Effect of Substrate Misorientation on Ordering in $Ga_{0.5}In_{0.5}P$

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ABSTRACT

Ordering produced in $Ga_{0.5}In_{0.5}P$ epitaxial layers grown by OMVPE can be controlled by variations in the substrate misorientation as well as the growth temperature and the growth rate. The ordering produced at a growth temperature of 620°C and a relatively low growth rate of 0.5 μm/hr is found to depend strongly on both the direction and angle of substrate misorientation. Transmission electron microscope images and transmission electron diffraction (TED) patterns as well as electrostatic force microscopy (EFM) and photoluminescence (PL) has been studied for misorientation angles of 0, 3, 6, and 9° from (001) toward the (111)B, (111)A, and [010] directions in the lattice. Misorientation in the (111)B direction (to produce [110] steps) increases ordering for angles of up to approximately 4°. Increasing the misorientation angle in the (111)A direction actually leads to a decrease in the degree of order observed. Misorientation in the [010] direction also decreases the degree of order, although the effect is much less than observed for misorientation in the (111)A direction. The most highly ordered material produced under these growth conditions is for a misorientation angle of 3° in the (111)A direction. Increasing the growth temperature to 720°C produces completely disordered material. This wide variation in ordering behavior has allowed the growth of an order/disorder heterostructure for a substrate misorientation of 3° in the (111)A direction. The heterostructure consists of a $Ga_{0.52}In_{0.48}P$ layer grown at 740°C followed by an ordered layer grown at 620°C. The x-ray diffraction results show that both layers are precisely lattice-matched to the GaAs substrate. TED patterns show that the first layer is completely disordered and the top layer is highly ordered, with only a single variant. EFM images of the order/disorder heterostructure show a pronounced contrast at the interface, attributed to the large difference in the nature of the surface states in the ordered and disordered materials. The 10 K PL spectrum consists of two sharp and distinct peaks at 1.995 and 1.830 eV from the disordered and ordered materials, respectively. The peak separation represents the largest energy difference between ordered and disordered materials reported to date. Such heterostructures may be useful for photonic devices.

INTRODUCTION

Atomic scale ordering, where a natural, monolayer superlattice is formed at the surface during vapor phase epitaxial growth is observed for a wide range of III/V alloys[1]. Epitaxial growth of III/V alloys on nominally (001)-oriented substrates yields the Cu-Pt structure, with ordering on {111} planes, for many growth conditions. Of the 4 possible variants, with ordering on the 4 sets of {111} planes, only 2 are observed. Misorientation by a few degrees in the (111)B direction, to introduce [110] steps on the surface has been reported to result in the formation of only one variant[1]. The properties of semiconductor alloys are altered by ordering. For example, the bandgap energy of $Ga_{0.52}In_{0.48}P$, lattice matched to GaAs, is predicted to decrease by 260 meV[2]. Thus, ordering must be avoided to obtain the shortest wavelength visible light-emitting diodes (LEDs) and injection lasers[3]. However, it has been suggested that a mostly disordered layer could be a desirable window layer for the partially ordered GaInP in solar cells[4]. Similarly, Lee et al [5] have reported the use of a disorder/order/disorder structure for a double heterostructure LED. An advantage of a heterostructure using ordering to control the bandgap energy is that the high bandgap layer does not contain Al. The use of Al causes growth difficulties due to the high reactivity of aluminum with oxygen and carbon. High level p-type doping is also found to be difficult in AlGaInP alloys[6].

Recent studies indicate that kinetic factors control the degree of order produced during epitaxial growth of GaInP alloys[1,7-9]. Thus, variations in growth parameters such as growth rate, temperature, and substrate misorientation can determine the degree of order in the alloy. Decreasing the growth rate would be expected to increase the degree of order, since more time is allowed for

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the atoms to find the lowest energy, ordered configuration. The decrease in order associated with an increase in growth rate has clearly been demonstrated for growth rates of from 4 to 12 μm/hr [10]. However, at lower growth rates other phenomena become important. For example, at 670°C decreasing the growth rate from 4 to 1 μm/hr results in a decrease in the degree of order[7]. Also for misorientation angles of greater than 6°, the degree of order is decreased by increasing the angle of misorientation, Θ_m. These effects are postulated to be due to annealing during growth[7-9]. Disordering due to annealing can be avoided by growth at lower temperatures, such as 570°C[8].

This paper explores the ordering produced at a growth temperature of 620°C and a growth rate of 0.5 μm/hr for nominally (001)-oriented substrates misoriented by angles of 0, 3, 6, and 9° toward each of three directions in the lattice: (111)A, (111)B, and [010], midway between. For small misorientation angles in the (111)B direction, the presence of [110] steps on the surface leads to increased ordering. For larger misorientation angles, the samples become more disordered. The presence of [$\bar{1}$10] steps appears to inhibit ordering. Thus, the most highly ordered material was grown on substrates misoriented by 3° in the (111)B direction. Increasing the growth temperature to 720-740°C results in totally disordered material. This large change in order parameter with substrate temperature is used to grow an order/disorder heterostructure. A difference in band gap energy of >160 meV was observed. This is the largest difference in bandgap energy between ordered and disordered material reported for GaInP. The EFM image shows a sharp contrast between the ordered and disordered materials.

EXPERIMENTAL

The $Ga_xIn_{1-x}P$ layers were grown by organometallic vapor phase epitaxy (OMVPE) on (001), semi-insulating GaAs substrates substrates misoriented by angles of 0, 3, 6, or 9° in either the (111)A, (111)B or [010] direction. Substrate preparation consisted on 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 (TMGa) and trimethylindium (TMIn) in temperature controlled baths at temperatures of -9 and 25°C, respectively, using a Pd-purified hydrogen carrier gas. The group V sources were 100% arsine and phosphine. The PH_3 partial pressure was always 2.3 torr for the experiments described here. The TMGa and TMIn flow rates were adjusted at each temperature to give a growth rate of 0.5 μm./hr and a solid composition, x, of 0.52. A 0.15 μm GaAs buffer layer was deposited first to improve the quality of the GaInP layers.

A bilayer structure was grown with the first layer grown at 740°C and the second at 620°C. Growth was interrupted for 5 minutes between layers, by stopping the group III flows with the phosphine partial pressure unchanged, to allow the change in temperature.

The layers were characterized using x-ray diffraction, using Cu K_a radiation. [110] cross-sectional view transmission electron microscopy (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.

For the EFM measurements, the sample is mounted on a piezoelectric scanner using a tungsten wire tip attached to a reflective glass cantilever. The cantilever serves as a mirror, and is glued to a piezoelectric bimorph element used to produce a vibration of the tip at its resonant frequency. As the tip approaches the sample, the force gradient of the tip-sample interaction modifies the effective spring constant of the cantilever, resulting in a resonant frequency shift. The feedback signal necessary to maintain a constant frequency is used to represent the topography of the sample surface. To electrostatically probe the sample surface, an A.C. voltage is applied to the tip.

10K photoluminescence (PL) measurements were performed by exciting with the 488 nm Ar ion laser line, dispersing the emitted radiation using an 1/2 meter monochromator, and then detection with a head-on photomultiplier using standard lock-in amplifier techniques.

RESULTS AND DISCUSSION

The nominally (001) oriented GaAs substrates were misoriented toward the (111)B direction in the lattice by angles of 0, 3, 6, and 9°. The resulting microstructures were presented in ref[11]. For a perfectly (001) substrate, two variants are produced with relatively small domain sizes. A high density of both antiphase boundaries (APBs) and order twins is observed. Increasing the misorientation angle to 3° or larger results in formation of only one variant. No order twins are observed in these samples and the APB spacing increases steadily as the angle of misorientation increases[7,8,11]. The 10K PL spectra for the sample with $\Theta_m = 3°$ at several excitation intensities are shown in Fig. 1. The spectra consist of a single peak that moves to higher energy with increasing excitation intensity. This is consistent with the PL spectra measured for growth at 670°C on substrates misoriented toward the (111)B direction[11].

In an earlier paper, we reported a good correlation between the PL peak energy and degree of order determined from the super spot intensities[7]. This is consistent with earlier work by other groups[13]. Comparing samples with the same composition, the energy of the PL peak is seen to decrease as the degree of order increases. From the plot of PL emission peak energy versus θ_m, Fig 2, the degree of order is seen to increase as the misorientation angle toward $[\bar{1}10]$ is increased from 0 to 3°. This is similar to earlier results[7] obtained at 670°C for growth rates of 1 and 2 μm/hr. Further increases in the misorientation angle result in an increased PL peak energy. Judging from the line representing a best fit to the data the maximum degree of order occurs for a value of θ_m of approximately 4°.

For substrates misoriented from (001) toward the (111)A direction, the TED patterns indicate the formation of two variants with a low degree of order. The intensity of the super spots appears to decrease monotonically with increased angle of misorientation. This is confirmed by the steady shift of the PL peak to lower energy with increasing θ_m, seen in Fig. 2. These data seem to indicate that the presence of the $[\bar{1}10]$ steps either decreases the rate of ordering during growth or increases the rate of annealing to produce disordered material. The intensities of the order spots are too weak to allow useful dark field images to be obtained.

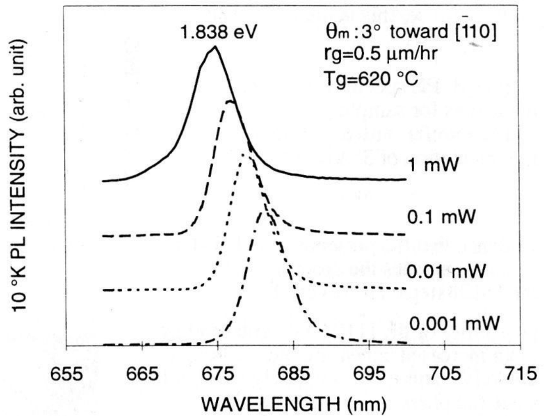


Figure 1: PL spectra for 4 excitation intensities for sample grown at 620°C and 0.5 μm/hr with an angle of misorientation of 3° in the (111)B direction.

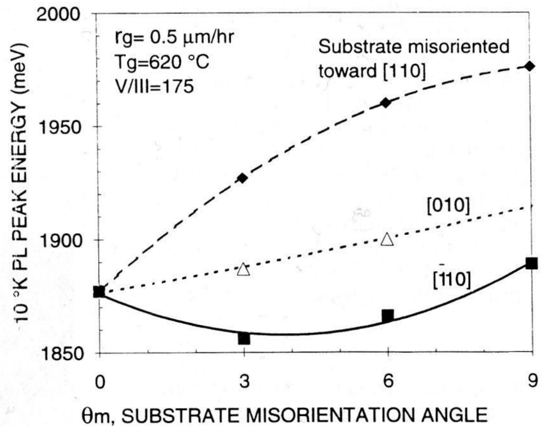


Figure 2: PL emission peak (excitation = 10 mW) versus θ_m for 620°C, 0.5 μm/hr layers misoriented in the (111)A, (111)B, and [010] directions.

The effect of $[\bar{1}10]$ steps is further clarified by examining the effects of misorientation in the [010] direction by angles of 3 and 6°. This presumably produces zig-zag steps with sections having the [110] orientation adjacent to $[\bar{1}10]$ sections. Again, the TED intensities for these samples are relatively weak. However, the degree of order appears to decrease with increasing misorientation angle. From the PL peak energies, plotted in Fig. 2, the degree of order is clearly seen to decrease with increasing misorientation angle. Again, since the ordering is much less than that expected from the [110] steps on the surface, this is interpreted as evidence that the presence of $[\bar{1}10]$ steps actually impedes the ordering effects of the [110] steps. However, the possibility of the $[\bar{1}10]$ segments leading to an increased annealing rate, although unlikely, cannot be completely ruled out, since the phenomenon is not well understood.

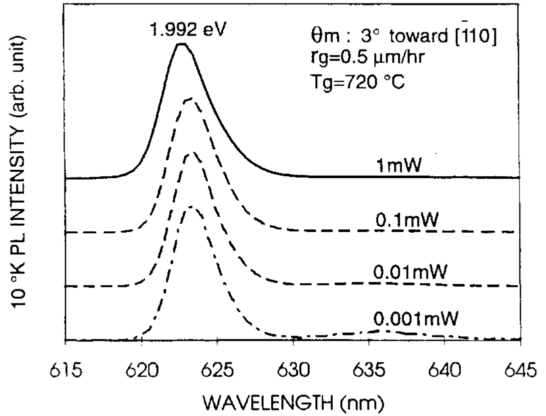
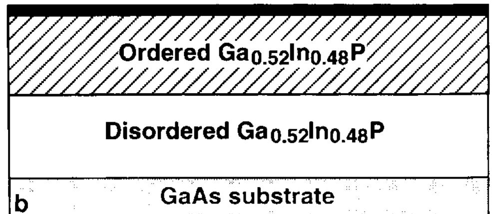


Figure 3: PL spectra for 4 excitation intensities for sample grown at 720 C and 0.5 μm/hr with an angle of misorientation of 3° toward (111)B.

Taken together, the PL data in Fig. 2 show that the most highly ordered sample was the one grown with a substrate misoriented by 3° in the (111)B direction. This sample is also more highly ordered than samples grown at 570°and 670°C at a rate of 0.5 μm/hr[8]. The ordering is also apparently slightly greater than for samples grown at higher rates of 1-4 μm/hr[7].

Growth at 720°C at 0.5 μm/hr yields material that is completely disordered, judging from the absence of spots in the TED pattern. The PL of a sample grown on a substrate misoriented by 3° in the (111)B direction is shown in Fig. 3 as a function of excitation intensity. The energy of the single peak at 1.992 eV is



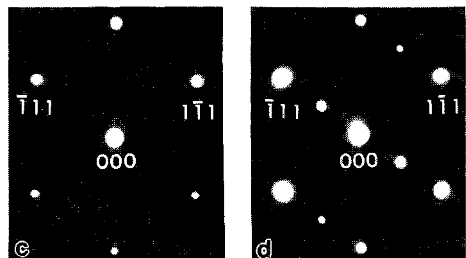


Figure 4. (a) Dark field and (b) schematic image of the order/disorder heterostructure. The arrow, on an under-exposed micrograph, indicates the GaAs/GaInP interface. (c) and (d) are the TED patterns for the bottom and top layers, respectively.

seen to be virtually independent of excitation intensity.

The large difference in degree of order between the layers grown at 720-740 and 620°C, with otherwise identical growth conditions, was exploited to produce an order/disorder heterostructure. A schematic diagram of the resultant structure is shown in Fig. 4(b). The corresponding TEM dark field image is shown in Fig. 4(a). The bottom layer, grown at 740 C to produce disordered material, has a thickness of 0.5 μm. The subsequent layer, grown at 620 °C to produce highly ordered material, has a thickness of 0.4 μm. The x-ray diffractometer scan for this structure shows a single, narrow Cu $K_{\alpha1}$-$K_{\alpha2}$ doublet, indicating that the compositions of the two layers are the same to within the 0.5 atomic % measurement accuracy. The TED patterns shown in Fig. 4 (c) and (d) indicate that the first layer is completely disordered and the top layer is highly ordered, with only one variant. The 10 K PL spectrum seen in Fig. 5 shows two narrow peaks. The position of the high energy peak is virtually independent of excitation intensity. The low energy peak shifts slowly to higher energy with increasing excitation intensity. From a comparison with the behavior of the PL from the individual layers, discussed above, the peaks can be identified. The high energy peak originates from the disordered region and the low energy peak from the ordered region. For the highest excitation intensity the peaks occur at 1.995 and 1.830 eV. This energy difference of 160 meV is due to ordering. It is the largest effect of ordering on the bandgap energy reported to date[11,14]. This is indicative of the high degree of order in the top layer.

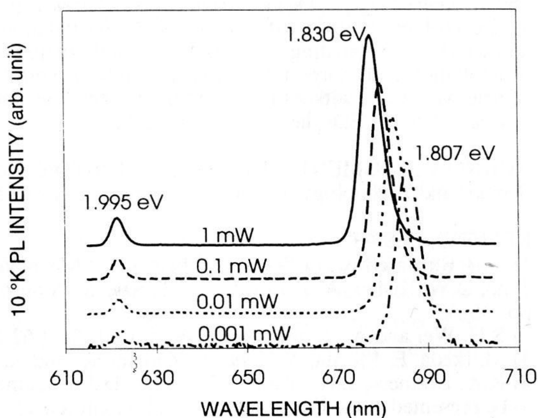


Figure 5. 10K PL spectra of the order/disorder heterostructure at 4 excitation intensities.

The ordered and disordered regions are clearly seen in the EFM image of the cross section of the order/disorder heterostructure. The high contrast observed in this A.C. measurement is believed to be due to a difference in the surface states of the various materials. The Fermi level appears to be pinned at the surface for the ordered material and to be unpinned for the disordered material[15]. The image also indicates that the Fermi level is pinned in the GaAs substrate, as expected. The reason for this remarkable difference in the surface states is not understood at the present time.

SUMMARY

In summary, the OMVPE growth of GaInP has been investigated at a low growth rate of 0.5 μm/hr for growth temperatures of 620 and 720-740°C. The emphasis has been on an investigation of the effect of the direction and angle of misorientation from the (001) plane on the ordering process. Misorientation to produce $[\bar{1}10]$ steps or kinks is found to decrease the degree of order. On the other hand, misorientation to produce [110] steps increases the degree of order for small misorientation angles. The highest degree of order is obtained for the sample with a misorientation angle of 3°. Growth at a temperature of 720°C at a growth rate of 0.5 μm/hr on a substrate with the same misorientation results in completely disordered material. An order/disorder heterostructure was produced by changing the growth temperature from 740 to 620°C during growth, with other growth conditions remaining the same for the two layers. X-ray diffraction results show that the two layers are both lattice matched to the GaAs substrate. The TED patterns shows no order-induced spots for the layer grown at 740°C and strong ordering, with one variant, for the layer grown at 620°C. The TEM dark-field image confirms that the structure is an order/disorder

heterostructure. EFM images of the heterostructure shows a marked contrast between the ordered and disordered layers. This is attributed to differences in the surface states for the two materials. 10K photoluminescence with a relatively high excitation intensity shows two sharp peaks at 1.995 and 1.835 eV, originating from disordered and ordered layers, respectively. The energy difference of >160 meV is the largest difference in bandgap energy due to ordering reported to date. This type of heterostructure, without the need for Al in the high bandgap layer, may be useful for photonic devices such as LEDs, lasers, and solar cells.

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