

Kinetically controlled order/disorder structure in GaInP

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A $\text{Ga}_{0.52}\text{In}_{0.48}\text{P}$ order/disorder heterostructure having a band-gap energy difference exceeding 160 meV has been grown by organometallic vapor phase epitaxy. The two layers were grown on a nominally (001)-oriented GaAs substrate misoriented by 3° toward the $[\bar{1}10]$ direction in the lattice. The disordered layer was grown first, at a temperature of 740°C . The temperature was then reduced to 620°C for the growth of the second, highly ordered, layer. X-ray diffraction shows that the two layers have the same composition and are both lattice matched to the GaAs substrate. Transmission electron diffraction patterns indicate that the first layer is completely disordered and that the second layer is highly ordered with only one variant. A low density of antiphase boundaries is observed in the dark field transmission electron microscope image of the top (ordered) layer. High resolution images demonstrate that the interface is abrupt with no dislocations or other defects. Photoluminescence measured at 10 K shows two sharp and distinct peaks at 1.998 and 1.835 eV for high excitation intensities. The peak separation is even larger at lower excitation intensities. The two peaks come from the disordered and ordered materials, respectively. The peak separation represents the largest energy difference between ordered and disordered material reported to date. This large energy difference, much larger than kT at room temperature, may make such heterostructures useful for photonic devices such as light emitting diodes and lasers.

Atomic scale ordering, resulting in natural monolayer superlattice structures, is seen in a wide range of III/V alloys.¹ The Cu-Pt structure, with ordering on $\{111\}$ planes, is normally produced for growth on nominally (001)-oriented substrates. For epitaxial growth on exactly (001) substrates two variants are typically formed, i.e., some domains are produced with ordering on the $(\bar{1}\bar{1}1)$ planes and others on $(1\bar{1}1)$ planes. By misorienting the substrate to produce $[\bar{1}10]$ steps on the surface, single variant samples can be produced.¹⁻³

The ordering phenomenon is of fundamental interest in terms of the thermodynamics and kinetics of formation of the ordered structures. It is also of practical interest because ordering has major effects on the properties. For example, the Raman scattering is altered by ordering,⁴ indicating a change in the phonon states, as expected for a superlattice structure. More important for most devices are changes in the electron states, notably, the band-gap energy. In $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$, ordering is predicted to reduce the band-gap by 260 meV.⁵ Thus, ordering is of technological importance. Ordering is normally avoided in visible light emitting diodes (LEDs) and injection lasers in order to produce the highest emission energies.⁶ However, it has also been suggested that ordering might be useful for optoelectronic devices. For example, Lee *et al.*⁷ suggested a disorder/order/disorder $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ structure for visible LEDs. An order/disorder structure might also be useful for the fabrication of high efficiency solar cells.⁸ An advantage of this structure is that it does not use Al to increase the band-gap energy. Al is well-known to cause growth difficulties due to increased incorporation of residual oxygen and carbon⁹ for OMVPE growth, problems with the Al distribution coefficient for growth by liquid or vapor phase epitaxy,¹⁰ and difficulties with p -type doping in AlGaInP alloys.¹¹

Our recent studies indicate that kinetic factors can be

used to control ordering in GaInP.³ We have identified a set of conditions, using unusually low growth rates of $0.5\ \mu\text{m/h}$, for the growth of highly ordered and completely disordered materials on GaAs substrates misoriented by 3° in the $[\bar{1}10]$ direction. This raises the possibility that a structure having adjacent highly ordered and disordered materials can be grown by simply changing the growth temperature during growth.

In this article we demonstrate the growth of an order/disorder heterojunction by changing the temperature midway through the growth cycle. The measured band-gap energy change of $>160\ \text{meV}$ is much higher than reported previously. Such a large band-gap energy shift, of greater than $6\ kT$ at room temperature, might be the basis for useful device structures. We report the growth procedure and a detailed x-ray and transmission electron microscope structural analysis as well as photoluminescence results.

The $\text{Ga}_x\text{In}_{1-x}\text{P}$ layers were grown by OMVPE on (001), semi-insulating GaAs substrates misoriented by 3° in the $[\bar{1}10]$ direction. Substrate preparation consisted of standard degreasing followed by etching for 5 min in a 1% Br in methanol solution. The OMVPE growth occurred in a horizontal, infrared-heated reactor using trimethylgallium and trimethylindium in temperature controlled baths at temperatures of -9 and 25°C , respectively, using a Pd-purified hydrogen carrier gas. The group V sources were arsine and phosphine. The PH_3 partial pressure was always 2.3 Torr for the experiments described. The group III flow rate were adjusted at each temperature to give a growth rate of $0.5\ \mu\text{m/h}$ and a solid composition, x , of 0.52. A $0.15\ \mu\text{m}$ GaAs buffer layer was deposited first to improve the quality of the GaInP layers.

The bilayer structure, with growth of the first layer at 740°C and the second at 620°C , is shown schematically in Fig. 1(b). Growth was interrupted for 5 min between layers,

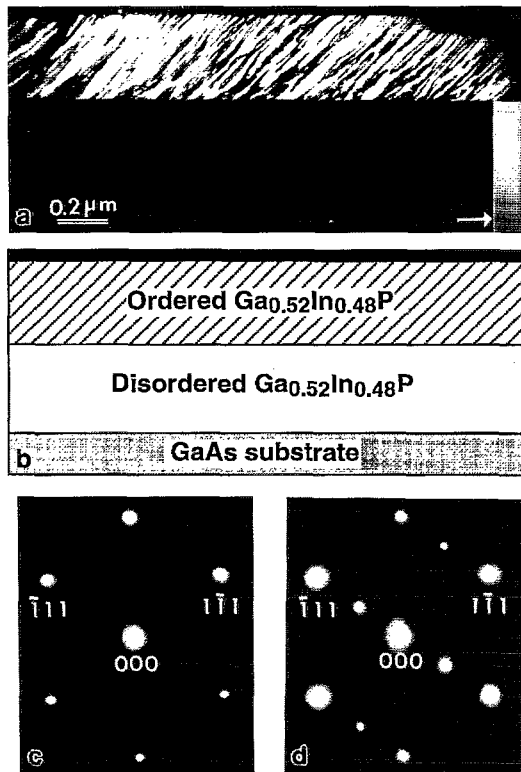


FIG. 1. (a) Dark field, cross-sectional image of the order/disorder heterostructure. The arrow indicates the GaAs/GaInP interface on an underdeveloped micrograph. (b) Schematic diagram for identification of the layers. (c) and (d) are the transmission electron diffraction patterns obtained with the electron beam entirely in the bottom and top layers, respectively.

by stopping the group III flows, to allow the change in temperature. The structure was characterized using x-ray diffraction, transmission electron microscopy (TEM), and photoluminescence (PL) measurements.

The x-ray diffraction measurements, using a Diano XRD 8000 diffractometer with $\text{Cu } K\alpha$ radiation showed a narrow (004) $\text{Cu } K\alpha_1$ - $K\alpha_2$ doublet. This indicates that the two layers have the same composition (within 0.5 at. %) with both closely lattice matched to the substrate.

[110] cross-sectional view TEM samples were prepared by cleaving two facets, glued face to face, and polishing mechanically followed by Ar-ion milling at 77 K to electron transparency. The transmission electron diffraction (TED) patterns and TEM images were obtained using a JEOL 200CX scanning transmission electron microscope operated at 200 kV. The TEM dark field image, made using the $1/2(113)$ superlattice spot, of the bilayer structure is shown in Fig. 1(a). The bottom layer, grown at a temperature of 740 °C to produce disordered material, has a thickness of 0.5 μm . The subsequent layer, grown at 620 °C to produce ordered material, has a thickness of 0.4 μm .

A TED pattern was taken with the electron beam entirely in the bottom layer. The result, shown in Fig. 1(c), indicates that the first layer is, indeed, completely disordered. No superlattice spots are seen. No trace of ordering was observed even when the negatives were carefully examined for faint superlattice spots. Moving the electron beam to the top layer



FIG. 2. High resolution TEM image of the interface of the order/disorder heterostructure obtained using the (000), $1/2(111)$, and $(\bar{1}11)$ diffraction spots. The difference in fringe spacings demonstrates that the ordered layer has twice the periodicity of the disordered layer. The arrow indicates the position of an anti-phase boundary.

yielded the TED pattern shown in Fig. 1(d). It indicates strong ordering with only one variant. Again, a careful examination of the negative shows virtually no diffraction due to the second variant. The faint streaking is caused by the presence of antiphase boundaries (APBs). The dark field image, Fig. 1(a), clearly shows the ordering in the top layer as well as the APBs. The high resolution TEM image of the interfacial region, Fig. 2, shows that the interface is abrupt, with no visible dislocations, stacking faults, or microtwins at the interface or propagating through the layer. This is consistent with the x-ray results showing that both layers are closely lattice matched to the substrate. However, an APB is clearly visible in Fig. 2. It originates exactly at the order/disorder interface.

The 10 K PL spectra were excited by the 488 nm Ar ion laser line, dispersed using a $\frac{1}{2}$ meter monochromator, and then detected with a Hamamatsu R1104 head-on photomultiplier using standard lock-in amplifier techniques. The spectrum for the order/disorder heterostructure, seen in Fig. 3, shows two narrow peaks. The high energy peak originates from the disordered region and the low energy peak from the ordered region, as determined by previous PL studies of individual layers¹² and high-resolution cathodoluminescence studies.¹³ For the highest excitation intensity, the peaks occur at 1.998 and 1.835 eV. This energy difference of >160 meV due to ordering is the largest reported.^{2,13-15} This is indica-

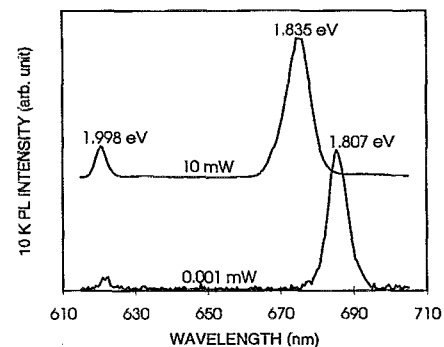


FIG. 3. 10 K PL spectra of the order/disorder heterostructure at high (10 mW) and low (0.001 mW) excitation intensities.

tive of the high degree of order in the top layer. The high energy peak is considerably less intense than the low energy peak. However, considering that the emission from the disordered layer must exit by passing through the smaller band-gap to layer before being collected, the ratio of peak intensities is not meaningful. It does, however, show the excellent quality of the ordered layer. The relatively narrow halfwidth of the emission from the ordered material also indicates that the ordering is relatively homogeneous.

Increasing the excitation intensity causes essentially no shift in the high energy PL peak. However, as noted previously,¹⁴ increasing the excitation intensity leads to a blue shift in the PL peak originating from the ordered material. The shift of approximately 6 meV/decade is typical of single variant ordered samples.¹⁴

Lee *et al.*⁷ previously reported the fabrication of a double heterostructure LED using undoped, ordered Ga_{0.5}In_{0.5}P, with a band-gap energy of 1.86 eV, as the active layer. The ordering was not investigated using electron microscopy, but the higher PL peak energy of their ordered material, as compared with the data presented here, is indicative of a lower degree of order. The growth temperature was 675 °C and the growth rate was not specified. The band-gap energy of the bottom cladding layer, grown at 730 °C, was not measured directly. However, they reported that the emission energy of a disordered LED is 1.896 eV, indicating that it may be partially ordered.

The band-gap offset in the heterostructure reported here is much larger than for the previous work.⁷ This is because today's more thorough understanding of the ordering process allows the growth of both more ordered and more disordered layers by proper selection of the growth parameters.

In summary, the OMVPE growth of an order/disorder GaInP heterostructure is reported. The growth rate of 0.5 μm/h on a GaAs substrate misoriented by 3° toward the [110] direction yields a disordered Ga_{0.52}In_{0.48}P layer for a high growth temperature of 740 °C. The TED pattern shows no order-induced spots. The second layer, grown at a lower temperature of 620 °C, is highly ordered. The TED pattern indicates that a single variant is formed. The dark field image shows widely spaced APBs. A high resolution image shows a planar, abrupt interface containing no defects other than the APBs, which are seen to originate at the order/disorder inter-

face. X-ray diffraction scans show that the two layers have the same composition. Photoluminescence measured at 10 K with a relatively high excitation intensity shows two sharp peaks at 1.998 and 1.835 eV, originating from the disordered and ordered materials, respectively. The difference of >160 meV represents the largest difference in band-gap energy due to ordering reported to date. The high energy peak remains virtually constant when the excitation intensity is decreased by 3 orders of magnitude, while the low energy peak moves to lower energy at a rate of 6 meV/decade. This type of heterostructure with a band-gap discontinuity of approximately 7 kT at room temperature, without the need for Al in the high band-gap layer, may be useful for photonic devices such as solar cells, LEDs, and lasers.

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