Surface photoabsorption studies of the chemical structure of GaInP grown by organometallic vapor phase epitaxy

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The surface structure of $Ga_{0.52}In_{0.48}P$ was studied by surface photoabsorption. An absorption peak due to P dimers on $Ga_{0.52}In_{0.48}P$ was observed at ~400 nm, shorter than for InP (430 nm). From comparison with results for GaAs and InP, the data are interpreted to indicate that at a tertiarybutylphosphine (TBP) pressure of 50 Pa for temperatures below 670 °C, the P-stabilized surface has P dimers aligned along the $[\bar{1}10]$ direction, i.e., it has a (2×4)-like structure. Above 670 °C, the 400 nm peak due to the P-dimer structure disappears because of P desorption from the surface at this TBP partial pressure. Epitaxial $Ga_{0.52}In_{0.48}P$ layers grown using TBP, trimethylgallium and ethyldimethylindium are nearly disordered at 670 °C and highly ordered at 620 °C. These data suggest a correlation between surface structure and ordering. © *1995 American Institute of Physics.*

It is well known that $Ga_{0.52}In_{0.48}P$ grown using trimethylgallium (TMGa), trimethylindium (TMIn), and PH_3 under certain conditions forms the Cu–Pt type structure with ordering along $\langle 111\rangle$ directions.[1] The degree of order is reported to vary with growth temperature,[2–5] growth rate,[4,6,7] V/III ratio,[4,8] and substrate orientation.[4,5,7,9,10] Although there are four equivalent $\{111\}$ planes in the zinc-blende structure, ordering on the (111) an $(\bar{1}\bar{1}1)$ planes is not typically observed.[1] The $(\bar{1}11)$ and $(1\bar{1}1)$ planes on which ordering has been observed intersect the (001) surface along the $[110]$ direction. This is interpreted to indicate that the chemical structure, in particular the surface reconstruction, plays an important role in the ordering process occurring at the surface during growth.[11,12] However, no studies of the surface reconstruction of $Ga_{0.52}In_{0.48}P$ have been reported previously.

Available techniques to observe the surface structure of epitaxial layers grown by organometallic vapor phase epitaxy (OMVPE) are more restricted than for molecular beam epitaxy (MBE), where reflection high-energy electron diffraction (RHEED) can be used. However, recently *in situ* surface measurements of GaAs grown by OMVPE have been reported by reflectance-difference spectroscopy (RDS)[13,14] and surface photoabsorption (SPA).[15,16] SPA has the advantage of a simple setup and high signal-to-noise (S/N) ratio.[17] The surface structure of InP grown by OMVPE determined by SPA has also been recently reported by Kobayashi *et al.*[18] It should be noted that these optical techniques can be used to determine the local structure at the surface, for example the presence of group V dimers, but cannot be used to determine the long range periodicity.

PH_3 is toxic and hazardous although it is widely used as a P source to grow $Ga_{0.52}In_{0.48}P$ layers by OMVPE. Thus, less toxic sources, such as tertiarybutylphosphine (TBP), are expected to replace PH_3. Takeda *et al.*[19] and Kawakyu *et al.*[20] previously studied $Ga_{0.52}In_{0.48}P$ growth using TBP. However, the effect of TBP on ordering of $Ga_{0.52}In_{0.48}P$ layers has not been fully discussed.

This letter reports the chemical surface structure determined using SPA of $Ga_{0.52}In_{0.48}P$ layers grown by OMVPE using TMGa, ethyldimethylindium (EDMIn), and TBP. The results suggest a correlation between the surface structure and the occurrence of ordering during epitaxial growth.

The $Ga_{0.52}In_{0.48}P$ layers were grown on semi-insulating (001)-oriented GaAs substrates in an atmospheric-pressure, horizontal OMVPE system. The sources were TMGa at −12 °C, EDMIn at 15 °C and TBP at −12 °C. The growth temperature and V/III ratio were 620 °C and 40, respectively. A SPA system was attached to the OMVPE reactor for *in situ* measurements. P-polarized light from a 150 W Xe lamp irradiated the $Ga_{0.52}In_{0.48}P$ layer at an incident angle of 70° through a polarizer and a chopper. The incident light direction was parallel to the direction of gas flow in the reactor. The reflected light was monochromatized and detected by a Si pnn^+ photodiode. The signal was processed by the standard lock-in amplifier technique. Each run consisted of the growth of two 0.15 μm layers, one where the $[110]$ direction of the GaAs was parallel to the gas flow and one where the substrate was rotated by 90°. SPA measurements were performed at 520, 570, 620, 670, and 720 °C.

Figure 1 shows the SPA spectra of $Ga_{0.52}In_{0.48}P$ with the incident light along the $[110]$ and $[\bar{1}10]$ directions at 520 °C. The quantity $[R(\mathrm{P})\text{-}R(\mathrm{III})]/R(\mathrm{III})$ was obtained from the reflectivity difference between the P-stabilized and the group III element-stabilized surfaces. 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. The spectra in Fig. 1 include both isotropic and anisotropic components. Since information about the dimer structure on the surface is obtained from only the anisotropic components, it is necessary to subtract one spectrum from the other. Figure 2 shows the result. The spectrum is similar to the results obtained for InP grown by OMVPE.[18] A strong absorption peak is observed at ~400 nm. Based on the similarity to the results reported for InP, this is attributed

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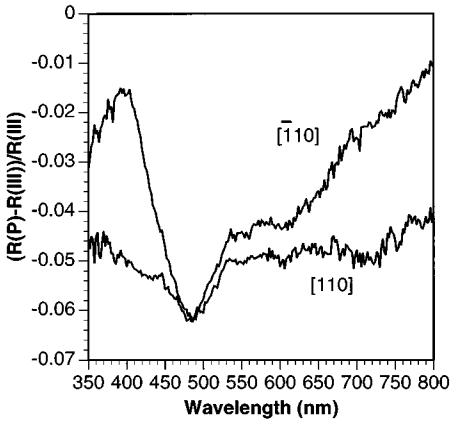

FIG. 1. SPA spectra of $Ga_{0.52}In_{0.48}P$ with the incident light along the [110] and [$\bar{1}$10] directions at 520 °C.

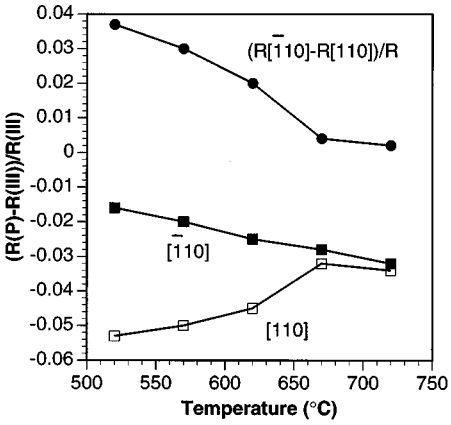

FIG. 3. Temperature dependences of the SPA signal at 400 nm.

to P dimers on the $Ga_{0.52}In_{0.48}P$ surface. The peak wavelength is shorter than that for P dimers on InP (430 nm),[18] because the bond length of P dimers on the $Ga_{0.52}In_{0.48}P$ surface will be shorter than on an InP surface. This would be expected to increase the splitting of the electron transition levels due to P dimers. The broad peak above 650 nm is regarded as being due to group III element dimers. Since both peaks have the same (positive) sign, it was concluded that the P dimers are aligned along [$\bar{1}$10], perpendicular to the group III-element dimers, which are known to be aligned along [110]. Since the (2×4) reconstructed surface is covered by [$\bar{1}$10] oriented P dimers, these data suggest that the $Ga_{0.52}In_{0.48}P$ surface reconstruction for these conditions is (2×4)-like. As mentioned above, the long range periodicity cannot be ascertained from optical measurements, thus the surface is referred to as "(2×4)-like." These data contrast with the data for GaAs grown by OMVPE, where the *c*(4×4)-like structure is formed, consisting of two As layers.[15,16] The As dimers in this case are aligned in the [110] direction. According to the phase diagram of Ref. 18, the vapor pressure of PH_3 over InP required to form the (2×4)-like structure is much higher than the AsH_3 pressure over GaAs required to form this structure, presumably due to the high group V pressure in equilibrium with InP.[21] Thus, the formation of the (2×4)-like structure for $Ga_{0.52}In_{0.48}P$ with a TBP partial pressure of 50 Pa is not surprising. Besides the (2×4)-like structure, the existence of amorphous P on the surface[18] is suggested from the largest isotropic signal observed at around 490 nm in Fig. 1.

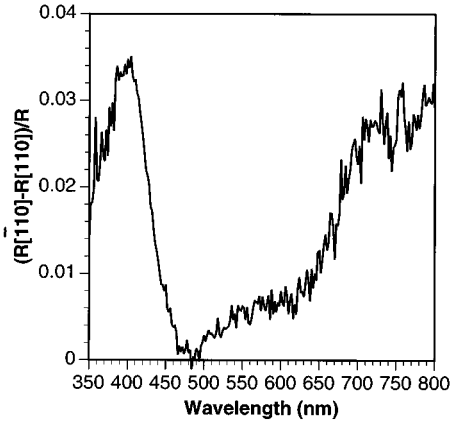

FIG. 2. Subtraction spectrum of $Ga_{0.52}In_{0.48}P$ at 520 °C.

For measurement temperatures above 520 °C, the measurement wavelength was fixed at 400 nm to measure the concentration of [$\bar{1}$10] oriented P dimers, since the surface degrades due to P desorption during the 7 min required for wavelength-scanning. The temperature dependence of the SPA signal at 400 nm is shown in Fig. 3. The lower two lines are the SPA signals at 400 nm along the [110] and [$\bar{1}$10] directions while the upper line is the difference, which will be proportional to the density of P dimers. The data indicate that the P-dimer concentration is highest at temperatures below 600 °C and decreases at higher temperatures. Above 670 °C, the difference approaches zero, suggesting the absence of P dimers on the $Ga_{0.52}In_{0.48}P$ surface at this TBP partial pressure because of the high P desorption rate.

To probe the relationship between ordering and surface structure, 0.3 μm thick $Ga_{0.52}In_{0.48}P$ epitaxial layers were grown on (001)-oriented GaAs substrates at 620 and 670 °C, two of SPA measurement temperatures, with a TBP partial pressure of 50 Pa using TMGa and EDMln as the group III sources. The growth rate and V/III ratio were held constant at 0.3 μm/h and 40, respectively. Ordering 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 and transmission electron microscope (TEM) observation. The PL peak energies at 20 K for $Ga_{0.52}In_{0.48}P$ grown at 620 and 670 °C are 1.891 and 1.971 eV, respectively. Su *et al.*[22] reported that the PL peak energy of the most ordered sample grown on a 3° misoriented substrate is ~1.84 eV and that of completely disordered sample is ~2.00 eV. This indicates that the sample grown at 620 °C is highly ordered, while that grown at 670 °C is nearly disordered. TEM examination of the sample grown at 620 °C shows order-induced superspots with two variants [stronger

$1/2(\bar{1}11)$ superspots and weaker $1/2(\bar{1}11)$ superspots]. The sample grown at 670 °C exhibits similar order-induced superspots but the intensities are much weaker.

It is significant that OMVPE growth using PH_3 produces ordered materials at both 620 and 670 °C, when the PH_3 partial pressure is between 130 and 670 Pa.[2–5] A comparison of resulting using TBP and PH_3 should be based on the P partial pressure at the interface. The PH_3 partial pressure is much larger than the TBP partial pressure. However, at low temperatures, the TBP is completely pyrolyzed ($T_{50}=\sim 450$ °C[23]), while the fraction of PH_3 pyrolyzed is low since $T_{50}=\sim 850$ °C.[23] Thus, at 620 °C the effective P pressure is probably comparable for the two P precursors, while at 670 °C the P partial pressure is expected to be much higher for growth using PH_3. The lower P pressure at 670 °C using TBP with an input partial pressure of 50 Pa probably accounts for the disappearance of the (2×4)-like surface reconstruction.

A comparison of the SPA and ordering results presented here suggests a strong correlation of order and surface structure during growth. This has been suggested by several models,[11,12] where the Cu–Pt ordering process is postulated to depend on the presence of [110] P-dimer rows, characteristic of a (2×4) surface reconstruction, on the surface. Further support comes from the observation that the growth on (115)A substrates produces nearly disordered material with a PL peak energy at 20 K of 1.989 eV. Our SPA results indicate that the P-dimer signal at ~400 nm nearly disappears on the $Ga_{0.52}In_{0.48}P$ grown on (115)A GaAs substrates.

In summary, SPA measurements indicate that the surface structure of $Ga_{0.52}In_{0.48}P$ grown by OMVPE using a TBP pressure of 50 Pa is (2×4)-like. The SPA spectrum indicates the presence of $[\bar{1}10]$ oriented P dimers, characteristic of the (2×4) reconstruction, but optical measurements are incapable of determining the long range order. It was observed that at this partial pressure the P dimers disappear at temperatures of 670 °C and above. This was found to correspond to the virtual disappearance of the Cu–Pt ordered structure as the growth temperature was increased from 620 to 670 °C for a TBP partial pressure of 50 Pa. This suggests a strong correlation between the surface structure and the ordering process. The temperature above which ordering disappears for TBP in this study is considerably below that reported for $Ga_{0.52}In_{0.48}P$ grown using PH_3. This is interpreted in terms of the much higher PH_3 partial pressure of 130–670 Pa. This will result in a much high P partial pressure at the interface at 670 °C, presumably resulting in the preservation of the (2×4)-like surface structure at higher temperatures and, hence, the production of ordered layers during growth at 670 °C.

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