Low-temperature (10 K) photoluminescence of $Ga_{1-x}In_xP_yAs_{1-y}$ quantum wells grown by metalorganic chemical vapor deposition

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$Ga_{1-x}In_xAs_{1-y}P_y/InP$ ($x = 0.72$, $y = 0.39$) lattice-matched quantum wells (QWs) are grown by low-pressure metalorganic chemical vapor deposition on (100) and 3° misoriented substrates, using different variations of growth technique. Low-temperature (10 K) photoluminescence is used to characterize the QWs. We find that substrates oriented closely to (100) (no intentional misorientation) produce QWs of consistently higher quality as judged by the width of the $n = 1$ photoluminescence peak. The use of growth interruptions at the well interfaces severely degrades the QW quality. The narrowest peak observed is 5.8 meV wide from a 70-Å-wide well.

The use of quantum wells (QWs) in optoelectronic devices has led to numerous demonstrations of enhanced device performance. Examples include reduced laser thresholds,[1] quantum-confined Stark effect modulators,[2] and bistable devices[3] in the AlGaAs material system, and more recently, enhanced laser performance in $Ga_{1-x}In_xAs$ graded-index separately confined heterostructure multiple QW (GRINSCH-MQW) structures.[4] Although most QW investigations have focused on the $Al_xGa_{1-x}As$ materials system, there is now heightened interest in QWs fabricated in the lattice-matched $Ga_{1-x}In_xAs_{1-y}P_y/InP$ (quaternary) alloy system, which is particularly attractive for 1.3 and 1.55 μm communications systems. In this wavelength region, both the QW width and emission energy may be optimized independently when the QWs are made of quaternary alloy. In contrast, the emission energy of a $Ga_{1-x}In_xAs$ QW is a unique function of well width. The intent in using QWs in the quaternary system is to achieve the same performance advantages in long-wavelength devices as those realized in QW AlGaAs devices. One of the primary difficulties, however, is that $Ga_{1-x}In_xAs_{1-y}P_y$ has proven less amenable to yielding high quality QW performance than $Al_xGa_{1-x}As$. The performance requirements are especially stringent in the case of Stark effect modulators, where sharply defined adsorption edges are necessary for high-speed operation.

Recently, the low-temperature photoluminescence (PL) half widths of $Ga_{1-x}In_xAs$ and quaternary QWs have been used to characterize the interfacial roughness and homogeneity of QWs grown by a variety of techniques.[5] Theory predicts that well-barrier interfacial roughness broadens PL linewidth when the well widths are narrow ($L_z < 50$ Å), and random alloy compositional fluctuations dominate the PL spectral width for wider wells.[6–8] The details of the crystal growth process on both interfacial roughness and alloy inhomogeneity bear directly upon QW quality. In the case of metalorganic chemical vapor deposition (MOCVD) QWs, Sugawara *et al.*[9] have discussed the influence of growth temperature on interfacial roughness, Bhat[10] has examined the importance of the thickness of the InP barrier layers, and Irikawa *et al.*[11] have studied growth interruptions using a vertical reactor geometry. In this letter we report on the effects of the details of the growth technique and substrate orientation on the PL peak widths of $Ga_{1-x}In_xAs_{1-y}P_y/InP$ ($y = 0.39$, $x = 0.72$, $E_g = 0.92$ eV, $\lambda = 1.33$ μm) QWs.

Two different InP:S ($n = 5\times10^{18}$ cm^{-3}, etch pit density < 1000 cm^{-2}) substrate orientations are used: (100) $\pm 0.2°$, and cut off the (100) orientation tilted 3° toward (110) (In). Both are cut from the same Czochralski boule[12] in order to eliminate possible differences inherent in the overall bulk growth quality. The epitaxial layers are grown in a low-pressure (76 Torr), horizontal, rf-heated reactor having a rectangular cross section. A SiC-coated graphite susceptor capable of holding two 2-in.-diam wafers is used. The gas handling system is designed for minimum dead space and is carefully pressure balanced between the reactor run and vent lines. The sources are trimethylindium (TMIn), triethylgallium (TEGa), 10% AsH_3, and 10% PH_3 in H_2. The alkyls are held at 17 °C temperature and a pressure of 1000 Torr; the hydrides are injected into a 76 Torr manifold. The average gas velocity is 90 cm/s over the substrate, and the growth temperature is 650 °C. Growth rates are 220 and 170 Å/min for quaternary and InP, respectively. All four reactant flows are held constant throughout the growth; the composition is changed only by switching the TEGa and AsH_3 flows. During growth, two wafers, one cut at each orientation, are placed adjacent to one another so that there is less than 10 mm separation between sample points. Since the two substrates used in each run are in such close proximity, variations in composition are minimized.

The quaternary compositions used, with one exception discussed later, are lattice matched to InP to within $\Delta a/a_0 = 2\times10^{-4}$ as determined by a double-crystal x-ray diffractometer. The test structure (undoped) for all growths is 2000 Å InP buffer, 2000 Å quaternary (used as reference for the bulk quaternary composition), four QWs ($L_z = 100$, 70, 40, and 25 Å) each separated by $L_b = 200$ Å InP, and 2000 Å InP cap. Four sets of growth conditions were chosen for examination. Under the first set of conditions, referred to as method (a), growth is interrupted (suspend alkyl flow, continue hydrides 5 s, switch AsH_3 and hold 5 s, resume new

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alkyl flow) at each well-barrier interface. Such interruptions are commonly used to flush out the growth chamber during composition changes, and to ensure that the flow controllers settle at new set points. In the remaining three samples, the growth interruptions are removed (all valves are switched simultaneously in less than 100 ms), and variations in a make-up H_2 flow are introduced. The second method, (b), is otherwise identical to the first. The third, method (c), is similar to the second, but the H_2 flow in the group V manifold is set higher (from 1 to 3 slpm), although the total H_2 flow in the growth chamber is held constant. In the fourth method, (d), conditions are identical to those in (c), except that the reactor chamber pressure is lowered to 38 Torr.

The PL is measured at 10 K using an Ar^+ laser operating at 514.5 nm. Typically 1 mW power is focused on a 50-μm-diam spot producing a carrier concentration around 5×10^{13} cm^{-3}, where band filling effects are negligible. The emitted light is focused on a 1 m grating spectrometer using 0.05 mm slits to produce a resolution approximately 0.05 nm. The detector is a LN_2-cooled photomultiplier tube. The resulting spectra are not corrected for detector response.

The surface morphology of the exact-oriented samples is consistently smooth and nearly defect-free, in contrast to the misoriented samples, which exhibit some roughness and a low density of small surface defects.

A useful comparison of the four growth techniques is the relative change in PL full width at half maximum (FWHM) from each well as a function of the quantized energy shift (ΔE_n). By comparing relative energy shifts rather than absolute transition energies, we eliminate errors due to small run-to-run variations in composition. Figure 1(a) shows such a plot for the exact-oriented wells. Notice that the wells grown with interruptions (curve a) have much broader PL FWHM compared to (b) and (c) (grown without interruptions), and that the energy shifts are significantly smaller. The PL FWHM of wells grown by method (d) is broadened, and bulk growths under the same conditions (lowered reactor pressure) show that the quaternary alloy composition shifts, producing strain ($\Delta a/a_0 = -2.9\times10^{-3}$, $\lambda_{(300)} = 1.32$ μm). The growth conditions of method (d) should have enabled yet faster gas changes above the substrate and hence wells with sharper PL transitions should have resulted. The data indicate otherwise. Thus, we attribute the broadening of the PL to strain effects. Regardless, the energy shifts for (d) are comparable to those observed for methods (b) and (c), indicating that the shape of the wells is very similar to those grown by methods (b) and (c).

Figure 1(b) shows a plot of the PL FWHM as a function of ΔE_n for the misoriented wells. The PL FWHM and ΔE_n are similar to those of Fig. 1(a), but the PL half widths of misoriented QWs grown with interruptions (method a) are notably larger than the exact-oriented QWs. The points on curve (a) are incomplete because the broadest PL peaks overlapped, rendering measurement meaningless. In most cases, the PL half widths are narrower for wells grown on exact-oriented wafers than for those grown on misoriented substrates. The exceptions are the strained wells, which are somewhat thinner when grown on misoriented substrates. For both orientations, the wells grown with no interruptions show dramatically narrower half widths, especially for narrower wells, and those in set (c) (higher manifold velocities) show the most improved PL FWHM.

A common comparison of QW quality is the behavior of the PL FWHM as a function of well width, L_z. In the narrow-well region ($L_z < 50$ Å), interface roughening is the most significant theoretical factor, while in the wide-well region, alloy inhomogeneities dominate. The half widths of

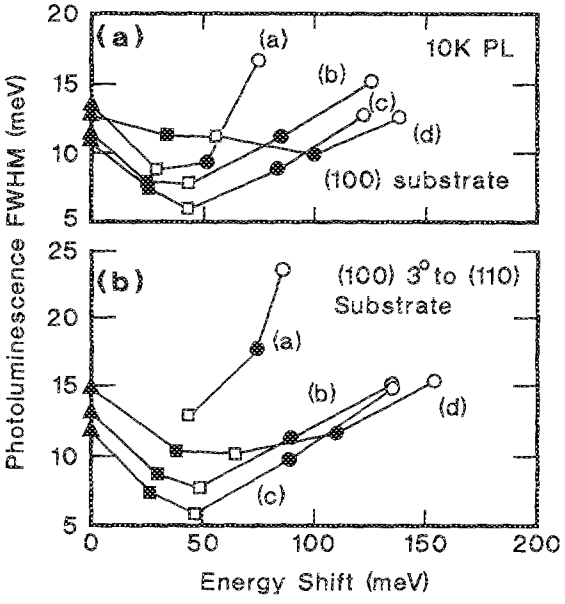

FIG. 1. Photoluminescence (10 K) full width at half maximum as a function of QW emission energy shift above the emission energy from the 2000-Å-thick layer (bulk) for QWs grown on (a) exact ⟨100⟩ oriented InP and (b) 3° misoriented towards ⟨110⟩ for the four QW widths (25 Å open circles, 70 Å solid circles, 40 Å open squares, 25 Å solid squares, 2000 Å solid triangles) from each of the four growth methods—a, b, c, and d. Solid lines serve only as a guide to the eye, linking points from the same growth method.

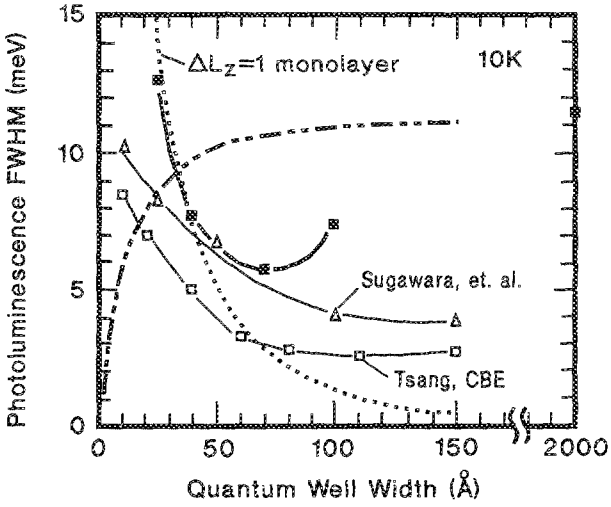

FIG. 2. Photoluminescence (10 K) full width at half maximum of $Ga_{0.28}In_{0.72}P_{0.39}As_{0.61}$/InP QWs as a function of well width. The dotted line is theoretical curve for $\Delta L_z = a_0/2$ (monolayer variation in well thickness) and dash-dotted line is a theoretical curve for compositional inhomogeneity broadening with 11.2 meV at the bulk limit. Solid squares are present work.

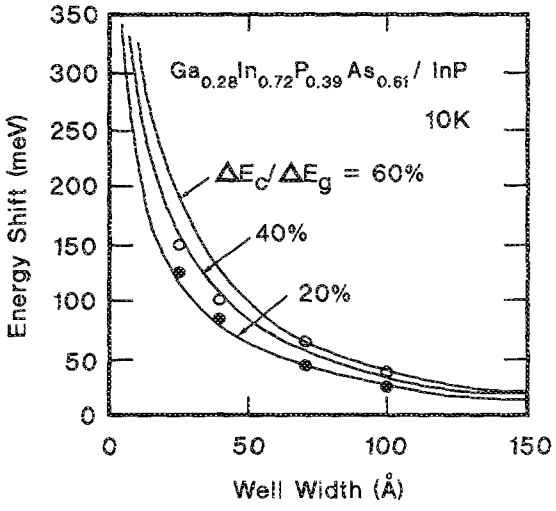

FIG. 3. $Ga_{0.28}In_{0.72}P_{0.39}As_{0.61}$/InP QW energy shift as a function of well width. Solid lines are theoretical curves for conduction-band offsets of 20%, 40%, and 60% of the heterojunction band-gap difference. Points are data taken from Fig. 1(a), curves (c) (unstrained, solid points) and Fig. 1(b), curve (d) (strained wells, open points).

our GaInPAs QW PL are plotted in Fig. 2 (solid squares) as a function of L_z. Data from two literature references are shown for comparison: Sugawara *et al.*[9] for quaternary QWs using 1.6 μm emitting bulk, and Tsang and Schubert[5] for chemical beam epitaxial $Ga_{0.47}In_{0.53}As$. A theoretical curve for broadening due to ΔL_z = one atomic monolayer (dotted) is also shown. The PL linewidth broadening expected from alloy composition inhomogeneities within the QW may be calculated from perturbation theory.[9] In this method, the measured bulk PL FWHM (11.2 meV in our material) becomes an asymptotic limit. The result of our calculation is shown in Fig. 3 (dash-dot curve). At small L_z, the PL FWHM measures slightly less than the theoretical monolayer fluctuation. In the wide-well case (L_z = 100 Å), the PL FWHM of the wells is 7.4 meV. It is not clear why the 100 Å QW should have a narrower spectrum than the bulk material. Because the bulk PL FWHM, measured at 11.2 meV, is substantially wider than the minimum theoretical value of 3.3 meV,[8] we believe that the quaternary alloy is not totally random. It is possible that as the quaternary layers are grown thicker, the growing surface becomes progressively rougher, so that at values of about 100 Å the linewidths broaden above half widths for narrower wells. As bulk thicknesses are approached, the inhomogeneous broadening mechanism reasserts. This odd behavior may indicate that the nonrandom nature of the quaternary alloy has a range longer than ~100 Å in the growth direction, or put more simply, short term instabilities exist in our MOCVD process which fluctuate at a period longer than the time needed to grow 100 Å.

The calculated energy shift of the $n = 1 \rightarrow$ hh transition (ΔE_n) as a function of L_z at 4 K is shown in Fig. 3 for these QWs. The experimental points shown (10 K) are from Fig. 1(a), curve (c) (solid points), and Fig. 1(b), curve (d) (open points). The agreement with theory is very good, especially for the wells with the highest ΔE_n when we use a conduction-band offset (ΔE_c) of 20% of the band-gap difference (ΔE_g). Irikawa *et al.*[11] and Kondo *et al.*[14] obtain best fits to their data with $\Delta E_c / \Delta E_g$ = 30% and 20%, respectively. The effective masses used in the calculation were taken from Adachi,[13] and are: $m^*_{eq} = 0.0564m_e$, $m^*_{hq} = 0.70m_e$ (quaternary), and $m^*_{eb} = 0.0803m_e$, $m^*_{hb} = 0.084m_e$ (InP) electron and heavy hole, respectively. The values of m^*_{eq} and m^*_{eb} differ from those used in Refs. 11 and 14, and this change accounts for the small discrepancy in the conduction-band offset which gives the best fit to the data when compared to Ref. 14.

In summary, we have grown $Ga_{1-x}In_xAs_{1-y}P_y$/InP QW stacks with widths ranging from 25 to 100 Å. In contrast to Irikawa *et al.*,[11] we find interrupted growth to be deleterious to QW quality. Increased manifold gas velocity (distinct from reactor tube gas velocity) in the group V manifold is the second most important factor. We find that substrates oriented to (100) $\pm$ 0.2° produce superior wells compared to substrates oriented (100) tilted 3° toward (110)(In). Strain also broadens the PL.

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