Particle localization and phonon sidebands in GaAs/$Al_xGa_{1-x}As$ multiple quantum wells

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We use time-resolved spectroscopy of the LO-phonon sidebands to study the in-plane localization of carriers and excitons in undoped GaAs/$Al_xGa_{1-x}As$ multiple quantum wells at low temperatures. We find three distinct populations contributing to the radiative recombination (excluding shallow background impurities): (a) weakly localized excitons, their localization dimension being larger than the exciton Bohr radius, (b) tightly localized excitons, (c) separately localized electrons and holes that decay radiatively on a microsecond time scale.

The radiative recombination in undoped multiple quantum wells (MQW's) is due to excitons confined in the wells. In most commonly studied MQW's, the luminescence band is Stokes shifted with respect to its excitation spectrum. This is generally understood to be due to excitons localized in the plane of the QW, either by interface roughness [e.g., in GaAs/$Al_{1-x}As$ MQW's (Ref. 1)] or by alloy concentration fluctuations [e.g., in $In_{1-x}Ga_xAs$/InP MQW's (Ref. 2)]. Localization effects have mainly been studied by energy transfer between localized exciton sites[3,4] or by exciton dephasing processes.[5] It has been shown[6,7] that the exciton radiative recombination rate in QW's is enhanced by the fact that the exciton in-plane motion is coherent over an area of dimension $A_{\rm coh} < \lambda^2$ (where λ is the wavelength of the exciton radiation). In this paper we examine the effects of in-plane localization on the LO-phonon sidebands (PSB's) of the luminescence of GaAs/$Al_xGa_{1-x}As$ MQW's, by using the method of time-resolved spectroscopy.

PSB's have long been related to the degree of e or h localization. Hopfield[8] has shown that in a direct gap semiconductor, an optical transition involving particles with a well-defined $\mathbf{k}$ has a vanishing small LO-PSB intensity relative to that of its no-phonon (NP) band. This is a direct result of momentum conservation. Localized particles, on the other hand, relax the $\mathbf{k}$ conservation rule and, therefore, are expected to show stronger PSB's. These PSB's are sharp, since the Fröhlich interaction is strong only for $k < 10^6$ cm^{-1}, a small fraction of the Brillouin zone in which the LO-phonon dispersion curve is flat.

We study the LO-PSB's photoluminescence (PL) and their excitation spectra at different time intervals after excitation by a laser pulse. We show that the results can be interpreted in terms of the radiative recombination of three different types of localized e-h pairs: (a) weakly localized excitons which do not show any LO-PSB's; (b) tightly localized excitons; and (c) electrons and holes which are separately localized at different sites in the QW (much like the case of donor-acceptor pairs in bulk semiconductors). The last two groups of localized e-h pairs show strong LO-PSB's. The temperature dependence of the 1LO-PSB intensity, which is typical of a localized particle with a small binding energy, and the nonexponential decay curve of that PSB, lends further support to the interpretation in terms of separate localization of electrons and holes.

The MQW's studied are GaAs/$Al_xGa_{1-x}As$ samples with $x=0.3$ or 1 and with well widths in the range of 40–70 Å. They were selectively excited by 6-psec dye laser pulses and the PL was measured with a temporal resolution of 350 ps. A time correlation technique was used for the time-resolved measurements: a specific delay time (t) was set and the spectrum was continuously recorded with a temporal window of 350 psec. The samples were either immersed in liquid He or in cold He vapor.

Figure 1 shows the time-resolved PL spectrum of a GaAs/AlAs MQW consisting of 100 wells, each of 70 Å width separated by 200-Å barriers. The PL was excited at 1.632 eV. Similar spectra were observed for all the other MQW's under study. The most intense feature [designated (a)] is the NP band of the (e1:hh1)1S exciton. The spectrum shown in Fig. 1(b) was measured at $t=300$ psec. This is the delay time at which this PL is maximal. LO_1 and LO_2 denote the PSB's associated with GaAs-like and AlAs-like LO phonons, respectively. The phonon energies were measured by Raman scattering. Thus it was found that $\hbar\omega_2$ corresponds exactly to the AlAs-like LO phonon of the $Al_xGa_{1-x}As$ MQW barrier material. Figure 1(c) shows the spectrum measured at $t=3.8$ nsec, a much longer delay time than the excitonic radiative decay time measured for this MQW (<400 psec). The 1LO-PSB now appears blueshifted by 2 meV. The same shift is observed in the higher-order PSB's. From this temporal behavior we conclude that the PSB's consist of two components. (1) A fast one, which follows the (e1:hh1) NP exciton luminescence decay; the $1LO_1$ fast

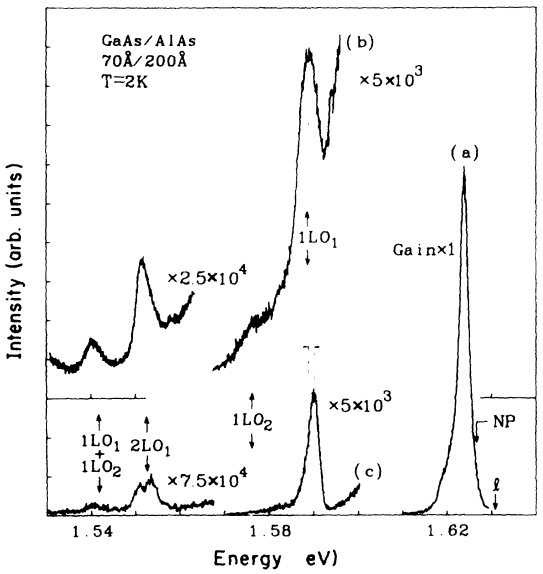

FIG. 1. Photoluminescence spectra excited at 1.632 eV. (a) The no-phonon band (observed either under cw or with psec pulse excitation). (b) Time-resolved spectrum monitored 300 psec after the laser pulse. (c) Same as in (b) but monitored 3.8 nsec after the laser pulse.

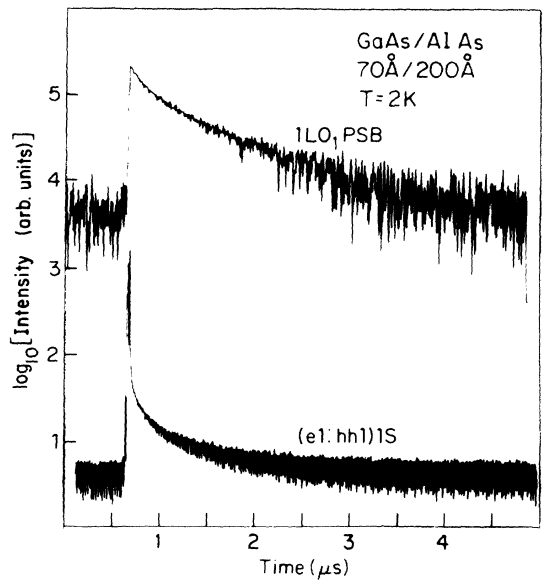

FIG 2. Photoluminescence decay curves of the no-phonon exciton band (bottom) and of the 1LO phonon sideband (top). The excitation energy was 1.631 eV. The top spectrum was arbitrarily shifted upwards. The overall time resolution of the system is 350 psec.

component is separated by $\hbar\omega_1 = 36.5$ meV from the NP exciton luminescence peak. (2) A slow component appearing at a higher energy; its corresponding NP transition energy is *above* the peak of the excitonic luminescence [its position is indicated by NP in Fig. 1(a)]. The decay curve of the $1LO_1$ PSB is shown in Fig. 2 (top) and it is compared to that of the NP exciton band [Fig. 2 (bottom)].

The PL excitation spectrum (PLE) of the NP exciton band (monitored at 1.621 eV) is shown in Fig. 3. It was obtained with cw excitation, but an identical spectrum is obtained with pulsed excitation and measured at a delay time of 300 psec. Such a spectrum has been reported for many similar MQW's. It contains the $(e1;hh1)1S$ and $(e1:lh1)1S$ bands, centered at 1.625 and 1.654 eV, respectively. In addition there are the corresponding higher nS excitonic features, with thresholds at 1.637 and 1.668 eV. Figures 3(b) and 3(c) show the PLE spectra of the $1LO_1$-PSB, monitored at 1.589 eV, and measured with cw or pulse excitation (with a 4-nsec delay), respectively. Note that the PSB-PLE spectrum is quite distinct from that of the $(e1:hh1)1S$ NP band: the lowest energy band of the former is blueshifted by ~ 3 meV with respect to the latter, the $(e1:1lh1)$ bands are virtually missing, and the band whose peak is at 1.636 eV does not appear in the exciton PLE spectrum.

The 1LO-PSB integrated intensity I_{1LO_1}, observed under cw excitation, decreases with increasing temperature. It shows a well-defined activation energy of $\Delta E = 5.0 \pm 0.1$ meV. The dependence of I_{1LO_1} on the exciting laser intensity I_L was measured at various delays after the laser pulse. It follows $I_{LO_1} \propto I_L^{0.45\pm0.02}$ for all delays, and does not show any saturation. On the other hand, the intensity of the NP exciton band has a linear dependence on I_L, and is virtually temperature independent over the range of 2–30 K (above which the PSB's vanish). These observations clearly show that the slow decaying component of the PSB is not related to the NP exciton band.

An indication of the origin of the PSB's can be gained by analyzing their intensity ratios. The relative PL intensity of the series of PSB's in which n LO phonons are

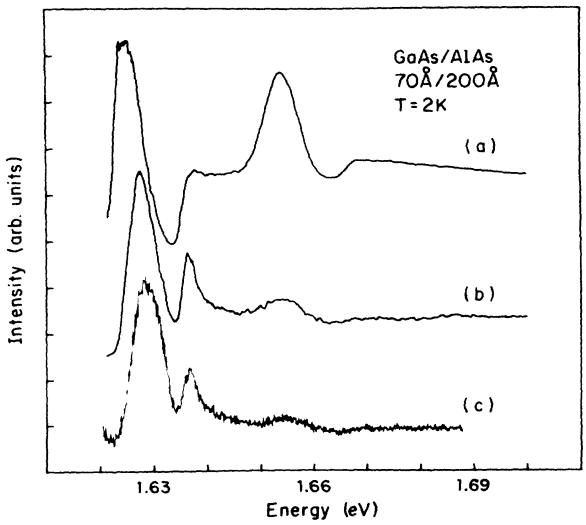

FIG. 3. Photoluminescence excitation spectra monitored at the following: (a) the no-phonon exciton band (1.6214 eV) under cw excitation. An identical spectrum is obtained under psec pulsed excitation and measured at $t = 300$ psec. (b) The peak of the 1LO-PSB (1.589 eV) and under cw excitation. (c) Same as (b) but with psec pulsed excitation and measured at $t = 4$ nsec.

emitted is given by

$$I_{n\mathrm{LO}}=\frac{S^n}{n!}\ , \tag{1}$$

where S is the Huang-Rhys (HR) factor which is a measure of the coupling strength of the radiative transition to the LO-phonon polarization field, and $n=0,1,2,\ldots$ ($I_0\equiv I_{\mathrm{NP}}$). S is given by[8,9]

$$S=\frac{1}{2\hbar\omega_{\mathrm{LO}}^3}\sum_q |D_q|^2\ , \tag{2}$$

where D_q is proportional to the qth Fourier-transform coefficient of the particle charge distribution, which is related to the degree of its localization. Thus, localized excitons show strong PSB's because their wave function contains large **q** components which allow them to couple to a wide range of LO phonons. In studying the relative intensities of the PSB's it is imperative to observe at least two successive PSB's in order to determine S. Using only $I_{1\mathrm{LO}}/I_{\mathrm{NP}}$ can lead to erroneous conclusions, as the NP band may consist of several radiation sources, each with its distinct coupling to phonons. Thus, using Eq. (1) and the measured intensity ratio $I_{2\mathrm{LO}_1}/I_{1\mathrm{LO}_1}$, we have calculated the HR factors for the fast and slow PSB's. They are $S_f=0.4$ and $S_s=0.1$.

A. Fast PSB: Exciton contribution

We might be tempted to link this PSB to the ($e1$:hh1)$1S$ exciton as they have similar decay rates. From the measured HR factor, and using Eq. (1), the expected intensity of the NP line should be $I_{\mathrm{NP}}/I_{1\mathrm{LO}_1}\cong 2.5$. However, the observed ratio is much greater: 10^4, for the laser power used in Fig. 1. Clearly, most of the ($e1$:hh1)$1S$ excitons do not contribute to the observed fast PSB's. From the measured value of $I_{\mathrm{NP}}/I_{1\mathrm{LO}_1}\geq 10^{-4}$ we obtain an upper limit for the HR factor for the majority of the ($e1$:hh1)$1S$ excitons: $S_{\mathrm{ex}}\leq 10^{-4}$. We now use Takagahara's[3,9,10] quasi-two-dimensional approximation adjusted for the exciton–LO-phonon Fröhlich interaction, an exciton Bohr radius of 100 Å, and a Gaussian wave function for the localized, in-plane motion of the whole exciton. The observed HR factor then corresponds to a calculated localization radius of $\xi_{\mathrm{ex}}\geq 200$ Å.

We are now left with only a very small subset of all exciton states that give rise to the fast components of the PSB's. We then find that the same approximation quoted above cannot yield such a large value of S_f ($=0.4$) with the material parameters appropriate to the studied MQW's. Therefore, we conclude that this is a subset of excitons which are tightly localized on dimensions much smaller than the well width.

The nature of the potential which determines the in-plane localization is related to the QW interface roughness. This issue has been intensely debated in various recent studies, since the description of this roughness in early spectroscopic papers[11] has been at variance with that of quantitative microscopic[12] and recent spectroscopic measurements.[13] In spite of their relevance, an exact knowledge of the interface structure is unnecessary for our present study. The PSB intensities depend only on the exciton localization extent [Eqs. (1) and (2)]. It should also be emphasized that since the excitons average out the potential fluctuations over an area of the order of the in-plane Bohr radius, the localization length scale does not correlate with that of the interface roughness.[14]

B. Slow PSB: Localized e-h pairs

The low-temperature radiative recombination of excitons in GaAs/$Al_xGa_{1-x}As$ QW's has a lifetime in the sub-nsec range. Therefore, the slow components of the PSB's cannot be due to exciton recombination. We propose that this slow PSB is due to e-h pairs which are spatially separated. Then, the radiative decay rate will depend on their separation. If the e-h localizing centers are randomly distributed, then the decay curve will show a nonexponential behavior, as the one shown in the upper curve of Fig. 2. The PLE spectrum of the slow PSB [Figs. 3(b) and 3(c)] shows that the separately localized e and h are excited in a relatively narrow band (peak energy at 1.628 eV). This band lies about 10 meV below the ($e1$:hh1) band gap, and this value is the total e and h binding energy. The small activation energy of the slow PSB luminescence shows that both particles have binding energies of less than 10 meV. The band whose peak is at 1.638 eV [in the PLE spectra of Figs. 3(b) and 3(c)], drops on its high-energy part as $[A=(E-1.638)]^{-1}$. This dependence fits the simple model of an e scattering from a neutral shallow center.

The model proposed here for the origin of the slow PSB's is very similar to that of donor-acceptor pair spectra observed in bulk materials. However, donors and acceptors must be ruled out as e and h binding centers because of their too large binding energies (8–14 meV for donors and more than 20 meV for acceptors[15]). Single-monolayer fluctuations in the well thickness can also be ruled out, as the hole binding energy for the monolayer step is of the order of 0.5 meV.[1] Although the e and h binding energies are small, the localizing centers must have a small areal size in order to yield a HR factor of $S_s=0.1$. We now use a three-dimensional Gaussian charge distribution and Hopfield's model,[8] and obtain a localization size of $\xi_s\sim 20$ Å for either e or h. A possible small-size center with a shallow bound state might be a deep potential fluctuation similar to the known isoelctronic traps in bulk semiconductors.[16] Potential fluctuations in crystalline, bulk alloys do not localize an e or an h separately (only an exciton). Thus, we propose that such potential fluctuations are unique to QW's. Note that this analysis of the PSB intensity accounts only for the extent of localization of the e and h. It does not provide any information either on their identification or on their spatial separation distribution.

The slow PSB is distinguished by a sublinear dependence on I_L (approximately $\propto\sqrt{I_L}$), whereas the NP exciton band is linearly dependent upon I_L. This peculiar feature can now readily be accounted for. Assuming that the photogenerated e-h pairs either produce excitons or are separately trapped by their localizing centers, the rate equation for free electrons (or holes) is

$$dn_e/dt = g - bn_e n_h - \beta n_e \ , \tag{3}$$

where g is the photogeneration rate, n_e (n_h) is the areal density of a free electrons (holes), $bn_e n_h$ is the rate at which free electrons and holes form excitons, and βn_e is the rate at which free electrons are trapped and become localized (we assume that the density of trapped electrons is much smaller than the concentration of localizing centers). When the process of exciton formation is much faster than the trapping process, the density of the free electrons (or holes) will be proportional to $\sqrt{g}$ (provided that the pulse duration $t_p > 2\sqrt{bg}$). The rate equation for the density of localized electrons or holes, N, is

$$dN/dt = \beta n_e - N/\tau \ . \tag{4}$$

τ^{-1} is the localized e-h recombination rate. (For the present discussion we disregard the nonexponential decay and assume a single value for τ.) In steady state, we readily find $N_{ss} = \beta\tau\sqrt{g/b}$. In the pulsed experiment, taking $n_e = \sqrt{g/b}$ at the end of the exciting pulse, we find for $t \gg t_p, N(t) \cong \beta\tau\sqrt{g/b}\, e^{-t/\tau}$. In both cases, then, the PL intensity due to the recombination of the separately localized e-h pairs is proportional to $\sqrt{g}$, namely, to $\sqrt{I_L}$.

In conclusion, we demonstrated the use of time-resolved spectroscopy in order to separate the slow and fast components of the LO-PSB's in GaAs/$Al_xGa_{1-x}As$ MQW's. We interpret our results in terms of various types of e-h pair localization in the plane of the QW. We find that nearly all excitons are localized on large-area centers and therefore couple very weakly to LO phonons. In addition we showed that there are two types of centers: one that tightly localizes excitons and another that separately localizes electrons and holes.

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