Observation of Phonon Modes through Resonant Mixing with Electronic States in the Secondary-Emission Spectra of a $GaAs/Al_{0.32}Ga_{0.68}As$ Single Quantum Well

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We report the first observation of a resonant mixing of the heavy hole (hh) and light hole (lh) plus one optical vibrational modes in a quantum well structure. A series of 27 peaks are observed between the hh and lh regions in the photoluminescence excitation spectra of the $GaAs/Al_{0.32}Ga_{0.68}As(100)$ *single* quantum well studied and correspond closely to sixteen vibrational modes belonging to the classes of confined in the well, confined in the barrier layers, confined at the interface, and unconfined. This remarkable first observation is made possible only in this quantum well with parameters such as to achieve double resonance conditions.

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In this Letter we report the first observation of an unexpectedly strong modification of the electronic density of states, brought about by a strong resonant mixing of the optical vibrational and electronic states of a quantum well structure when the separation between the latter is comparable to the energy of the former.[1] As schematically indicated in Fig. 1, the $GaAs/Al_{0.32}Ga_{0.68}As(100)$ *single* quantum well (QW) studied is such that the separation of the light-hole (lh)–first-electron and heavy-hole (hh)–first-electron free excitons is near resonance with an optical vibrational mode of the quantum-well layer. Consequently, the usual two-dimensional-like nearly constant density of electronic states (dashed lines) can acquire considerable structure induced by the various confined (in the well or barrier layers), interface, and unconfined vibrational modes. The photoluminescence excitation (PLE) spectra can manifest the presence of this structure in the density of states of the coupled electron-phonon system, and is indeed observed here for the first time. The double-resonance condition achieved by excitation at the lh free exciton and detection at the heavy-hole free exciton also leads to dramatic enhancement of the Raman-scattering (RS) cross section so that Stokes lines associated with several phonon modes in near double resonance are also observed in the photoluminescence (PL) spectra from such a single QW.[2] The phonomenon is *not* observed in quantum wells of well widths different by even ± 1 monolayer (ML) from the unique value at which the lh+phonon to hh resonant condition is achieved, thus indicating the effect to be undoubtedly due to a strong resonant mixing of such states.

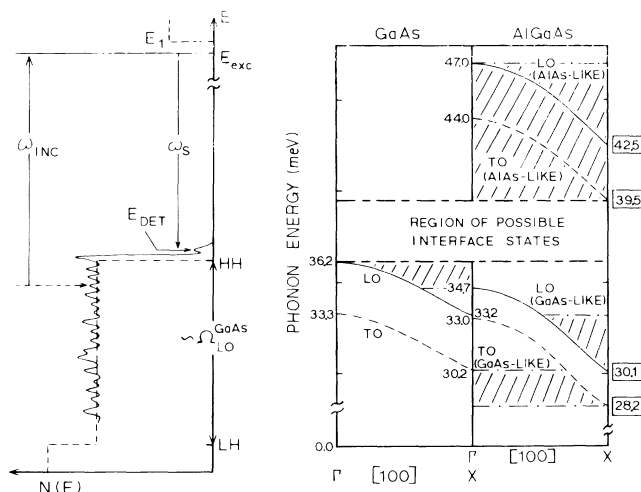

FIG. 1. Schematic representation of the overlapping nature of the bulk phonon branches of the well and barrier layers in a quantum well such as $GaAs/Al_{0.3}Ga_{0.7}As(100)$. The values shown correspond to reported experimental values except for the X-point values of $Al_{0.35}Ga_{0.7}As$ which are experimentally not known and are thus estimated (see text). The solid and dashed lines are only schematic and do not represent the dispersion curve which, for $Al_{0.3}Ga_{0.7}As$, is not known. The cross-hatched area indicates regions where confined and interface states may arise. (a) Schematic representation of the expected modification of the quasi two-dimensional density of hole states due to strong resonant mixing when lh+optical-phonon states become degenerate with the hh states.

For completeness we note that a variety of RS, resonant RS, and PL studies of heterojunctions, multiple QW's, and superlattices have been carried out to examine their vibrational and electronic states.[3-14] In particular, the recent Raman-scattering studies[9] of GaAs-AlAs(100) superlattices by Sood *et al.* provided evidence for the presence of interface modes and of confined LO and TO phonons in the GaAs well layers arising from the *nonoverlapping* nature of the bulk GaAs and AlAs optical-phonon branches. The confined modes, defined by $m\pi/d$ where m is an integer and d the well thickness,[15] were found[9] to have energies well approximated by the *bulk* GaAs optical-phonon branches at the discrete values of the wave vector $q = m\pi/d$. Confined modes belonging to both the $A_1(m=\text{even})$ and $B_2(m=\text{odd})$ symmetry of the D_{2d} point group were observed,

the former only near resonant conditions when the excitation energy is near the first electron–heavy-hole exciton energy. By contrast, the most commonly studied and technologically important systems, $GaAsAl_xGa_{1-x}As$ ($x=0.3$) and $InP/In_xGa_{1-x}As$ ($x=0.53$), involve ternary alloys which are known to exhibit the so-called "two-mode" behavior, i.e., two LO and two TO optical-phonon branches, referred to as the A-like and B-like, where A and B are the binary components (see Fig. 1). The issue of interface and confined phonon states in quantum well structures made of such components is thus more complex since, depending upon the alloy composition, both overlapping and nonoverlapping regions of the well and barrier-layer phonons can exist (see Fig. 1).

The quantum well structure was grown via molecular-beam epitaxy employing the technique of growth interruption.[12-14] The details of the growth conditions, as well as some results of initial PL studies, have been previously reported.[14] The sample consists of one quantum well made of an intended nine-ML GaAs well region sandwiched between forty-ML-thick $Al_{0.32}Ga_{0.68}As$ barrier layers. The growth rates and the individual layer thicknesses were monitored via the oscillation periods and number of oscillations in the specular beam intensity of the reflection high-energy electron diffraction pattern during growth.[12-14] This ensures that the Al concentration and the delivered layer thicknesses are known to an accuracy of 1% and 0.1 ML, respectively.

The PL and PLE data were taken in the backscattering geometry at about 25° from the normal to the sample surface. The excitation source was an Ar^+-ion-pumped dye laser with a full width at half maximum of 0.25 meV. The detection was achieved via photon counting and the resolution was 0.20 meV. In the data reported here the excitation energy was kept below the $Al_{0.32}Ga_{0.68}As$ barrier-layer band gap to avoid creation of excitons in the barrier layers and the possible ambiguities in interpretation that could arise from their subsequent thermalization into the GaAs well layer. All data shown here were taken at 5 K with an incident power of $\simeq 0.5$ W/cm^2. Systematic studies as a function of temperature, incident power, and polarization dependence have, however, also been carried out and found to be consistent with the inferences derived in this paper. Such details will be reported elsewhere.[16]

The PL behavior, taken at an incident energy of 1.7694 eV, is shown in Fig. 2(a). One observes two broad ($\simeq 8$ meV) features centered near 1.7155 and 1.7308 eV which respectively correspond to the $n=1$ electron-to-hh free-exciton recombination in regions of the sample with nine- and eight-ML-wide GaAs wells. The presence of well regions differing by ± 1 ML from the intended well thickness in samples grown with growth interruption is by now a well documented phonomenon.[12-14] Of greater significance is the presence of the far narrower ($\simeq 0.5$ meV) peaks labeled P_1, P_2, and P_3. These peaks are

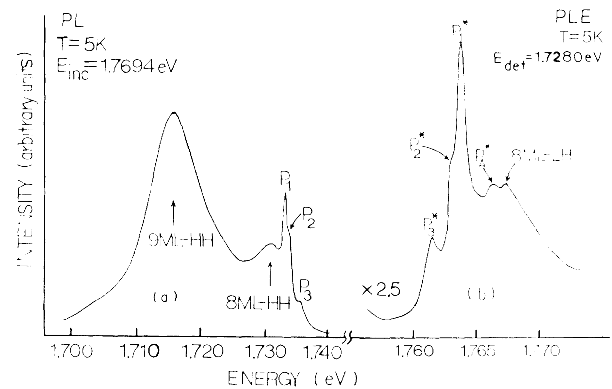

FIG. 2. (a) Low-temperature (5 K) photoluminescence spectra of a single quantum well structure grown with growth interruption and intended GaAs well thickness of nine ML (25.5 Å) sandwiched between forty-ML (113.2 Å) $Al_{0.32}Ga_{0.68}As(100)$ barrier layers. Peaks P_1, P_2, and P_3, are doubly resonant Raman-scattered peaks, Stokes shifted by $\Omega_1 = 36.2 \pm 0.2$ meV, $\Omega_2 = 35.5 \pm 0.2$ meV, and $\Omega_3 = 33.7 \pm 0.2$ meV, respectively. (b) Low-temperature PL excitation spectra for the eight-ML light-hole region, taken with detection set at 1.7280 eV in the heavy-hole region. Peaks P_1^*, P_2^*, and P_3^* are Stokes shifted by the same energies Ω_1, Ω_2, and Ω_3 as the peaks P_1, P_2, and P_3 seen in the PL spectra of (a). P_A^* is a new peak, Stokes shifted by $\Omega_A = 38.7 \pm 0.2$ meV. The eight-ML lh is marked.

Stokes shifted from the incident photon energy by $\Omega_1 = 36.2 \pm 0.2$ meV, $\Omega_2 = 35.5 \pm 0.2$ meV, and $\Omega_3 = 33.7 \pm 0.2$ meV and *move rigidly with the incident energy*. Their remarkably large strength is a consequence of the double resonance condition since, as seen in the PLE spectrum [Fig. 2(b)], the incident energy is very near the eight-ML $n=1$ to lh free-exciton transition at 1.7674 eV. The PLE spectrum was taken with detection set at 1.7280 eV (i.e., in the eight-ML hh exciton region). The peaks labeled P_1^*, P_2^*, P_3^*, and P_A^* are separated from the detection energy by $\Omega_1^* = 36.1$ meV, $\Omega_2^* = 35.3$ meV, $\Omega_3^* = 33.7$ meV, and $\Omega_A^* = 38.7$ meV and *shift rigidly with the detection energy*. The peak at 1.7674 eV, however, does not shift with the detection energy and is thus identified as the eight-ML light-hole free exciton. Similar studies for the nine-ML lh region give the nine-ML lh exciton energy as 1.7515 eV. The shifts Ω_1^*, Ω_2^*, and Ω_3^* are the same as Ω_1, Ω_2, and Ω_3 seen in PL. Hence, the peaks P_1^*, P_2^*, and P_3^* in PLE are simply the resonant-RS counterpart of the peaks P_1, P_2, and P_3 seen in PL. The peak P_A^* is also a resonant-RS peak, although its counterpart peak in the PL spectra was not detected. The shifts Ω_1 and Ω_3 are very close to the known Γ-point LO and TO modes of bulk GaAs (36.2 and 33.3 meV, respectively). The shift Ω_2 corresponds closely to the energy at which the real parts of the GaAs and $Al_{0.32}Ga_{0.7}As$ dielectric functions cross.[17] It may thus be an interface mode or may be a confined

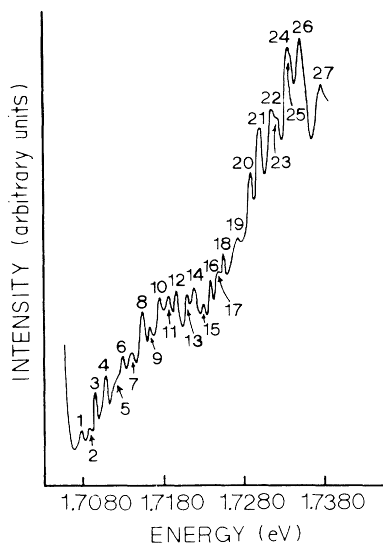

FIG. 3. 5-K PLE spectrum in the nine-ML hh to eight-ML hh region with detection at 1.7040 eV (i.e., in the low-energy tail of the nine-ML hh luminescence line). Peaks labeled 1 through 13 are at phonon energy separations from the nine-ML lh, whereas peaks 14 through 27 are at phonon energy separations from the eight-ML lh (see Table I).

mode of the GaAs well. Note that Ω_A^* does not correspond to any previously reported phonon mode of bulk GaAs, bulk $Al_{0.3}Ga_{0.7}As$, or quantum well structure. Of the known frequencies of these bulk materials (see Fig. 1), it lies between the LO of GaAs (36.2 meV) and the AlAs-like TO frequency at the X point (39.5 meV, see Fig. 1) of $Al_{0.3}Ga_{0.7}As$. We will return to its identification in the following.

Extending the excitation spectra to the energy region between the nine-ML hh and eight-ML hh free excitons we find a remarkable 27 peaks (Fig. 3). Samples grown under identical conditions but with only well width different by even ± 1 ML *do not* exhibit such structure. The energies of the peaks are summarized in Table I. Within the detection resolution of 0.25 meV, *their energy position does not shift with detection energy.* The separations of these peaks from the detection energy is too small compared to any optical phonon of the system. However, the separation of the first 13 peaks from the nine-ML lh (1.7515 eV) and the next 14 peaks from the eight-ML lh (1.7674 eV) free exciton, also shown in Table I, corresponds closely to many of the phonon energies expected from the bulk-phonon branches of GaAs and $Al_{0.32}Ga_{0.68}As$ indicated in Fig. 1. The identification of the confined phonons, denoted by LO_m or TO_m, is based upon the nonoverlapping regions of the dispersion curves of Fig. 1. Peaks denoted by $\Omega(LO_m)$ or $\Omega(TO_m)$ are such that, within the uncertainties of the phonon energies of Fig. 1 and these measurements, their energy coincides well with that estimated from the corresponding bulk-phonon branch. However, given the Γ-point and X-point values of the relevant GaAs and $Al_{0.32}Ga_{0.68}As$ branches, their wave functions cannot be totally of the confined nature. The modes labeled "AlAs-like" are the modes confined in the barrier layer. However, in the absence of a knowledge of the precise dispersion curves of the AlAs-like LO and TO modes of $Al_{0.32}Ga_{0.68}As$, they cannot be identified with an m value. We attribute their coupling to the electrons to the significant penetration of electron and light-hole wave functions into the barrier for a well of eight-ML width. Finally, the unlabeled peaks 6 and 7 ($\Omega = 38.7$ and 37.5 meV, respectively), and possibly even peak 5 ($\Omega = 39.4$ meV), would correspond to the energy region where only interface modes would be possible if the X-point energy of AlAs-like TO mode, estimated with use of the work of Yip and Chang[18] to be 39.5 meV, is correct. If this value is lower, peaks 5, 6, and 7 could be confined AlAs-like TO modes. Since no crossing of the real parts of the dielectric functions of GaAs and $Al_{0.32}Ga_{0.68}As$ occurs in this region,[17] our data suggest that the X-point value of the AlAs-like TO mode is likely to be significantly lower than the best estimates available in the literature and that peaks 5, 6, and 7 are most likely confined in the barrier layers. A firm assignment of some of the peaks observed in the present experiments can be made only if the phonon dispersion curves of $Al_{0.3}Ga_{0.7}As$ were available.

We ascribe the observation of each of these peaks to resonant excitation from peaks present in the electronic density of states between the hh and lh energies and arising from strong mixing between the one-particle hh band states and the lh electron plus one of each of the different phonons. It is important to recognize that this is an inherent consequence of quantum-mechanical mixing of nearly degenerate states and does not require the presence of thermally excited phonons. Such a situation has been discussed[1] theoretically some years ago and, in fact, resonant mixing and modification of density of states was predicted. It is also to be recognized that the differences in the peak positions in Fig. 3 correspond to differences in the phonon energies. As such, a contribution from certain second-order Raman processes, which otherwise would have a negligible cross section, could be present in the peaks because of enhancement of such cross sections near the double-resonance conditions.

In summary, we have reported here (i) the first observation of resonant mixing of electron and phonon states, (ii) the first *simultaneous* observation of all four possible types of vibrational modes (i.e., confined in the well, confined in the barrier layers, unconfined, and interface) of a QW made of components with overlapping phonon branches, and (iii) the remarkable enhancement of optical cross sections under double-resonance–induced mixing of states so that even a single quantum well is sufficient to provide strong Raman signals from several phonons in the secondary-emission spectra.

TABLE I. Assignment of PLE peaks of Fig. 3.

PEAK NUMBER	ENERGY (eV)	DIFFERENCE From 9 ML LH (1.7515eV) (meV)	PEAK NUMBER	ENERGY (eV)	DIFFERENCE From 8 ML LH (1.7674eV) (meV)	ASSIGNMENT
			14	1.7215	45.9	LO_m-AlAs-like
			15	1.7228	44.6	LO_m-AlAs-like
1	1.7076	43.9	16	1.7237	43.7	Ω (LO_m)/ Ω (TO_m)-AlAs-like
2	1.7086	42.9	17	1.7245	42.9	Ω (LO_m)/ Ω (TO_m)-AlAs-like
3	1.7094	42.1	18	1.7253	42.1	TO_m-AlAs-like
4	1.7109	40.6	19	1.7271	40.3	TO_m-AlAs-like
5	1.7121	39.4				
6	1.7128	38.7	20	1.7287	38.7	
7	1.7136	37.6	21	1.7299	37.5	
8	1.7152	36.3	22	1.7314	36.0	LO_2-GaAs
9	1.7162	35.3	23	1.7323	35.1	LO-GaAs or Interface mode
10	1.7172	34.3	24	1.7333	34.1	Ω (LO_m)-GaAs/Ω (LO_m)-GaAs-like
11	1.7182	33.3	25	1.7342	33.2	Ω (LO_m)/ Ω (TO_m)-GaAs/ Ω (LO_m)-GaAs-like
12	1.7195	32.0	26	1.7353	32.1	Ω (TO_m)-GaAs/ Ω (TO_m)/ Ω (LO_m)-GaAs-like
13	1.7206	30.9				Ω (TO_m)-GaAs/ Ω (TO_m)/ (LO_m)-GaAs-like
			27	1.7372	30.2	Ω (TO_m)-GaAs/ Ω (TO_m)-GaAs-like

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