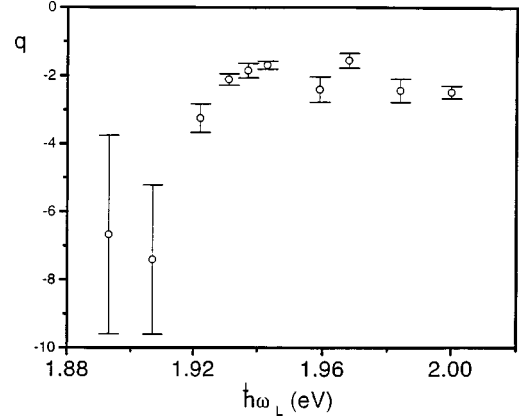

FIG. 6. Variation of the Fano resonance parameter q with the laser energy for sample 2, as obtained from the fittings shown in Fig. 4.

Figure 6 shows the variation of the Fano interference parameter q with the laser energy. It shows a behavior in sharp contrast with that obtained by Pusep *et al.*[9] However, the formula that fits the variation of $q(\hbar\omega_L)$ used by Pusep *et al.* is theoretically predicted only for conditions of near resonance[13] and probably the behavior obtained by them is not universal. It was not obtained for any of the samples that we investigated.

III. DISCUSSION

The set of data on Raman scattering in δ-doped crystals, obtained here and in the previous studies, present some paradoxical facts that we could understand only partially. Let us start considering the broad background band that appears in all spectra. For high values of the laser energy, that band has peaks at energies that are invariant with respect to the laser energy and correspond to ''Raman'' shifts as high as 0.15 eV (see Figs. 1–3). Also, preliminary calculations using the same procedure as in Anjos, Ioriatti, and Nunes[15,16] show that for $\hbar\omega_L = 2.00$ eV the Raman scattering is at least fifty times weaker than that obtained near resonance. Therefore, definitely the high shift spectral bands observed at high laser energies are luminescence. On the other hand, the Fano interference and the resonant Raman scattering, together with the very good agreement between the calculations by Anjos, Ioriatti, and Nunes[15,16] and the experiments by Maciel *et al.*,[8] indicate that the spectra observed for lower laser energies is dominated by Raman scattering. In order to understand this apparent conflict, we have to consider that the rate of nonequilibrium luminescent recombination involving the conduction-band electrons and holes in the split-off valence band is proportional to the population of photogenerated holes in this latter band. Consequently, this luminescence intensity is proportional to the absorption coefficient involving the split-off band. For laser energies $\hbar\omega_L \gg E_g = E_0 + \Delta_0 = 1.86$ eV, the luminescence intensity is proportional to $(\hbar\omega_L - E_g)^{1/2}$. For lower laser energies, the crystal modulation modifies this relation, which becomes steplike, but anyhow, as the variation of the laser energy is large compared with the energy width of the steps, the luminescence intensity decreases as the laser energy approaches the lowest energy transition between the split-off band and the electron

subbands. At the same time, the Raman scattering increases by resonant enhancement. Thus, for decreasing laser energies the luminescence disappears gradually, whereas the Raman scattering increases the intensity. The conclusion is that the spectra observed by us and by others changes gradually from luminescence to electronic Raman scattering as the laser energy is decreased towards resonance. We believe that this is a universal phenomenon that has manifested in many published resonant Raman experiments.

In Figs. 1 and 2 for the laser energy 2.016 eV, the polarized spectra are more intense than the unpolarized one. This fact was observed for all samples under investigation. Once those spectra are assigned as nonequilibrium luminescence, the fact deserves some attention. The nonequilibrium luminescence, involving transitions from the conduction band to the split-off valence band is a very fast phenomenon because the decay time of the holes from the split-off band to the fundamental valence band is smaller than 10^{-12} s. Owing to that, the nonequilibrium luminescence is partially polarized, as already demonstrated by previous investigations.[17]

Another subject for discussion is the spectral anomaly near the LO phonon energy. Nunes *et al.*,[14] Pusep *et al.*,[9] and ourselves could successfully fit that spectral anomaly using the Fano formula for the resonance between a discrete level and a continuum. According to Ioriatti,[13] that interference originates in the Fröhlich mechanism for Raman scattering, in which the phonon dynamics participates explicitly. However, the data by Maciel *et al.*[8] could be reproduced with

remarkable precision in the calculation by Anjos,[16] where the LO phonons participate only to screen the electron dynamics via the longitudinal dielectric function. This creates a scattering window around $\hbar\omega_{LO}$. Our speculation is that both phenomena (lattice screening and Fröhlich interaction) participate in that anomaly. When the Fröhlich mechanism gives little contribution to the Raman scattering, there appears only that antiresonance (scattering window) observed by Maciel *et al.* and theoretically reproduced by Anjos. When the Fröhlich mechanism is dominant for the scattering near the LO phonon, the Fano-like line shapes are observed. In the experiments here reported, it is clear that the resonant enhancement of the Fröhlich mechanism makes it very strong in the laser energies for which the Fano resonance was observed. It is also interesting to notice that in the experiments by Wagner *et al.*, the Fano-like interference showed up for laser resonant with the E_1 gap, but not with the $E_0+\Delta_0$ gap; this reinforces the idea that the appearance of the Fano interference depends on the dominant mechanism in the scattering.

It is also interesting to notice that the Fano-like interference, which was predicted by Ioriatti[13] only for the condition of near resonance, revealed to hold in some cases even at extreme resonance, as observed by Pusep *et al.*[9] and by us.

As stated before, the Fano-like interference was not observed for sample 3, with nominal parameters $d=30$ nm and $N_S=1.0\times10^{11}$ cm^{-2}. This demonstrates that the interference requires a minimum concentration in the electron gas.

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