High quality quantum wells of InGaP/GaAs grown by molecular beam epitaxy

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High quality quantum wells of GaAs confined by barriers of InGaP have been grown by gas-source molecular beam epitaxy. High-resolution lattice images obtained with transmission electron microscopy of single quantum wells reveal high quality interfaces for both the normal InGaP/GaAs and the inverted GaAs/InGaP interface. Multiple-line low-temperature photoluminescence emission is observed for the thinnest GaAs quantum well. The range of well thicknesses examined was 0.6–5.2 nm, with the smallest well producing a quantum confinement energy shift of over 410 meV, corresponding to photoluminescence emission at 640 nm (1.94 eV) from GaAs.

The materials system AlGaAs/GaAs has been used extensively for synthesis of quantum well (QW) optoelectronic and transport devices. The III-V alloy InGaP provides an alternative to AlGaAs for confinement of GaAs QWs. At the composition for lattice matching to GaAs, In$_{0.48}$Ga$_{0.52}$P exhibits a room-temperature band gap of 1.89 eV, somewhat larger than that of Al$_{0.3}$Ga$_{0.7}$As, and the In$_{0.48}$Ga$_{0.52}$P/GaAs valence-band offset ($\Delta E_v$) is about 0.24–0.30 eV,1,2 larger than that of the Al$_{0.3}$Ga$_{0.7}$As/GaAs heterojunction. The inverted GaAs/AlGaAs interface is known to be significantly smoother than the normal AlGaAs/GaAs interface, resulting in monolayer fluctuations in the well width, most notably observed in narrow quantum wells.3 As shown here, both normal InGaP/GaAs and inverted GaAs/InGaP interfaces are found to be very smooth on the atomic scale. Finally, InGaP does not oxidize as readily as AlGaAs, and InGaP exhibits a much lower concentration of deep levels than AlGaAs when both materials are doped with Si.4 InGaP/GaAs QWs have been recently reported by Razeghi et al., who used metalorganic chemical vapor deposition to grow wells as narrow as 1.5 nm.5 We report here the growth of InGaP/GaAs single QWs by gas-source molecular beam epitaxy (GSMBE) and demonstrate that wells as thin as a few monolayers can be obtained by this technique.

The InGaP/GaAs QW heterostructures were grown nominally lattice matched on (100) oriented semi-insulating GaAs substrates after desorption in an As$_2$ beam at 630 °C of an oxide layer formed in de-ionized water. Epitaxial growth was carried out at a substrate temperature of 500 °C using P$_2$ and As$_2$ molecular beams produced by thermal decomposition of the gaseous hydrides PH$_3$ and AsH$_3$, respectively, in a low-pressure cracking oven held at 900 °C. The use of gas sources provided a means of rapidly switching between InGaP and GaAs growth while maintaining precise control of the group V molecular flux.6 During InGaP layer growth at 0.5 μm/h, the PH$_3$ flow rate was 5 sccm, and during GaAs layer growth at 0.3 μm/h, the AsH$_3$ flow rate was 2 sccm. All samples were grown using a computer to switch the gas flows and the Ga and In effusion cell shutters, with a 24 s pause programmed at each heterointerface. A detailed description of GSMBE growth of high quality InGaP has been reported elsewhere.7

The samples used in this study consisted of a 0.5–1.0 μm buffer layer of unintentionally doped (p-type) GaAs followed by a series of five unintentionally doped GaAs QWs of decreasing thickness, each confined by an In$_{0.48}$Ga$_{0.52}$P barrier layer of 12 nm. Growth was then terminated by a cap layer of InGaP of 65–100 nm in thickness. Based on the growth conditions, the GaAs QW thicknesses were expected to be approximately 0.6, 0.9, 1.7, 3.4, and 5.1 nm. All InGaP layers were unintentionally doped (n type) with an approximate carrier concentration of $3 \times 10^{16}$ cm$^{-2}$ and were found to exhibit a lattice mismatch with respect to the GaAs substrate of less than $7 \times 10^{-4}$, measured using double-crystal x-ray diffraction.

Both [011] and [010] cross sections of the InGaP/ GaAs samples were examined by transmission electron microscopy (TEM) using a JEM 2000EX microscope operated at 200 kV. The microscope is equipped with an ultrahigh resolution pole piece which has a spherical aberration coefficient of 0.7 mm and yields a point resolution of 2.0 Å at the operating voltage. Figure 1 shows a low magnification [011] cross-section bright field image. The five QWs are clearly discernible; the wells are uniform in thickness with smooth distinct interfaces. The values of the GaAs well thicknesses as determined by TEM are listed in Fig. 1 and are in good agreement with the expected values.

Figure 2 shows a [010] cross-section high-resolution TEM lattice image of the smallest QW. The defocusing and the thickness of the area for this imaging were chosen to yield the dominance of 200 type diffracted waves in the formation of the image. Due to the large difference in the amplitude of 200 type diffracted waves between GaAs and InGaP crystals, the QW having two monolayers (i.e., a well thickness of 0.57 nm) is clearly seen in the image. Interfaces between the GaAs well and InGaP barriers appear to be atomistically abrupt and smooth, being similar to those of high quality GaAs/AlAs interfaces.8 In all the lattice-matched GSMBE InGaP/GaAs heterostructures that we have examined, the
interfaces were found to be free from dislocations and interfacial contamination, showing atomistically smooth images similar to those in Fig. 2. A recent study of high-resolution electron microscope images of GaAs/AlAs heterostructures, however, has suggested that considerable fine scale roughness exists even in the high quality GaAs/AlAs interfaces. The analysis of detailed atomic structures of interfaces of these GSMBE heterostructures, therefore, requires further close examination of observed images.

The InGaP/GaAs samples were characterized by photoluminescence (PL) at 10–300 K using an Ar-ion laser at 514.5 nm, a 0.5 m monochromator, and a Si detector. Figure 3 shows the 10 K PL spectra for the sample of Fig. 1. The emission peaks for the five QWs are clearly evident, except for the largest well whose broad weak peak is partially obscured by the exciton bound to neutral donor ($D^0,X$) and donor to acceptor ($D_A$) emissions from the GaAs buffer layer. Emission from the InGaP layers, expected to be at a wavelength of 6300 Å for this sample, is not detected. An examination of the band diagram shown in the inset of Fig. 3 indicates that any electron-hole pairs generated in the InGaP layers would most likely be swept into the QWs where they recombine, and thus emission characteristic of InGaP would be unlikely. The energy of each peak was measured as a function of temperature from 10 to 300 K and the QW peak energies were found to follow the GaAs energy gap temperature dependence, indicating that the observed QW PL is due to recombination of free excitons.

In Fig. 3 the exciton peak of the narrowest QW shows double-line emission. The wavelength difference of 18 Å between the two peaks (i.e., an energy difference of 52 meV) corresponds to a difference in well thickness of one atomic layer. Thus, the multiple-line emission is due to monolayer thickness variation within the smallest QW. In AlGaAs/GaAs QWs and InGaAsP/InP QWs, multiple-line emission from a single well implies that the interfaces are atomically smooth over distances large compared to the diameter ($\sim 100$ Å) of the two-dimensional QW exciton. The TEM image of Fig. 2 supports this interpretation. Thus, for the smallest QW of Fig. 3, emission is obtained from excitons in the regions where the well is two monolayers thick and from where the well is one monolayer thick. For the thicker QWs of Fig. 3, multiple-line emission is not observed, presumably because the individual emission peaks are weaker and

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**FIG. 1.** TEM bright field image of a [011] cross section of a sample with five GaAs quantum wells of differing thicknesses confined by InGaP barrier layers of 12 nm each.

**FIG. 2.** TEM lattice image of a [010] cross section of the smallest InGaP/GaAs quantum well of Fig. 1. The (200) atomic planes are resolved and the well is two monolayers (0.57 nm) thick.
broader and thus overlap significantly.

The energy shift due to quantum confinement for the In$_x$Ga$_{1-x}$P/GaAs QWs is summarized in Fig. 4, where the dependence of the PL peak energy (relative to the band gap of GaAs at 10 K) on well thickness is shown for two samples with slightly different alloy composition $x$. Also shown is the theoretical ground-state electron, heavy hole energy shift calculated using a finite square well model assuming an InGaP/GaAs band-gap difference $\Delta E_g$ of 0.46 eV and a conduction-band offset $\Delta E_c$ of 0.22 eV, and using an electron effective mass of $0.45m_0^{13}$ and a hole effective mass of $0.60m_0^{14}$ for InGaP. Reasonably good agreement is obtained between the simple square well theory and the experimental data. Finally, for the smallest QW grown an energy upshift of over 410 meV was obtained, the largest value yet reported for an InGaP/GaAs QW.

In summary, single QWs of InGaP/GaAs as thin as two monolayers have been reproducibly grown by GSMBE. The QWs exhibit high quality interfaces that extend laterally for distances exceeding the diameter of the QW exciton. For the smallest investigated, low-temperature PL emission from GaAs at wavelengths as short as 640 nm was observed.

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10The static band diagram was calculated numerically assuming low-level injection and that the Fermi level is pinned near midgap on the free-InGaP surface, based on previously reported Schottky barrier measurements. See T. F. Kaneh and J. C. McAlindon, J. Vac. Sci. Technol. B 7, 891 (1980).