Quantum wells due to ordering in GaInP

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CuPt ordering results in a reduction of the band-gap energy of GaInP. Thus, heterostructures and quantum wells can be produced by simply varying the order parameter, without changing the solid composition. Changes in the order parameter can be induced by changes in growth conditions. The disordered/ordered/disordered quantum wells described here are grown by changing the PH_3 flow rate. Transmission electron microscopy results show that the quantum wells produced in this way are clearly defined, with abrupt interfaces. Low-temperature photoluminescence spectra show distinct peaks from quantum wells (QWs) of different widths. The QW photoluminescence peak energy increases with decreasing well width due to quantum size effects. The difference in band-gap energy between the ordered and disordered single layers is determined from photoluminescence excitation spectroscopy to be 0.06 eV. © *1998 American Institute of Physics.*
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CuPt ordering is a phenomenon observed in many III/V alloys[1] and has a significant effect on the band-gap energy.[2] For example, the band-gap energy was experimentally found to be as much as 0.16 eV lower in partially ordered $Ga_{0.52}In_{0.48}P$ than in a random alloy of the same composition.[3] A theoretical prediction of the band-gap reduction in perfectly ordered material is 490 meV.[2] The degree of CuPt order in GaInP is dependent on the organometallic vapor phase epitaxial (OMVPE) growth parameters such as temperature,[4] input partial pressure of the P precursor (P_p),[5] substrate orientation,[6] and growth rate.[7] Thus, in principle, it is possible to vary the degree of order, and hence, the band-gap energy, at will during growth. Heterostructures[8] and quantum wells (QWs)[9] have been prepared by changing the growth temperature. However, a more convenient method for changing the degree of CuPt order in GaInP layers is simply to change P_p. This allows the degree of order to be modulated simply with no other change in growth parameters.[10] The maximum range of low-temperature band-gap energy caused by varying P_p is approximately 0.07 eV.[11] It is important to thoroughly characterize disordered/ordered/disordered (D/O/D) QW structures in order to assess their potential for light-emitting diode and laser applications. Preliminary studies indicate that D/O heterostructures would be type-II,[9] which will limit applications involving efficient radiative recombination.

This letter presents the results of studies of disordered/ordered/disordered QWs grown by changing P_p during OMVPE growth and of the corresponding single layers. All the GaInP layers discussed here are partially ordered. The terms ordered and disordered are used throughout to refer to more and less ordered layers, respectively. The interfaces of the quantum wells are clearly defined and abrupt in the dark-field transmission electron microscopy (TEM) images. The 5 K photoluminescence (PL) peak energy from the QWs increases as the well width decreases, clearly demonstrating the presence of quantum confinement.

The $Ga_{0.52}In_{0.48}P$ single layers and QWs were grown on semi-insulating (001) GaAs substrates misoriented by 3° in the $(111)B$ direction in an atmospheric pressure, horizontal OMVPE system.[12] Substrate preparation consisted of standard degreasing followed by a 1 min etch in a solution of $12H_2O:2NH_4OH:1H_2O_2$. The substrates were then rinsed in deionized water for 5 min and blown dry with N_2 before being loaded into the reactor. The group III sources were trimethylgallium at 7 °C and trimethylindium at 25 °C with Pd-diffused hydrogen as the carrier gas. The phosphorus source was PH_3 and the growth temperature was 670 °C with a total flow rate of 4 standard liters per minute. The group III flow rates were kept constant and the growth rate was 0.6 μm/h. The V/III ratios were either 30 or 480, corresponding to values of P_p of 0.75 or 12 Torr, respectively. All epilayers discussed here have a lattice parameter misfit $\Delta a/a$ of $<0.1\%$, as confirmed by x-ray diffraction. Mirror-like surface morphologies of the epilayers were observed using Normarski phase contrast optical microscopy. Since there is only one source line for PH_3 in the apparatus and it takes 60 s to change P_p, it is necessary to switch the group III sources to ''vent'' while changing P_p to avoid a transition layer.

The samples were held at 5 K for PL and PL excitation (PLE) spectroscopy measurements. Standard lock-in amplifier techniques were used. The PLE was excited with 615–680 nm light from a Coherent CR-599 dye laser with DCM dye. The [110] cross-sectional TEM samples were prepared using standard argon-ion milling at 77 K. Dark-field images

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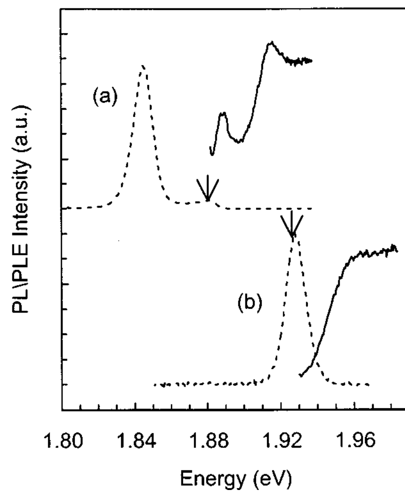

FIG. 1. PL (dashed lines) and PLE (solid lines) spectra for more ordered (a) and less ordered (b) GaInP single layers. The arrows indicate the PLE detection energy.

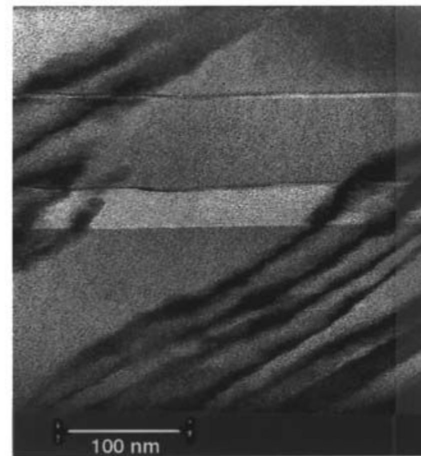

FIG. 2. Dark-field TEM image for the 6.5 nm GaInP D/O/D QW (thin bright region near the top). The 45 nm thick ordered region is also seen nearer the substrate.

from superspots were obtained using a JEM 2010 scanning TEM operated at 200 kV. The undoped single layers were measured by the van der Pauw method and were found to be *n* type with a carrier concentration of $\sim 10^{16}\,\mathrm{cm}^{-3}$ and a room-temperature Hall mobility of $\sim$2600 $\mathrm{cm^2/V\,s}$.

Figure 1(a) shows typical low-temperature PL and PLE spectra from an ordered $Ga_{0.52}In_{0.48}P$ single layer grown under the same conditions (V/III=480) as the well layers in the D/O/D QWs. There are two PL peaks. The low-energy peak shifts to higher energy with increasing excitation intensity at a rate of about 5 meV/decade in agreement with earlier reports.[13,14] The energy of the high-energy peak is nearly independent of excitation intensity. The PLE spectra show two excitonic absorption peaks due to valence-band splitting in ordered GaInP.[15,16] The difference of excitonic resonances from light and heavy holes is 26 meV. The band edge as defined by the heavy-hole excitonic resonance is 1.888 eV. The data are consistent with the results of Ernst *et al.*[15]

The PL and PLE spectra from a disordered single layer [Fig. 1(b)], grown under the same conditions (V/III=30) as the barrier layers in the D/O/D QWs, are different from the spectra in Fig. 1(a). There is only one PL peak at an energy about 0.02 eV lower than the absorption edge measured by PLE. The PL peak shifts to higher energy with increasing excitation intensity at a rate of about 1 meV/decade. This shift rate is similar to that previously attributed to conduction-band to acceptor recombination.[17] Attribution of the PL peak [Fig. 1(b)] from the disordered layers to conduction-band to acceptor recombination is supported by the growth conditions of the disordered layer. At low (high) V/III ratios there are more group V (III) vacancies. The group IV residual impurities would more likely sit on group V (III) sites and become acceptors (donors).[18] Ge and Si are typically the residual impurities in PH_3;[19] C is typically present due to the methyl radicals from the group III sources. Even though conduction-band to acceptor recombination dominates in the PL spectra for the disordered layers grown at the low V/III ratio, Hall-effect measurements indicate that the single layer is still *n* type. A comparison of the PLE spectra in Fig. 1 indicates that the band-gap energy from the single disordered layer is 0.06 eV greater than that from the single ordered layer.

Figure 2 shows the [110] TEM dark-field image from a D/O/D QW. The sample consists of a 270 nm barrier layer grown at $P_p = 0.75$ Torr, a 45 nm well layer grown at $P_p = 12$ Torr, another 90 nm barrier layer, a 6.5 nm well layer, and the top 90 nm barrier layer. In this dark-field image, the more ordered well layers are brighter. The interfaces between the ordered and disordered layers are well defined and abrupt. The dark stripes running diagonally through the image are antiphase boundaries,[20] i.e., interfaces between two ordered domains of the same variant with Ga and In ordering planes out of phase.

PL spectra from three D/O/D QW samples are shown in Fig. 3. Each shows a band-edge peak from the barrier layers as well as distinct peaks from the two QWs. The only difference in the spectra is in the peak originating from the thinner well, which varies in thickness from 4 to 10 nm in the three different samples. It is clearly seen that the PL peak energy

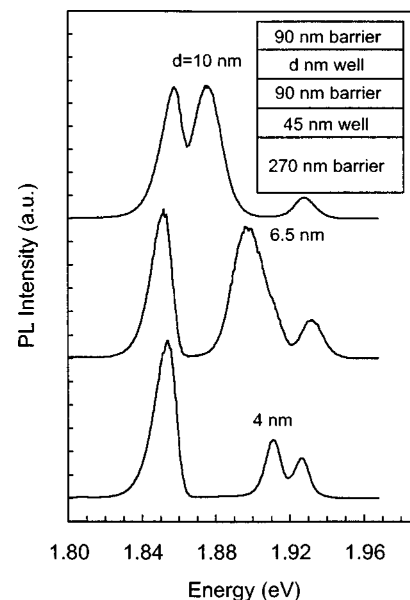

FIG. 3. 5 K photoluminescence spectra for GaInP D/O/D QWs. The PL peak at about 1.85 eV corresponds to the reference 45 nm well.

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from the QW increases with decreasing well width. The trend is consistent with the expected well-width dependence of the quantized energy in QWs. These PL spectra together with the TEM results definitively establish the existence of the quantum wells. The PL peak energies from the 10 and 45 nm QWs are lower than the highest peak energy ($\sim$1.88 eV) in Fig. 1(a), and hence, is lower than the band-gap energy of the more ordered single layer. This anomalously low energy has previously been attributed to a type-II band alignment between the two layers of the O/D heterostructure.[9]

In summary, by simply changing the input partial pressure of PH_3 during growth, GaInP D/O/D QWs have been successfully grown. The TEM dark-field images from the order-induced superspots show clearly defined, abrupt interfaces between the ordered and disordered layers. The 5 K PL peak energy from D/O/D QWs increases with decreasing well width. This is interpreted as due to the quantum confinement effect. The PLE spectra show that the band-gap difference between the ordered and disordered single layers is 0.06 eV. A discussion of the peak energies and other evidence for a type-II band alignment between ordered and disordered GaInP will be the subject of a future paper.

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