

Surface photoabsorption study of the effect of V/III ratio on ordering in GaInP

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Cu–Pt ordering is widely observed in Ga_{0.5}In_{0.5}P layers grown by organometallic vapor phase epitaxy. The degree of order is a strong function of the input partial pressure of the phosphorus precursor, i.e., the V/III ratio, during growth. By observing the surface structure using *in situ* surface photoabsorption (SPA) measurements, the concentration of $[\bar{1}10]$ -oriented P dimers, characteristic of the (2×4) reconstructed surface, has been measured as a function of the growth conditions. For growth at 670 °C, the P-dimer concentration is found to increase systematically as the input tertiarybutylphosphine pressure is increased from 10 to 200 Pa. This corresponds directly to a monotonic increase in the degree of order, measured using transmission electron microscopy and low-temperature photoluminescence. These data strongly suggest that the (2×4) surface reconstruction is necessary for formation of the Cu–Pt structure. The step structure at the surface was also observed for these layers using atomic force microscopy. For high V/III ratios the structure of the layers grown on exactly (001) oriented GaAs substrates consists of islands surrounded mainly by bilayer (5.7 Å) steps. As the V/III ratio is reduced, the step height transforms to 2.8 Å (one monolayer). © 1996 American Institute of Physics. [S0003-6951(96)01413-7]

Ga_{0.5}In_{0.5}P is a material that has been found to be useful for the fabrication of visible light emitting diodes¹ 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) typically form the Cu–Pt ordered structure, i.e., the Ga and In atoms spontaneously segregate into alternating {111} monolayers during growth rather than forming a disordered alloy with the Ga and In atoms randomly distributed on the group III sublattice.⁴ This has profound implications for device performance. For example, the Ga_{0.5}In_{0.5}P band-gap energy is found to decrease dramatically in ordered material.^{5,6}

This somewhat surprising spontaneous superlattice formation phenomenon is now believed to be driven by the thermodynamics at the surface. Energy minimization calculations by Zhang *et al.*⁷ indicate that the periodic surface stresses resulting from the formation of $[110]$ rows of $[\bar{1}10]$ -oriented phosphorus dimers on the (2×4) reconstructed (001) surface result 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 typically observed for layers grown by OMVPE. However, until recently, no information about the surface reconstruction of Ga_{0.5}In_{0.5}P during OMVPE growth has been available. This has been somewhat rectified by the recent discovery that surface photoabsorption (SPA) measurements indicate the presence of $[\bar{1}10]$ -oriented P dimers on the surface of Ga_{0.5}In_{0.5}P layers grown by OMVPE under certain conditions.⁸

The ordering mechanism has been postulated to involve the motion of $[110]$ monatomic steps across the nominally (001) surface during epitaxial growth.^{9–11} Again, the physical structure of the surface during OMVPE growth has not

been known until the recent discovery that ambient atomic force microscope (AFM) measurements give a clear picture of the step structure of the surface after growth.¹² For vicinal Ga_{0.5}In_{0.5}P surfaces misoriented by a few degrees toward the $[\bar{1}10]$ direction, the steps are found to be bunched for most growth conditions.^{13–15} For exactly (001)-oriented substrates, the surface of 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.¹⁶

Previous studies have indicated a strong dependence of the degree of order on the growth parameters. Both high growth temperatures¹⁷ and high growth rates¹⁸ have been found to lead to the elimination of ordering in Ga_{0.5}In_{0.5}P. The former has been determined to be due to the loss of the (2×4) reconstruction at high temperatures⁸ and the latter to the limited time for atomic rearrangement to form the ordered structure on the surface at high growth rates.¹⁸

The degree of order has also been found to be function of the input phosphorus flow rate.^{19,20} The degree of order is found to be strongest at an intermediate value of the V/III ratio. The layers become disordered as the V/III ratio falls below a certain critical value and the degree of order decreases gradually as the V/III ratio is increased above the optimum value. The reasons for these two phenomena are not entirely clear. Kurtz *et al.*²⁰ have postulated that the reduction in ordering at low V/III ratios is due to an alteration of the chemical structure of the surface and the reduction in Cu–Pt ordering at high V/III ratios is due to a reduction in the group III surface diffusion coefficient. Neither mechanism has been verified experimentally.

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), (p_{TBP}^0). A direct correlation is ob-

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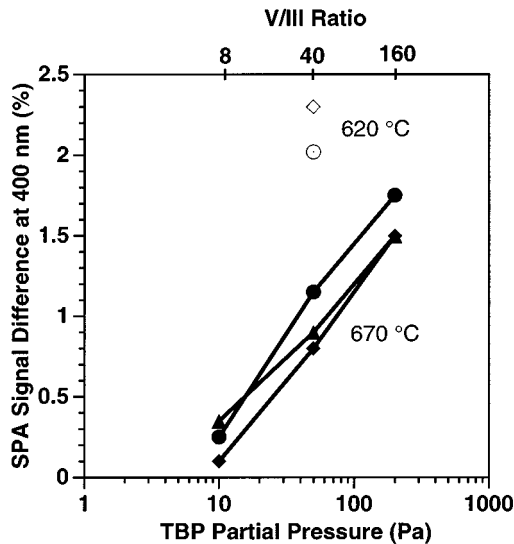


FIG. 1. TBP partial pressure dependencies of SPA signal difference between $[110]$ and $[\bar{1}\bar{1}0]$ directions at 400 nm for GaInP layers grown with several combinations of temperature and V/III ratio: (●) 670 °C/40, (◆) 670 °C/160 (No. 1), (▲) 670 °C/160 (No. 2), (○) 620 °C/40 (No. 1), (◇) 620 °C/40 (No. 2).

served between the concentration of $[\bar{1}\bar{1}0]$ phosphorus dimers on the surface ($[P_{[\bar{1}\bar{1}0]}^2]$), which are characteristic of the (2×4) reconstruction, and the degree of Cu–Pt order in the epitaxial layers. An abrupt change in the surface structure is also observed, from monolayer steps for low values of p_{TBP}^0 to bilayer steps at high values of p_{TBP}^0 .

All $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ layers described here were grown on semi-insulating exactly (001)-oriented GaAs substrates in an atmospheric pressure, horizontal OMVPE reactor using trimethylgallium (TMGa) at -10 °C, ethyldimethylindium (EDMIn) at 15 °C and TBP at 7 °C. The growth rate was 0.3 $\mu\text{m}/\text{h}$. A SPA system was attached to the OMVPE system for *in situ* measurements. P-polarized light from a 150-W Xe lamp irradiates the $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ 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 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 $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ 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 measurement wavelength was fixed at 400 nm to measure $P_{[\bar{1}\bar{1}0]}^2$.⁸ The SPA measurement can be used to determine the local structure at the surface, for example the presence and orientation of phosphorus dimers, but not for determination of the long range periodicity.

p_{TBP}^0 was varied from 10 to 200 Pa at 670 °C and fixed at 50 Pa at 620 °C. Values of p_{TBP}^0 of 10, 50, and 200 Pa correspond to V/III ratios of 8, 40, and 160, respectively, since the group III flow rates are fixed. Figure 1 shows the effect of p_{TBP}^0 on the 400 nm SPA signal difference between $[110]$ and $[\bar{1}\bar{1}0]$ directions, $\{[(R(\text{P}) - R(\text{III}))/R(\text{P})]_{[\bar{1}\bar{1}0]} - [(R(\text{P}) - R(\text{III}))/R(\text{P})]_{[110]}\}$, where $R(\text{P})$ and $R(\text{III})$ are the reflectivities of the P stabilized and the group III stabilized sur-

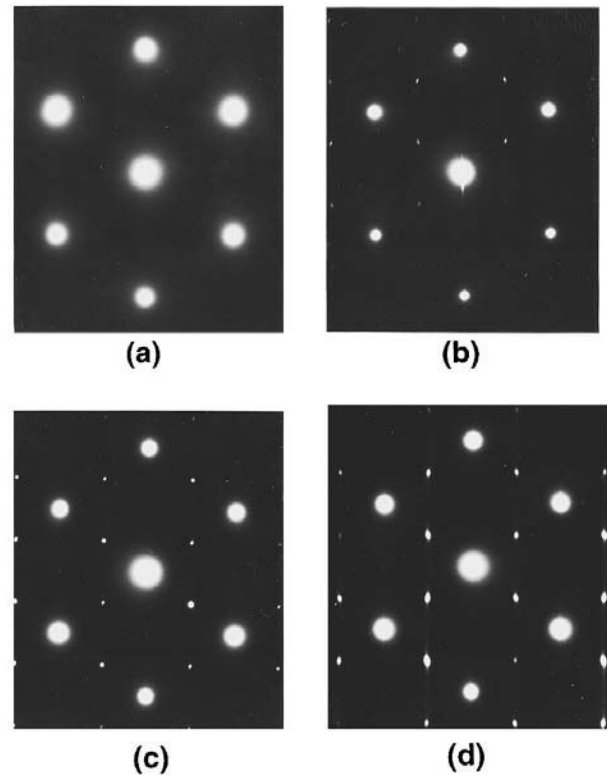


FIG. 2. $[110]$ pole TED patterns for GaInP layers grown with various combinations of growth temperature (°C) and V/III ratio: (a) 670/8, (b) 670/40, (c) 670/160, and (d) 620/40.

faces, respectively. The magnitude of this quantity is taken to be proportional to $[P_{[\bar{1}\bar{1}0]}^2]$.⁸ The $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ layers are 0.15 μm thick in all cases. The multiple data sets are included individually to demonstrate the reproducibility of the measurements. It is clear that the SPA signal difference, i.e., $[P_{[\bar{1}\bar{1}0]}^2]$, increases as p_{TBP}^0 increases at 670 °C. The concentration of P dimers is determined by a balance between P adsorption onto the surface from the TBP and P desorption. At 670 °C, as p_{TBP}^0 decreases to 10 Pa the SPA signal approaches zero, suggesting the virtual absence of $[\bar{1}\bar{1}0]$ -oriented P dimers. The SPA signal of 620 °C and 50 Pa was larger than that at 670 °C and 200 Pa, presumably due to the reduction of the P desorption rate due to the 50 °C lower temperature.

To probe the relationship between ordering and $[P_{[\bar{1}\bar{1}0]}^2]$, 0.3 μm $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ 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 ordering was evaluated using transmission electron microscopy (TEM) observation and low-temperature (20 K) photoluminescence (PL) measurements.

In Fig. 2, $[110]$ pole TED patterns show order-induced superlattice spots due to two variants [stronger $1/2(\bar{1}\bar{1}1)$ superspots and weaker $1/2(1\bar{1}\bar{1})$ superspots] for all samples except those grown at 670 °C with a V/III ratio of 8. From the SPA results mentioned above, the disappearance of the Cu–Pt ordering at 670 °C and a V/III ratio of 8 is attributed to the disappearance of the (2×4) surface reconstruction, deduced from the absence of $[\bar{1}\bar{1}0]$ -oriented P dimers on the surface. The intensities of the superlattice spots became

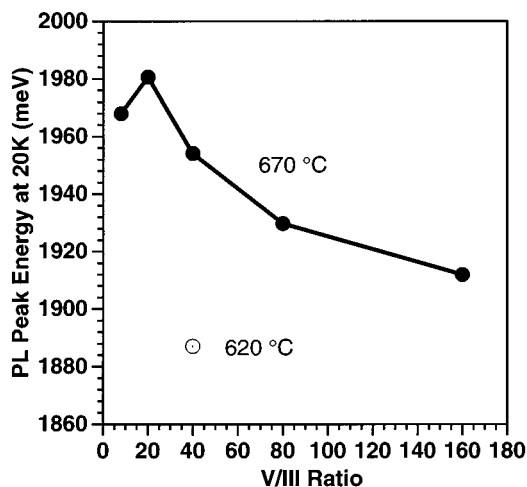


FIG. 3. V/III ratio dependence of 20 K PL peak energy for an excitation power of 10 mW.

stronger for the samples grown at higher V/III ratios. The sample grown at 620 °C with a V/III ratio of 40 is even more highly ordered. A monotonic relationship between the degree of order and the SPA intensity is clearly observed.

Figure 3 shows the PL peak energies at 20 K with excitation by the 488 nm line of an Ar⁺ laser with a power of 10 mW. As mentioned above, the band-gap energy decreases as the degree of order increases.⁵ For growth at 670 °C, the PL peak energy increases systematically with decreasing V/III ratio. The PL peak for the sample grown at V/III=8 was relatively weak and broad. This sample had a hazy surface. Thus, the PL peak might be due to defects due to the very low V/III ratio during growth. The peak energy for the sample grown at 620 °C and a V/III ratio of 40 was even lower than that for the sample grown at 670 °C and V/III ratio of 160, indicating a higher degree of order. These PL results are consistent with the TEM results and strongly support the correlation between ordering and the (2×4) surface reconstruction.

The surface structure was characterized using a Nano-scope 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.^{12,15} When only monolayer and bilayer steps were taken into account, 80% of surface steps were bilayers, having a height of 5.7 Å, for the Ga_{0.5}In_{0.5}P layer grown on an exactly (001) GaAs substrate at 670 °C with a V/III ratio of 160. This is similar to the results obtained for Ga_{0.5}In_{0.5}P layers grown at 620 °C with V/III ratios of between 160 and 220 using TMGa, trimethylindium and phosphine.¹⁵ As the V/III ratio decreased, the ratio of bilayer steps to monolayer steps decreased monotonically. For the Ga_{0.5}In_{0.5}P layers grown at 670 °C with V/III ratios of 8 and 20 the fraction of bilayer steps was smaller than 10%, i.e., the steps are mostly one monolayer (2.8 Å) in height. It was also found that the fraction of bilayer steps was only 46% on the sample grown at 620 °C and V/III ratio of 40, which is more ordered than the sample grown at 670 °C and V/III ratio of 160 (fraction of bilayer steps=80%). From this result, it is concluded that

the step structure is not directly linked to the ordering mechanism.

In summary, the surface structure of Ga_{0.5}In_{0.5}P grown on (001) GaAs substrates by OMVPE at 620 and 670 °C using various ratios of the P precursor, TBP, and the group III precursors, TMGa and EDIn, was studied using SPA. The peak at ~400 nm was ascribed to [110]-oriented P dimers on the surface, which are characteristic of the (2×4) surface reconstruction. The degree of order of epitaxial layers, grown using the same conditions as used for SPA, was measured using transmission electron microscopy and low-temperature photoluminescence spectroscopy. At 670 °C, both the SPA intensity due to P dimers and the degree of order were observed to increase monotonically with increasing input V/III ratio. Decreasing the substrate temperature to 620 °C resulted in an increase in both the concentration of [110]-oriented dimers and the degree of order. These data strongly suggest a correlation between formation of the Cu-Pt ordered structure and the surface reconstruction. Apparently, the (2×4) surface reconstruction is necessary for the formation of the ordered structure during growth. The step structure of the surface was also found to be dependent on the V/III ratio. For the lowest V/III ratios, monolayer steps were observed on the surface. As the V/III ratio increased, bilayer steps became dominant.

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- ¹F. A. Kish, F. M. Steranka, D. C. DeFever, D. A. Vandewater, K. G. Park, C. P. Kuo, T. D. Ostenowshi, M. J. Peanasky, J. G. Yu, R. M. Fletcher, D. A. Steigerwald, and M. G. Craford, *Appl. Phys. Lett.* **64**, 2839 (1994).
- ²T. Katsuyama, I. Yoshida, J. Shinkai, J. Hashimoto, and H. Hayashi, *Appl. Phys. Lett.* **59**, 3351 (1991).
- ³H. K. Yow, P. A. Houston, C. C. Button, T. W. Lee, and J. S. Roberts, *J. Appl. Phys.* **76**, 8135 (1994).
- ⁴G. B. Stringfellow, in *Common Themes and Mechanisms of Epitaxial Growth*, edited by P. Fuoss, J. Tsao, D. W. Kisker, A. Zangwill, and T. Keuch (Materials Research Society, Pittsburgh, 1993), pp. 35–46.
- ⁵A. Gomyo, T. Suzuki, and S. Iijima, *Phys. Rev. Lett.* **60**, 2645 (1995).
- ⁶L. C. Su, S. T. Pu, G. B. Stringfellow, J. Christen, H. Selber, and D. Bimberg, *Appl. Phys. Lett.* **62**, 3496 (1993).
- ⁷S. B. Zhang, S. Froyen, and A. Zunger, *Appl. Phys. Lett.* **67**, 3134 (1995).
- ⁸H. Murata, I. H. Ho, T. C. Hsu, and G. B. Stringfellow, *Appl. Phys. Lett.* **67**, 3747 (1995).
- ⁹G. B. Stringfellow and G. S. Chen, *J. Vac. Sci. Technol. B* **9**, 2182 (1991).
- ¹⁰B. A. Philips, A. G. Norman, T. Y. Seong, S. Mahajan, G. R. Booker, M. Skowronski, J. P. Harbison, and V. G. Keramidias, *J. Cryst. Growth* **140**, 249 (1994).
- ¹¹S. B. Ogale and A. Madhukar, *Appl. Phys. Lett.* **60**, 2095 (1992).
- ¹²C. C. Hsu, J. B. Xu, and I. H. Wilson, *Appl. Phys. Lett.* **64**, 2105 (1994); H. Bluhm, U. D. Schwarz, F. Herrmann, and P. Paufler, *Appl. Phys. A* **59**, 23 (1994).
- ¹³G. B. Stringfellow, L. C. Su, Y. E. Strausser, and J. T. Thornton, *Appl. Phys. Lett.* **66**, 3155 (1995).
- ¹⁴G. B. Stringfellow, L. C. Su, Y. E. Strausser, and J. T. Thornton, *J. Electron. Mater.* **24**, 11 (1995).
- ¹⁵L. C. Su and G. S. Stringfellow, *J. Appl. Phys.* **78**, 6775 (1995).
- ¹⁶L. C. Su and G. B. Stringfellow, *Appl. Phys. Lett.* **67**, 3626 (1995).
- ¹⁷L. C. Su, I. H. Ho, and G. B. Stringfellow, *Appl. Phys. Lett.* **65**, 749 (1994).
- ¹⁸D. S. Cao, E. H. Reihlen, G. S. Chen, A. W. Kimbal, and G. B. Stringfellow, *J. Cryst. Growth* **109**, 279 (1991).
- ¹⁹A. Gomyo, K. Kobayashi, S. Kawata, I. Hino, and T. Suzuki, *J. Cryst. Growth* **77**, 367 (1986).
- ²⁰S. R. Kurtz, D. J. Arent, K. A. Bertness, and J. M. Olson, *Mater. Res. Soc. Symp.* **340**, 117 (1994).