Surface photoabsorption study of the effects of growth temperature and V/III ratio on ordering in GaInP

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Surface photoabsorption (SPA) measurements were used to clarify the Cu–Pt ordering mechanism in $Ga_{0.5}In_{0.5}P$ layers grown by organometallic vapor phase epitaxy. The Cu–Pt ordering is strongly affected by the growth temperature and the input partial pressure of the phosphorus precursor, i.e., the V/III ratio. SPA was used to measure the concentration of $[\bar{1}10]$-oriented phosphorus dimers on the surface, which are characteristics of the (2×4) reconstruction, as a function of the growth temperature and V/III ratio. The degree of order decreases markedly with increasing growth temperature above 620 °C at a constant V/III ratio of 40 [tertiarybutylphosphine (TBP) partial pressure of 50 Pa]. This corresponds directly to a decrease of the P-dimer concentration on the surface. Below 620 °C, the degree of order decreases as the growth temperature decreases, even though the concentration of P dimers increases. This is most likely due to the slow migration of adatoms on the surface during growth. The degree of order is found to decrease monotonically with decreasing V/III ratio in the range from 160 to 8 at 670 °C. This corresponds directly to the decrease of the P-dimer concentration on the surface. The direct correlation of the $[\bar{1}10]$-oriented phosphorus dimer concentration and the degree of order with changes in both temperature ($\geq$620 °C) and V/III ratio suggests that the (2×4) surface reconstruction is necessary to form the Cu–Pt structure, in agreement with published theoretical studies. The physical structure of the surface of these $Ga_{0.5}In_{0.5}P$ layers was also characterized, using atomic force microscopy. For growth at 670 °C and a V/III ratio of 160, the structure of the layers growth on exactly (001) oriented GaAs substrates consists of islands surrounded mainly by bilayer (approximately 6 Å) steps. As the V/III ratio is reduced, the step height transforms to one monolayer. Exclusively monolayer steps are formed at a V/III ratio of 8. This is interpreted in terms of the stabilization of the bilayers by formation of the (2×2) reconstruction on the (111)B step face at high V/III ratios. © *1996 American Institute of Physics.* [S0021-8979(96)05509-8]

I. INTRODUCTION

$Ga_{0.5}In_{0.5}P$ is a material used for the manufacture of visible light-emitting diodes[1] and injection lasers.[2] It is also potentially useful for electronic switching devices such as bipolar transistors.[3] $Ga_{0.5}In_{0.5}P$ layers grown by organometallic vapor phase epitaxy (OMVPE) using typical growth conditions form the Cu–Pt ordered structure spontaneously at the surface during growth. This structure consists of {111} monolayers alternately enriched in Ga and In.[4] This has profound implications for device performance. For example, the GaInP band gap energy is found to decrease markedly in ordered material.[5] Thus, ordering must be controlled in material to be used for device fabrication. The degree of order is found to vary widely for different growth conditions. For example, growth rate,[6–8] substrate misorientation,[7–11] substrate temperature,[7,9,12,13] and V/III ratio during growth[7,14] all have major effects on the degree of order of layers grown by OMVPE.

Formation of this superlattice structure, rather than a disordered alloy with the Ga and In atoms randomly distributed on the group III sublattice, was at first somewhat surprising. It is not predicted by reliable total energy minimization calculations for the bulk alloy nor is it a stable surface phase for the unreconstructed surface.[15] This phenomenon is now widely accepted to be driven by the thermodynamics at the (2×4) reconstructed surface.[15,16] Calculations summarized by Zunger and Mahajan[15] indicate that the periodic surface stresses resulting from the formation of [110] phosphorus dimer rows on the (2×4) reconstructed surface and the related dimer row buckling results in a segregation of the subsurface group III atoms into alternating [110] rows of In and Ga atoms. This, in turn, results in the formation of the two *B* variants of the Cu–Pt structure with ordering on the $(\bar{1}11)$ and $(1\bar{1}1)$ planes commonly observed for layers grown by OMVPE. Implicit in the above description is the assumption that the subsurface atoms to the fourth buried layer are able to diffuse rapidly,[17] a hypothesis seemingly at odds with the slow bulk diffusion in III/V alloys. Chen *et al.*[18] suggested an alternate explanation, that the group V dimer rows are formed above the alternating Ga and In rows in a synergistic relationship between the positions of the surface dimers and the Cu–Pt ordered structure in the solid alloy.

The actual mechanism for the formation of the Cu–Pt ordered structure during growth is suggested by the strong influence of misorientation from the nominal (001) surface on the degree of order in the GaInP alloy. The data indicate that [110] steps assist in the formation of the ordered structure and the direction of their motion determines the variant formed.[19] These data have been interpreted in terms of a mechanism involving the motion of monolayer [110] steps across the surface.[20–22]
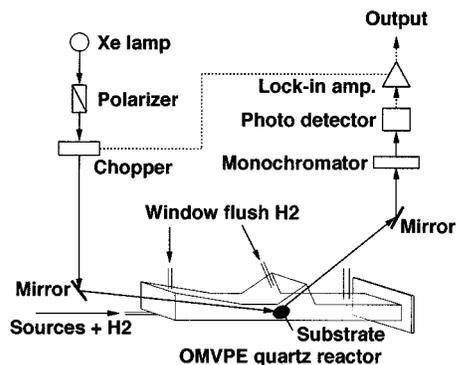
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FIG. 1. Experimental setup for the SPA monitoring of growth in a horizontal OMVPE reactor system.

Until recently, no experimental information about either the surface reconstruction or the physical structure of the surface during OMVPE growth of GaInP has been available. Of course any interpretations of the mechanisms of formation of the Cu–Pt structure during growth must be treated as speculative without such information. Two techniques have recently become available which offer the possibility of providing this missing information. Surface photoabsorption (SPA) measurements have recently been used to indicate the presence of the $[\bar{1}10]$-oriented phosphorus dimers characteristic of the (2×4) reconstruction on the surface of GaInP layers grown by OMVPE under certain conditions.[23] Atomic force microscopy (AFM) measurements have been shown to be capable of detecting and characterizing even monolayer steps on the surface after growth.[24] For exactly (001)-oriented substrates, the surface of GaInP layers grown using the trimethyl-group III alkyls combined with phosphine at 670 °C with an input V/III ratio of 160 has been reported to consist of small islands surrounded by bilayer steps.[25]

The research presented here uses both SPA and AFM to characterize the surfaces of $Ga_{0.5}In_{0.5}P$ layers grown on exactly (001)-oriented GaAs substrates as a function of the input partial pressure of the phosphorus precursor, tertiarybutylphosphine (TBP) in this case, and the growth temperature. A direct correlation is observed between the concentration of $[\bar{1}10]$ phosphorus surface dimers and the degree of Cu–Pt order in the epitaxial layers. A transition of the surface structure is also observed, from monolayer steps for low V/III ratios to bilayer steps at high V/III ratios.

II. EXPERIMENT

The $Ga_{0.5}In_{0.5}P$ layers were grown on semi-insulating, exactly (001)-oriented GaAs substrates in an atmospheric-pressure, horizontal OMVPE reactor. The substrates were degreased, then etched in H_2SO_4 for 3 min followed by another 4 min in a solution of $4H_2SO_4:1H_2O_2:1H_2O$. They were then rinsed in de-ionized water for 5 min and blown dry with N_2 before loading into the reactor. The sources were trimethylgallium (TMGa) at -10 °C, ethyldimethylindium (EDMIn) at 15 °C, and TBP at -12 °C (for the growth temperature dependence series of runs) or 7 °C (for the V/III

ratio dependence series). The $Ga_{0.5}In_{0.5}P$ growth rate was constant at 0.3 μm/h. Fig. 1 shows the SPA system attached to the OMVPE reactor for *in situ* measurements. P-polarized light from a 150 W Xe lamp irradiates the $Ga_{0.5}In_{0.5}P$ layer at an incident angle of 70° through a polarizer and a chopper. The direction of the incident light is parallel to the direction of the gas flow in the reactor. The reflected light is monochromatized and detected by a Si PNN^+ photodiode using standard lock-in amplification techniques. Each run consisted of the growth of two $Ga_{0.5}In_{0.5}P$ layers, one where the [110] direction of the GaAs substrate was parallel to the gas flow and one where the substrate was rotated by 90°. The spectra are found to have a dominant peak at 400 nm. The peak position and asymmetry are consistent with data for InP where the peak is identified as being due to $[\bar{1}10]$-oriented P dimers.[26] As discussed in an earlier paper, the measurement wavelength was fixed at 400 nm to measure the concentration of the $[\bar{1}10]$-oriented P dimers on the surface, $[P^2_{[\bar{1}10]}]$.[23] The SPA measurement can be used to determine the local structure at the surface, e.g., the presence and orientation of phosphorus dimers, but not for determination of the long-range periodicity. However, the (2×4) surface reconstruction is the only common surface reconstruction reported for III/V alloys that consists primarily of $[\bar{1}10]$-oriented P dimers. Thus, the concentration of $[\bar{1}10]$-oriented P dimers is taken as a measure of the degree to which the (2×4) reconstruction is formed.

A. Growth temperature studies

SPA measurements were performed on 0.15-μm-thick $Ga_{0.5}In_{0.5}P$ layers grown at 620 °C and a V/III ratio of 40, corresponding to an input TBP partial pressure (p^0_{TBP}) of 50 Pa. The measurement temperatures were 520, 570, 620, 670, and 720 °C.

To probe the relationship between surface reconstruction and ordering, 0.3-μm-thick epitaxial layers were grown at 520, 570, 620, 670, and 720 °C with a fixed V/III ratio of 40. The degree of order was evaluated using low-temperature (20 K) photoluminescence (PL) measurements with excitation by the 488 nm line of an Ar^+ laser with a power of 10 mW.

B. V/III ratio studies

For SPA measurements p^0_{TBP} was varied at temperatures of 620 and 670 °C on 0.15 μm $Ga_{0.5}In_{0.5}P$ layers. The p^0_{TBP} values of 10, 50, and 200 Pa were used, corresponding to V/III ratios of 8, 40, and 160, respectively, since the group III flow rates were fixed. Again, 0.3 μm $Ga_{0.5}In_{0.5}P$ layers were grown at 670 °C with V/III ratios of 8, 20, 40, 80, and 160 and at 620 °C with a V/III ratio of 40. The degree of order for these layers was evaluated by low-temperature PL measurements. The surface structure was characterized using a Nanoscope III AFM in the tapping mode. Etched single-crystalline Si tips were used with an end radius of about 5 nm and a sidewall angle of about 35°. This technique has been demonstrated to allow imaging of features a single atomic layer in height.[24,25]
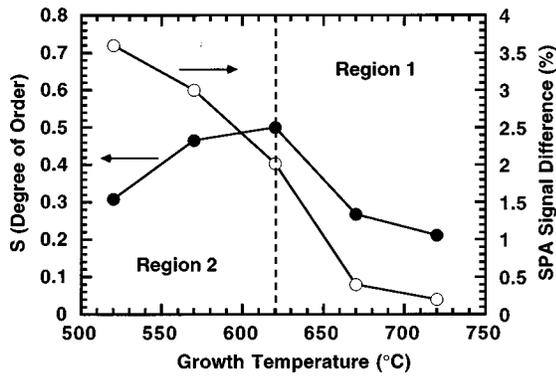
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FIG. 2. The effect of growth temperature on the degree of order, S, and the SPA signal difference at 400 nm: (●) degree of order for a V/III ratio of 40 (TBP partial pressure of 50 Pa), (○) SPA signal difference for a TBP partial pressure of 50 Pa.

FIG. 3. The effect of V/III ratio (input TBP partial pressure) on the degree of order and SPA signal difference at 400 nm: (●) S, degree of order, at 670 °C, (■) S, degree of order, at 620 °C, (○) SPA signal difference at 670 °C, (□) SPA signal difference at 620 °C.

III. RESULTS AND DISCUSSION

A. Growth temperature studies

The effect of growth temperature on the SPA signal difference at 400 nm between [110] and [$\bar{1}$10] directions is shown in Fig. 2. The SPA signal difference plotted is $\{[(R(\text{P})\text{-}R(\text{III}))/R(\text{P})]_{[\bar{1}10]}\text{-}[(R(\text{P})\text{-}R(\text{III}))/R(\text{P})]_{[110]}\}$, where $R(\text{P})$ and $R(\text{III})$ are the reflectivities of the P-stabilized and the group-III-stabilized surfaces, respectively. The P-stabilized and group III element-stabilized surfaces were formed by switching TBP with a constant partial pressure of 50 Pa to reactor and vent, respectively. It is seen that the SPA signal difference, $[P^2_{[\bar{1}10]}]$, decreases monotonically as the temperature increases. The phosphorus concentration on the surface is obviously determined by a balance between P adsorption onto the surface from the pyrolyzed TBP and P desorption. At low temperatures the thermally activated P desorption rate is low, resulting in a P-rich surface which appears to form the (2×4) reconstruction, consisting of [$\bar{1}$10]-oriented P dimers. As the temperature increases, the P desorption rate becomes larger, resulting in a decrease in $[P^2_{[\bar{1}10]}]$. The SPA difference signal approaches zero at a temperature of 720 °C.

The degree of order, S, is also plotted versus substrate temperature in Fig. 2. The degree of order was determined from the calculated S^2 dependence of the band gap energy on the degree of order.[15,27] The calculated value of band gap energy difference between $Ga_{0.5}In_{0.5}P$ that is completely disordered and totally ordered, 490 meV,[27] is in good agreement with the experimental value of 471 meV[28] and the experimental value of the band gap energy for totally disordered $Ga_{0.5}In_{0.5}P$ is approximately 2.005 eV.[9,28] Thus, S is calculated as

$S(\text{degree of order})$

$$= \sqrt{\frac{2005 - \text{PL peak energy at 20 K(in meV)}}{471}}.$$

The data plotted in Fig. 2 indicate that the temperature dependence of the order parameter is complex, with a maximum degree of order at 620 °C and a clear decrease in order
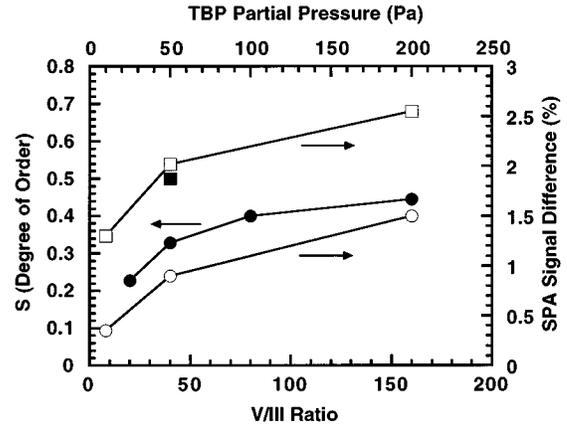
for both higher and lower temperatures. This leads to the division of the temperature range into two regions, as indicated in Fig. 2. In region 1, both the degree of order and $[P^2_{[\bar{1}10]}]$ decrease with increasing growth temperature. This suggests that loss of the (2×4) surface reconstruction results in a reduction in the degree of Cu–Pt ordering. As discussed above, this is consistent with theoretical predictions summarized in Ref. 15. In region 2, the degree of order decreases with decreasing temperature although $[P^2_{[\bar{1}10]}]$ increases in this range. This indicates that the lack of the (2×4) reconstruction is not the factor limiting ordering in this temperature range. It is likely that the degree of order decreases for kinetic reasons. Lower temperatures lead to lower rates of atomic migration on the surface, which prevents formation of the Cu–Pt structure during the time available before the surface layer is covered by the next layer deposited. This mechanism is basically the same as that postulated to account for the decreased degree of order with increasing growth rate at a constant temperature.[6]

B. V/III ratio studies

Figure 3 shows the effect of V/III ratio (p^0_{TBP}) on the degree of order and the SPA signal difference at 400 nm between the [110] and [$\bar{1}$10] directions. $[P^2_{[\bar{1}10]}]$ increases monotonically as p^0_{TBP} increases at both 620 and 670 °C. This is expected for any isotherm. For example, the simple Langmuir isotherm gives a surface coverage that is proportional to $Kp^0_{\text{TBP}}/(1+Kp^0_{\text{TBP}})$, where K is the adsorption coefficient, assuming that the TBP is completely pyrolyzed.[29] The saturation of the SPA signal with increasing TBP partial pressure is simply due to the high coverage expected for these high partial pressures of 100–200 Pa. The SPA signal difference approaches zero for low TBP partial pressures. This behavior supports the idea that the SPA signal being measured is, in fact, due to P species on the surface.

For growth at 670 °C, the degree of order is seen to increase systematically with increasing V/III ratio. The sample grown at 620 °C with a V/III ratio of 40 is even more

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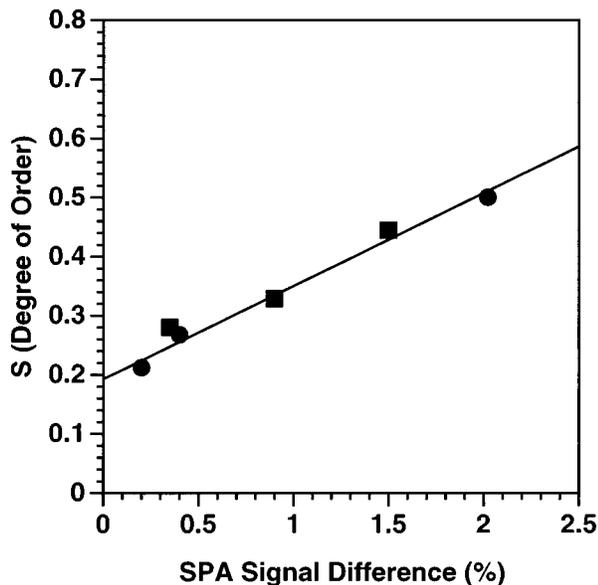
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FIG. 4. Degree of order vs SPA signal difference for layers grown at a series of different temperatures for V/III=40 (■) and at a series of different V/III ratio at a temperature at 670 °C (●).
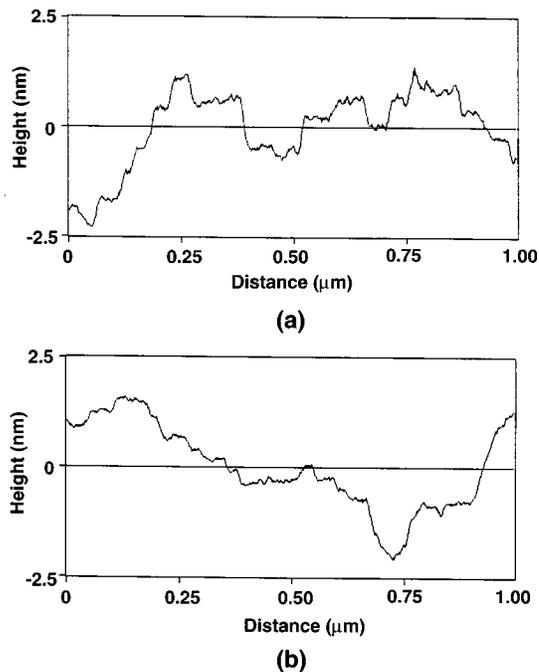

FIG. 5. AFM section scans of the surface structure for GaInP grown on exactly (001) GaAs substrate at 670 °C (a) V/III ratio=160, (b) V/III ratio =40.

highly ordered than the most ordered sample grown at 670 °C with a V/III ratio of 160. A monotonic relationship between the degree of order and the SPA intensity is clearly observed.

The data obtained from the variable temperature and variable V/III ratio series are combined in the plot of degree of order versus the SPA difference signal in Fig. 4. The plot neglects the data obtained at temperatures of 570 and 520 °C, where the degree of order is limited by kinetic factors. A remarkable correlation is observed. This provides strong support for the assertion that the ordering is driven by the (2×4) reconstructed surface.

The surface structure was characterized by AFM. Fig. 5 shows sectional scans of the $Ga_{0.5}In_{0.5}P$ surfaces grown on exactly (001) GaAs substrates at 670 °C with V/III ratios of 40 and 160. For a V/III ratio of 160 the surface steps are highly uniform, with an average height of approximately 6 Å. Only a single larger step is seen in Fig. 5(a). The AFM images indicate that the surface is covered by islands. The sectional scan indicates that the islands are surrounded by exclusively bilayer steps. This result is similar to that reported for $Ga_{0.5}In_{0.5}P$ layers grown using TMGa, trimethylindium (TMIn), and phosphine at 670 °C with a growth rate of 0.1 μm/h.[25]

For the layer grown using a lower V/III ratio of 40, the sectional scan shown in Fig. 5(b) shows the virtual absence of bilayer steps. It appears that the islands are terminated mainly by monolayer steps that are theoretically 2.8 Å in height. Similar results were obtained for the layers grown using V/III ratios of 8 and 20. Nearly equal numbers of monolayer and bilayer steps were observed for layers grown using a V/III ratio of 80. When only monolayer and bilayer steps are taken into account, the average step height is plotted versus V/III ratio in Fig. 6 for the $Ga_{0.5}In_{0.5}P$ layers grown at 670 °C.

It was also found that the average step height was 1.46 monolayers on the surface of the sample grown at 620 °C with a V/III ratio of 40, which is more ordered than the sample grown at 670 °C with a V/III ratio of 160 (average step height=1.80 monolayers). This suggests that the step structure is not closely related to the ordering mechanism. The hypothesis that the step structure is relatively unimportant for ordering is supported by the nearly perfect correspondence between the SPA signal difference and the degree of order, which indicates that the effects observed here are mainly determined by the chemical structure of the surface.

A plausible explanation for the alteration of step structure with changing V/III ratio is related to the structure of the riser at the step edge. A monolayer step will have a series of dangling P bonds running along the [110] step edge with no
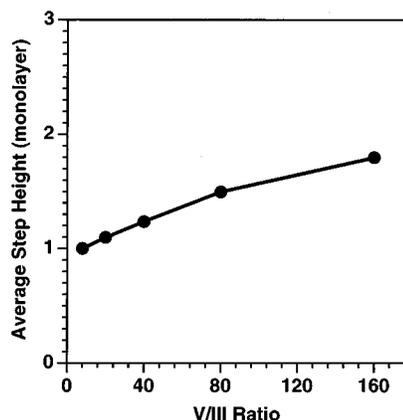

FIG. 6. V/III ratio dependence of average step height for GaInP layers grown on exactly (001) GaAs substrates at 670 °C.

obvious way to reconstruct to reduce the step energy. A bilayer step will form a thin ribbon of (111)B surface that will be just large enough to accommodate the (2×2) reconstruction reported for (111)B GaAs surfaces.[30] This structure has a layer of As trimers bonded to the underlying surface, so they would be expected to form only for group-V-rich conditions. Thus, formation of the reconstructed bilayer structure at the step edge on the GaInP surface would be stabilized only for high TBP flow rates.

IV. CONCLUSIONS

The effects of growth temperature and V/III ratio (input TBP partial pressure) were studied using SPA and AFM. The SPA signal difference at approximately 400 nm was ascribed to $[\bar{1}10]$-oriented P dimers on the surface, which are characteristic of the (2×4) surface reconstruction. At growth temperatures above 620 °C, the degree of order varies directly with the concentration of $[\bar{1}10]$-oriented P dimers on the surface. For temperatures below 620 °C, the degree of order is determined not by the (2×4) surface reconstruction but by atomic surface migration during growth. The SPA signal difference due to P dimers and the degree of order were observed to increase in tandem with increasing V/III ratio (input TBP partial pressure) at 670 °C. Both the temperature and V/III ratio results strongly suggest a correlation between formation of the Cu–Pt ordered structure and the surface reconstruction. Apparently, the (2×4)-like surface reconstruction is necessary for the formation of the ordered structure during growth.

The step structure of the surface was also found to be markedly dependent on the V/III ratio. For the low V/III ratios of 8 and 20, mainly monolayer steps were observed. As the V/III ratio increased, a transition to bilayer steps was observed. This is interpreted in terms of stabilization of bilayer steps by formation of a (2×2) structure on the (111)B step edge.

ACKNOWLEDGMENTS

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