Correlation between surface structure and ordering in GaInP

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Ga and In atoms in $Ga_{0.52}In_{0.48}P$ layers spontaneously segregate to form alternating In- and Ga-rich {111} monolayers during organometallic vapor phase epitaxial (OMVPE) growth on (001) oriented GaAs substrates, thus forming the CuPt ordered structure. This ordering phenomenon is believed to be driven by surface processes, although little direct experimental information is available. This work presents evidence, based on surface photoabsorption data, that $[\bar{1}10]$ oriented P dimers are present on the surface during OMVPE growth using trimethylgallium and ethyldimethylindium combined with tertiarybutylphosphine, suggesting a (2×4)-like surface reconstruction. Furthermore, when the growth temperature is increased above 620 °C, with other parameters constant, both the concentration of these P dimers and the degree of order are observed to decrease. A similar correlation of decreased P-dimer concentration with decreased degree of order is observed for decreases in V/III ratio. Thus, the changes in order parameter for variations in temperature and TBP flow rate are found to be closely correlated with the changes in the order parameter. A third parameter studied was the misorientation of the substrate from (001) toward either the $\{111\}_A$ or $\{111\}_B$ planes. The concentration of P dimers decreased as the misorientation increased in either direction. The degree of order was also observed to generally decrease, supporting the connection between surface reconstruction and ordering. However, the difference in order parameter observed for the two misorientation directions suggests the importance of a second parameter, the step structure, itself. For exactly (001) oriented substrates the surface was observed, using high resolution atomic force microscopy, to consist of islands, elongated in the [110] direction, with heights of 30–60 Å. Monolayer steps are observed for some growth conditions, but for most conditions the boundaries are formed exclusively of bilayer (5.7 Å) steps. Predominantly monolayer steps are formed for low V/III ratios and bilayer steps for high V/III ratios.

I. INTRODUCTION

The spontaneous formation of monolayer superlattices during vapor phase epitaxial growth is a phenomenon of both fundamental and technological importance. The most widely studied example of this phenomenon is the formation of the CuPt ordered structure, with ordering on {111} planes, during organometallic vapor phase epitaxial (OMVPE) growth of $Ga_{0.52}In_{0.48}P$.[1,2] The thermodynamic driving force for CuPt ordering is believed to be related to formation of the (2×4) surface reconstruction,[1–3] since this ordered structure is not stable in the bulk.[2] The ordered structure is formed at the surface during epitaxial growth.[1–4] Evidence of this is the change in ordered structure correlated with the change in surface reconstruction for GaInP grown by molecular beam epitaxy (MBE).[3,4] The initial studies of Murata *et al.*[5] have demonstrated that for GaInP grown by OMVPE a (2×4)-like surface reconstruction can be detected *in situ* using the optical technique of surface photo absorption (SPA). This allows the opportunity to probe the correlation between the degree of CuPt order or order parameter, S, and the extent of formation of the (2×4)-like reconstruction as a function of growth parameters such as temperature, V/III ratio, and substrate misorientation from (001), all of which are known to have marked effects on the degree of order observed in the GaInP epitaxial layers grown by OMVPE.[1,2]

This article will present the results of a study of the effects of the three growth parameters mentioned above on the SPA spectrum and the degree of order determined from the photoluminescence peak energy as well as the step structure of the surface determined using atomic force microscopy (AFM). The results suggest a direct correlation between the (2×4)-like reconstruction determined by SPA and the degree of CuPt order in the GaInP epitaxial layers, although changes in the step structure are also found to be important.

II. EXPERIMENT

The epitaxial layers studied in this work were grown by OMVPE in a horizontal, atmospheric pressure apparatus[6] using the newly developed, less hazardous phosphorus source tertiarybutylphosphine (TBP). The flow rates of the group III precursors trimethylgallium (TMGa) and ethyldimethylindium (EDMIn) were adjusted to give the solid composition lattice matched to the GaAs substrates, i.e., $Ga_{0.52}In_{0.48}P$, and a growth rate of 0.3 μm/h. The TBP flow rate was varied to give the various V/III ratios used. The semiinsulating GaAs substrates were nominally (001), misoriented by angles of 0°, 3°, 6°, 11°, and 15.8° toward either the $[\bar{1}10]$ or the [110] direction in the lattice.

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For the SPA measurements, P-polarized light from a 150 W Xe lamp irradiates the GaInP layer at an incidence angle of 70° through a polarizer and a chopper.[7] 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 consists of the growth of two epitaxial layers, one where the [110] direction of layer is parallel to the gas flow and one where the substrate is rotated by 90°. The P-stabilized and group III element-stabilized surfaces were formed by switching the TBP flow between reactor and vent, respectively.[5,7]

The characterization of the surface structure was carried out using a Nanoscope III atomic force microscope (AFM) in the tapping mode. Etched single-crystalline Si tips were used with an end radius of about 5 nm, with a sidewall angle of about 35°. Scan rates of 1 to 2 lines per second were used and data were taken at 512 points/line and 512 lines per scan area. This technique has been shown capable of revealing atomic-scale features on the surface.[8] Monolayer steps have been observed *ex situ* for GaInP layers grown by OMVPE.[9]

The solid composition of the GaInP layers was determined, using Vegard's law, from x-ray diffraction measurements using Cu $K\alpha$ radiation. The 20 K PL was excited with the 488 nm line of an Ar^+ laser. The emission was dispersed using a Spex Model 1870 monochromator and detected using a Hamamatsu R1104 head-on photomultiplier tube.

III. RESULTS AND DISCUSSION

The major feature of the SPA spectrum, i.e., the difference in SPA signal with incident light along [110] and $[\bar{1}10]$, is a strong absorption peak observed at approximately 400 nm.[5] This has been attributed to the $[\bar{1}10]$ oriented P dimers on the surface[5] based on the similarity to the SPA results for InP reported by Kobayashi and Kobayashi.[10] These $[\bar{1}10]$ oriented group V dimers are the major characteristic of the (2×4) reconstructed surface.[11] Thus, in what follows, the intensity of this peak is taken as a measure of the degree of (2×4) order on the surface during growth, although SPA is a probe of the local bonding, so it cannot be used to determine the long range order on the surface. For this reason, the reconstruction will be referred to as "(2×4)-like."

The effect of growth temperature on the SPA difference signal at 400 nm is shown in Fig. 1. The SPA signal difference, and hence the concentration of $[\bar{1}10]$ oriented P dimers, $[P^{2-}_{[110]}]$, decreases monotonically as the temperature increases from 620 to 720 °C. This is simply due to a shift in the P adsorption/desorption balance at the surface. The SPA difference signal approaches zero at 720 °C. The SPA signal at 400 nm continues to climb as the temperature is further reduced to 520 °C.[7]

The degree of order is included in Fig. 1. It was determined from the S^2 dependence of the band gap energy on the degree of order,[2] with a band gap energy difference between ordered and disordered $Ga_{0.5}In_{0.5}P$ of 471 meV.[12] The PL peak energy is used to determine the band gap energy. A potential problem with this approach is the possibility of nonband edge emission dominating the PL spectra. Impurities are one possible source of such low-energy emission peaks, although impurity emission is not normally dominant for the high purity GaInP layers considered here. Impurity effects can normally be minimized by using high excitation energies. A more serious problem for these samples is the possibility of band tailing effects associated with the inhomogeneity of the order parameter or the presence of antiphase boundaries. Such effects have been studied by several workers.[12,13] Again in this case, the best method for minimizing these problems is the use of high excitation intensities. Thus, all order parameters have been deduced from PL spectra measured at a laser power of 10 mW. For the size of the laser spot used here, this corresponds to an excitation power density of 30 W/cm^2.

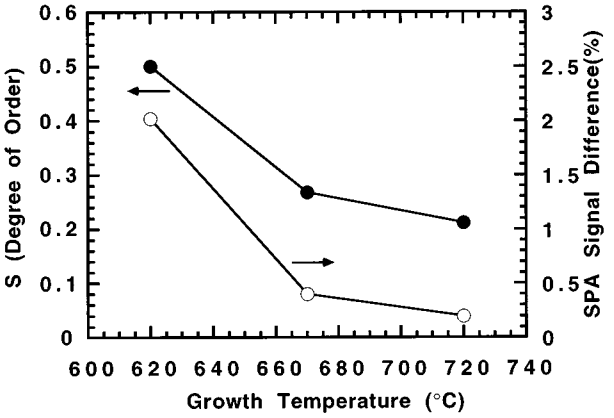

FIG. 1. The effect of growth temperature on the degree of order, S, and the SPA signal difference at 400 nm: (●) degree of order for a V/III ratio of 40 (TBP partial pressure of 50 Pa), (○) SPA signal difference for a TBP partial pressure of 50 Pa.

The data plotted in Fig. 1 indicate that for temperatures of 620 °C and above, both the degree of order and $[P^{2-}_{[110]}]$ decrease with increasing growth temperature. This suggests that loss of the (2×4)-like surface reconstruction results in a reduction of the degree of CuPt ordering. As discussed above, this is consistent with theoretical predictions summarized in Ref. 2. The order parameter is a maximum at approximately 620 °C. A clear decrease is observed with decreasing temperatures below 620 °C.[5,7] Thus, the degree of order decreases with decreasing temperature even though $[P^{2-}_{[110]}]$ increases in this range. This suggests that the degree of order decreases at low temperatures for kinetic reasons. Lower temperatures lead to lower rates of atomic migration on the surface, which may prevent formation of CuPt structure during the time available before the surface layer is covered by the next layer deposited.[7] This mechanism is basically the same as that postulated to account for the decrease in degree of order with increasing growth rate at a constant temperature.[14]

The effect of V/III ratio on both ordering and the surface reconstruction deduced from the SPA measurements is also significant. As seen in Fig. 2, for layers grown using TBP on exactly (001) substrates, a decrease in the TBP partial pres-

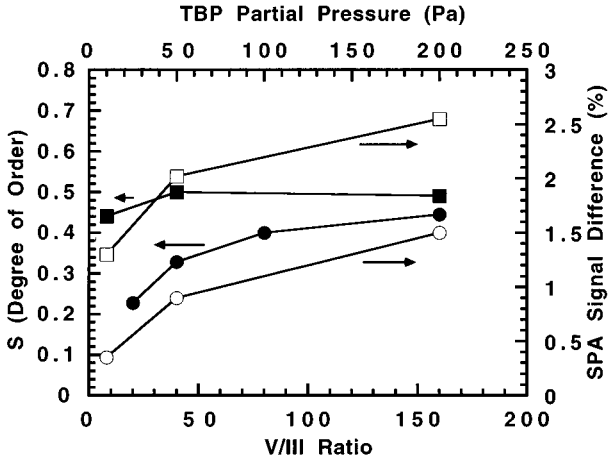

FIG. 2. Influence of input TBP partial pressure on the SPA difference signal at 400 nm and the degree of order, deduced from the 15 K PL peak energy, for GaInP samples grown lattice matched to exactly (001) GaAs substrates. ○, □: 670 °C and ●, ■: 620 °C.

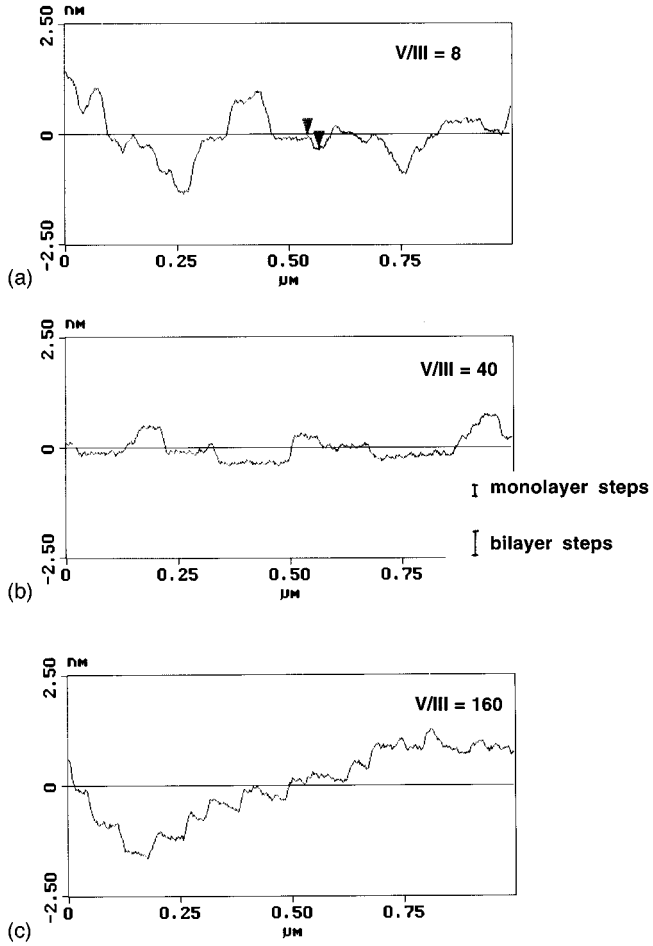

FIG. 3. Cross sectional AFM scans of the surfaces of GaInP layers grown on exactly (001) GaAs substrates at a temperature of 620 °C. (a) V/III=8; (b) V/III=40; and (c) V/III=160.

sure from 200 to 10 Torr results in a significant decrease in the extent of (2×4)-like reconstruction at both 620 and 670 °C. Consistent with the temperature effect discussed above, the SPA signal is always larger at the lower growth temperature. The degree of order deduced from the PL peak energy is also plotted versus input TBP partial pressure in Fig. 2 for growth at both 620 and 670 °C. The monotonic trend of decreasing degree of order for decreasing (2×4)-like reconstruction observed at 670 °C is qualitatively similar to the correlation observed when the growth temperature is changed. At 620 °C, the behavior is more complex. At high V/III ratios at this lower growth temperature, the degree of order is observed to decrease slightly. This is consistent with previous observations for growth using either phosphine or TBP.[15] This behavior at high P surface coverages is not completely understood. However, evidence of formation of an isotropic P dimer on the surface at high group V flow rates and low temperatures observed in InP[10] is also seen in the GaInP layers studied here. This change in surface reconstruction may be responsible for the observed decrease in the degree of order. This also provides an alternate possibility for the reduced ordering observed at lower growth temperatures.

The step structure, another factor that may affect ordering, is also found to be dependent on the V/III ratio. Figure 3 shows AFM scans for layers grown at 620 °C with V/III ratios of 8, 40, and 160. The surfaces for V/III ratios of 40 and 160 are smooth, giving easily interpreted AFM profiles. Growth at the low V/III ratio of 8 is difficult, resulting in rougher surfaces. The scan shown in Fig. 3 is representative of the smoothest areas observed. The [110] steps are seen to be mainly monolayers (2.8 Å) at low V/III ratios and mainly bilayers at high V/III ratios. The average step height is plotted versus input TBP flow rate in Fig. 4 for growth temperatures of both 620 and 670 °C. The formation of bilayer (5.7 Å) steps at high TBP partial pressures has been attributed to the stabilization of the (2×2) structure on the (111)B step edge at high phosphorus partial pressures.[7] Biegelsen *et al.*[16] observed the As-rich (2×2) structure on (111)B GaAs surfaces at high As pressures. The (2×2) unit cell will just fit on the (111)B face of a bilayer step.[7] Recent calculations indicate that bilayer type A ($[\bar{1}10]$) steps become more stable for high anion/cation ratios,[17] although the effect for B type ([110]) steps has not been considered.

The bilayer step structure observed for growth at high V/III ratios apparently explains one type of defect observed in GaInP layers.[9] For growth on exactly (001) oriented substrates, both the $(\bar{1}11)$ and $(1\bar{1}1)$ variants of the CuPt ordered structure are observed. The domains of the two variants are separated by order twin boundaries having the (001) orientation. The thicknesses of the (001) laminae of the two variants are found experimentally to be always equal to an even number of atomic layers.[18] The results presented here suggest that this is due to the formation of the CuPt structure via propagation of bilayer steps. The order twin boundaries are apparently due to a change in the direction of step propagation due to the undulating nature of the surface as growth proceeds.

The SPA spectra for GaInP layers grown at 620 °C with a V/III ratio of 40 on substrates with misorientation angles of 0°, 6°, 11°, and 15.8° toward the $[\bar{1}10]$ direction are super-

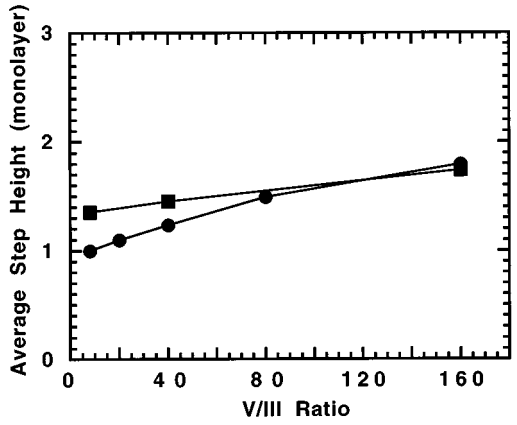

FIG. 4. Average step height (neglecting bunched steps) vs V/III ratio of GaInP layers grown on exactly (001) oriented GaAs substrates at temperatures of 620 (■) and 670 °C (●).

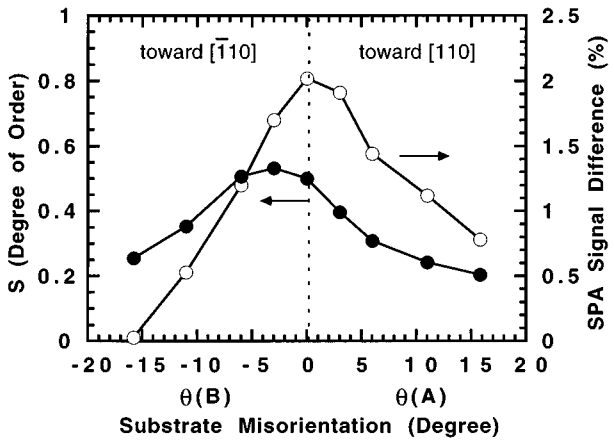

FIG. 6. SPA difference intensity at 400 nm vs misorientation angle, for misorientations in both the A and B directions, to produce [$\bar{1}$10] and [110] steps, respectively. Also plotted are the order parameters determined for these samples.

imposed in Fig. 5. The substrate with a misorientation of 15.8° is, of course, the (115)B surface. Clearly, the feature at approximately 400 nm is strongly dependent on the substrate misorientation. As mentioned above, this strongly anisotropic feature is attributed to [$\bar{1}$10] oriented P dimers on the surface. The SPA difference intensity is plotted in Fig. 6 versus misorientation angle, for misorientation in the [110] direction, to produce A-type steps, and in the [$\bar{1}$10] direction, to produce B-type steps. The data clearly show the decrease in the (2×4)-like reconstruction with increasing misorientation angle. The effect is stronger for misorientation in the B direction. Also included in Fig. 6 are the order parameters calculated as described above from the PL peak energies. The degree of order decreases monotonically with increasing θ_A, as reported previously for GaInP growth using phosphine.[19] For misorientation in the B direction, the degree of order increases with increasing misorientation angle for angles of less than approximately 3°. However, for larger misorientation angles, a decrease in order parameter with increasing misorientation angle is observed, similar to the data for misorientation in the A direction. These data are similar to those obtained earlier using PH_3.[6,19]

By combining these observations, it is clear that the decrease in the (2×4)-like reconstruction induced by increasing the misorientation angle corresponds to a decrease in the degree of order, as for the data obtained for variations in both temperature and V/III ratio. However, a second factor also appears to be important. The [110] steps themselves clearly assist the ordering process and the [$\bar{1}$10] steps have a disordering effect.

The effect of the surface [$\bar{1}$10] P-dimer concentration on the degree of order measured in the GaInP layers can be seen most clearly by directly examining the relation between the degree of order, deduced from the PL peak energy, and the

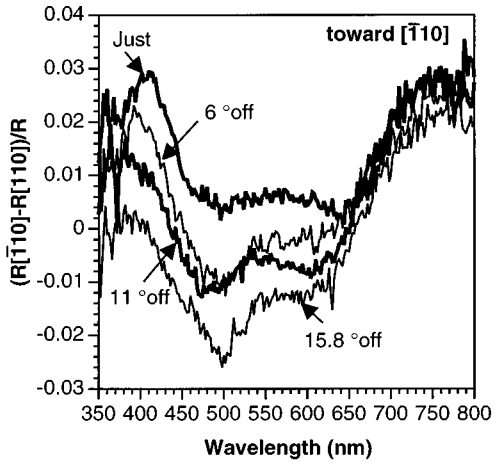

FIG. 5. Superimposed SPA spectra for GaInP samples grown at 620 °C on substrates misoriented from (001) by angles of 0°, 6°, 11°, and 15.8° toward the [$\bar{1}$10] direction in the lattice.

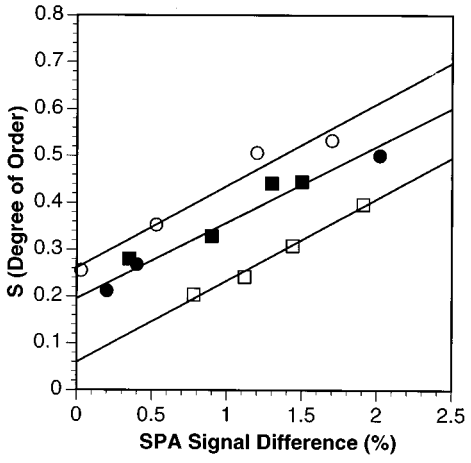

FIG. 7. Degree of order vs SPA difference signal: (●) Ref. 7 for samples grown at several temperatures for exactly (001) substrates; (■) Ref. 7 for samples grown at several values of V/III ratio for exactly (001) substrates; (□) substrates misoriented toward [110]; (○) substrates misoriented toward [$\bar{1}$10].

SPA difference signal measured at 400 nm. The data are plotted in Fig. 7. For samples with the exact (001) orientation, the correlation between the degree of order and the SPA signal intensity induced by changing either the growth temperature or the input TBP flow rate is nearly perfect. The general trends for changes in the misorientation angle are similar, although it is apparent that [110] steps have an additional beneficial effect and the $[\bar{1}10]$ steps have an additional deleterious effect.

The disappearance of the (2×4)-like reconstruction with increasing misorientation angle is thought to relate to the inability to form dimers involving all atoms on the (001) facets between steps. For an exactly (001) oriented surface having the (2×4) reconstruction, all P surface atoms will be able to reduce the energy of their dangling bonds via formation of [110] dimer rows. The introduction of [110] steps produces (001) facets of finite widths. This interferes with the ability of all surface atoms to form dimers. For example, if the (001) facet in a particular location consists of an odd number of [110] rows of P atoms, one row will not be able to participate in the reconstruction. The fraction of surface P atoms not able to participate generally increases with increasing misorientation angle. In terms of the simplest surface structure involving P dimers, the (2×1) reconstruction, one can see qualitatively that a larger fraction of the surface P atoms will be able to dimerize on the surface in the presence of $[\bar{1}10]$ steps, in agreement with the results presented in Fig. 6.

For both the A and B misorientations, the steps on the surface are also expected to affect the reconstruction. Simple electron counting (local charge density) arguments are often used to understand the stabilities of particular surface reconstructions.[16] The presence of steps will certainly affect the electron counting results for large misorientation angles, leading to the expectation that other reconstructions may form.

The general effects of surface steps, in addition to the effect on the surface reconstruction, have been considered qualitatively. For example, simple models to explain the formation of the B variants of the CuPt structure involve [110] steps.[1,20] Additional factors related to the attachment of adatoms at steps were discussed qualitatively by Asahi.[21] For example, a group III adatom approaching a [110] step makes no bonds in addition to the two bonds to the underlying (001) surface. This is expected to lead to a small sticking coefficient which leads, in turn, to a higher probability for ordering, since the lowest energy structure is more likely to form when many adsorption/desorption steps occur at the step edge before the final configuration is attained. On the other hand, for high V/III ratios, the group V adatom approaching a $[\bar{1}10]$ step will be able to form third bond. This is expected to result in a high sticking coefficient, which would not be conducive to formation of an ordered structure. For example, if the sticking coefficient were unity, the step propagation rate would be a maximum, the $[\bar{1}10]$ step would be extremely rough, and the arrangement of the Ga and In atoms would be random. This simple model is consistent with the observation that islands on exactly (001) surfaces of GaInP grown by OMVPE are elongated in the $[\bar{1}10]$ direction.[9] Thus, [110] steps are expected to enhance the formation of the B variants of the CuPt structure and $[\bar{1}10]$ steps are expected to have a deleterious effect.

Examination of the data collected here for variations in growth temperature, V/III ratio, and substrate misorientation suggests that formation of the CuPt ordered structure is intimately related to the formation of the (2×4)-like ordered structure on the surface during growth. However, it is too early to claim a direct mechanistic relationship. Recent efforts to produce order/disorder heterostructures by changing the flow rate of the P precursor during growth have resulted in a clear memory effect. The degree of order in the bottom layer apparently "propagates" into the top layer for a significant distance, i.e., the change in order parameter is not abrupt.[22] The change in the SPA signal is virtually instantaneous. This suggests that the step structure may play an important role in ordering. Investigations of the dynamics of the change is step structure are currently underway.

IV. CONCLUSIONS

The effects of three growth parameters, temperature, V/III ratio, and substrate misorientation, on both the occurrence of CuPt ordering and the surface structure have been studied. Considering first the data for singular (001) substrates, increasing growth temperature above 620 °C is found to decrease the degree of order and to result in a dramatic decrease in the SPA signal at 400 nm attributed to the $[\bar{1}10]$ dimers characteristic of the (2×4)-like surface reconstruction. Decreasing the input TBP flow rate, giving V/III ratios of <160 at 620 and 670 °C is similarly found to decrease both the 400 nm SPA signal and the degree of order measured in the GaInP epitaxial layers. Together, these data strongly suggest a correlation between the concentration of $[\bar{1}10]$ P dimers on the surface, characteristic of the (2×4) reconstruction, and the degree of order produced during epitaxial growth. In addition, the structure of [110] steps is found to change from predominately bilayer at high V/III ratios to monolayer at low V/III ratios. Increasing the concentration of [110] steps by misorientation of the (001) substrate is found to decrease the concentration of $[\bar{1}10]$ P dimers on the surface. It is found to increase the degree of order for angles of $<3°$ and to decrease the degree of order for larger angles. Increasing the concentration of $[\bar{1}10]$ steps is found to decrease both the concentration of P dimers and the degree of order. This supports the relationship between the (2×4)-like reconstruction and ordering, but indicates that a second factor is the concentration of steps. [110] steps assist the ordering process and $[\bar{1}10]$ steps lead to disordering.

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