

Surface photoabsorption transients and ordering in GaInP

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Heterostructures and quantum wells can be produced in GaInP without changing the solid composition by simply varying the order parameter. Since CuPt ordering reduces the band-gap energy, changes in the order parameter induced by changes in growth conditions result in heterostructures with band-gap energy discontinuities as large as 160 meV. The most convenient growth parameter to change is the flow rate of the P precursor. However, previous work has shown that under some conditions the change in order parameter is sluggish, giving rise to graded heterostructures. The cause of the slow change in order parameter is the topic of this article. CuPt ordering has been shown to be driven by the formation of $[\bar{1}10]$ P dimers, characteristic of the (2×4) surface reconstruction. Thus, this study of the transient in the degree of order induced by changing the flow rate of the P precursor has relied on the use of surface photoabsorption (SPA) to monitor the surface reconstruction during the period after the partial pressure of the P precursor was reduced. The SPA transient has then been correlated with the abruptness of the heterostructure interface, determined from the transmission electron microscopy images and the photoluminescence spectra, for organometallic vapor phase epitaxial (OMVPE) growth at temperatures of 620 and 670 °C using the P precursors phosphine (PH_3) and tertiarybutylphosphine (TBP). For TBP at both 620 and 670 °C, the SPA reflectance transient is extremely short, with a time constant of less than 10 s, corresponding to the time response of the OMVPE growth system. Abrupt interfaces are produced using these conditions. For PH_3 , the SPA reflectance transient is abrupt at 670 °C; however, at 620 °C the SPA response is extremely sluggish, with a time constant of approximately 6.5 min. The effect is tentatively attributed to a surfactant effect due to H on the surface. Corresponding heterostructures were abrupt at 670 °C and graded at 620 °C. © 1998 American Institute of Physics. [S0021-8979(98)00206-0]

I. INTRODUCTION

Ordering, i.e., the spontaneous formation of short period superlattice structures during epitaxial growth, has been observed for many semiconductor alloys.^{1,2} Formation of the CuPt ordered structure, with ordering on $\{111\}$ planes, is now believed, based on both theoretical³ and experimental⁴⁻⁶ evidence, to be driven by the thermodynamics of the (001) surface phase. Formation of $[\bar{1}10]$ group V dimer rows on the (2×4) -like surface gives rise to stresses in the third buried layer that lead to a reduction in the microscopic strain energy when the two variants of the CuPt ordered structure with ordering on the $(\bar{1}11)$ and $(1\bar{1}1)$ planes are formed.

CuPt ordering is a phenomenon of both technological and fundamental interest. For example, a 50/50 GaInP alloy lattice matched to GaAs that is completely disordered has a band-gap energy hundreds of meV higher than for a completely ordered alloy.² This means that the degree of order must be tightly controlled for materials to be used in photonic devices. It also presents the opportunity to intentionally vary the degree of order during the growth process to produce heterostructures with absolutely no change in solid

composition. For example, by changing the temperature during organometallic vapor phase epitaxy (OMVPE) growth, Su and Stringfellow⁷ were able to produce order/disorder (O/D, really a less ordered layer grown on top of a more ordered layer) heterostructures with a 160 meV difference in band-gap energy. Heterostructures and quantum wells are important elements of modern, high performance photonic and electronic devices. Thus, the ability to modulate the band-gap energy rapidly and easily during growth offers obvious technological applications.

The most convenient method for changing the degree of CuPt order in GaInP layers grown by OMVPE is to simply change the flow rate (or partial pressure) of the P precursor. In principle, this allows the degree of order to be modulated simply with no change in other growth parameters. However, the early studies of heterostructure produced in this way have been somewhat confusing. The initial studies, using PH_3 as the P precursor at a growth temperature of 620 °C, resulted in O/D heterostructures with nonabrupt interfaces, i.e., a change in the PH_3 flow rate was found to result in a very gradual change in the degree of CuPt order as determined by transmission electron microscopy (TEM) images. The variation in the band-gap energy is also gradual, as indicated by the low-temperature photoluminescence (PL) results.⁸ More

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recent studies have produced abrupt O/D and D/O heterostructures, as indicated by TEM and PL results, using TBP as the P precursor at a growth temperature of 670 °C.^{9,10} Hsu *et al.*¹¹ demonstrated that neither the degree of order nor the SPA signal due to $[\bar{1}10]$ P dimers at 400 nm was a function of the choice of P precursor. They also presented initial results showing that at 620 °C the SPA transient was slow when the PH_3 partial pressure was varied.

The purpose of this article is to present the results of a systematic study of the SPA transient induced by a change in the partial pressure of the P precursor for both PH_3 and TBP at temperatures of 620 and 670 °C. These results are compared with the corresponding heterostructure abruptness, evaluated using PL and TEM techniques.

II. EXPERIMENT

The $\text{Ga}_{0.52}\text{In}_{0.48}\text{P}$ layers were grown on semi-insulating (001) GaAs substrates in an atmospheric pressure, horizontal OMVPE system. Substrate preparation consisted of standard degreasing followed by a 1 min etch in a solution of $12\text{H}_2\text{O}:2\text{NH}_4\text{OH}:1\text{H}_2\text{O}_2$. The substrates were then rinsed in deionized water for 5 min and blown dry with N_2 before loading into the reactor. The sources were trimethylgallium (TMGa) at -10 °C and ethyldimethylindium (EDMIn) at 15 °C with Pd-diffused hydrogen as the carrier gas. The phosphorus source was either PH_3 or TBP. The growth rate of $\text{Ga}_{0.52}\text{In}_{0.48}\text{P}$ was constant at 0.3 $\mu\text{m}/\text{h}$ and all layers were approximately 0.15 μm in thickness.

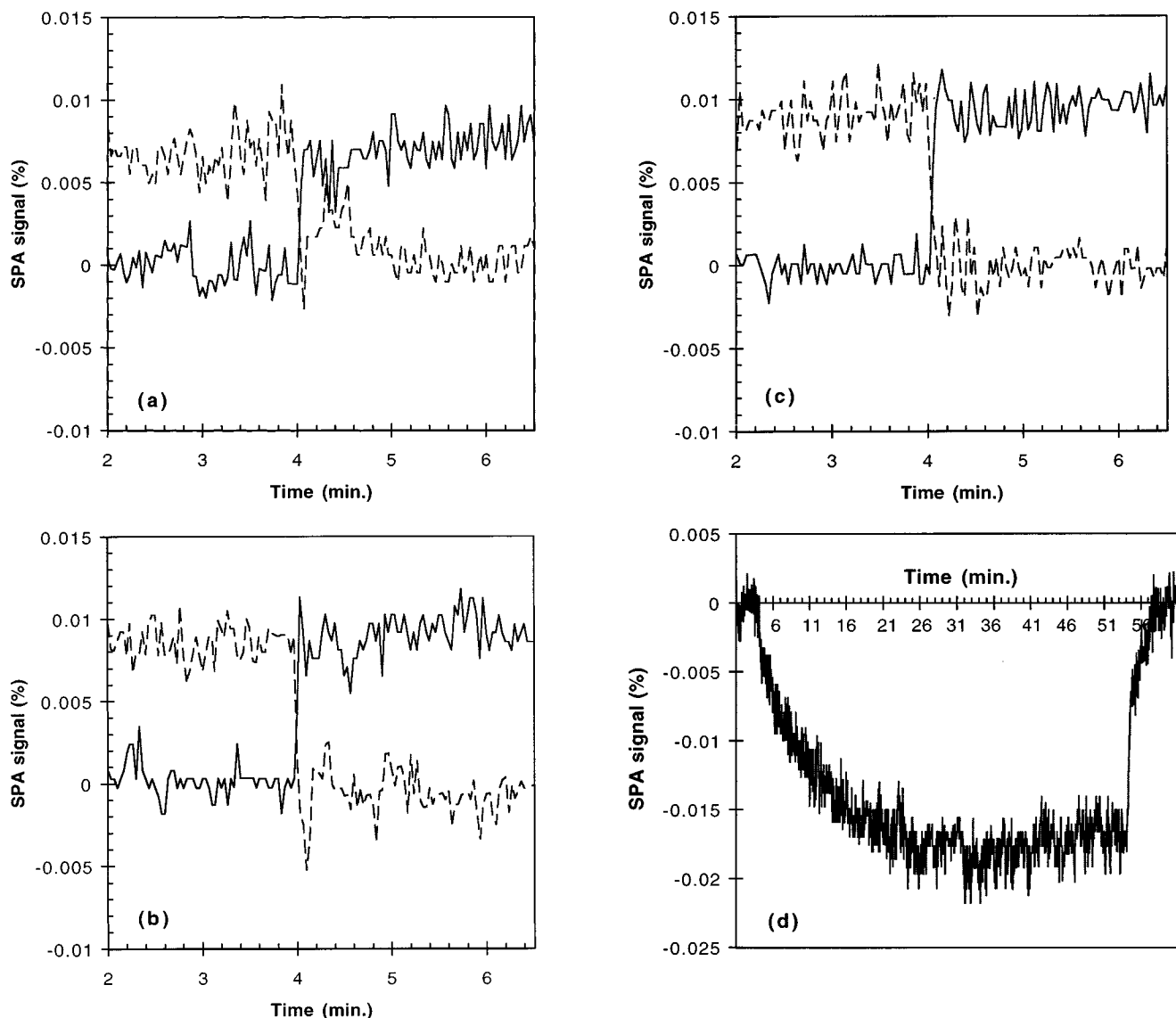


FIG. 1. SPA signal ($[\bar{1}10]$ - $[110]$) transients for signals measured at 400 nm. The group III precursors were switched to vent at time=0 and the flow rate of the P precursor was changed at time=4 min, (---) is for high to low switching and (—) represents low to high switching. (a) TBP at 670 °C for a variation of the partial pressure between 0.375 and 1.5 Torr. Transients for both an increase and a decrease in the TBP flow rate are shown. (b) TBP at 620 °C as the partial pressure was varied between 0.075 and 0.375 Torr. Transients for both an increase and a decrease in the TBP flow rate are shown. (c) PH_3 at 670 °C as the partial pressure was varied between 0.45 and 3.00 Torr. Transients for both an increase and a decrease in the PH_3 flow rate are shown. (d) PH_3 at 620 °C as the partial pressure was varied between 0.10 and 0.75 Torr. 0–4 min, 0.75 Torr; 4–54 min., 0.1 Torr; 54–60 min., 0.75 Torr.

The SPA system was attached to the OMVPE reactor for *in situ* measurements. *P*-polarized light from a 150 W Xe lamp was used to irradiate the surface of the $\text{Ga}_{0.52}\text{In}_{0.48}\text{P}$ layer at an incidence angle of 70° through a polarizer and a chopper. The direction of the incident light was parallel to the direction of gas flow in the reactor. The reflected light was monochromatized and detected by a Si PNN^+ photodiode using standard lock-in amplification techniques. The SPA measurements were done using both $[\bar{1}10]$ and $[110]$ azimuths at 400 nm, the wavelength where the signal is proportional to the $[\bar{1}10]$ P dimer concentration.

The sample was held at 20 K for PL measurements, with excitation by the 488 nm line from a focused argon ion laser with an intensity of 10 mW. The detector was a photomultiplier and standard lock-in amplifier techniques were used.

$[110]$ cross-sectional TEM samples were prepared using standard Ar-ion milling at 77 K. The transmission electron diffraction (TED) patterns and TEM images were obtained using a JEM 2010 scanning transmission electron microscope operated at 200 kV.

III. RESULTS AND DISCUSSION

The change in the SPA signal, $[\bar{1}10]$ - $[110]$ at a wavelength of 400 nm, due to the $[110]$ P dimers, when the flow of the TBP precursor is reduced from 1.5 to 0.375 Torr is shown in Fig. 1(a) for a temperature of 670°C . A $0.15\ \mu\text{m}$ layer was grown at 1.5 Torr. The group III flows were switched to vent at time=0 on this plot and the change in TBP flow rate occurred after a time of 4 min. The SPA signal when the TBP flow rate was increased from 0.375 to 1.5 Torr is also shown. In both cases, the change in the SPA signal is very rapid. It reflects the time constant of the system, i.e., the SPA signal follows the changing TBP partial pressure.⁹ Growth using these conditions is now well established to give abrupt D/O and O/D heterostructures, respectively, as reported by Chun *et al.*¹⁰

The SPA signal transients for a change in the TBP partial pressure between 0.075 and 0.375 Torr at a temperature of 620°C are seen in Fig. 1(b). Again, the transients for both an increase and a reduction in the TBP partial pressure are abrupt and limited by the response time of the flow system. An O/D heterostructure was grown by reducing the TBP partial pressure from 0.375 to 0.075 Torr at 620°C . The thickness of each layer is $0.15\ \mu\text{m}$. The 20 K PL spectrum from this heterostructure is shown in Fig. 2(a). The PL peaks are seen to be located at the energies of individual layers grown using the identical conditions. The peak separation is approximately 25 meV. The TEM cross section shows an abrupt change in order parameter. Apparently, even at 620°C , abrupt heterostructures can be produced using TBP. This appears to be due to the rapid change in surface reconstruction associated with a change in the TBP partial pressure.

At a temperature of 670°C , using PH_3 as the P precursor, the SPA signal transients associated with a change in partial pressure between 0.45 and 3.0 Torr are abrupt, as seen in Fig. 1(c). As seen from the PL spectrum in Fig. 2(b), the O/D heterostructure grown using the same conditions, with

layer thickness of $0.15\ \mu\text{m}$ each, consists of two peaks at the same energies as observed for single layers grown using the same conditions, also indicated on the figure. The peak separation is approximately 45 meV, larger than the TBP results at 620°C due to the larger change in order parameter induced by this change in the PH_3 partial pressure. The TEM cross section for this sample is shown in Fig. 3(a). It clearly shows an abrupt change in the order parameter at the interface. The TED patterns from the two layers show a distinctly higher degree of order in the lower layer. Even using PH_3 , at a temperature of 670°C abrupt heterostructures can be produced by changing the flow rate. This appears to be consistent with the rapid change in the surface reconstruction as the PH_3 pressure is changed.

The results using PH_3 at 620°C are distinctly dissimilar to all of the above results. The SPA signal transient due to a reduction in the PH_3 pressure from 0.75 and 0.1 Torr is shown in Fig. 1(d). Again, a $0.15\ \mu\text{m}$ GaInP layers was grown using a PH_3 partial pressure of 0.75 Torr. The TMGa and EDMIn flows were stopped at time=0 on this plot and the PH_3 flow rate was reduced after a period of 4 min. The 400 nm SPA signal due to $[\bar{1}10]$ P dimers on the surface falls off gradually. The exponential decay has a time constant of approximately 6.5 min. The PL from the corresponding heterostructure grown using the same conditions, as indicated in the inset, with each layer having a thickness of $0.15\ \mu\text{m}$ is shown in Fig. 2(c). The PL spectra for the individual layers grown using the same conditions are indicated. Clearly, the peak at approximately 1.89 eV corresponds to the bottom, more ordered layer. No peak is observed corresponding to the top, less ordered layer. Instead a peak is observed between the energies measured for the individual layers. This is indicative of a "memory" effect. The order from the bottom layer obviously continues for some distance into the top layer. As seen in Fig. 3(b), the TEM results are consistent with this assessment. No abrupt heterostructure is observed. Instead, the dark-field intensity appears to gradually decrease beyond the interface.

The results shown above make it clear that the graded heterostructure corresponds closely with the long time constant associated with the change in the surface reconstruction, i.e., the concentration of $[110]$ P dimers on the surface. The cause of the long SPA transient involves both the use of PH_3 and the lower temperature of 620°C . The cause for the long time constant for the change of surface structure is unclear. It is certainly not due to the vapor pressure of *P* on the surface, since the transient is rapid for TBP at 620°C . One possible explanation for the slow decrease in the SPA signal using PH_3 at 620°C is the presence of a surfactant which accumulates at the surface during growth, desorbs slowly at 620°C , and acts to reduce the rate of evaporation of *P* from the surface.¹¹ The only element known to be present that is expected to have a higher concentration for PH_3 than for TBP is H. Atomic H is expected to be produced by the heterogeneous pyrolysis of both P precursors. The H concentration might be expected to be larger for PH_3 than for TBP, although direct evidence of the H concentration on the surface is unavailable. The presence of small concentrations of dopant atoms on the surface is well known to change the

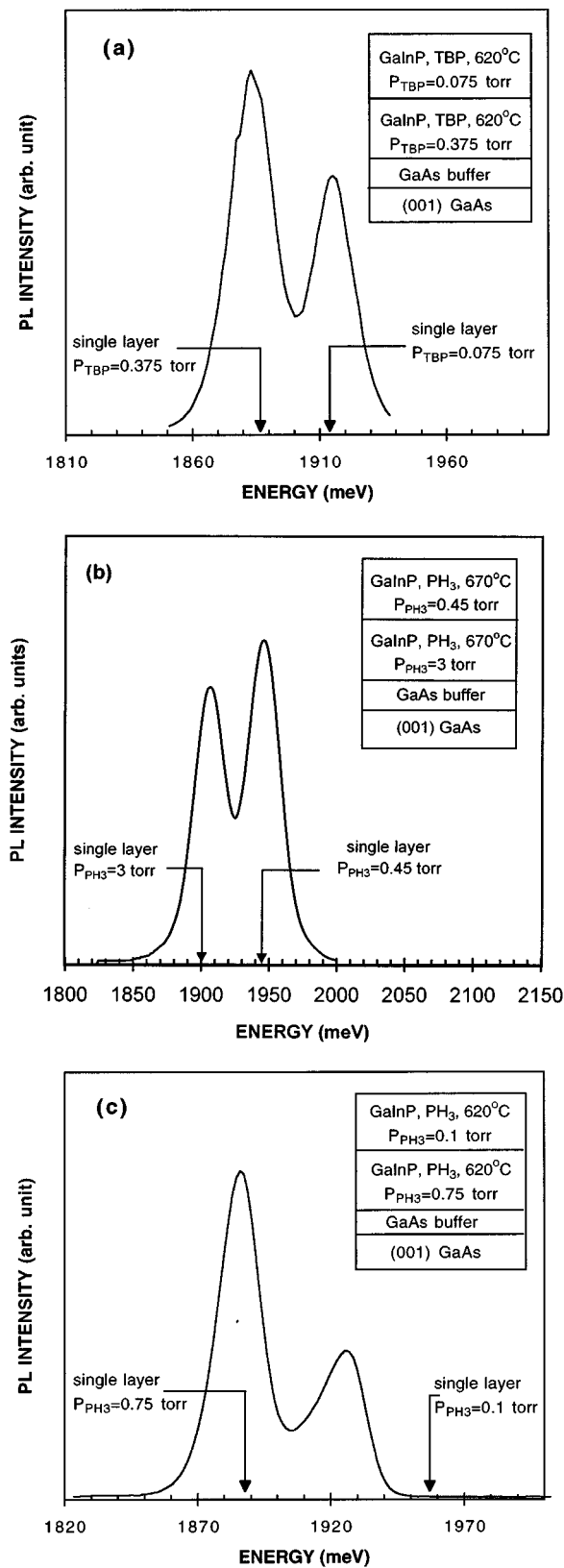


FIG. 2. 20 K photoluminescence spectra for heterostructures, shown in the insets, produced using conditions similar to those used for the SPA experiments in Fig. 1. In each case the energies of the PL peaks observed for single layers grown using the same conditions are indicated. (a) TBP at 620 °C—partial pressure varied from 0.375 to 0.075 Torr. (b) PH_3 at 670 °C—partial pressure varied from 3.00 to 0.45 Torr. (c) PH_3 at 620 °C—partial pressure varied from 0.75 to 0.10 Torr.

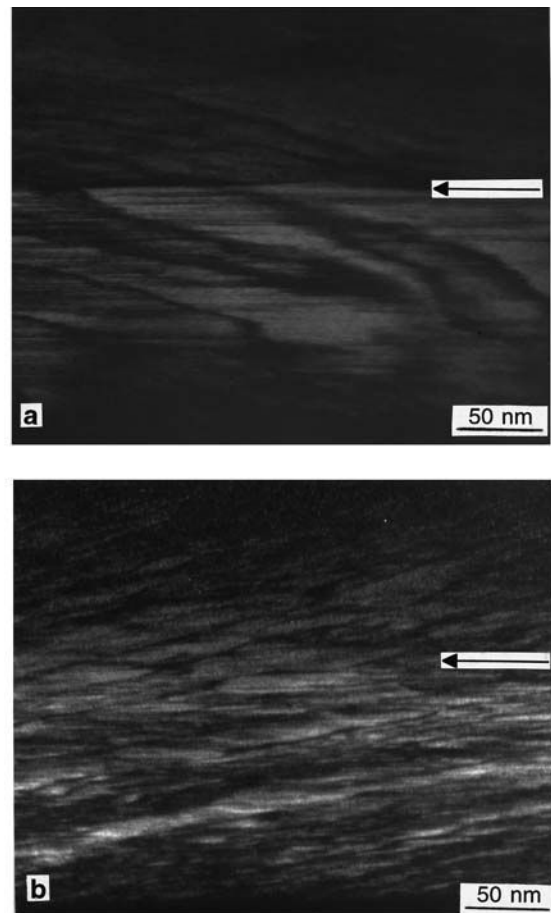


FIG. 3. TEM cross-sectional micrographs for the heterostructures included in Fig. 2. In each case, the position at which the partial pressure of the P precursor is changed is indicated by an arrow. (a) PH_3 at 670 °C—partial pressure varied from 3.00 to 0.45 Torr. (b) PH_3 at 620 °C—partial pressure varied from 0.75 to 0.10 Torr.

surface morphology, presumably by collecting at steps and kinks where adatom attachment occurs.^{12,13} It seems entirely reasonable that atomic H, which likes to make a single bond, would also accumulate at steps and kinks, producing the change in step structure observed.¹¹ Since the ordering process must occur at these sites on the surface, it might be expected that H would affect ordering. An influence of H on the rate of P desorption also appears plausible, although the mechanism is not known. P is known to evaporate as P_2 , presumably from the P dimers on the surface. The presence of a significant concentration of H on the surface might retard P_2 formation and evaporation, perhaps by blocking P_2 loss at step edges. This effect is postulated to control the SPA transient using PH_3 at 620 °C. At 670 °C, the vaporization rate is apparently rapid enough that the SPA response time is controlled by the system. Clearly, this mechanism is speculative. The mechanistic details must await further more specific surface studies.

The transient in SPA signal for PH_3 at 620 °C was studied further by examining the effects of the growth of a series of very brief GaInP layers at times of 3, 6, 9, and 12 min after the PH_3 partial pressure was reduced from 0.75 to 0.1 Torr. The thickness of each layer was estimated from the

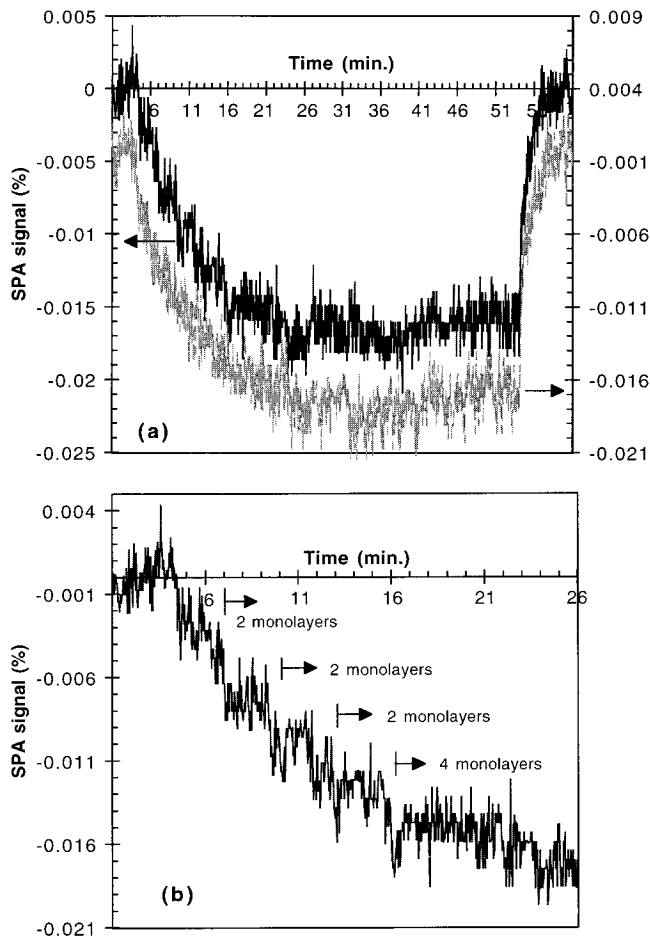


FIG. 4. SPA signal transient for PH_3 at 620°C with the inclusion of 6 \AA GaInP layers after times of 3, 6, 9, and 12 min. (a) Overall transient, including the SPA transient from Fig. 1(d), (—): with GaInP layers and (---) without GaInP layers. (b) Expanded time scale.

growth time to be approximately 6 \AA . As seen in Fig. 4(a), the SPA transient is virtually unaffected by the thin GaInP layers. The SPA transient without the GaInP layers is included for comparison. Apparently the growth of the GaInP layers does not increase the removal of P from the surface. Adding Ga and In should remove the “excess” P. The results are consistent with the H surfactant model, providing that the addition of TMGa and EDMin does not remove the H. This would be consistent with the long transient in the change in order parameter during growth. The results appear to solidify the connection between the transients in SPA and order parameter.

Figure 4(b) shows the detail of the SPA transient with the thin layers. The behavior appears to be odd. The SPA signal seems to drop during the growth of each thin GaInP layer and to be nearly constant in between. This is unexpected and unexplained, since the overall transient appears to be virtually the same with and without the intermittent GaInP layers.

To further probe the memory effect on the ordering transition, a variable interrupt time was inserted between the growth of the bottom layers with a PH_3 partial pressure of 0.75 Torr and the top layer with a pressure of 0.1 Torr. In

TABLE I. Summary of 20 K PL peak energies for heterostructures grown using PH_3 at 620°C with different interruption time.

	PL peak energy from ordered layer (meV)	PL peak energy from disordered layer (meV)
Single layer	1888.6	
$P_{\text{PH}_3} = 0.75$ Torr		
Heterostructure with 2 min interruption	1885.7	1925.2
Heterostructure with 8 min interruption	1894.4	1941.8
Heterostructure with 25 min interruption	1892.9	1949.5
Heterostructure with 50 min interruption	1892.9	1949.5
Single layer		1957.2
$P_{\text{PH}_3} = 0.1$ torr		

this experiment, the bottom $0.15 \mu\text{m}$ GaInP layer was grown as for all of the other experiments described. The group III sources were removed for a period of 4 min after which the PH_3 partial pressure was reduced to 0.1 Torr. A period of either 2, 8, 25, or 50 min passed with the lower PH_3 flow rate before the group III elements were reintroduced into the reactor, after which the top $0.15 \mu\text{m}$ layer was grown. The 20 K PL results for the several resulting heterostructures are summarized in Table I. The PL peak from the highly ordered bottom layer is nearly the same as for a single layer grown using the same conditions, independent of the interruption time. The PL peak of the less ordered top layer moves progressively to higher energies as the interrupt time increases, approaching the peak energy for a single layer grown at 0.1 Torr for the longest interrupt time. In order to compare these

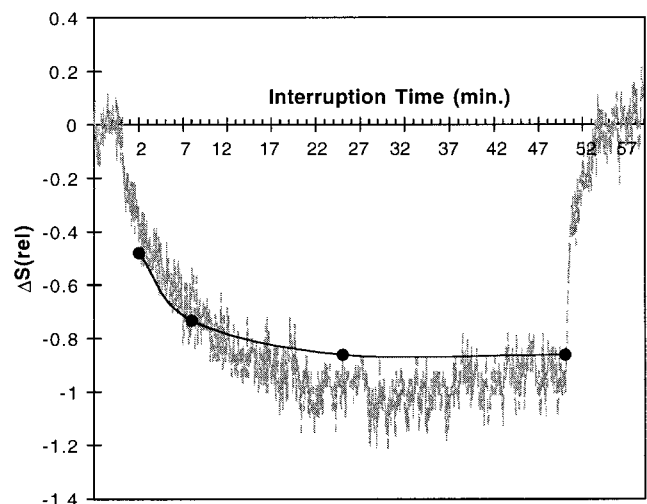


FIG. 5. $\Delta S(\text{rel})$, from Eq. (2), vs interrupt time for the growth of heterostructures at 620°C using PH_3 . For comparison the normalized SPA difference transient from Fig. 1(d) is included.

results with the SPA transient, the order parameter, S , was calculated from the PL peak energy using the equation¹⁴

$$S = [2005 - \text{PL peak energy at 20 K (in meV)} / 471]^{1/2}. \quad (1)$$

The value of order parameter was then compared with the value for a single highly ordered layer grown at 0.75 Torr of PH_3 and normalized to correspond to the normalized SPA transient,

$$\Delta S(\text{rel}) = S(\text{top layer}) - S(0.75 \text{ Torr layer}) / [S(0.1 \text{ Torr layer}) - S(0.75 \text{ Torr layer})] \quad (2)$$

The results are plotted in Fig. 5 with the normalized SPA transient superimposed. The similar behavior of the two curves appears to qualitatively confirm that the transient in the change in order parameter is related to the time required for the change in the surface structure detected by SPA.

IV. CONCLUSIONS

Heterostructures produced by changing the partial pressure of the P precursor have been studied using SPA for *in situ* measurement of the transient in the surface structure after changing the flow rate of the P precursor. Studies have included the use of either TBP or PH_3 and growth temperatures of 670 or 620 °C. A close correlation between the SPA transient and the heterostructure abruptness is observed. For a temperature of 670 °C, reducing the flow rate of either TBP or PH_3 produces abrupt heterostructures and the SPA transients follow the response time of the system, approximately 10 s. At 620 °C the use of TBP produces abrupt heterostructures and rapid SPA transients, while the use of PH_3 produces a slow SPA transient, with a time constant of approximately 6.5 min, and a graded heterostructure. The insertion of thin GaInP layers has little effect on the transient. By

including a pause between the two layers after the PH_3 flow rate has been reduced the magnitude of the memory effect is reduced, corresponding approximately to the time required for the change in the surface structure seen by SPA. The results are tentatively interpreted in terms of the effect of H acting as a surfactant to retard P desorption from the surface for growth using PH_3 at 620 °C. TBP produces less H on the surface and for either precursor at 670 °C the P desorption rate is rapid enough to avoid the long delay in the reduction in concentration of $[\bar{1}10]$ P dimers on the surface.

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