Surface photoabsorption study of the effect of substrate misorientation on ordering in GaInP

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Substrate orientation strongly affects Cu–Pt ordering in $Ga_{0.5}In_{0.5}P$ layers grown by organometallic vapor phase epitaxy. *In situ* surface photoabsorption (SPA) measurements were used to measure the concentration of [$\bar{1}$10]-oriented P dimers, characteristic of the (2×4) reconstructed surface, as a function of substrate misorientation from (001). For substrates misoriented toward either [110] [or (111)A] or [$\bar{1}$10] [or (111)B], the P-dimer concentration is found to decrease systematically as the misorientation angle increases from 0° to 15.8° at 620 °C with tertiarybutylphosphine (TBP) partial pressures of 10, 50, and 200 Pa. The P-dimer concentrations on substrates misoriented toward [110] are higher than for those misoriented toward [$\bar{1}$10]. The $Ga_{0.5}In_{0.5}P$ layers were found to form the Cu–Pt structure during growth. The degree of order, determined from 20 K photoluminescence measurements, shows a strong correlation with the concentration of [$\bar{1}$10]-oriented P dimers. The data also clearly show the effect of step structure on Cu–Pt ordering. They indicate that [110] steps formed by misorientation toward [$\bar{1}$10] enhance ordering while [$\bar{1}$10] steps formed by misorientation toward [110] retard ordering. *© 1996 American Institute of Physics.* [S0003-6951(96)03116-2]

$Ga_{0.5}In_{0.5}P$ layers grown on (001)-oriented GaAs substrates by organometallic vapor phase epitaxy (OMVPE) typically form the Cu–Pt ordered structure.[1] Cu–Pt ordering is believed to be driven by the thermodynamics at the surface. The periodic surface stresses resulting from the formation of [110] rows of [$\bar{1}$10]-oriented phosphorus dimers on the (2×4) reconstructed (001) surface result in a segregation of the subsurface group III atoms into alternating [110] rows of In and Ga atoms.[2] This results in the formation of the two B variants of the Cu–Pt structure with ordering on the ($\bar{1}$11) and (1$\bar{1}$1) planes typically observed for layers grown by OMVPE.

The degree of order is found to vary widely for different growth conditions.[3–9] Our recent results,[10–12] obtained using surface photoabsorption (SPA) to determine the concentration of [$\bar{1}$10]-oriented P dimers on the surface ($[P^2_{[\bar{1}10]}]$), showed a direct correlation between the P-dimer concentration and the degree of order with changes in either growth temperature (⩾620 °C) or V/III ratio. This indicates that the (2×4)-like surface reconstruction is, indeed, necessary for formation of the Cu–Pt structure during growth.

Substrate misorientation from (001) also has a major effect on the degree of order for layers grown by OMVPE.[3,9,13,14] When the misorientation angle θ_B increases from the exact (001) toward [$\bar{1}$10] [or (111)B] to produce [110] (or B) steps, the band-gap energy (E_g) decreases until it reaches a minimum value at between 3° and 6°. The presence of [110] steps on the surface apparently increases the rate of Cu–Pt ordering.[14] As θ_B increases above 6°, the value of E_g increases. Increasing the misorientation angle θ_A from the exact (001) toward [110] [or (111)A] to produce [$\bar{1}$10] (or A) steps, results in a monotonic increase in E_g. In contrast to [110] steps, [$\bar{1}$10] steps appear to hinder the Cu–Pt ordering process.[13,14] This is probably due to the high group III sticking probability at [$\bar{1}$10] steps, where 3 bonds are formed at high V/III ratios. This would be expected to result in the growth of disordered material.

The purpose of this research is to characterize the surface structure of $Ga_{0.5}In_{0.5}P$ layers grown on misoriented GaAs substrates by using SPA measurements to determine $[P^2_{[\bar{1}10]}]$, which is characteristic of the (2×4) reconstruction. The change in $[P^2_{[\bar{1}10]}]$ with increasing misorientation angle is correlated with the degree of Cu–Pt order in the epitaxial layers in an effort to further our understanding of the mechanism leading to Cu–Pt ordering during growth.

All $Ga_{0.5}In_{0.5}P$ layers described here were grown at a rate of 0.3 μm/h in an atmospheric pressure, horizontal OMVPE reactor using trimethylgallium (TMGa) at −10 °C, ethyldimethylindium (EDMIn) at 15 °C, and tertiarybutylphosphine (TBP) at 7 °C. A SPA system was attached to the OMVPE system 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 incidence angle of 70° through a polarizer and a chopper. The reflected light is monochromatized and detected by a Si pnn^+ photodiode using standard lock-in amplification techniques. The wavelength was fixed at 400 nm to measure $[P^2_{[\bar{1}10]}]$.[10] 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. Thus, the term ''(2×4)-like'' is used to describe surfaces with a high concentration of [$\bar{1}$10] phosphorus dimers.

The GaAs substrates used for this study were nominally (001), misoriented by angles of 0°, 3°, 6°, 11°, and 15.8° toward either the [110] direction, in which case the misorientation is denoted θ_A, or the [$\bar{1}$10] direction where the angle is denoted θ_B. Prior to SPA measurements, 0.15 μm thick $Ga_{0.5}In_{0.5}P$ layers were grown at 620 °C with a V/III ratio of 40. The TBP partial pressure (p°_{TBP}) was varied

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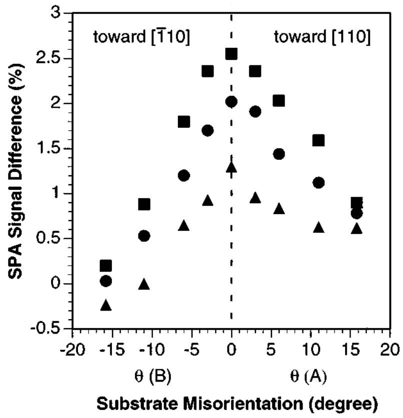

FIG. 1. The effect of substrate misorientation on the SPA difference signal at 400 nm for GaInP at 620 °C; TBP partial pressures of 10 Pa (▲), 50 Pa (●), and 200 Pa (■).

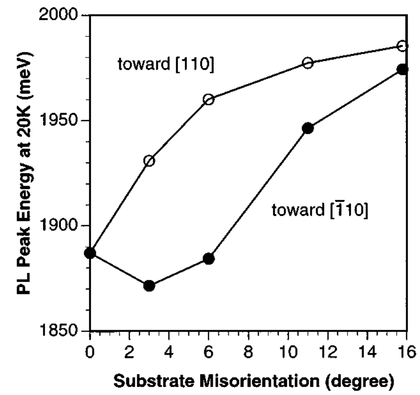

FIG. 2. Dependence of 20-K PL peak energy on substrate misorientation for an excitation power of 10 mW; (○) substrates misoriented toward [110], (●) substrates misoriented toward [$\bar{1}$10].

from 10 to 200 Pa at 620 °C during SPA measurements, corresponding to V/III ratios of 8 to 160.

Figure 1 shows the effect of substrate misorientation angle on the 400 nm SPA signal difference between [$\bar{1}$10] and [110] directions, $\{[(R(\mathrm{P})-R(\mathrm{III}))/R(\mathrm{P})]_{[\bar{1}10]}-\{[R(\mathrm{P})-R(\mathrm{III})]/R(\mathrm{P})\}_{[110]}\}$, where R(P) and R(III) are the reflectivities of the P stabilized and the group III stabilized surfaces, respectively. The magnitude of this quantity is taken to be proportional to $[\mathrm{P}^2_{[\bar{1}10]}]$. It is clear that the SPA signal difference, i.e., $[\mathrm{P}^2_{[\bar{1}10]}]$, decreases as both θ_A and θ_B increase.

For very small misorientation angles, the surface consists of large (001) regions separated by monolayer or bilayer steps.[15] At the high V/III ratios and low temperatures used in this study, the (001) terraces will have the (2×4)-like reconstruction.[10–12,15] Virtually every surface P atom will participate in the formation of [$\bar{1}$10]-oriented P dimers. With increasing misorientation angle, the terrace width becomes narrower. Each terrace is presumably composed of a number of (2×4) unit cells with ''leftover'' atoms not able to form the low energy P dimers. As the misorientation angle increases, the fraction of P atoms not participating in formation of the (2×4) unit cells necessarily increases. This may result in the formation of faceted surface, such as those observed previously in GaAs[16] and Si.[17] For specific high index planes, new stable ordered structures may also form.[17] Naturally, these phenomena will depend on whether the misorientation is toward the [110] or the [$\bar{1}$10] direction in the lattice. Presumably, these factors, that are not well understood for GaAs and certainly not for GaInP, control both the decrease in the concentration of P dimers with increasing misorientation angle and the difference between misorientations in the [110] and [$\bar{1}$10] directions.

For all substrate misorientations the SPA signal difference increases with increasing $\mathring{p}_{\mathrm{TBP}}$ from 10 to 200 Pa. This is consistent with the results for exactly (001) substrates.[11,12] To probe the relationship between ordering and $[\mathrm{P}^2_{[\bar{1}10]}]$, 0.3 μm $Ga_{0.5}In_{0.5}P$ layers were grown at 620 °C with a V/III ratio of 40 on the misoriented substrates described above. The ordering was evaluated using low-temperature (20 K) photoluminescence (PL) measurements. Figure 2 shows the 20 K PL peak energy versus substrate misorientation for excitation by the 488 nm line of an Ar^+ laser with a power of 10 mW. For the substrates misoriented toward [$\bar{1}$10], the PL peak energy is a minimum for the misorientation angle of 3° and then increases with increasing misorientation angle. This is very similar to the data of Su *et al.*[9] for layers grown using PH_3 at 670 °C using a V/III ratio of 160. On the other hand, for the substrates misoriented toward [110], the PL peak energy increases monotonically with increasing misorientation angle. These results are consistent with other published work.[3,1,14]

The degree of order S, was determined from the calculated S^2 dependence of the band-gap energy on the degree of order.[18,19] 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[20] is in good agreement with the experimental value of 471 meV.[19] The experimental value of the band-gap energy for totally disordered $Ga_{0.5}In_{0.5}P$ is ~2.005 eV.[4,18] Thus, S is calculated as

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

Figure 3 shows the degree of order versus SPA difference signal. As mentioned above, $[\mathrm{P}^2_{[\bar{1}10]}]$ and the degree of (2×4)-like reconstruction on the surface are taken to be proportional to the SPA difference signal.[10] The results for exactly (001) substrates in Fig. 3 are taken from Ref. 12 where the effects of growth temperature (⩾620 °C) and V/III ratio were studied. The *slopes* for the data for exactly (001) substrates, the substrates misoriented toward [110], and those misoriented toward [$\bar{1}$10] are nearly identical. However, the magnitude of the order parameter for a given value of $[\mathrm{P}^2_{[\bar{1}10]}]$ is dependent on the direction of misorientation. The data suggest that two factors are important. The strong dependence on the P-dimer concentration suggests that the (2×4)-like ordered structure is necessary for the formation of the Cu–Pt ordered structure during growth, in agreement with theoretical results.[2,18] Clearly, even for misoriented substrates, the (2×4)-like surface reconstruction is formed and plays an important role in formation of the Cu–Pt structure. The second factor is related to the relative displacements of

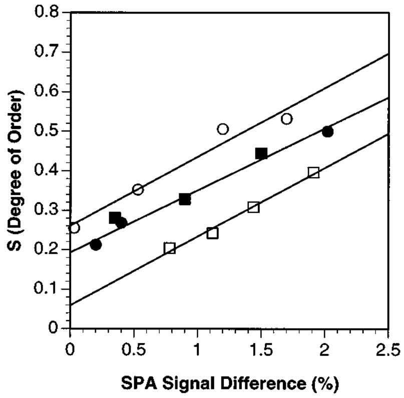

FIG. 3. Degree of order vs SPA signal difference; (●) Ref. 12 for samples grown at several temperatures for exactly (001) substrates. (■) Ref. 12 for samples grown at several values of V/III ratio for exactly (001) substrates, (□) substrates misoriented toward [110], (○) substrates misoriented toward [$\bar{1}$10].

the data for [$\bar{1}$10] misoriented substrates to higher order parameters and for the [110] misoriented substrates to lower order. These observations represent clear evidence that the step structure is also important for formation of Cu–Pt ordering during growth. The [110] steps formed by misorientation toward [$\bar{1}$10] apparently assist in the formation of alternating [110] rows of Ga and In atoms necessary for formation of the ($\bar{1}$11) and (1$\bar{1}$1) variants of the Cu–Pt structure observed. On the other hand, [$\bar{1}$10] steps formed by misorientation toward [110] apparently hinder formation of the [110] Ga and In rows. This may be due to the extremely high sticking coefficients for Ga and In atoms expected at [$\bar{1}$10] steps for high P pressures, where each group III atom can form 3 bonds at the step edge.

In summary, the surface structure of $Ga_{0.5}In_{0.5}P$ epitaxial layers grown on substrates misoriented toward the [110] and [$\bar{1}$10] directions in the lattice was studied using SPA. The SPA intensity due to [$\bar{1}$10]-oriented P dimers on the surface decreases as the misorientation angle increases, indicating that large misorientation angles prevent formation of the (2×4)-like surface reconstruction on the (001) terraces between steps. The P-dimer concentration on GaInP layers grown on substrates misoriented toward [110] is higher than for substrates misoriented toward [$\bar{1}$10] especially for large misorientation angles. The degree of order is found to be proportional to the SPA signal difference for exactly (001) substrates as well as those misoriented toward both the [110] and [$\bar{1}$10] directions. However, the degree of order corresponding to a particular SPA signal intensity is highest for misorientation toward [$\bar{1}$10] and lowest for misorientation toward [110]. These results indicate that Cu–Pt ordering is affected by both (2×4)-like surface reconstruction and the step structure. Formation of [$\bar{1}$10] oriented P dimers on the surface provides the driving force for formation of the Cu–Pt structure and [110] steps enhance the ordering process while [$\bar{1}$10] steps inhibit ordering.

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