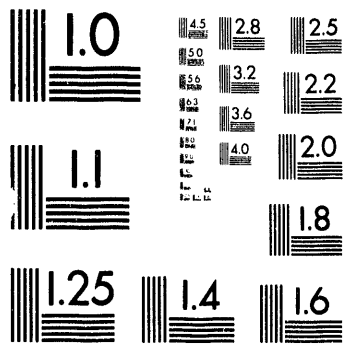
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ORDERING AND PHASE SEPARATION IN MOCVD InGaP ALLOYS AND UNICOMPOSITIONAL QUANTUM WELLS

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ABSTRACT

The microstructures of $In_{0.5}Ga_{0.5}P$ alloys grown on (100) GaAs by MOVPE have been characterized with cross-section TEM and their optical emission examined with photoluminescence at low temperatures. All the alloys exhibit spinodal-like decomposition with compositional modulations along directions in the growth plane. Alloys grown at 775°C have the highest emission energy, 2.0 eV, while those at 675°C have the lowest, 1.89 eV, due to strong CuPt-type ordering of In and Ga. The ordered domains are platelets 20 to 200 nm wide and 10-20 nm thick with antiphase boundaries 1-2 nm apart. We have also formed "unicompositional" quantum wells of thin (1.3-20 nm) ordered layers grown at 675°C between disordered barriers grown at 775°C. Ordering is found only in the active layer, with domains similar to those of thick layers. The emission energy increases by 90 meV as the well thickness is decreased from 10 to 1.3 nm, thus demonstrating quantum size effects solely through disorder-order phenomena.

INTRODUCTION AND APPROACH

Alloys of InGaP have the highest direct bandgap of ternary III-V systems, making them attractive candidates for optoelectronic devices operating in the visible range (green to red). Compositions of $In_{0.5}Ga_{0.5}P$ can be grown by metal organic vapor phase epitaxy (MOVPE) with a lattice constant matching that of GaAs. The optical emission energy of these alloys varies with growth temperature [1] and is lowest near 675°C [2]. It is now well established that the reduced energy is due to CuPt-type ordering of In and Ga on {111} planes, as confirmed with electron diffraction [3,4]. Our laboratory has previously examined the emission characteristics with photoluminescence (PL) as a function of growth temperature and substrate orientation [2]. In order to determine the microscopic origin of the PL variations and control them, we have characterized key alloys of that work with transmission electron microscopy (TEM) [4]. All the alloys exhibit contrast modulations like those of spinodally decomposed materials [5]. We find strong ordering for growth at 675°C but none for 750°C, consistent with the PL energies [2].

We have also used the growth-temperature dependence to form "unicompositional" disorder-order-disorder (DOD) quantum wells by growing thin ordered layers at 675°C between disordered "barrier" layers grown at 775°C [6]. We use dark-field TEM to demonstrate that the quantum well is indeed ordered and has a domain structure like that of thick layers. The PL energy of these structures increases with decreasing thickness of the ordered layer, consistent with quantum confinement of carriers in a low-energy well. The DOD quantum wells thus provide size quantization solely through order-disorder phenomena, and may give a unique perspective on optical transitions in nominally ordered material. More generally, our work shows that ordering can be an additional tool to tailor electronic properties of III-V alloys.

The alloys were grown using triethylindium, triethylgallium and phosphine in a low-pressure horizontal quartz reaction chamber with IR-lamp heating. Substrates were (100) GaAs or GaAs

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tilted 6° from (100) toward the nearest $<111>_A$. A pressure of 110 mbar and total flow rate of ~11 slm were used with a V/III ratio of ~150. These conditions gave a growth rate of 2.5 μm/hr. Growth temperatures between 600 and 775°C were used, and the ~1 μm-thick alloys cooled ~600°C in about 20 minutes. More details of the growth are given in Ref. [2]. X-ray diffraction showed that the alloys are lattice-matched to GaAs to within $\Delta a/a < 5x10^{-4}$, and the composition is thus deduced to be $In_{0.48}Ga_{0.52}P$. Dislocations were observed in a some layers on (100) GaAs, but may have been introduced during TEM specimen preparation. Numerous dislocations were observed in GaAs buffer layers grown on the tilted substrates prior to InGaP growth. Dislocations were not found at the alloy/substrate interfaces, and the alloys are believed to be fully coherent with the substrate. The PL energies were determined between 1.4 and 19 K by exciting with an Ar^+ laser (514 nm) at relatively low power densities (~1 w/cm^2) [2,6].

Cross-section transmission electron microscopy (XTEM) specimens were prepared by gluing two alloy surfaces together, cutting 3 mm disks and mechanically polishing them. Specimens from wafer pieces with no remaining orientation flats were prepared by rotating the two surfaces 90° to each other to insure that one of the two <011> orientations would contain the $<111>_B$ directions in the specimen plane, since ordering occurs only along them and not the $<111>_A$ [7,8]. The disks were "dimpled" by mechanically polishing with a rotating felt wheel and 1 μm diamond paste to a thickness of 15 μm. Specimens were ion milled with Ar until perforated, followed by additional milling with I_2 vapor present in order to remove In residue seen on specimens without this treatment. Curing the glue and mounting specimens with wax for dimpling required heating to 100°C for ~30 minutes and to 130°C for a total of ~30 minutes, respectively. Ion milling was done with some specimens at ambient temperature, which could rise to perhaps ~100°C, while others were on a cold stage in contact with liquid N_2 at 77 K.

SPINODAL-LIKE DECOMPOSITION

All alloys exhibit contrast like that of composition-modulated spinodal alloys. Bright-field images with $(02\bar{2})$ two-beam contrast and dark-field images using this reflection show light/dark modulations in the $[01\bar{1}]$ direction, as seen in Fig. 1 for a 750°C alloy. Spacings between modulations varied from tens to a few nanometers; finer spacings are more readily seen at higher magnification. Consistent with this variability, satellites due to the modulations were not detected around fundamental diffraction spots. The modulations are apparently not as periodic as those in spinodal metal alloys [5], other InGaP alloys [8] and InPSb alloys [9], which exhibit satellites, although the images are similar. Tilting 45° to [010] and imaging with (002) and (004) beams also showed modulations, but satellites were not detected. Thus a specific modulation direction was not identified in our alloys. In spite of the inhomogeneity seen in Fig. 1, this particular layer exhibited the narrowest PL peak ever observed in InGap alloys, 4.3 meV [4].

We use the term "spinodal-like" because this structure in III-V MOVPE alloys is thought to be formed by elemental segregation on the surface during growth, which becomes incorporated into the bulk. Such a mechanism differs from that of conventional spinodal alloys, which set up compositional fluctuations within the bulk to lower their free energy by separation into two phases [10]. Other work indicates that the modulations in (100) InGaP are along [010] and [001], which lie in the growth plane [8] and are elastically soft, preferred directions [11]. This has been interpreted to mean that decomposition occurs on the growing surface. However, that model seems to conflict with the observation of CuPt order in the same specimen (below), which is also thought to form on the growing surface. An alternative mechanism would be for alloys

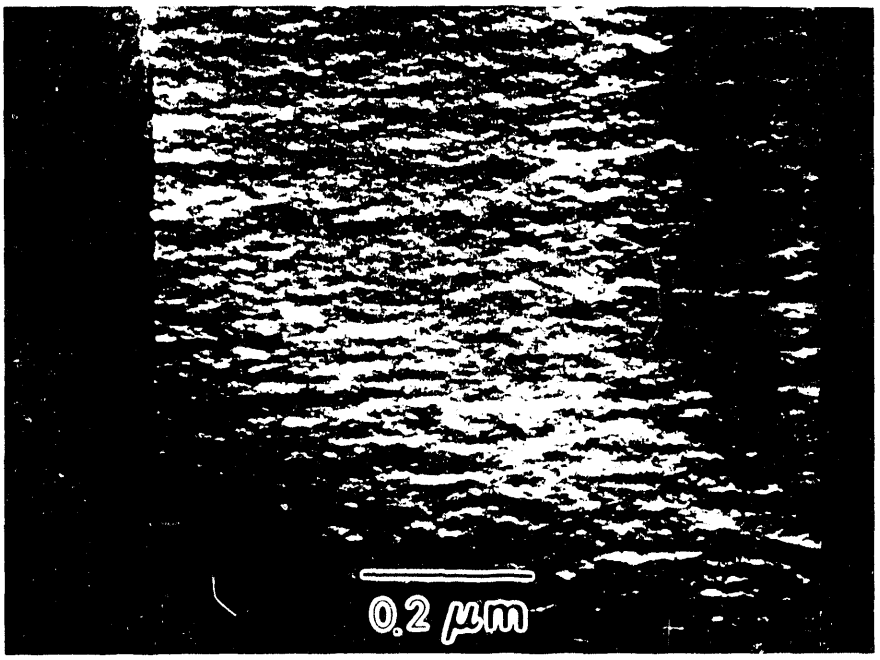
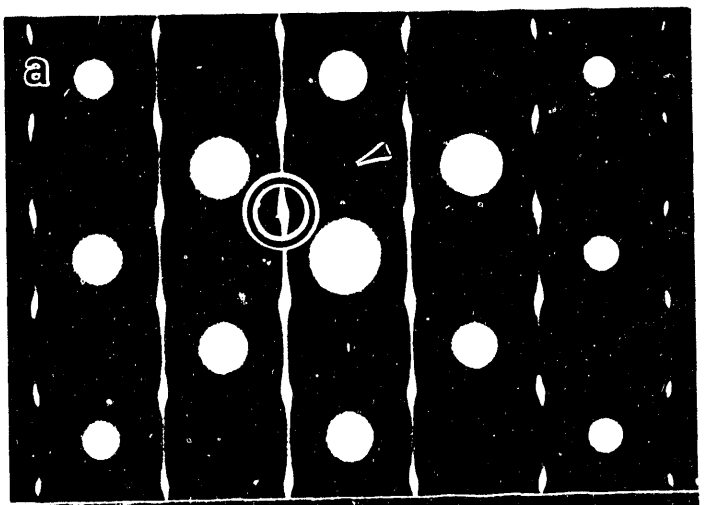
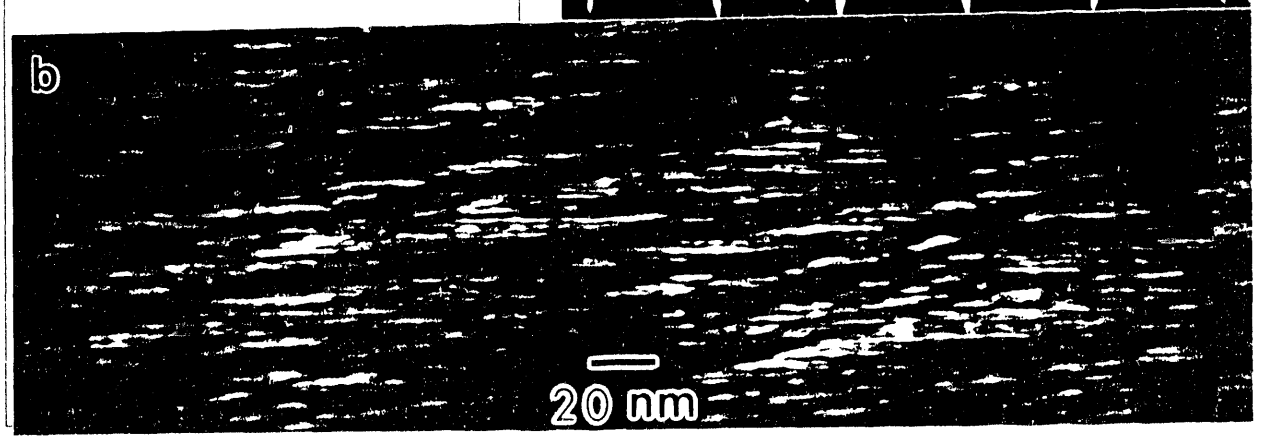


Figure 1. Dark-field (011) XTEM image of $In_{0.48}Ga_{0.52}P$ alloy grown by MOCVD at 750 C on GaAs (at left) obtained with (022) reflection, showing spinodal-like contrast modulations with 10 nm spacing. The large-scale contrast variations across the image are diffraction contours. (Specimen 0912d)

formed at 600-750 C to enter a two-phase spinodal regime and decompose throughout the layer during cooling or during subsequent heating to prepare TEM specimens. However, coherent spinodal decomposition is not expected at the temperatures of this work [12], and minimal bulk diffusion is expected at 130°C and even at the growth temperature [10]. Additional work is needed to specify precisely how this structure forms in MOVPE alloys.

Figure 2. a) Diffraction pattern from $In_{0.48}Ga_{0.52}P$ alloy grown by MOVPE at 675 C. Note the elongation of the ordering reflections and their tilt by ~8 from (100). b) Dark-field TEM image obtained with the ordering reflection circled in a). The domains show a fine structure of antiphase boundaries 1-2 nm apart. (Specimen 0923d).





MICROSTRUCTURE OF ORDERED DOMAINS

A diffraction pattern from the 675°C alloy is shown in Fig. 2a [4]. Elongated CuPt ordering reflections are seen at $\frac{1}{2}\{11\bar{1}\}$ (circled) and related positions for the two $<111>_B$ ordering variants. Quantification of electron diffraction intensities would be difficult; however, these reflections appear stronger than those of ordered InAsSb [13]. Dark-field imaging with the circled reflection illuminates the ordered domains, seen in Fig. 2b. The domains are platelets 10-20 nm thick with widths ranging from 20 to 200 nm; they are tilted by 7-12° from parallel to the growth surface, consistent with the slight tilt (see Fig. 2a) of the elongated ordering reflections from [100]. The domains also show a fine structure of dark lines 1-2 nm apart and parallel to the (100) growth surface, which we interpret to be antiphase boundaries (APBs). Thin APBs account for the streaks in the [100] direction passing through the ordering reflections in Fig. 2a.

Dark-field imaging with the other $<111>_B$ variant as well as lattice imaging show that the two sets of domains are interspersed. Their close association is also indicated by the very weak double diffraction spot at the (100) position (arrowed in Fig. 2a), which is produced by diffracting the beam first by one variant and then the other. Ordering is also believed to be produced at the surface during growth, which complicates interpretation of spinodal-like decomposition in the same specimen. The two metal elements are thought to occupy alternating dimer rows on the reconstructed (100) surface, with subsequent layers locking into a registry with their previous layer to form alternating Ga/In-rich $\{111\}_B$ planes in the group III sublattice [14]. The fine structure noted above (small domains, antiphase boundaries, and change between variants) indicate that the elemental alternation is laterally uniform over ~100 nm on the surface. The registry between subsequent layers is maintained for only ~2 nm. Weaker ordering reflections were detected in alloys grown at 600 and 725°C; these reflections are very elongated like those in Ref. [3]. Ordering was not detected at 750°C nor at 775°C (see below).

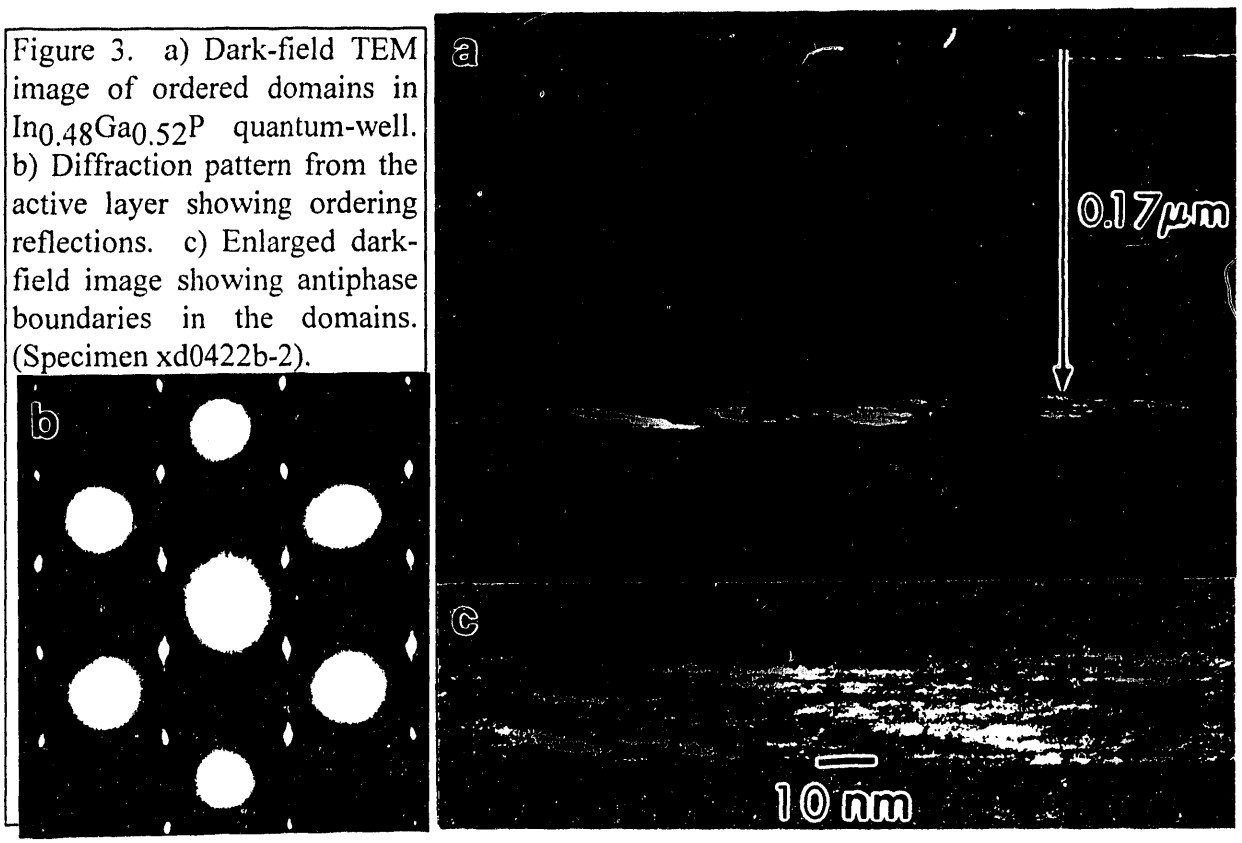


Figure 3. a) Dark-field TEM image of ordered domains in $In_{0.48}Ga_{0.52}P$ quantum-well. b) Diffraction pattern from the active layer showing ordering reflections. c) Enlarged dark-field image showing antiphase boundaries in the domains. (Specimen xd0422b-2).

UNICOMPOSITIONAL QUANTUM WELLS

The DOD quantum well structure was formed by first growing a layer of disordered $In_{0.5}Ga_{0.5}P$ on GaAs at 775°C. Growth was halted, the temperature lowered to 675°C and stabilized. A thin layer (1.3-20 nm) of the same composition was grown at 675°C using a growth rate ~4x slower to improve the greater degree of ordering. After stabilizing at 775°C, a second barrier layer of disordered material was grown. Because the quantum well and barrier layers have the same composition, we call this heterostructure a "unicompositional" quantum well.

Ordering is present in the lower-temperature layer and is limited to it, as demonstrated for the 20 nm layer in Fig. 3a, a dark-field image obtained with the ordering reflection circled in Fig. 3b. The ordered layer is illuminated at a depth of 0.17 μm below the surface. The illuminated width varied from 17 to 22 nm; this could indicate that some variations occurred in starting and stopping ordered growth, but the image could also vary in width because only one variant is imaged. The ordering reflections are weaker than in the corresponding figure for thick layers (Fig. 2a) because the quantum well is thinner than the selected area diameter (~250 nm) used to obtain the diffraction pattern. Higher-magnification, dark-field imaging of the ordered layer shows details of its domain structure as seen Fig. 3c. Domains 10-20 nm thick are seen, with antiphase boundaries ~1 nm apart. These features are essentially the same as those noted above for the thick alloy grown at 675°C. Based on these considerations, the active layer is thought to be about as well ordered as the thick layers. Imaging with the $(02\bar{2})$ reflection showed spinodal-like decomposition throughout this heterostructure, just as for thick alloys. No dislocations were observed between the ordered and disordered layers, nor at the interface with the GaAs substrate.

The TEM observations indicate that the above growth strategy produced an ordered active layer typical of 675°C layers with a reduced emission energy of ~1.9 eV, positioned between two disordered barrier layers [6]. The retention of order after growth of the (disordered) top layer for 4 min. at 775°C directly indicates that the highest temperature attained does not determine whether ordering will be present in InGaP. Ordered InGaP may not be the equilibrium phase, but it is stable at the higher temperature where it does not form during MOVPE.

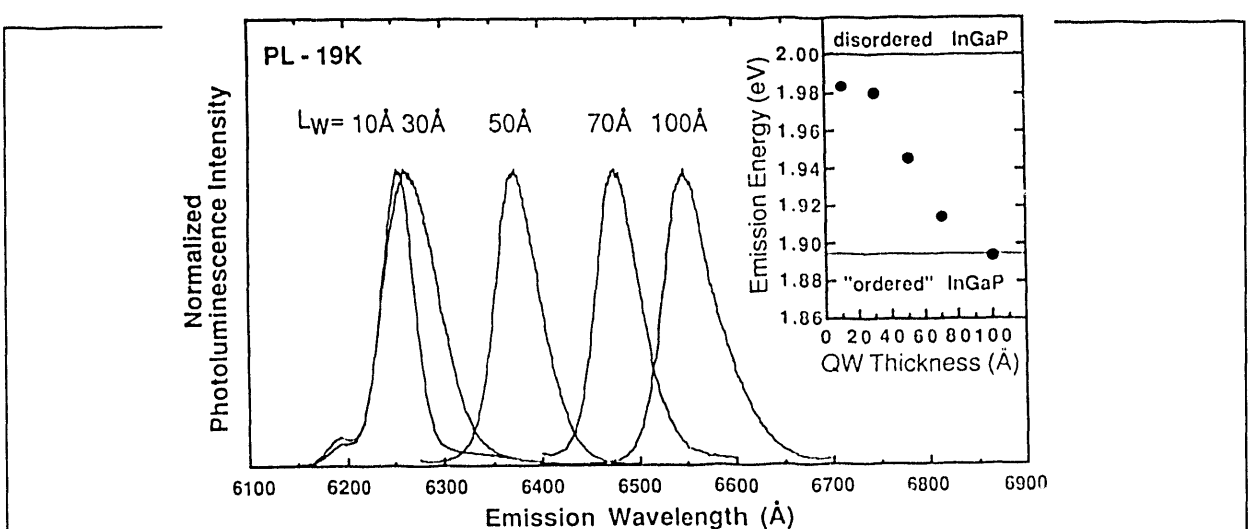


Figure 4. Normalized PL spectra showing increasing emission energies (shorter wavelengths) with decreasing DOD quantum well thickness. Inset: Increase of PL emission energy from that of the ordered alloy to near that of the disordered alloy with decreasing quantum well thickness.

Shown in Fig. 4 are PL spectra from DOD quantum wells and their peak emission energies plotted versus active layer thickness (inset). The thickest well (10 nm) has an emission energy of 1.89 eV as expected for a thick ordered layer. The energies of confined electrons and holes are expected to increase as the width of the confinement well decreases. As the DOD quantum well width decreases to 3 nm and lower, the PL energy increases to 1.98 eV, just below the energy of the 775°C disordered alloy, 2.00 eV. This increase demonstrates that carriers are confined in a lower-energy well of ordered alloy surrounded by barriers of disordered alloy.

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