Quantum-confined excitonic states at high-quality interfaces in GaAs(n type)/$Al_xGa_{1-x}As$(p type) double heterostructures

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We report 1.8-K H-band photoluminescence (PL) from abrupt, high-quality GaAs(n type)/$Al_{0.3}Ga_{0.7}As$(p type) double heterostructures prepared by metalorganic chemical vapor deposition, versus GaAs thickness (0.1–2.0 μm), to study dynamics of carriers quantum confined near heterointerfaces. Our time decays yield bimolecular kinetics, spectral peak shifts in time, and lifetimes (across the H-band PL) varying from nanoseconds to >50 μs. Numerical modeling yields a two-dimensional-exciton description—with quantitative predictions for exciton binding energies, transition energies, charge densities, oscillator strengths, and lifetimes—which, upon radiative decay, give rise to the observed H-band dynamics. We thus explain the observed kinetics and prove that H-band PL arises not from impurities, but from *intrinsic bound excitons* involving both heterointerfaces. Further, we find that such highly polarizable, spatially indirect, electron-hole systems may only be adequately understood in wide (non-quantum-well) structures.

Molecular-beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD) have recently produced high-quality semiconductor heterostructures with virtually atomically abrupt heterointerfaces.[1–3] Such microscopically, and hopefully electronically, superior structures may thus provide for careful study of *intrinsic* heterointerface properties.[4–7] Among phenomena possibly traceable to such interfaces is a photoluminescence (PL) band found in GaAs/$Al_xGa_{1-x}As$ heterostructures, and referred to as the H band.[8] While some suggest that this PL may be due to intrinsic states within the band bending near the heterointerface,[9–11] others insist that these recombination processes arise from carriers bound to defects at, or near, the heterointerfaces.[12–15]

Here we report extensive PL time-decay measurements aimed at testing these models, while elucidating the carrier dynamics responsible for H-band emission. Previous studies of H-band dynamics in liquid-phase epitaxy heterostructures or MBE quantum wells have proven largely inconclusive, simply showing lifetimes that, depending on conditions, may range from $\sim$1 to 100 ns.[16,17] In contrast, we show here that these earlier reported kinetics were most probably dominated by both *unrelated interfacial recombination,* and influence of the *companion* heterointerface of the double heterostructure—and, therefore, the truly intrinsic H-band dynamics remained elusive. Further, through lifetime measurements in virtually "ideal" structures and extensive theoretical modeling we have uncovered the true carrier dynamics leading to H-band emission. In so doing, we find H-band lifetimes more than 500 times longer than those reported previously.

Our samples were MOCVD-prepared GaAs/$Al_{0.3}Ga_{0.7}As$ double heterostructures, with GaAs layer thicknesses ranging from 0.1 to 2.0 μm. All $Al_{0.3}Ga_{0.7}As$ layers were 0.5 μm thick and unintentionally p-type doped at $\sim 3\times10^{16}$ cm^{-3}, while the GaAs layers were undoped, n type at $\sim 1\times10^{15}$ cm^{-3}. To ensure abrupt interfaces, all growths were interrupted at each heterointerface. Photoluminescence was excited by a synchronously pumped (Ar^+), cavity-dumped 4-dicyanomethylene-2-methyl-6-(p-dimethylaminostyryl)-4H-pyran dye laser with a 1-ps pulse width. Emission was dispersed by a 0.85-m double spectrometer, and detected by a RCA C31034A photomultiplier using the time-correlated single-photon-counting technique (0.5-ns response).

The low-temperature (1.8 K) time-integrated PL from all samples, regardless of GaAs thickness, yielded the same basic spectral structure, dominated by the near-gap free-exciton (F,X) emission of Fig. 1, thus reflecting the exceedingly high and uniform quality of our heterostructures. Secondarily, relatively weak neutral-donor-bound exciton (D^0,X) and band-to-carbon-acceptor (BA_C) luminescence were also evident. In addition, however, each sample also showed emission lying energetically between the edge excitons and the band-to-acceptor emission. Such emission, first identified as the H band by Yuan *et al.*,[8] is the focus of this study.

Prior to H-band study, all samples were assessed according to their "interface quality," as quantified by the interface recombination velocity S. Appropriately, this quantity reflects the nonradiative decay of carriers at each heterointerface as this spurious recombination pathway affects, and is detected in, PL efficiencies and/or lifetimes.[18–20] Because the H band originates from carriers near heterointerfaces, serious nonradiative interfacial decay might be expected to significantly influence, if not dominate, carrier dynamics. We have thus determined S in our samples through room-temperature lifetime measurements versus GaAs layer thickness,[18] with a result of $S\simeq 40$ cm/s—a value among the lowest yet reported for any GaAs/$Al_xGa_{1-x}As$ structure. These virtually "ideal" heterointerfaces should thus allow photoexcited carriers to reside nearby, for long periods, largely uninfluenced by spurious nonradiative decay, thus allowing for detailed study of other possible intrinsic interfacial recombination.

To prove our Fig. 1 emissions were indeed those of the H band, experiments parallel to those of Yuan *et al.*[8] were performed, wherein the top $Al_{0.3}Ga_{0.7}As$ was chem-

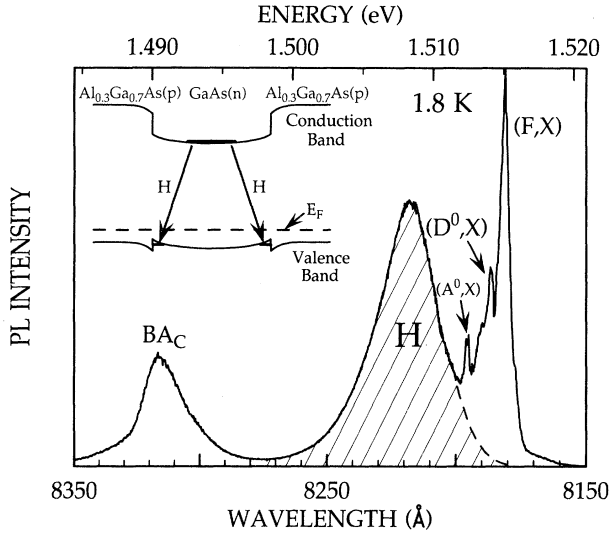

FIG. 1. Time-integrated PL (1.8 K) from a GaAs/$Al_{0.3}Ga_{0.7}As$ structure; free excitons (F,X) dominate. Inset shows double-heterostructure band structure, with band bending responsible for intrinsic H band.

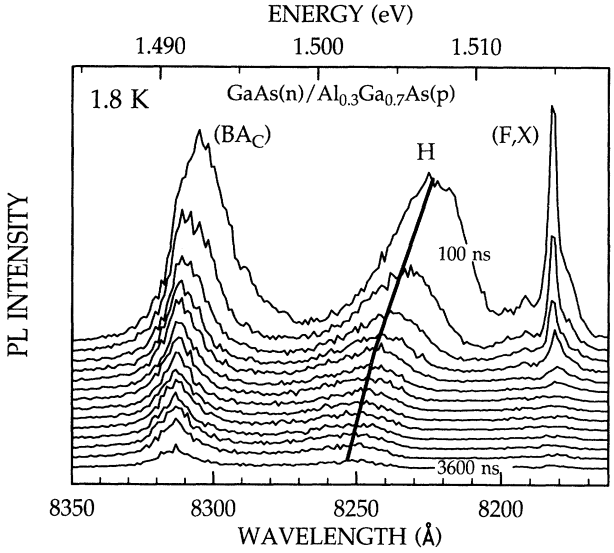

FIG. 2. Time-resolved PL (1.8 K) from a GaAs/$Al_{0.3}Ga_{0.7}As$ double heterostructure with a 0.2-μm GaAs layer. Spectra (top to bottom) represent 250-ns time intervals after excitation.

ically removed, leaving a bare GaAs surface. H-band PL, previously strong in all samples, became fully quenched. Thus the bare GaAs surface served to effectively "drain" all photoexcited carriers from the GaAs layer through nonradiative surface recombination,[18] thereby eliminating carriers before they might recombine as the H band. In a related experiment, PL was also measured versus excitation power, with the result that peak H-band emission shifted to higher energies as the log of the power density, as initially reported.[8,9] Further, versus increasing temperature, H-band PL intensity was also found to drop precipitously and vanish above 15 K, again as found in Ref. 9, and here with an extremely small activation energy of 0.75 meV. The H band thus confirmed, we proceeded with dynamics.

From time-resolved PL spectra we find, as in Fig. 2, that the H band is not spectrally fixed, but instead progressively shifts to lower energy with increasing time after pulsed excitation, by as much as 25 meV. To quantify such dynamics 1.8-K lifetimes were measured at various energies within the H band for all structures, with a typical result being shown in Fig. 3(a) and combined results being shown in Fig. 3(b). All decays were nonexponential, but readily fit to a *bimolecular-type* decay, with results for GaAs thicknesses of 0.5, 1.0, and 2.0 μm being virtually identical. Lifetimes thus obtained, characteristic of the exponential tail of the decays, ranged from several nanoseconds to more than 50 μs. (Such long lifetimes are indeed only attainable in samples with truly superior interfaces.)

Results for thinner GaAs layers (<0.5 μm) differ markedly, however. Here we find, for example, lifetimes for 0.2- and 0.1-μm GaAs layer thicknesses reach only (at low emission energies) to 700 and 380 ns, respectively. (High-energy emission decays remain identical, however, for all samples.) Thus H-band lifetimes saturate at decreasing values, while the energy at which this saturation occurs increases, as the GaAs layer thickness decreases. This is not, however, a consequence of differing amounts of interfacial recombination among the samples, since our initial room-temperature lifetime measurements in all samples (yielding the interface recombination velocities of $S \simeq 40$ cm/s) were consistent. Also, the fact that different structures with virtually identical interfaces (as

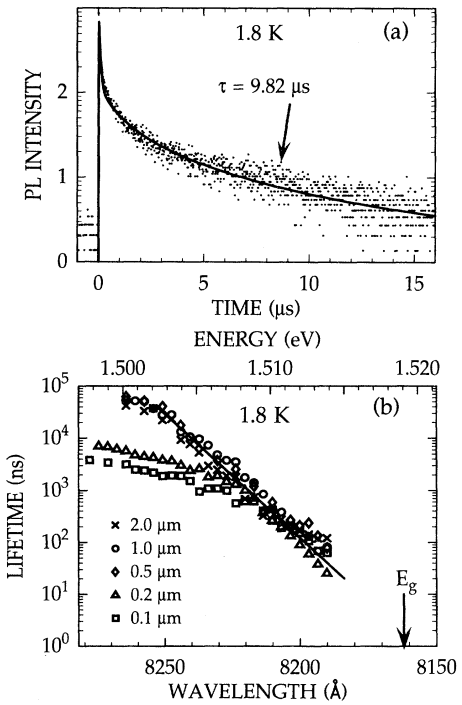

FIG. 3. (a) Typical PL decay (1.8 K) at 1.503 eV from a 0.5-μm structure with bimolecular fit. (b) Lifetimes at energies across the H-band profile.

determined by S) show different emission dynamics gives further support as to the origin of this emission being intrinsic and not impurity induced.

We have next modeled the H band to help clarify the role of the heterointerfaces in the dynamics. Yuan *et al.*[8] interpreted the H band in their n-n (n-p) double heterostructures as the recombination of electrons (holes) confined in the potential notch of the conduction (valence) band at the heterointerface, which is formed by the band bending there, with free holes (electrons). While this indeed qualitatively explains the observed spectral position of the H-band emission, it does not explain the above noted extreme temperature-dependent (~ 0.75 meV) H-band quenching. Thus our H-band calculation includes, as does Balslev's[21] the static Coulomb interaction between electrons and holes, while the dynamics are accounted for by parametrizing heterointerface band bending. The H band—in our n-p heterostructures—thus becomes the radiative decay of a *quasi-two-dimensional (2D) exciton,* formed by the Coulomb interaction between a hole bound intrinsically at the heterointerface and a conduction electron.

We begin by determining the band structure of the entire double heterostructure. This is done by solving, self-consistently, Poisson's equation, yielding band bending at the heterointerfaces resulting from the differences in properties of the GaAs(n type) and $Al_{0.3}Ga_{0.7}As$(p type) layers, in the absence of photoexcited carriers. Because additional photogenerated carriers may screen the heterointerface field, thereby reducing the band bending there, photoexcitation of carriers and their subsequent radiative and nonradiative decay will dynamically alter the heterointerface band bending. Dynamics are thus accounted for by parametrizing the valence and conduction bands at each heterointerface, respectively, as

$$\phi_v(z)=F_i d_i a_B e^{-(|z|/d_i a_B)}, \tag{1}$$

$$\phi_c(z)=\phi_v(z)+E_g, \tag{2}$$

where $i=1,2$ corresponds to the GaAs(n type) and $Al_{0.3}Ga_{0.7}As$(p type) layers, respectively. Here, F_i represents the maximum heterointerface field, and d_i is the screening length measured in units of the 3D exciton bohr radius a_B. Thus the equivalent of increasing time after pulsed excitation corresponds, in the calculation, to increasing d_i.

Since we photoexcited below the $Al_{0.3}Ga_{0.7}As$ band gap and the photocarriers reside in the GaAs, we have parametrized d_1 only, leaving the remaining constants fixed and equal to the values obtained by fitting Eqs. (1) and (2) to the self-consistent solution of Poisson's equation (in the absence of additional photogenerated carriers), denoted by superscript eq. The case $d_1 \rightarrow d_1^{\rm eq}$ corresponds to no additional photogenerated carriers, or equivalently to the long-time limit after photoexcitation, as the number of these additional carriers becomes small due to both radiative and nonradiative decay. The companion case $d_1 \rightarrow 0$ corresponds to a large number of additional photogenerated carriers, or equivalently to the short-time limit immediately after photoexcitation.

Next we solved numerically Schrödinger's equation, wherein, for simplicity, we also restricted d_1 to $\gtrsim 1$. By assuming Schrödinger's equation and the excitonic wave function are separable into electron and hole parts the respective ground-state envelope wave functions (which comprise the exciton), and their corresponding energies, may then be calculated. From here the H-band emission energies—which are almost entirely determined by the hole confinement energy—and the exciton binding energy may be determined. In the end, the theoretical results agree quantitatively with all of our data.[22] The calculated binding energy thusly obtained fully explains both the temperature dependence (~ 0.75 meV) of the integrated H-band PL and the maximum energy shift versus time of the PL, as measured from the GaAs band gap.

Further, the model also shows that for $d_1 \simeq 1$, both species of carriers are uniformly distributed throughout the GaAs layer, but as d_1 increases the holes immediately become bound at *both* heterointerfaces. In this early-time regime the electrons then follow the holes to the interface as a result of the Coulomb interaction, thus forming a compact interface exciton. In the opposite long-time regime, as $d_1 \rightarrow d_1^{\rm eq}$, the conduction-band potential changes force electrons to the center of the GaAs layer, hence forming a very extended, highly polarized 2D exciton *shared by both interfaces.*

With these calculated envelope wave functions the spatial overlap of the electron and hole may then be readily calculated. Since the oscillator strength of the transition f is directly proportional to the square of the wavefunction overlap, and the lifetime of the transition is related to the oscillator strength as $\tau^{-1} \sim f$, the relative change in oscillator strength, and hence lifetime, may also be calculated. Figure 4 shows these results for the sample with a 0.2-μm GaAs layer, together with the corresponding experimental results from Fig. 3(b), where good agreement is found. The model calculation thus accurately predicts the saturation behavior for the structures with thin GaAs layers. In contrast, calculations for thicker GaAs structures do not show this saturation—also in agreement with experiment. Further, it is found, from the calculation, that the saturation in lifetime occurs at higher energies for thinner structures. These facts are due to the finite size of the GaAs layer, or, equivalently, to the effects of the *companion heterointerface.* The carriers thus reach their maximum separation, equal to half of the GaAs layer thickness, at progressively smaller values of d_1—and higher transition energies—as the GaAs thickness decreases. This causes the spatial overlap integral to become approximately constant, thus yielding the lifetime saturation. Moreover, the calculation shows that the transition is "indirect" in real space, which qualitatively explains the observed long (nonexponential) lifetimes.

In comparison to our H-band data, Yuan, Merz, and Vawter[16] found an H-band lifetime at 8220 Å of approximately 1.3 ns. Zhao *et al.*[17] have also measured the lifetime versus emission energy in a GaAs/Al-Ga-As double heterostructure with a 500-Å GaAs layer thickness; their lifetimes also increased with decreasing energy, but were shorter than those reported here by a factor of 500. We have found that samples with poorer interfaces (as

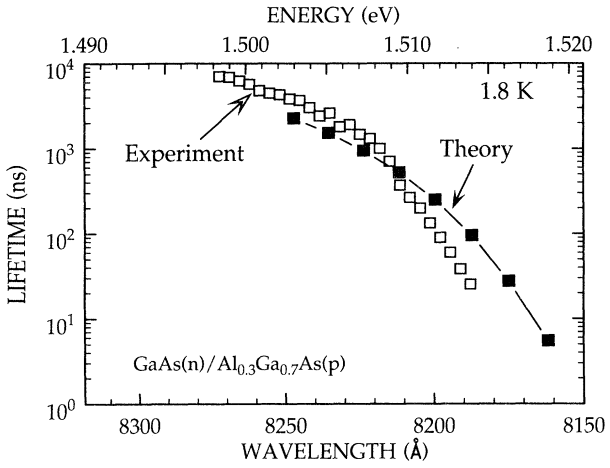

FIG. 4. Model calculation and experimental results for the double heterostructure with a 0.2-μm GaAs layer.

quantified by S) yield shorter lifetimes than those reported here, while neither of these previous studies[16,17] included any form of interface characterization. It is thus clear that earlier studies were hampered, if not perhaps flawed, by nonradiative interface recombination and the saturation effects (associated with the finite GaAs layer thickness) noted above. Thus we believe our results to be the first to definitively measure carrier dynamics responsible for the H band, unimpeded by competing interfacial decays.

In summary, we have made extensive optical measurements of the H-band emission dynamics in GaAs(n type)/$Al_{0.3}Ga_{0.7}As$(p type) double heterostructures, and observed differences in the decay kinetics which depend critically on the GaAs layer thickness. Our accompanying model calculation showed the importance of the double heterointerface to the dynamics of heterointerface-confined excitons. We have shown conclusively that meaningful studies of the dynamics of carriers confined at a single GaAs/$Al_xGa_{1-x}As$ heterointerface—unaffected by other heterointerfaces and the nonradiative decay there—may only be done in double heterostructures with wide GaAs layers (>1 μm) and in structures with very low interfacial recombination. Results here are thus unencumbered by these complicating factors, and represent the dynamics of carriers confined at a single heterointerface which give rise to the H band. Our theoretical results are also in excellent agreement with data, thus further confirming observation of truly *intrinsic* H-band dynamics.

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[22]Assumptions made were the following: (i) We assume the Coulomb potential between carriers affects only electrons (valid only when the hole confinement energy is greater than the quasi-2D exciton binding energy) which limits our model to $d_1 \gtrsim 1$. (ii) We calculate only ground-state envelope wave functions, but find excited-state energy spacings to be significantly larger than kT (at temperature of 1.8 K), thus justifying this simplification.