Alloy Clustering in $Al_xGa_{1-x}As$-GaAs Quantum-Well Heterostructures

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Data on spontaneous and stimulated emission, in the photon-energy range $E_g + 5\hbar\omega_{LO} \gtrsim \hbar\omega \gtrsim E_g$, are presented on $Al_xGa_{1-x}As$-GaAs quantum-well heterostructures with $Al_xGa_{1-x}As$ ($x \sim 0.4$–0.5) coupling barriers of size $L_B \sim 40$–70 Å and GaAs wells of size $L_z \sim 30$–40 Å. For $L_z, L_B \lesssim 50$ Å, Al-Ga disorder (clustering) in the alloy barriers is consistent with the observed spectral broadening and downward energy shift of the confined-particle transitions. A simple substitution of binary (AlAs) for ternary (AlGaAs) barriers eliminates alloy clustering and its effects, and makes unambiguous the identification of clustering in alloy barriers.

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In contrast to earlier work,[1,2] stimulated emission has been observed recently at energy $5\hbar\omega_{LO}$ to $6\hbar\omega_{LO}$ below the confined-particle transitions of $Al_xGa_{1-x}As$-GaAs multiple–quantum-well heterostructures (QWH) with narrow wells ($L_z \lesssim 50$ Å) and narrow alloy barriers ($L_B \lesssim 50$ Å). An example is illustrated in Fig. 1, *a*. The lowest energies are a little above that of the GaAs energy gap, E_g. With increased pump power, stimulated emission is transferred to the neighborhood of the confined-particle states [Fig. 1, *b*]. In this paper, we show that because of disorder and clustering in the narrow ternary barriers (which can be removed by the use of binary barriers, AlAs), a continuum of states may exist in the QWH, the lowest with energies extending down to the band edge of pure GaAs. It is suggested that real phonon transitions take the electrons down to these levels, from which stimulated emission then occurs. With higher power, emission from the confined-particle states is enhanced and electrons do not have time to cascade to the lower levels.

The $Al_xGa_{1-x}As$-GaAs quantum-well heterostructures of interest here are grown by metalorganic chemical vapor deposition.[3,4] Gas flow rates and layer growth times are electronically controlled to ensure layer reproducibility. Growth rates are controllable in the range 2–50 Å/sec for GaAs and in the range 2.5–100 Å/sec for AlGaAs ($x \sim 0.40$), which makes it practical to grow layers as thin as 10 Å. The first layer grown on the {100} GaAs substrate is a GaAs buffer layer to provide a good crystallographic surface for succeeding layers. The next layer is a relatively thick (~1 μm) $Al_xGa_{1-x}As$ ($x \sim 0.50$) confining layer. This is followed by the QWH active region, which consists of a series of GaAs quantum wells and $Al_xGa_{1-x}As$ (or AlAs) barrier layers. The final layer is a second relatively thick (~0.3 μm) $Al_xGa_{1-x}As$ ($x \sim 0.50$) confining layer. All layers are undoped ($n_d - n_a \lesssim 10^{15}/cm^3$). Samples for photoluminescence experiments are prepared by polishing and selectively etching off[5] the GaAs from the substrate side. Cleaved portions (20–100×100–300 μm^2) of the remaining thin wafer (~1.3 μm thick) are imbedded for heat sinking into In under a sapphire window (77-K experiments)[6] or into annealed Cu under a diamond window (300-K experiments),[7] and are photoexcited with an Ar^+ (5145 Å) or a dye-tunable (6540-Å)

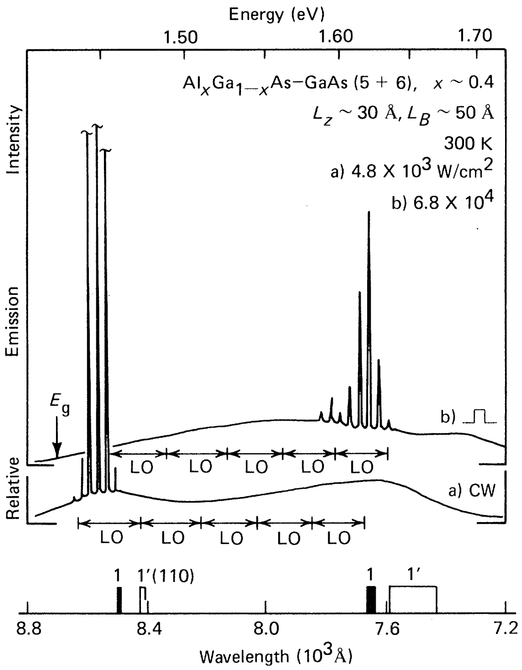

FIG. 1. Laser spectra (300 K) of a photopumped QWH grown by metalorganic chemical vapor deposition with an active region consisting of six ~ 30 Å GaAs wells and five ~ 50 Å $Al_xGa_{1-x}As$ ($x \sim 0.40$) barriers. The 1 and 1′ markers indicate the allowed electron-to-heavy-hole and electron-to-light-hole transitions, respectively, for 30 Å wells separated by perfect 50-Å barriers (i.e., no alloy clustering). The 1 and 1′ (110) markers indicate the lowest transitions of a 110-Å well. Typical cw laser operation (a, 4.8×10^3 W/cm^2) occurs slightly below the 1 (110) marker, while the spontaneous background extends to higher energy. Pulsed operation of a narrower sample (b, 6.8×10^4 W/cm^2) produces lasing at the expected energy of the $n = 1$ transition (30-Å well).

laser.

The 300-K laser data of Fig. 1 demonstrate the range of laser mode energies attainable from a QWH with an active region consisting of six $L_z \sim 30$ Å GaAs quantum wells coupled by five $L_B \sim 50$ Å, $Al_xGa_{1-x}As$ ($x \sim 0.4$) barrier layers. At 4.8×10^3 W/cm^2 cw excitation (a), a 39×110 μm^2 sample exhibits laser operation at $\lambda \sim 8560$ Å, which is in the anomalous range $\sim 5\hbar\omega_{LO}$ lower in energy than the lowest ($n = 1$) confined-carrier electron-to-heavy-hole ($e \rightarrow hh$) or lowest ($n' = 1'$) electron-to-light-hole ($e \rightarrow lh$) transitions of ~ 30 Å GaAs quantum wells coupled by ideal (microscopically uniform) ~ 50 Å, $Al_xGa_{1-x}As$ ($x \sim 0.4$) barriers. By exciting narrower samples at high level, we observe laser emission as high as 1.63 eV ($\lambda \sim 7600$ Å) as is shown by the 23×94 μm^2 sample of curve b (6.8×10^4 W/cm^2, pulsed). This high emission energy, which is expected ($L_z \sim 30$ Å), serves to identify the lowest confined-carrier transitions ($n = 1, n' = 1'$) of an ideal structure.

Alloy clustering in the $Al_xGa_{1-x}As$ barrier layers, which is a form of disorder and is inevitable, allows further interpretation of these spectra. In the extreme case of very large scale clustering, which would allow GaAs to extend across a barrier (~ 50 Å) and connect two or even more wells, the carrier recombination can approach E_g(GaAs) or $\lambda \sim 8707$ Å (300 K). Even for a smaller average cluster size it is possible that regions exist in the $Al_xGa_{1-x}As$ barriers where the Al concentration is nearly zero. The resulting local potential-well size is effectively increased from $L_z \sim 30$ Å to as much as $L_z + L_B + L_z \sim 110$ Å. The location (energy) of the lowest confined-carrier transitions of a ~110-Å GaAs quantum well are also labeled in Fig. 1. Note that alloy clustering in the barrier layers sufficient to create GaAs paths through the $Al_xGa_{1-x}As$ barriers is expected to have a drastic effect in broadening and lowering the energy spectrum of this quantum system. For example, the $n = 1$ confined-electron state shifts downward by ~140 meV for a size shift from $L_z \sim 30$ Å to $L_z + L_B + L_z \sim 110$ Å.

A result of this shift is that the density of states of a QWH with alloy clustering in the barriers will not exhibit an abrupt step to zero at energies below the lowest confined-particle states of an ideal structure. Instead, the density of states is expected to be small but significant below these "lowest" confined-carrier states, and then drop to zero for energies less than E_g(GaAs). Besides depending upon the barrier size L_B, the exact form of the density of states will depend on the average cluster size, the form of the cluster size distribution, and on the composition x of the Al_x-$Ga_{1-x}As$. Also, cluster-induced quantization in the x, y dimensions will play a role.

These additional lower-energy states are expected to play an important part in radiative emission from a QWH. The existence of small areas or patches within the active region with lower-energy states (areas that increase in number with the number of barriers) increases the probability of LO-phonon–assisted recombination processes[8] at energies $E_{1,1'} > \hbar\omega > E_g$ since virtual transitions are no longer required. Instead, real transitions in this range at multiples of $\sim\hbar\omega_{LO}$ below the $n = 1$ and $n' = 1'$ transitions of the $L_z \sim 30$ Å well are possible.

Further evidence for alloy clustering in the $Al_xGa_{1-x}As$ barriers is shown (Fig. 2) by the form of the high-level spontaneous emission spectra of a two-well, one-barrier ($x \sim 0.5$) QWH (a different QWH wafer) with all three layers ~40 Å thick. Note that in this case the barrier size is smaller (40 Å) and approaches and helps identify the average cluster size. As in Fig. 1, the confined-carrier transitions of the ideal $L_z \sim 40$ Å quantum well and also of the larger $L_z + L_B + L_z$ ~120 Å composite quantum well are labeled in Fig. 2. The two samples (a, 4×10^4 W/cm², 90 ×360 μm²; b, 10^5 W/cm², 56×195 μm²) exhibit very similar spectra as, in fact, do all of the samples from this wafer. A large peak in the range of $n'=1'$ is observed. The emission does not drop to zero just below the $n=1$ $e \to hh$ transition, as would be expected in the ideal cluster-free limit, but extends downward in energy to nearly the location of the $n=1$ (120) and $n'=1'$ (120) transitions, which are near a distinct shoulder in the emission. An increase in the barrier thickness to ~70 Å results in cutoff of most of this lower energy emission.[9] As the barrier thickness L_B is decreased from ~70 Å (Ref. 9) to ~50 Å (Fig. 1) to ~40 Å (Fig. 2) and approaches the average cluster size, tunneling filaments are likely to appear in the $Al_xGa_{1-x}As$ barriers, which results in a major increase of the effective well dimension from $\sim L_z$ to $\sim L_z + L_B + L_z$. The observation of spectra such as those of Fig. 2 allow an estimate to be made of the cluster size ($\lesssim 40$ Å).

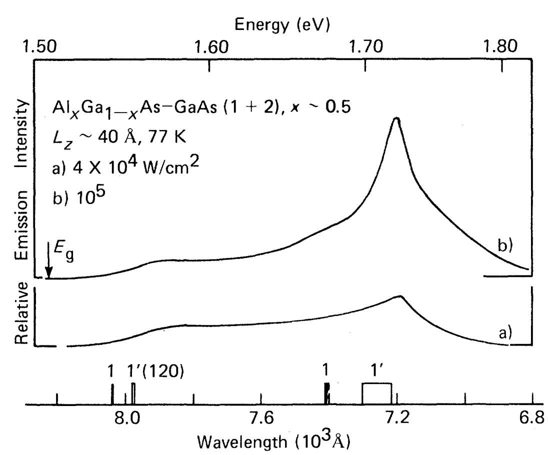

FIG. 2. Photoemission (77 K) of two QWH samples with active regions consisting of two 40-Å GaAs wells separated by one 40-Å $Al_xGa_{1-x}As$ ($x \sim 0.50$) barrier. These spectra (a, 4×10^4 W/cm²; b, 10^5 W/cm²) exhibit a peak near the $n'=1'$ transition of a 40-Å well, with emission extending to lower energy. Note that this emission rolls off near the lowest-energy transitions of a composite-layer 120-Å well, indicated by the 1 and 1′ (120) markers.

Further 300-K laser data on a 29-barrier, 30-well $L_z \sim 30$ Å, $L_B \sim 50$ Å superlattice structure (not shown) demonstrate that laser operation below E_g is also attainable. This fact, along with recent laser data on QWH's consisting of a large quantum well (or in some cases a bulk layer) coupled to a phonon-generating and -reflecting array of smaller quantum wells,[8] indicate that *virtual* phonon-assisted recombination processes with $\hbar\omega < E_g$ can occur and are not inconsistent with the present data. Alloy clustering *(in ternary barriers)*, however, allows actual states to exist between the bulk band edge and the lowest quantum states characteristic of an ideal QWH and thus permits *real* phonon processes to scatter the electrons to lower energies before recombining.

It is worth mentioning that a reinterpretation of previous investigations of disorder scattering[10-13] indicates that cluster models might have to be involved to explain successfully the experimental results for electron mobilities in III-V alloys. For example, negligible alloy scattering seems to exist[12] in $In_{1-x}Ga_xAs$ and strong alloy scattering in the quaternary system $In_{1-x}Ga_xP_{1-z}As_z$,[13] which (for the latter) cannot be explained on the basis of random-compositional-disorder models alone. In addition, these models do not take into account, in detail, the peculiarities of crystals such as $Al_xGa_{1-x}As$ or $GaAs_{1-x}P_x$ that undergo a direct-indirect transition in the range $x \equiv x_c = 0.4$–0.5, nor whether such crystals are particularly prone to clustering. It is also worth mentioning that data are not presently available indicating how sensitive cluster formation is to the specific process (vapor-phase epitaxy, liquid-phase epitaxy, molecular-beam epitaxy) used to grow a III-V alloy.

In any case, the basic features of the $Al_xGa_{1-x}As$ alloy clustering described above are clear since, besides the data of Figs. 1 and 2, simple substitution of binary barriers (including very narrow barriers, ~10 Å) for the ternary barriers employed here eliminates recombination below the expected (ideal) confined-particle transitions of a QWH. These further data are shown in Fig. 3, which is for the case of a QWH with twelve GaAs wells ($L_z \sim 50$ Å) interleaved in the active region with thirteen *binary* (nonclustered) AlAs barriers ($L_B \sim 10$ Å). The laser operation of the sample (50×90 μm²) occurs exactly on the $n=1$,

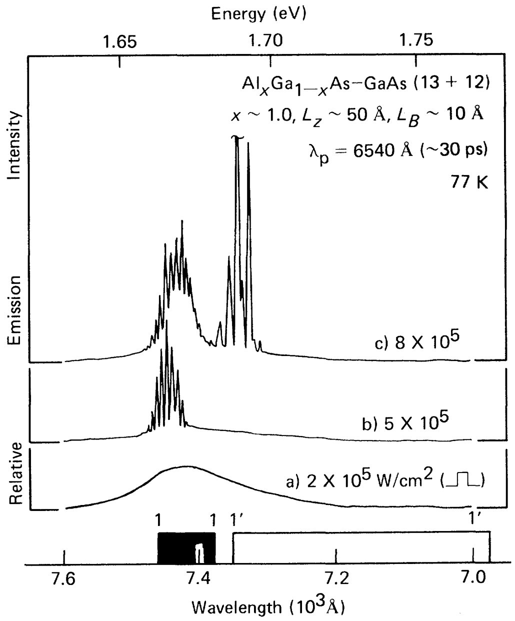

FIG. 3. Photoluminescence (laser) spectra (77 K) of a QWH sample with an all-binary (cluster-free) active region consisting of twelve ~ 50-Å GaAs wells alternating with thirteen ~ 10-Å AlAs barriers. The excitation power densities are high (~ 10^5 W/cm^2) since absorption of the incident pump beam (λ_p ~ 6540 Å) occurs only at the 50-Å GaAs wells. Spontaneous (a) and stimulated (b, c) emission occur only on the $n = 1$ and $n' = 1'$ transitions, and not at lower energy as in Figs. 1 and 2.

$e \rightarrow hh$ and $n' = 1'$, $e \rightarrow lh$ "bands" with no recombination radiation between E_g ($\lambda \sim 8224$ Å) and E_1($\lambda \sim 7460$ Å), and with only minor spectral broadening just below E_1 as would occur for small growth fluctuations in layer size.

Finally we emphasize that the consequences of alloy clustering are very different for QWH layers and for bulk semiconductors. In a bulk III-V alloy the changes in the scattering rates (e.g., decrease in carrier mobility) due to clusters are quite small,[10] whereas in layered structures size-quantization effects can be totally destroyed. It is exactly these effects of size quantization that are probed with QWH laser emission, which is therefore a sensitive new tool to investigate clustering.

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