Optical investigation of atomic steps in ultrathin InGaAs/InP quantum wells grown by vapor levitation epitaxy

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Ultrathin InGaAs/InP single quantum well structures, grown by chloride transport vapor levitation epitaxy, have been investigated by low-temperature photoluminescence (PL). Well-resolved multiple peaks are observed in the PL spectra, instead of an expected single peak. We attribute this to monolayer ($a_0/2 = 2.93$ Å) variations in quantum well (QW) thickness. Separate peak positions for QW thicknesses corresponding to 2–6 monolayers have been determined, providing an unambiguous thickness calibration for spectral shifts due to quantum confinement. The PL peak corresponding to two monolayers occurs at 1.314 eV, corresponding to an energy shift of 524 meV. Experimental data agree very well with a simple effective mass theory.

Ultrathin (20 Å or less) quantum wells (QWs) of InGaAs, lattice matched to InP, have been reported for organometallic vapor phase epitaxy (OMVPE),[1–3] low-pressure OMVPE,[4] molecular beam epitaxy (MBE),[5] gas-source MBE (GSMBE),[6] and chemical beam epitaxy (CBE).[7] Low-temperature photoluminescence (PL) has been used to study these structures in order to relate the electron-hole energy shift, due to quantum confinement, with the QW thickness as determined by transmission electron microscopy (TEM) or extrapolated from thicker reference layers. There is considerable disagreement as a result of the studies, however. For the thinnest QWs reported, values of PL spectral shift differ by more than 200 meV for the same nominal thickness of two monolayers.

In this letter we report low-temperature (< 10 K) PL measurements on ultrathin single quantum well structures of InGaAs/InP grown by vapor levitation epitaxy[8] that should help to resolve the discrepancies found in the literature. The measured spectra show highly resolved multiple peaks which we attribute to monolayer ($a_0/2 = 2.93$ Å) variations in QW thickness, similar to what has been observed for high quality GaAs/GaAlAs QW samples.[9] Similar features have been previously observed in the PL spectra of OMVPE-grown InGaAs/InP single QW samples and ascribed to monolayer fluctuations of thickness by Wang *et al.*[3] However, they calibrated their thicknesses with PL results published for CBE-grown QWs.[7] Our results differ considerably from those of Wang *et al.*[3] and also from the results of Tsang and Schubert,[7] but agree quite well with a simple theory using no adjustable parameters. We observe five individual peaks for 2–6 monolayers, sufficiently narrow and close in energy to the InP band gap that they provide an unambiguous thickness calibration for comparison with theory and with previously published experimental data.

Samples were grown by vapor levitation epitaxy which, as presently used, is a dual chamber, atmospheric pressure, chloride transport vapor phase epitaxial growth technique. It has been described in detail elsewhere.[10] For this study, a low growth temperature of 550 °C was used in order to make timing more precise and to minimize transition effects. The InP growth rate was ≈2 Å/s. The InGaAs growth rates were 0.5 Å/s for sample *A* and 0.2 Å/s for sample *B*. Sample *A* was grown on a Sn-doped InP substrate oriented 2° off the (100) toward the (111). It consists of a 2400 Å InP buffer, followed by the InGaAs single QW and a 360 Å InP cap. A cross-sectional lattice image of the QW of sample *A*, taken along the InP [100] axis with a JEOL 4000FX transmission electron microscope (TEM), is shown in Fig. 1. The micrograph indicates that the InGaAs layer is ≈4 monolayers thick with structural coherence to the InP cladding layers. The interfaces do not appear atomically sharp, indicating a few monolayers of thickness variation over the TEM sample thickness of tens of nanometers. Sample *B* was grown on an Fe-doped InP substrate nominally oriented to the (100) direction and consists of an InP buffer, followed by the InGaAs QW and a 600 Å InP cap. A TEM image of sample *B* was not obtained. The InGaAs QW thickness (growth time = 15 s), as extrapolated from a TEM cross section of a 36 Å QW grown for 150 s, is nominally 3.6 Å. Near-lattice-matched composition of the QWs was established with a separately grown 2000 Å InGaAs reference layer.

A conventional lock-in detection technique was used in the PL measurements. The 5145 Å line from an argon ion laser was chopped and focused to a ≈150 μm spot on the

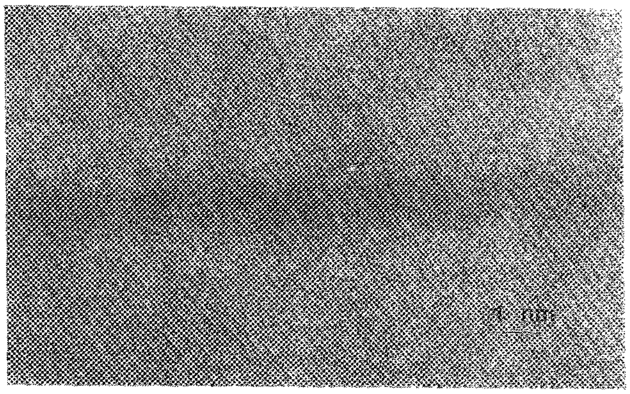

FIG. 1. High-resolution cross-sectional transmission electron micrograph of an InGaAs layer clad above and below by InP.

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sample to give ≈ 0.2 W/cm^2 excitation intensities. The samples were cooled to less than 10 K and the PL spectra were recorded using a liquid-nitrogen-cooled Ge detector. Figure 2 shows the PL spectrum of sample *A* (nominal QW thickness = 11 Å) and sample *B* (nominal QW thickness = 3.6 Å). The narrow peaks at 0.904 μm for both samples are acceptor-related emissions from the InP layer.[11] Three features of the PL data to be noted are (i) the upshift in energy with decreasing nominal well width; (ii) the multipeaked spectra associated with the single QWs; and (iii) the evolution from one multipeak spectrum to another without loss of the peak alignment. We attribute upshift to the well-known quantum confinement effect. The PL peak at 0.943 μm is an indication that we are close to the limit of 1 monolayer.

We explain the presence of a multipeaked single quantum well PL spectrum by considering monolayer steps in the InGaAs layer. In the present case, growth is not interrupted between layers. The InP substrate and the InP surface upon which the InGaAs grows are not perfectly planar and have steps and groupings of steps of monolayer height ($a_0/2 = 2.93$ Å). For sample *A*, nominally misoriented 2° from the (100), a perfect surface is assumed to have monolayer ledges spaced 84 Å apart. Deviation from planarity would be accommodated by variation in spacing and curvature of the nominally straight monolayer ledges. The InGaAs is expected to nucleate and advance from each step existing on the InP surface resulting in local variations of InGaAs thickness but with atomically abrupt InGaAs/InP interfaces. This results in large flat regions of InGaAs consisting of discrete numbers of monolayers. Our results indicate that the flat regions are larger than the exciton diffusion length and small compared with the illuminated spot area. Therefore, the PL spectra result primarily from excitonic recombination inside atomically flat InGaAs layers. If we move the spot to different points on the wafer, the PL peaks change intensities but not positions.

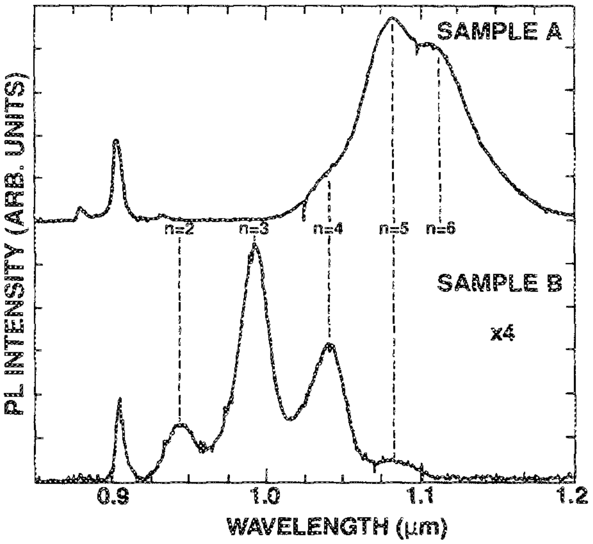

FIG. 2. Photoluminescence (< 10 K) of InGaAs/InP single quantum wells of sample *A* (nominal 11 Å thickness) and sample *B* (nominal 3.6 Å thickness). Both spectra show peak splitting due to monolayer variations in well thickness. The number of monolayers, *n*, responsible for each peak or shoulder is indicated. Note the alignment of peaks between samples for $n = 4$ and $n = 5$. The small peak at 0.904 μm for both samples is due to acceptor-related emission from InP. The other InP peaks discernable for sample *A* are at 0.879 μm (bound excitons) and at 0.932 μm (probably an LO phonon replica of the acceptor peak).

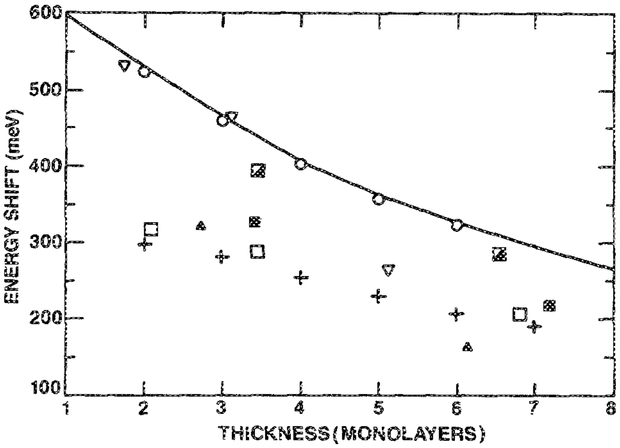

FIG. 3. Photoluminescence energy shift vs InGaAs quantum well thickness for this work (○), Panish *et al.*[6] (▽), Carey *et al.*[2] (◪), Miller *et al.*[1] (▩), Razeghi *et al.*[4] (▲), Tsang and Schubert[7] (□), and Wang *et al.*[3] (+). The solid line represents theory using effective mass approximation for a finite well with 58% valence-band offset.

The spectra from samples *A* and *B* were fitted assuming three PL peaks for *A* and four peaks for sample *B*. The left shoulder (1.1912 eV) of *A* matches quite well the third peak (1.1919 eV) of *B* as does the right shoulder (1.1478 eV) of *B* and the second peak (1.1472 eV) of *A*. The five different peak positions obtained from fitting the spectra from samples *A* and *B* were converted to energy upshift from the peak position (0.7899 eV) of the separately grown bulk InGaAs reference layer. The energy shifts are plotted in Fig. 3 (open circles) as a function of *n*, where *n* is the number of InGaAs monolayers assigned to each peak position. The solid line (see Fig. 3) connects values calculated for integral numbers of monolayers. Other points are from the literature and are discussed in detail below. We calculated the electron and hole confinement energies in the effective mass approximation for electrons and holes in a finite potential well.[12] We used well-established values of effective masses for electrons (0.041 m_0) and heavy holes (0.470 m_0) in InGaAs. The band gap used for InP was 1.4205 eV.[13] For InGaAs, we used the value 0.7899 eV determined from the peak position of the InGaAs reference layer. The band offsets for the conduction band (42%) and the valence band (58%) came from recent measurements performed by Lang *et al.*[14]

The excellent agreement between experiment and theory (see Table I) using no adjustable parameters indicates

TABLE I. Experimental and calculated energy upshifts (meV) related to InGaAs layers composed of discrete numbers (*n*) of monolayers (2.93 Å thick), as shown in Fig. 3. The values are related to the PL peak position of the 2000-Å-thick InGaAs reference layer as discussed in the text.

Number of monolayers (*n*)	1	2	3	4	5	6
Theory	597	529	462	407	362	325
Sample *A*	···	···	···	401	357	323
Sample B	···	524	459	402	358	···

that the assignment of two monolayers for the highest energy peak is correct. The use of such thin layers showing monolayer fluctuations in thickness allows the correlation to be made with little ambiguity. The combined factors of large energy separation for monolayer differences in thickness (>60 meV), narrow PL lines associated with the thinnest layers ($n=2$ and $n=3$), and close proximity to the band gap of InP (1.42 eV) make any other choice unlikely. The thickness ranges for both samples, however, differ significantly from the nominal values. In the case of sample A for which we have TEM calibration of 11 ± 2 Å, it is clear that we have luminescence from 4, 5, and 6 monolayers (11.7–17.6 Å), which would certainly have been misinterpreted without the calibration provided by the peak splittings. The thicker portions of the well, though perhaps small in absolute area, are strongly favored in the PL spectra. The excitons from thinner regions diffuse toward the thicker regions where recombination can occur at lower energy.[15]

The QWs for this study are considerably thinner than the 50 Å QWs reported by Kodama *et al.* using chloride transport VPE[16] or the 100 Å QWs studied by DiGiuseppe *et al.*[17] and grown by hydride VPE, so a comparison with their results cannot be made. The data from other growth techniques which have reported ultrathin QWs are plotted in Fig. 3. The results from Panish *et al.*[6] agree well with our 2 and 3 monolayer values and those of Carey *et al.*[2] agree within $\approx 1/2$ monolayer for 4 and 7 monolayers. Most of the points, however, fall well below our theoretical line and experimental points. We attribute this wide deviation, in part, to the difficulty of determining precise layer thicknesses. In the ultrathin layer regime of the present study, it is possible to resolve this difficulty. By using the natural quantization of thickness imposed by the InGaAs/InP lattice spacing, we have established an essentially unambiguous correlation between QW thickness and PL spectral position. The excellent agreement of our results with theory establishes vapor levitation epitaxy as an important new technique for the growth of high quality ultrathin QW structures.

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