Control of ordering in $Ga_{0.5}In_{0.5}P$ using growth temperature

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The kinetic processes leading to ordering in $Ga_{0.52}In_{0.48}P$ have been studied by observing the effects of substrate misorientation (0°–9°), growth rate (0.1–0.5 μm/h), and substrate temperature (570–670 °C) during growth. The ordered structure and degree of ordering are determined using transmission electron microscopy and photoluminescence (PL) spectroscopy. Low growth rates were used for samples with misorientations of 0°–9° toward the [$\bar{1}$10] lattice direction to elucidate the ordering mechanism; however, due to the long times required to grow layers thick enough for PL characterization (≈1 μm), at a temperature of 670 °C the samples became less ordered with increasing misorientation angle. This was attributed to a disordering annealing process occurring during growth which leads to disorder. In order to reduce the rate of this annealing process, the growth temperature was reduced from 670 to 570 °C. At this temperature, a growth rate of 0.5 μm/h produces material with an increasing degree of order as the angle of substrate misorientation is increased from 0° to 9°. This shows that the kinetics of the ordering process are assisted by an increasing density of [110] steps on the surface.

I. INTRODUCTION

Atomic-scale ordering is a topic of increasing interest both for fundamental studies of the thermodynamic and kinetic aspects of the phenomenon itself, and for practical applications of ordering for the control of the properties of semiconductor alloys. This phenomenon, which involves the formation of natural, monatomic superlattices during epitaxial growth,[1] is observed for virtually all III/V semiconductor alloys as well as for Ge-Si alloys. Ordering is predicted[2] and experimentally observed[3] to result in a decrease in the bandgap energy for III/V alloys, notably GaInP. Thus, control of this phenomenon is vitally important for devices such as GaInP (and AlGaInP) high-efficiency solar cells[4] and visible laser diodes.[5]

The thermodynamic driving force for ordering is understood mainly from theoretical studies. In III/V alloys, all of which have positive values of the enthalpy of mixing,[6] the ordered structure is stable only at the surface. Annealing studies[7] support the results of calculations indicating that the ordered structure is not stable in the bulk at ordinary growth temperatures.

The Cu-Pt structure, with ordering on the {111} plane, is most commonly observed for III/V alloys grown on nominally (001)-oriented substrates. The stability of the Cu-Pt-ordered structure at the surface during epitaxial growth is believed to be determined by the surface reconstruction.[8] Surface reconstructions involving the formation of group-V dimers apparently lead to the formation of the ordered structures by the motion of [110]-oriented bilayer steps across the surface.[1]

The detailed formation mechanism and kinetics of ordering during epitaxial growth are not well understood; however, ordering is found experimentally to depend on the surface structure, mainly determined by the exact orientation[1,9] and the growth parameters such as the growth rates,[10,11] substrate temperature,[11] and V/III ratio.[12]

At normal growth temperatures for GaInP, 650–670 °C, two competing kinetic phenomena are observed to determine the degree of order[11,13]: the ordering process occurring at the surface and an annealing process occurring below the surface. The latter dominates at high growth temperatures and at low growth rates, since the annealing time is increased.

The purposes of this study are to verify the importance of the annealing effect during organometallic vapor-phase-epitaxial (OMVPE) growth and to obtain better information on the effects of growth rate and the degree of substrate misorientation on the kinetics of ordering for $Ga_{0.52}In_{0.48}P$ grown on nominally (001)-oriented GaAs substrates. To do this, a very low growth rate of 0.1 μm/h, much lower than normally used for OMVPE growth, was used at a growth temperature of 670 °C to enhance the surface processes leading to ordering. In addition, a lower growth temperature of 570 °C was used to suppress disordering due to annealing at the low growth rates employed. The spacing of [110] steps on the surface is varied using substrate misorientations ranging from 0° to 9° in the [$\bar{1}$10] direction.

II. EXPERIMENT

The $Ga_{0.52}In_{0.48}P$ epitaxial layers were grown by OMVPE on nominally (001)-oriented semi-insulating GaAs substrates. For many runs the substrates were intentionally misoriented (with an accuracy of ±0.5°) by angles of 3°, 6°, and 9° in the [$\bar{1}$10] direction. Directly before growth the substrates were degreased and then etched in a 1% bromine-in-methanol solution for 5 min. They were then rinsed in methanol and blown dry with N_2, after which they were loaded into the quartz reactor tube.

A horizontal atmospheric pressure OMVPE reactor was used in this study. The source materials were trimethylgallium (TMGa at −9 °C), trimethylindium (TMIn at 25 °C), carried by Pd-diffusion hydrogen with a flow rate of 4 slm, and phosphine. For layers grown with r_g=0.5 μm/h, two growth temperatures, 670 and 570 °C, were used with a con-

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stant phosphine pressure of 2.3 Torr. Since the growth efficiency is somewhat lower at 570 °C, the group-III flow rate was increased to obtain the desired growth rate. This yields two values for the input V/III ratio of 220 and 145 at the two temperatures. For a layer grown with $r_g = 0.1$ μm/h, a mass flow controller with full scale value of 1 sccm was used since the input molar flow rate of the TMGa must be very low. The growth temperature, phosphine partial pressure, and V/III ratio were 670 °C, 4.5 Torr, and 2000, respectively. A 0.15–0.2 μm GaAs buffer layer was deposited first, using TMGa and arsine, to improve the quality of the GaInP layers.

The surface morphologies of the GaInP epilayers were observed using a Nomarski differential interference contrast optical microscope. The growth rate was calculated from the growth time and the epilayer thickness measured using a scanning electron microscope. The composition of the GaInP layers was determined by a Diano XRD 8000 x-ray diffractometer with CuK_α radiation. The 2θ position of the (004) peak for the epilayer relative to that of the GaAs substrate was used to determine the lattice constant and, using Vegard's law, the solid composition. For misoriented substrates, a sample holder with a goniometer was used to properly orient the substrate.

[110] cross-sectional view transmission electron microscope (TEM) samples were prepared by cleaving two facets, glued face to face, and polishing mechanically. The samples were then 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 10 K photoluminescence spectra were excited by the 488 nm Ar-ion laser line, dispersed using a $\frac{1}{2}$ m monochromator, and then detected with a Hamamatsu R1104 head-on photomultiplier using standard lock-in amplifier techniques.

III. RESULTS

A. Growth at 670 °C and 0.5 μm/h

The first experiments to be described involve the use of low growth rates at the "normal" growth temperature of 670 °C, used in many earlier studies, including our own.[13] For a growth rate of 0.5 μm/h and a misorientation angle of 0° the TED pattern, Fig. 1(a) shows the presence of the both the $(\bar{1}11)$ and $(1\bar{1}1)$ variants of the Cu-Pt structure. The superlattice spots are nearly circular, more so than for comparable growth conditions at a growth rate of 1 μm/h reported in Ref. 13, indicating a fairly large spacing between antiphase boundaries (APBs). The pronounced [001] streaking is indicative of the presence of closely spaced (001) order twin boundaries.[13,14] In the dark-field TEM image for this

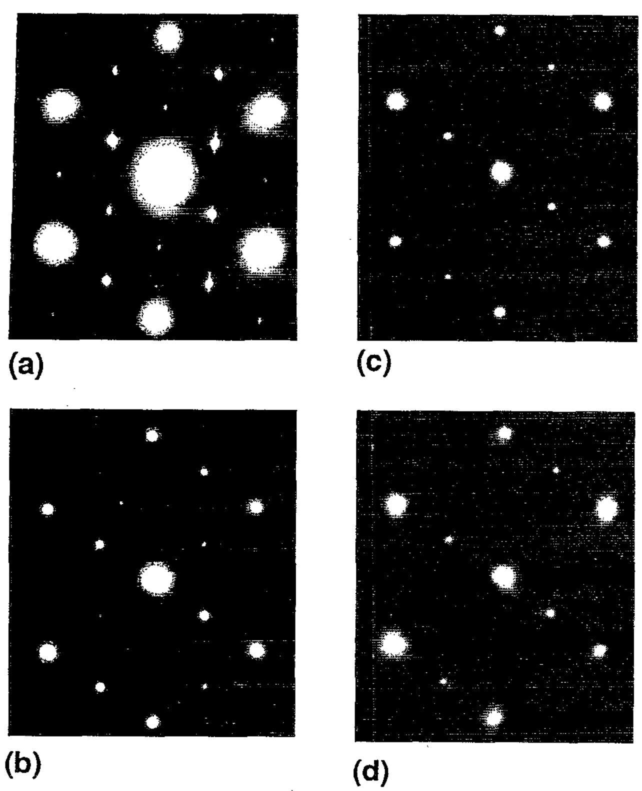

FIG. 1. TED patterns for $Ga_{0.52}In_{0.48}P$ layers grown at 670 °C with a growth rate of 0.5 μm/h. The substrates were misoriented by angles of (a) 0°, (b) 3°, (c) 6°, and (d) 9°.

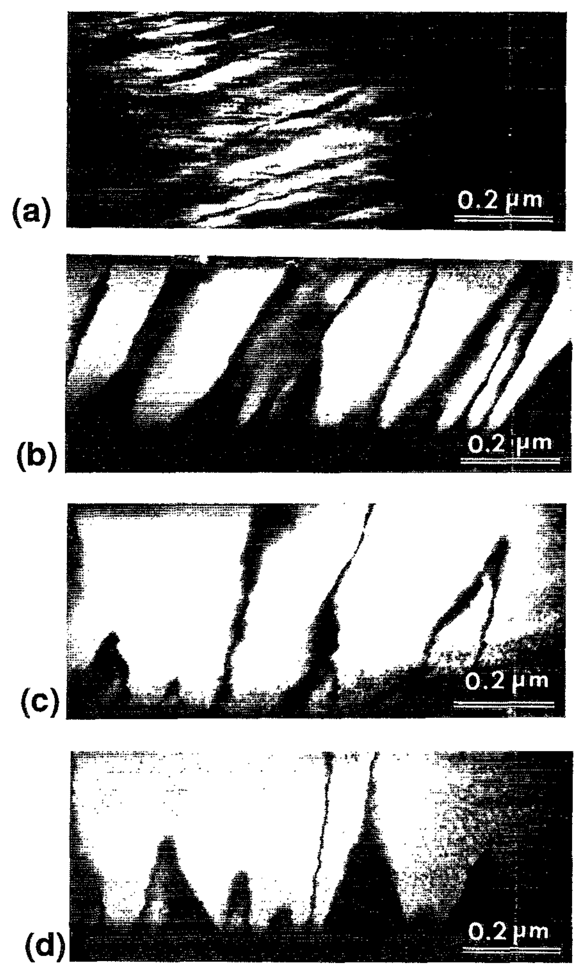

FIG. 2. TEM dark-field images for $Ga_{0.52}In_{0.48}P$ layers grown at 670 °C with a growth rate of 0.5 μm/h. The substrates were misoriented by angles of (a) 0°, (b) 3°, (c) 6°, and (d) 9°.

sample, shown in Fig. 2(a), APBs are seen with an orientation sharply angled from the vertical direction. The order twin boundaries, lying in the (001) plane, are barely visible.

Misorienting the substrate by 3° in the [$\bar{1}$10] direction results in a structure still containing two variants, as seen in Fig. 1(b), although the intensity of one set of superlattice spots is considerably weakened, indicating that the [110] surface steps favor the formation of the ($\bar{1}$11) variant. As seen by comparing the TEM dark-field images in Figs. 2(a) and 2(b), the presence of [110] steps dramatically increases the APB spacing. The [001] streaking and associated order twin boundaries are completely absent for this sample.

Misorientation by $\theta_m = 6°$ results in the complete elimination of the (1$\bar{1}$1) variant, as seen in Fig. 1(c). The TEM image of this sample, seen in Fig. 2(c), shows large, well-defined domains separated by APBs that are becoming nearly perpendicular to the substrate, as reported previously for other growth rates.[13] As seen in Fig. 3, the growth rate has little effect on the misorientation angle. The lateral dimensions appear to be larger than for samples grown under similar conditions at higher growth rates,[13] as expected from the comparison between growth rates of 4, 2, and 1 μm/h. The domain size is plotted versus misorientation angle for various growth rates, including 0.5 μm/h, in Fig. 4.

As expected, for a substrate misorientation of 9°, a single set of nearly circular superlattice spots is observed, Fig. 1(d). The degree of order appears to be lower for this sample than for the samples with values of θ_m of 3° and 6°, similar to results presented in Ref. 13 for growth rates of 4, 2, and 1 μm/h. From the TEM image in Fig. 2(d), the domain size is seen to be larger than for the 6° misorientation and the APBs are nearly perpendicular to the (001) plane. Data for these samples are also contained in Figs. 3 and 4.

The photoluminescence (PL) peak energy, measured at 10 K, is plotted versus the angle of substrate misorientation in Fig. 5. For these samples, all grown using the same conditions and with compositions within 0.5% of the lattice-matched composition, the PL peak, and hence the band-gap energy, steadily increases with increasing misorientation angle. Since the band-gap energy is known to decrease with increased degree of order,[9,13,15,16] this indicates that increasing θ_m leads to a decrease in the degree of order. A comparison of these results with those published in Ref. 13 for higher growth rates, indicates that the reduced growth rate has led to a decrease in ordering. This might be attributed to the effects of annealing during growth, for the increased growth times as described above. The effect of misorientation angle on this disordering effect is not well established; however, preliminary results of Williams, Jen, and Meehan[17] indicate that the disordering rate during annealing is larger for samples with larger domain sizes. This would be consistent with an increasing disordering rate for higher values of θ_m.

B. Growth at 670 °C and 0.1 μm/h

The growth rate was reduced even further, to 0.1 μm/h at 670 °C. Attempts to grow at this rate, by decreasing the

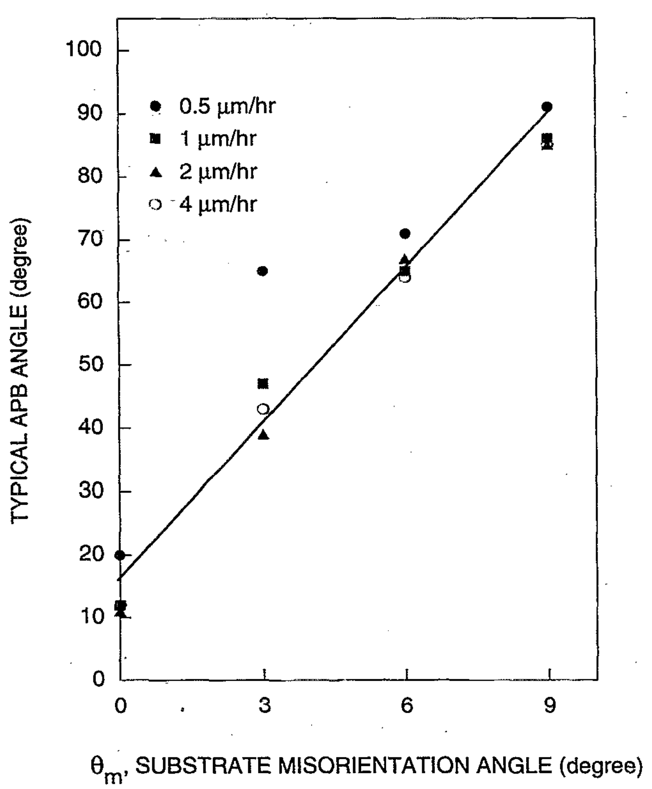

FIG. 3. Angle of antiphase boundaries, measured from the (001) plane, vs substrate misorientation in the [$\bar{1}$10] direction for several growth rates.

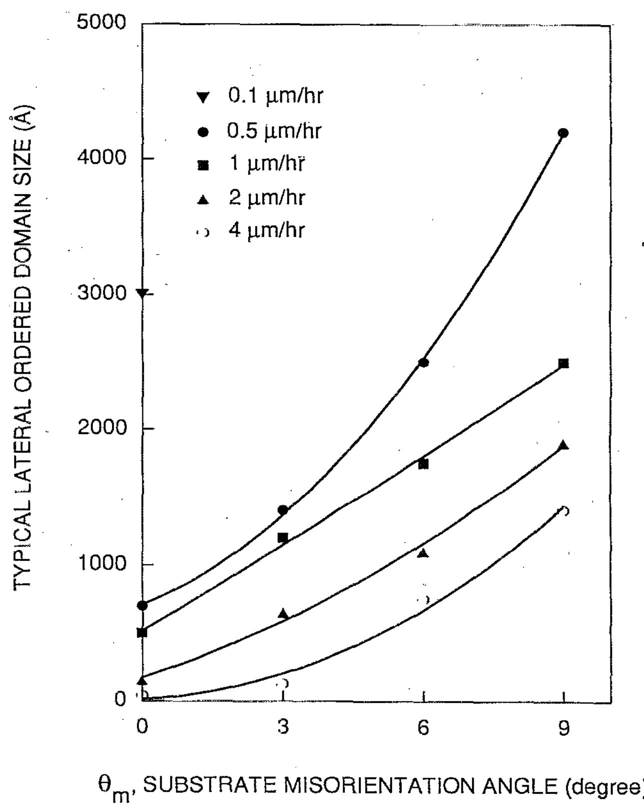

FIG. 4. Lateral domain size (APB spacing) vs substrate misorientation in the [$\bar{1}$10] direction for several growth rates.

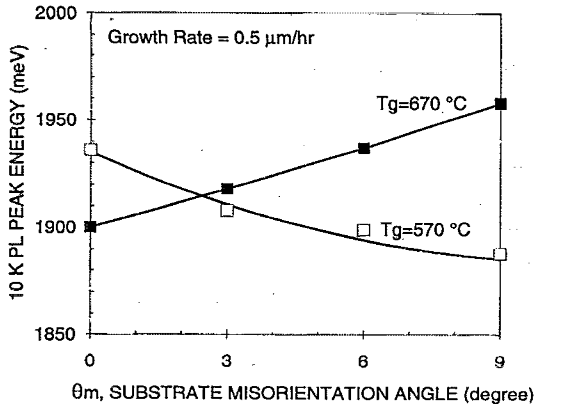

FIG. 5. 10 K PL peak energy vs misorientation angle for growth temperatures of 570 and 670 °C.

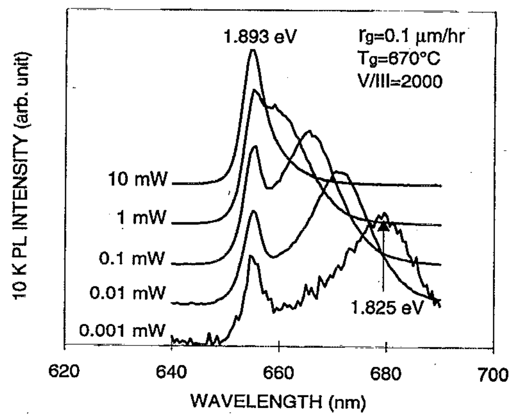

FIG. 7. 10 K PL spectra for sample grown at 670 °C at a rate of 0.1 μm/h for several excitation intensities.

TMIn and TMGa flow rates, led to poor morphologies. In order to preserve the surface from P loss, a certain PH_3 partial pressure is required. Thus, the input V/III ratio required for good morphologies (2000) is much higher than for the growth rate of 0.5 μm/h (220); however, at the interface the V/III ratio is probably not significantly different, as described in Ref. 18. Figure 6(a) shows a TED pattern and Figs. 6(b) and 6(c) the TEM images for the sample grown at 0.1 μm/h for a precisely (001)-oriented GaAs substrate. Two variants are formed, with order spots that are nearly circular, indicative of widely spaced APBs, as confirmed in the TEM images. The APBs are not straight, but appear to meander. The distance between APBs increases markedly as the growth rate decreases as shown in Fig. 4. The TED pattern shows strong [001] streaking, indicative of a high density of closely spaced (001) order twin boundaries,[13,14] that are clearly seen in Fig. 6.

Associated with the microstructure produced at low growth rates for $\theta_m=0°$ is a PL spectrum, seen in Fig. 7, consisting of a high-energy peak, with an energy nearly independent of excitation energy, and a second peak that shifts rapidly to higher energy as the excitation intensity is increased, as described by Su *et al.*[3] for $r_g=0.5$ μm/h. Decreasing the growth rate to 0.1 μm/h gives rise to a peak moving even more rapidly with increased excitation intensity, 17.6 meV/decade, as seen in Fig. 7, the largest value reported to date. A recent theoretical analysis associates this "rapidly moving emission" with an intermixing of the two variants at the order twin boundaries.[19]

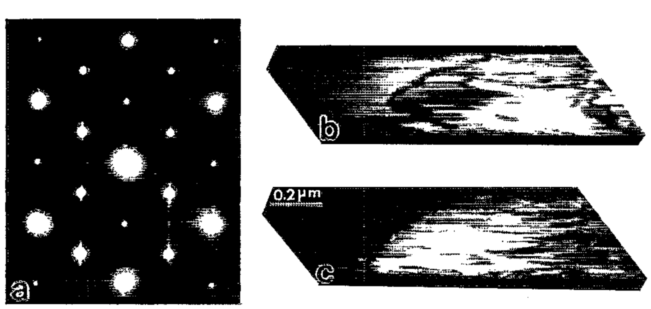

FIG. 6. TED and TEM results for $Ga_{0.52}In_{0.48}P$ sample grown at 670 °C at a rate of 0.1 μm/h; (a) TED pattern; (b) $\frac{1}{2}(1\bar{1}3)$ dark-field image; (c) $\frac{1}{2}(\bar{1}13)$ dark-field image.

C. Growth at 570 °C and 0.5 μm/h

In an effort to decrease the rate of the annealing process, the growth temperature was reduced to 570 °C. As mentioned above, the V/III ratio has been decreased slightly to 145 for these layers, however, the input phosphine partial

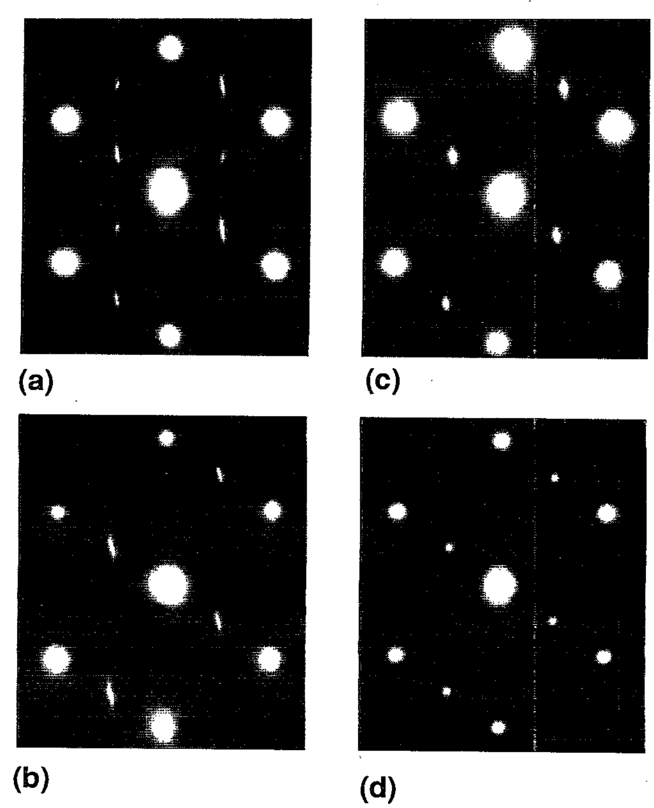

FIG. 8. TED patterns for $Ga_{0.52}In_{0.48}P$ layers grown at 570 °C with a growth rate of 0.5 μm/h. The substrates were misoriented by angles of (a) 0°, (b) 3°, (c) 6°, and (d) 9°.

(a)
(b)
(c)
(d)

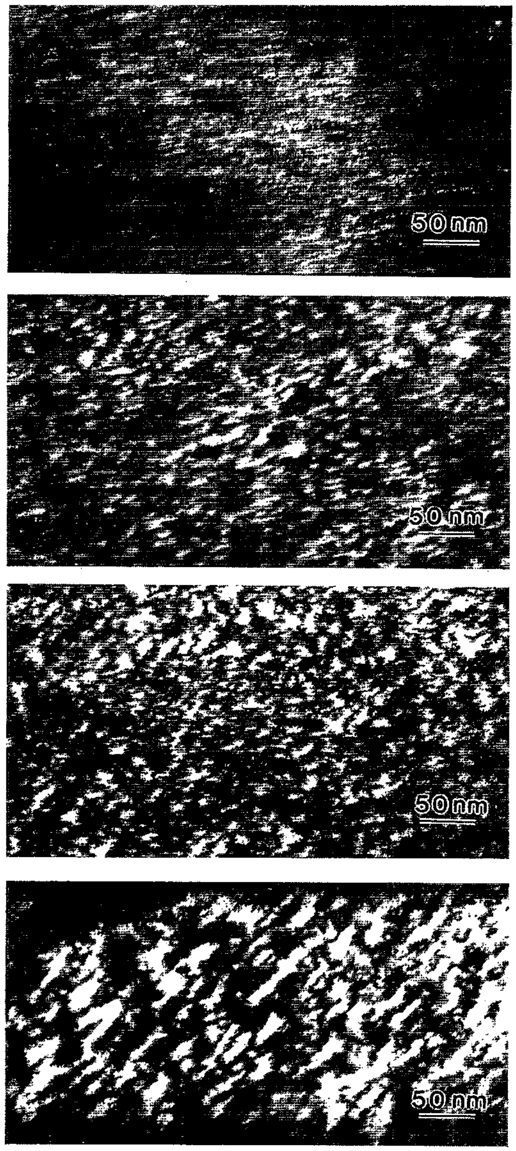

FIG. 9. TEM dark-field images for $Ga_{0.52}In_{0.48}P$ layers grown at 570 °C with a growth rate of 0.5 μm/h. The substrates were misoriented by angles of (a) 0°, (b) 3°, (c) 6°, and (d) 9°.

pressure has been kept constant. For a misorientation angle (in the $[\bar{1}10]$ direction) of 0°, the TED pattern, shown in Fig. 8(a) indicates the formation of two variants, as expected. The marked elongation of the order-induced spots and the strong streaking are indicative of very small APB spacings. Increasing the misorientation angle to 3° nearly eliminates the second variant; however, the distorted superlattice spots and streaking indicate that the APBs are still closely spaced. The streaking persists even for a misorientation angle of 6° and 9°. The intensity decreases monotonically with increasing values of θ_m. The TEM images, Fig. 9, show microstructures completely different than those seen for samples grown at the higher temperatures. Small ordered domains are dispersed in a disordered matrix. No APBs are seen in the images, but APB spacings considerably smaller than the domain size would be required to give the TED patterns seen in Fig. 8. As the angle of misorientation increases, the domains appear to cluster into platelets oriented at an angle of approximately 54° to the (001) plane.

The PL data, plotted in Fig. 5, indicate that for $\theta_m=0°$, the sample is less ordered than for growth at 670 °C. This is probably due to the changes in ordering leading to the dramatically different microstructure seen in Figs. 8 and 9. An important result of this part of the study is the steady decrease in PL peak energy with increasing angle of misorientation, corresponding to an increase in the degree of order with increasing θ_m. This apparently indicates that an increase in the [110] step density acts to increase the ordering kinetics at these low growth temperatures where annealing effects are insignificant. This trend is postulated to also exist at the higher growth temperatures;[20] however, the effect is obscured by the increase in annealing rate with increasing θ_m at higher growth temperatures.

IV. SUMMARY

The effects of OMVPE growth parameters on ordering in $Ga_{0.52}In_{0.48}P$ have been studied in an effort to elucidate the kinetics of the ordering process. At a growth temperature of 670 °C, an increase in the angle of substrate misorientation from (001) toward the $[\bar{1}10]$ direction caused an increase in the annealing process occurring during growth that leads to more disordered material. This was confirmed by decreasing the growth rate to 0.1 μm/h where the long growth times required to produce samples thick enough to characterize significantly decreased the degree of order. The PL emission originating in the ordered material in these samples was found to move to higher energy with increasing excitation intensity at a rate of 17.6 meV/decade, the largest reported to date. It was found that decreasing the growth temperature from 670 to 570 °C resulted in a monotonic increase in the degree of order with increasing misorientation angle. This indicates that [110] steps assist in the ordering process.

ACKNOWLEDGMENT

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