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Fano-like resonant interference in Raman spectra of electronic and LO-vibronic excitations in periodically δ-doped GaAs

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The asymmetry in the one-phonon Raman lines of a Si:GaAs δ-doped doping superlattice is interpreted as a quantum-mechanical interference process in which an incident photon is inelastically scattered by a resonance excitation composed of a bulk LO one-phonon state mixed to a continuum of electron intersubband transitions. The dependence of the line shape on the frequency as well as on the polarizations relative to the crystal axis of the incident and the inelastically scattered radiation is produced by the difference in Raman-scattering amplitudes associated with each component of the mixed excitation.

In polar semiconductors, longitudinal-optical (LO) phonons are known to form coupled modes with the collective charge-density oscillations of a bulk electron plasma that are admixtures of electron and lattice oscillations.[1] A similar coupling also occurs between LO phonons and the collective intersubband charge-density oscillations of quasi-two-dimensional electron systems that exists in modulation-doping GaAs-$Al_xGa_{1-x}As$ single heterostructures and quantum wells where band-gap discontinuities and space-charge fields modify electronic motion normal to the semiconductor interfaces into discrete subband states.[2] In this paper we demonstrate that a resonance structure previously seen in the Raman spectra of a Si:GaAs δ-doped doping superlattice in the region of the LO phonon[3] is caused primarily by a coupled electron-phonon excitation of a different nature, viz., a bulk LO one-phonon state of polarization normal to doping layers mixed to a continuum of electron intersubband transitions. Possibility for excitations of this kind was suggested in a recent theoretical paper[4] and attributed to the inhomogeneous periodical distribution of space-charge characteristic of these systems which quantizes electronic motion along the normal direction of the doping layers (the superlattice axis) into miniband states whose nature and energy spectra are very dependent on the values of the doping parameters used in the design of such structures. For moderately high sheet carrier densities and sufficiently large superlattice periods, the low-lying miniband states have narrow widths and correspond to the quantized subband states of an isolated δ layer whose existence have been experimentally established through magnetotransport measurements[5] and theoretical models.[6] For sheet carrier densities chosen so that electron confinement energies in each δ layer are less than the LO one-phonon energy, occupied states at low temperatures in this system consist of a few minibands with the lowest accounting for more than 75% of the total number of electrons. The remaining ones, having energies lying very close to the Fermi energy near the top of the confining self-consistent potential, are dispersed into nearly-free-electron (NFE) bands before any interwell coupling starts to significantly affect the lowest miniband state that remains as a discrete subband state.[4] Owing to the low electron occupation of these bands and because matrix elements associated with one-electron transitions from the lowest subband state to those of the NFE continuum are nonzero in a wide energy interval, here charge-density fluctuations in the spectral region of the LO phonon are not followed by significant macroscopic electric fields as in the case of a bulk electron plasma of the same density. Thus, a broad unscreened continuum of single-particle excitations overlapping in energy with that of LO one-phonon states may be seen in light scattering by these structures. Since a LO phonon of polarization normal to the doping layers is mixed to this intersubband continuum through Fröhlich coupling, the quantum-mechanical picture for the electron-phonon interaction is analogous to the Auger-type electronic transitions treated by Fano.[7] The effects of an intersubband continuum on LO phonons have not been investigated previously. Here we report detailed measurements of the dynamical structure factor $S(k,\omega)$ of a Si:GaAs δ-doped doping superlattice in the spectral region of the LO phonon using resonance Raman spectroscopy.

The sample used in the present study consisted of sheets of silicon donors (the δ-doping layers) periodically implanted in single atomic monolayers during the molecular-beam-epitaxial growth of an otherwise intrinsic GaAs film on a semi-insulating (001) oriented GaAs substrate. The sample was grown at a temperature of 540 °C in order to reduce impurity diffusion.[8] It contained 10 repetitions of such doping layers separated from one another by 500 Å sandwiched between a 1-μm-thick buffer and a 500-Å-thick cap layer. The nominal sheet carrier density of each layer, as determined from Hall measurements, was 1.0×10^{12} cm^{-2}.

Three similar samples cut from the same wafer were mounted next to each other in the cold finger of a cryo-

stat together with a fourth of intrinsic GaAs used as reference. The samples were oriented so that measurements in the polarized $z(x',x')\bar{z}$, $z(y',y')\bar{z}$, $z(x,x)\bar{z}$ and depolarized $z(x',y')\bar{z}$ and $z(y,x)\bar{z}$ backscattering configurations could be performed by means of a parallel translation of the samples and a 90° rotation in the polarization of the exciting radiation. As usual, we adopt the notation x, y, z, x', and y' to denote the (100), (010), (001), (110), and $(1\bar{1}0)$ crystal directions, respectively. Raman measurements at 77 K were taken using the variable frequency output of a cw dye laser with dicyanomethylene as a dye pumped by all lines (6W) of an Ar-ion laser. Measurements at room temperatures were performed at a fixed frequency using the 6471-Å line of a Kr-ion laser as the exciting source. A Spex double monochromator equipped with single-photon counting and a homemade data acquisition system were used for the detection of the scattered radiation.

We found for a range of exciting frequencies between 1.86 eV and 1.99 eV, a characteristic fine structure in the polarized Raman spectra measured at 77 K which is absent in the corresponding $z(x',y')\bar{z}$ depolarized spectra. The discrete points in Fig. 1, for example, are experimental results in the $z(y',y')\bar{z}$ scattering geometry for various exciting photon energies $\hbar\omega_L$ tuned to resonance near the spin-split $E_0+\Delta_0$ optical gap of GaAs at 1.85 eV (77 K). The observed resonance profiles have a critical Raman frequency that is close to the LO one-phonon frequency of intrinsic GaAs and are characterized by a relative maximum followed by a steep descent and a relative minimum, or vice versa, depending on whether the exciting laser energy $\hbar\omega_L$ is tuned to near resonance above or below a certain "effective" energy gap $\tilde{E}_g$ defined by the condition that the electronic Raman scattering is maximum at the frequency of the LO phonon.[4] As is evident from Fig. 1, resonance profiles become increasingly asymmetric as the exciting laser frequency approaches a critical energy near 1.916 eV, where the resonance excitation is manifested as a "scattering window" (an antiresonance) in a intense (partially luminescent) underlying background centered at the frequency of the LO phonon. For the other polarized configurations investigated in the same range of exciting frequencies, asymmetric profiles of similar linewidth and critical frequency as those shown in Fig. 1 were also observed.

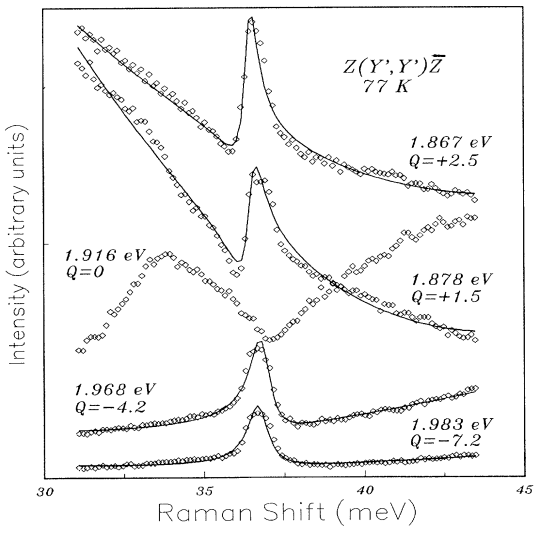

FIG. 1. Resonance Raman spectra in the $z(y,'y')\bar{z}$ scattering configuration of a Si:GaAs δ-doped doping superlattice for various laser energies. The lines are theoretical fits to Fano profiles superimposed on smooth backgrounds as described in the text. The curves have been shifted vertically with respect to each other for reasons of clarity.

As noted, we interpret these profiles as Fano interferences between an electronic charge-density continuum and the discrete vibronic Raman scattering originated in a "quasiparticle" consisting of a bulk LO phonon mixed via final-state interactions to a intersubband continuum of one-electron transitions. Consistent with this interpretation and the fact that depolarized spectra yield spin-density excitations which do not directly couple to LO phonons, no interference profiles were seen in the $z(x,y)\bar{z}$ depolarized spectra. Instead, Raman spectra in this geometry consisted of symmetrical profiles superimposed on backgrounds similar to those in Fig. 1. The complex line-profile parameter $q=q_r+\imath q_i$ that determines the asymmetry of the resonance lines is proportional to the ratio of the transition matrix associated with the discrete state to that associated with the continuum.[7] In near-resonance conditions when the difference between the energy of the light and $\tilde{E}_g$ is still larger in magnitude than typical transition energies associated with the intersubband continuum, i.e., $\hbar\omega_{\rm LO}$, the dependence of q on $\hbar\omega_L$ apart from a frequency-independent positive quantity is given by[4]

$$q \propto \imath(\tilde{E}_g-\hbar\omega_L)(\hat{\mathbf{e}}_S\cdot\mathbf{R}\cdot\hat{\mathbf{e}}_L), \tag{1}$$

where $\hat{\mathbf{e}}_L \parallel \hat{\mathbf{e}}_S$ denote the polarization vectors of the incident and scattered fields, respectively, and $\mathbf{R}$ the Raman polarizabity tensor.

As in the case of a bulk GaAs, two LO-phonon scattering mechanisms are expected to contribute to this tensor, namely, "allowed" (deformation potential plus eletrooptic) and "forbidden" (Fröhlich intraband).[9] The former is represented by

$$\mathbf{R}=\begin{pmatrix}0 & a_D & 0\\ a_D & 0 & 0\\ 0 & 0 & 0\end{pmatrix}, \tag{2}$$

where a_D is the "allowed" Raman polarizability. The latter corresponds to a diagonal tensor with a diagonal element a_F that in contrast to a_D strongly resonates with the $E_0+\Delta_0$ optical gap. It can become comparable to or even larger than the "allowed" process for photon energies near this energy gap particularly when in the presence of impurities[9] or macroscopic electric fields[10] originated, in the present case, in the periodical self-consistent space-charge potential.

The solid curves in Fig. 1 represent theoretical fits to a Fano profile,

$$\sigma(\omega)=\sigma_b(\omega)+\sigma_{el}\frac{(q_r^2+q_i^2-1)+2q_r\epsilon}{1+\epsilon^2}, \tag{3}$$

where ajustable parameters in this equation are the amplitude $\sigma_{el}(q_r^2+q_i^2-1)$ and the Fano line-profile parameter Q $[Q-1/Q=(q_r^2+q_i^2-1)/q_r]$ associated with each resonance line. The slowly varying, partially luminescent background underlying each fitted curve in Fig. 1 $[\sigma_b(\omega)$ of Eq. (3)], was taken as the corresponding $z(y',x')\bar{z}$ depolarized spectra fitted to a smooth curve. The procedure is consistent with the theoretical expectation that in the absence of collective fields resonant Raman spectra of spin- and charge-density excitations should be identical. It is also consistent with our experimental measurements which yield nearly identical spectral intensities in the polarized $z(y',y')\bar{z}$ and depolarized $z(x',y')\bar{z}$ geometries in wide spectral regions on each side of all resonances in Fig. 1. In Eq. (3), $\epsilon=(\omega-\omega_{\rm LO}-\Delta\Omega)/\Gamma$ represents a reduced frequency where Γ is a linewidth parameter and $\Delta\Omega$ a line shift. For laser exciting frequencies well above the $E_0+\Delta_0$ gap where Raman-scattering amplitudes are expected to be nonzero only for phonon modes that satisfy (or nearly satisfy) the momentum selection rules, resonance profiles could be consistently fitted using Eq. (3) with constant $\Delta\Omega$ and Γ, i.e., $\Delta\Omega=1.5$ $\rm cm^{-1}$ and $\Gamma=3.2$ $\rm cm^{-1}$. These values are to be compared with those of Ref. 4, viz., $\Delta\Omega=0.8$ $\rm cm^{-1}$ and $\Gamma=2.8$ $\rm cm^{-1}$ that have been theoretically computed from the self-energy of a bulk one-phonon state of wave vector k normal to the doping layers interacting with the charge-density excitations of a Si:GaAs δ-doped doping superlattice having the same parameters as those reported here. We emphasize, however, that calculations were performed in the limit of zero temperatures and, more importantly, valid when photon energies are only in near resonance with the "effective" gap $\tilde{E}_g$. On the other hand, when incident photon energies lie in close resonance with this gap, electronic Raman spectra in the region of the LO phonon are not simply those given by the spectrum of charge-density fluctuations in the conduction band but must depend on the details of the energy level structure of conduction- and valence-band states participating in the light-scattering process. For incident photon energies lying below this energy gap, on the other hand, values for the line-shift and linewidth parameters used in the fits were somewhat less than the corresponding ones used in the high side of the excitation spectrum. Although this may be taken as evidence for a distinctive phonon mode associated with the (resonant) Fröhlich mechanism, one cannot exclude the possibility of an artifact due to the presence of an intrinsic line associated with light penetration into the substrate which was not resolved from the resonance line due to the finite spectrometer resolution (3.5 $\rm cm^{-1}$)

Figure 2 shows Raman spectra taken at room temperatures using the 6471-Å output from a Kr-ion laser as the exciting source. As is evident from the figure, polarized Raman spectra are asymmetric and, more importantly, *not* invariant under a 90° rotation of the sample. The $z(y,x)\bar{z}$ spectra, on the other hand, are symmetric as expected for a noninteracting electronic background. In all three scattering configurations, Raman spectra were complicated by the appearance of an additional structure at precisely the LO-phonon frequency of intrinsic GaAs

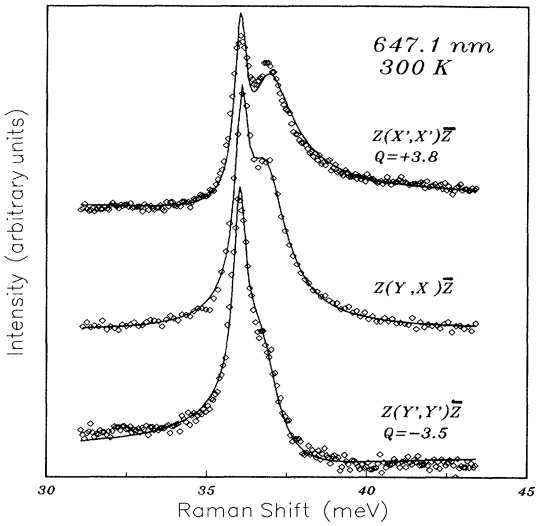

FIG. 2. Room-temperature Raman spectra of a Si:GaAs δ-doped doping superlattice line in three scattering configurations using the 6471-Å line of a Kr-ion laser. The lines are theoretical fits assuming a frequency-independent base line for each spectrum as described in the text. The critical energy and the linewidth parameter are the same for all curves.

whose presence is ascribed to changes that occur in the surface depletion layer[10] by the influence of the temperature on the rate of electron return from the δ layers to electron surface states.[11]

The solid lines in Fig. 2 are theoretical curves fitted to the experimental data using Eq. (3) with an additional Lorentzian line of the same width and critical frequency as that observed in the reference sample. The symmetric $z(y,x)\bar{z}$ spectrum was fitted in the same way except for the fact that it consisted of the sum of two Lorentzians. It is interesting to note that the frequency shift $\Delta\Omega=6.1$ $\rm cm^{-1}$ associated with these spectra is considerably larger than the corresponding one observed at 77 K. This is understood in terms of a larger number of electrons populating excited NFE bands which would confer a more three-dimensional behavior to the electron system at these temperatures. In fact, recent self-consistent calculations done for the present system[12] show that at room temperatures only 37% of the total number of electrons remains in the lowest subband state, all the rest being distributed among various NFE bands. If a bulk plasma frequency is ascribed to electron oscillations in these bands, one arrives at a L^+ LO-phonon-plasmon vibration frequency[1] that is in close correspondence with that observed here for the resonance excitation. Electrons that remain in the lowest subband state, on the other hand, give rise to the line-shape asymmetries seen in Fig. 2. As indicated in the figure, the line-profile parameter Q associated with the $z(x',x')\bar{z}$ scattering configuration is positive, a fact that lends support to Eqs. (1) and (2) which predicts a positive q_r with the use of a positive imaginary part of the "allowed" Raman polarizability.[9] The corresponding $z(y',y')\bar{z}$ spectrum, on the other hand, exhibits a negative Q of approximately the same magnitude as the one

found for the previous spectrum. This is also in accordance with the predictions of Eqs. (1) and (2) which indicate line-profile parameters of the same magnitude but opposite signs for these two spectra. We remark that no distinctive structure was observed in the $z(x,x)\bar{z}$ scattering geometry, except for a faint antiresonance that could be barely resolved from the underlying scattering background.

Finally we note some limitations of Eqs. (1) and (3) in describing the Raman data in the extreme resonant case when the resonance excitation is manifested as a scattering window in a rapidly varying scattering background. Attempts to fit the antiresonance profiles observed near 1.916 eV on the assumption of a frequency-independent electronic Raman-scattering amplitude have produced linewidths about three times larger than those observed in the near-resonance region of the excitation spectrum. Except for the expected strong dependence of the electronic transition matrix on the Raman frequency which renders the use of Eq. (3) with constant q and σ_{el} invalid in these circumstances, we have no other explanation for this fact.

In summary, our results show that the peculiar form of electron confinement produced by a spiked periodical distribution of dopants expected from δ doping leads to profound modifications in the behavior of bulk electron–LO-phonon coupled excitations in GaAs and constitutes clear manifestation of a true quantum-mechanical feature originating in a continuum of intersubband transitions that is present in this system even at room temperatures.

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[1] B. B. Varga, Phys. Rev. **137**, A1896 (1965); A. Mooradian and A. L. MacWhorter, Phys. Rev. Lett. **19**, 849 (1967).

[2] See, e.g., G. Abstreiter, R. Merlin, and A. Pinczuk, IEEE J. Quantum Electron. **QE-22**, 1771 (1986), and references therein.

[3] A. C. Maciel, M. Tatham, J. F. Rayan, J. M. Worlock, R. E. Nahory, J. P. Harbinson, and L. T. Florez, Surf. Sci. **228**, 251 (1990).

[4] L. Ioriatti, Phys. Rev. B **43**, 14 742 (1991)

[5] A. Zrenner and F. Koch, Surf. Sci. **196**, 671 (1988); A. Zrenner *et al.*, Semicond. Sci. Technol. **3**, 1203 (1988).

[6] L. Ioriatti, Phys. Rev. B **41**, 8340 (1990).

[7] U. Fano, Phys. Rev. **124**, 1866 (1961).

[8] E. F. Schubert, J. B. Stark, B. Ulrich, and J. E. Cunningham, Appl. Phys. Lett. **52**, 1508 (1988).

[9] J. Menendez and M. Cardona, Phys. Rev. Lett. **51**, 1297 (1983); A. Cantarero, C. Trallero-Ginner, and M. Cardona, Phys. Rev. B **40**, 12 290 (1989).

[10] G. Abstreiter, A. Pinczuk, and M. Cardona, in *Light Scattering in Solids IV*, edited by M. Cardona and G. Güntherrodt (Springer, Berlin, 1983), Sec. 2.6.

[11] Weimin Zhou, Clive H. Perry, Lin Ma, Kyu-Seok Lee, J. M. Worlock, A. Zrenner, F. Koch, and K. Ploog, J. Appl. Phys. **69**, 4075 (1991).

[12] J. C. Barbosa and L. Ioriatti (unpublished).