Adsorption and desorption of the surfactant Sb on GaInP grown by organometallic vapor phase epitaxy

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Abstract. It has been determined that ordering has a profound effect on the bandgap energy of many compound semiconductor alloys. Therefore, ordering must be controlled for devices such as solar cells, light emitting diodes and diode lasers. Since ordering depends on the surface properties during organometallic vapor phase epitaxy (OMVPE), the ability to control the surface has been shown to be important for controlling ordering and for producing heterostructures and quantum wells. However, perhaps equally as important as the affect of ordering on the bandgap is the fundamental information that it can provide about the surface during growth.

This paper reports on the use of time dependent surface photoabsorption (SPA) measurements to determine the rate of change in the P dimer concentration when TESb is added to and removed from the reactor. In particular, the time constants for the transients are presented and compared with the Langmuir model for adsorption and desorption of the surfactant. Transients in the Sb surface concentration were also indirectly determined from secondary-ion mass spectroscopy (SIMS) measurements on a GaInP heterostructure where TESb was added during growth of one of the layers.

Introduction

The use of surfactants to control the surface morphology, growth mode, and surface reconstruction during vapor phase epitaxy (VPE) of elemental [1] and III/V [2,3,4,5,6] semiconductors has been demonstrated. However, the use of surfactants to change the major semiconductor properties, such as the bandgap, had not been reported until recently [7,8,9].

In VPE, surfactants typically refer to substances that accumulate at the surface during growth and alter the surface properties. Generally, surfactants are substances with a low solubility (i.e., they are rejected from the solid) and a low vapor pressure (i.e., they do not readily evaporate). This results in a high surface concentration of the surfactant that in turn changes the surface energy and the adatom attachment at steps and thus affects the growth processes at or near the surface [4].

CuPt ordering frequently occurs in GaInP layers grown by OMVPE on (001) oriented GaAs substrates [10,11]. Spontaneous segregation of the Ga and In atoms occurs during growth due to alternating stresses from the [-110] oriented P dimers on the (2x4)-like reconstructed surface. The P dimers thermodynamically stabilize the CuPt variants with ordering on the (-111) and (1-11) planes [11,12,13]. The bandgap energy of partially ordered GaInP grown by OMVPE

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can be as much as 160 meV less than for the completely disordered material [11,14]. Consequently, ordering has significant technological importance. It must be controlled in order to produce GaInP solar cells [15], light emitting diodes [16] and visible lasers [17].

Perhaps more important than the technological application of ordering is the fundamental information that it can provide about the surface during growth, since ordering is controlled by surface processes. In-situ optical measurements during OMVPE growth, such as surface photoabsorption (SPA), can be used to measure the P dimer concentration on the surface and indirectly the surface reconstruction. It has been shown that reducing the concentration of [-110] P dimers on the surface by adding a small amount of the surfactant Sb during growth, reduces ordering. In fact, a GaInP disorder-on-order heterostructure (D/O) produced by adding a small amount of triethylantimony (TESb) during growth of the top layer resulted in a change in the band gap of 135 meV from the ordered layer to the disordered layer with no significant change in the solid composition [7,8].

This paper reports on the rate of change in the P dimer concentration on the surface of GaInP as TESb is added to and removed from the reactor. The P dimer concentration was directly measured by time dependent SPA. Surprisingly, the measured time dependent P dimer concentration fits the Langmuir model for adsorption and desorption of a material from a surface. The results indicate that the Sb does not completely cover the surface.

Experimental

All of the GaInP layers reported in this paper were grown in a horizontal, infrared-heated, atmospheric pressure, OMVPE reactor. Semi-insulating GaAs substrates with both singular (001) and vicinal (misoriented 3° toward (111)B direction) orientations were used. The substrates were cleaned by standard degreasing followed by a 1 minute etch in a 2 NH_4OH: 12 H_2O: 1 H_2O_2 solution. The substrates were then rinsed in de-ionized water for 5 minutes and blown dry with N_2 before being loaded into the reactor. Trimethylgallium (TMGa) at 7°C, ethyldimethylindium (EDMIn) at 15.9 °C, and tertiarybutylphosphine (TBP) at –7°C were used as the organometallic precursors. TESb at –7°C was used as the surfactant precursor. The TESb molar flow rate was 1.32×10^{-7} moles/minute. The carrier gas was Pd-diffused H_2. All of the layers were grown at a temperature of 620 °C with a V/III ratio of 40, a total flow rate of 5500 ml/min and a growth rate of 1.3 μm/hr. A heterostructure was produced by growing undoped GaInP for 10 min. on a GaAs substrate followed by growing a GaInP:Sb middle layer for 20 min. by adding TESb and finally growing another undoped GaInP top layer for 30 min.

In situ, time dependent SPA measurements of the surface were made after growth of an ordered GaInP layer while TESb was added to and removed from the reactor. Chopped, p-polarized light from a 150 W Xe lamp was used to irradiate the surface of the sample in the direction of the gas flow at the Brewster angle for GaInP of approximately 70°. The reflected light was dispersed with a compact monochromator and detected with a Si PNN+ photodiode using standard lock-in amplifier techniques. The reflectivity of the surface at 400 nm and 650 nm with the incident light parallel to the [-110] and [110] directions was measured. The reflection anisotropy was calculated as $\{R(V)-R(III)]/R(III)\}_{[-110]}$ - $\{R(V)-R(III)]/R(III)\}_{[110]}$ where R(V) and R(III) are the reflectivities of the group V and group III terminated surfaces, respectively. The reflection anisotropy (RA) at 400 nm is representative of the concentration of [-110] oriented P dimer concentration on the surface. The (2X4)-like reconstructed GaInP surface was normalized to unity. The dimer bond length of Sb on (2X4) reconstructed GaAs has been measured to be approximately 2.9 Å. This is also expected to be the dimer bond length for

Sb on GaInP, since it is lattice matched to GaAs. Harrison's model predicts that a dimer bond length of 2.9Å will absorb strongly at approximately 650 nm [18]. The reflection anisotropy (RA) at 650 nm is likely representative of the [-110] oriented Sb dimer concentration on the surface.

All of the GaInP layers were mirror-like when examined using Nomarski phase contrast optical microscopy. The solid composition of the layers was determined using standard x-ray diffraction techniques. Only the results for lattice matched layers are reported.

The secondary-ion mass spectroscopy (SIMS) depth profile of the GaInP heterostructure was performed by Applied Microanalysis Laboratory using a Cameca ims-3f system with Cs^+ bombardment. The Sb in the GaInP layer was measured as Sb^-.

Results

Fig. 1 shows the time dependent reflection anisotropy at 400 nm for a GaInP surface as TESb was added to and removed from the reactor. The reflection anisotropy signal was normalized so that the (2X4)-like reconstructed surface has a signal near unity. It can be seen that there is some drift in the signal during the experiment; however, the drift is insignificant. At t = 2 min., TBP was removed from the reactor. The sharp decrease in the signal indicates the rapid decrease in the P-dimer concentration to produce a group III terminated surface. At t = 4 min., the TBP flow was introduced back into the reactor at which point the signal quickly recovers (i.e. the P dimers reform on the surface). TESb was added to the reactor at t = 6 min. with a Sb/P mole ratio in the vapor of $4x10^{-4}$. The signal again decreases, but not as quickly as when the TBP was removed. At t = 10 min., TESb was removed from the reactor and the surface gradually recovered to the P dimer terminated state. At t = 14 min., the experiment was repeated with a Sb/P mole ratio of $1.6x10^{-3}$. At the higher Sb concentration, the signal decreases more quickly when TESb was added to the reactor. The P dimer signal recovers more slowly after the TESb was again removed at t = 18 min.

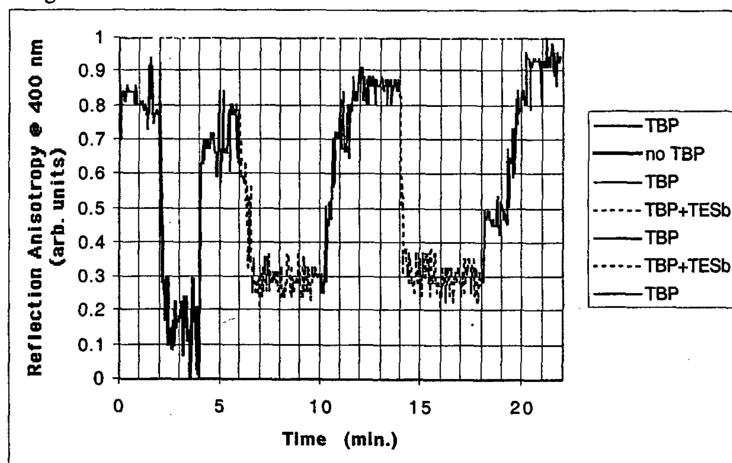

Fig. 1. Reflection anisotropy at 400 nm of a GaInP surface as TESb is added to and removed from the reactor. The change in signal intensity directly correlates to a change in the P dimer concentration on the surface.

Fig. 2 shows the time dependent reflection anisotropy signal at 650 nm. The reflection anisotropy was normalized so that the Sb dimer terminated surface has an signal near unity. SPA can not be used to determine the surface reconstruction, but it does appear that the Sb dimers are oriented in the same direction as the P dimers they replace. After exposing the surface to TBP for 2 min., TESb was added to the reactor with an Sb/P mole ratio of $4x10^{-4}$. The signal gradually increases as the P dimers were replaced by Sb dimers. At t = 6 min., the TESb was removed from the reactor. The signal decreases as the Sb evaporates and the surface gradually recovers to the P dimer terminated state. The experiment was repeated with an Sb/P mole ratio of $1.6x10^{-3}$. The signal increases more quickly at t = 14 min. when a higher TESb concentration was used. The signal also recovers more slowly at t = 18 min. after the TESb was removed. The concentration of Sb-dimers on the surface appears to have been higher with a higher TESb concentration.

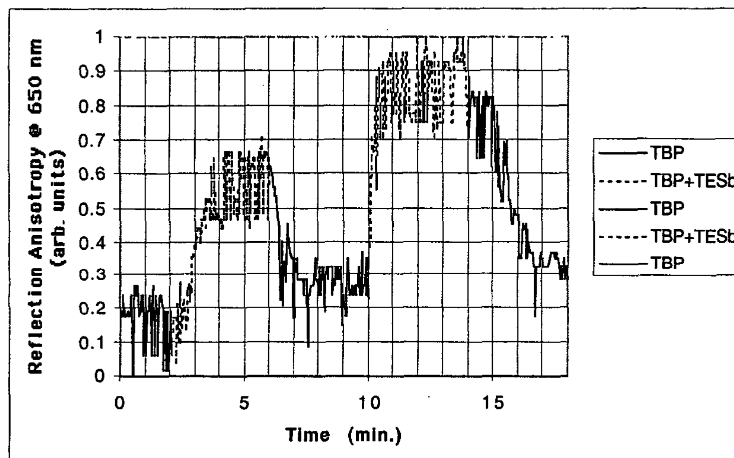

Fig. 2. Reflection anisotropy at 650 nm of a GaInP surface as TESb is added to and removed from the reactor. The change in signal intensity directly correlates to a change in the Sb dimer concentration on the surface.

Fig. 3 shows the results of a SIMS depth profile for a GaInP heterostructure. The heterostructure is composed of an approximately 0.18 μm thick undoped GaInP bottom layer on the GaAs substrate, an approximately 0.35 μm thick GaInP:Sb layer grown with the addition of TESb, and an approximately 0.53 μm thick undoped GaInP top layer. It indicates that Sb is incorporated into the GaInP:Sb layer at a low concentration of approximately $1x10^{-18}$ at/cc. The Sb concentration in the bulk directly correlates to the Sb concentration on the surface as measured by SPA (i.e. the bulk Sb concentration increases sharply when TESb was added to the reactor, but decreases gradually after TESb was removed).

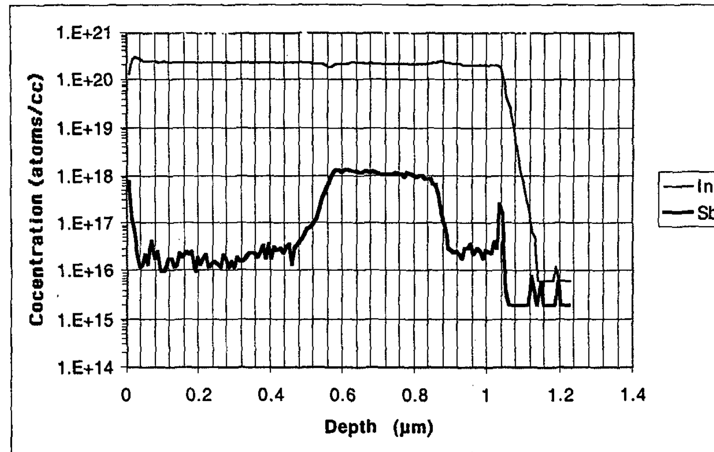

Fig. 3. SIMS depth profile of a GaInP heterostructure. The undoped top layer is approximately 0.53 μm thick. The approximately 0.35 μm thick GaInP:Sb middle layer was grown with the addition of TESb. The undoped GaInP bottom layer on the GaAs substrate is approximately 0.18 μm thick.

Discussion

Sb appears to accumulate quickly on the surface when TESb is added to the reactor. The rate at which it collects is roughly proportional to the concentration of TESb in the vapor. When TESb is removed from the reactor to grow an ordered layer, the Sb on the surface begins to evaporate (or be incorporated) more slowly than it accumulated. When a higher concentration of TESb is used, the P dimers recover more slowly. This suggests that within the time interval of the SPA measurements, the concentration of Sb on the surface achieved a higher level when a higher concentration of TESb was used. It was expected that Sb would evaporate more slowly than was indicated in the SPA data, since the vapor pressure of Sb is a relatively low at 620 °C ($2x10^{-3}$ torr). However, it is possible that Sb actually leaves the surface as a more volatile hydride. Since the SIMS results indicate that very little Sb was incorporated into the bulk, the time dependent SPA results suggest that Sb accumulates at the surface. From the effect of Sb on ordering it is clear that Sb destroys the [-110] P dimers that drive the CuPt ordering. This confirms that Sb acts as a surfactant in GaInP.

The P dimer and Sb dimer surface concentration transients that were measured by SPA look surprisingly like the curves generated by the Langmuir model [19] for the concentration of occupied sites during the adsorption and desorption of a material from a surface. Although the Langmuir model has been shown to be valid for dilute levels of a material on a surface, it still appears to describe the correct behavior for the higher concentrations of Sb that have been observed during OMVPE growth. The following form of the Langmuir model was used to fit the data:

$$d\theta/dt = P_{Sb}k_a (1-\theta) - k_d\theta - k_i\theta \qquad \text{(Eq. 1)}$$

where θ is the fraction of surface sites occupied by Sb, P_{Sb} is the mole fraction of Sb in the vapor ($4x10^{-4}$ and $1.6x10^{-3}$) k_a is the adsorption constant for Sb, k_d is the desorption constant for Sb and

k_i is the incorporation constant for Sb. For the adsorption of Sb on the surface when the surface coverage is small, the transient (slope of the adsorption curve) is given by:

$$d\theta/dt = P_{Sb}k_a.$$

This suggests that a higher Sb partial pressure will result in a steeper transient which agrees with the measured SPA data at 650 nm. Assuming that Sb and P occupy the same sites, the P transient will be 1- θ_{Sb}. For the desorption of Sb from the surface in the case where the steady state surface coverage is large (i.e. P_{Sb} is large), the Sb transient is given by:

$$d\theta/dt = -(k_d + k_i).$$

This suggests that for $P_{Sb}k_a > (k_d + k_i)$ the transient will always be steeper for adsorption than for desorption of Sb. This agrees with the measured SPA results at both 650 nm and 400 nm for adsorption and desorption of Sb. Integration of Eq. 1 for $\theta(0) = 0$ and $P_{Sb}k_a > (k_d + k_i)$ yields an equation for adsorption:

$$\theta = (1 - e^{-t/\tau})$$

where $\tau_a = 1/(P_{Sb}k_a)$. Integration of Eq. 1 for $\theta(0) = 1$ and $P_{Sb} = 0$ yields an equation for desorption from a completely covered surface:

$$\theta = e^{-t/\tau}$$

where $\tau_d = 1/(k_d + k_i)$. τ_a and τ_d are the time constants for the adsorption and desorption transients, respectively. The time constants calculated from the measured SPA and SIMS data at $t = \tau$ are given in Table I.

Table I: Adsorption and Desorption Transients

Type	Sb/III ratio	τ_a (min.)	τ_d (min)
SIMS	$1.6\text{x}10^{-3}$	0.6	1.5
SPA (400 nm)	$1.6\text{x}10^{-3}$	0.1	1.4
	$4\text{x}10^{-4}$	0.5	0.7
SPA (650 nm)	$1.6\text{x}10^{-3}$	0.2	1.9
	$4\text{x}10^{-4}$	0.9	1.5

The fact that the desorption transients change somewhat with a change in the Sb/III ratio suggests that $\theta_{Sb} \neq 1$ at the lower value of P_{Sb}. However, the surface coverage is likely close to unity for the higher Sb partial pressure.

The small amount of Sb in the bulk ($1\text{x}10^{18}$ atoms/cc) with an Sb surface concentration approaching unity suggests that the incorporation constant (k_i) is small.

Conclusion

Time dependent SPA analysis indicates that Sb accumulates on the surface during growth and produces disordered material by eliminating the P dimers. The transients for the adsorption and desorption of Sb from a GaInP surface fit the Langmuir model. Analysis of the desorption time constants suggest that the Sb surface concentrations are high (approaching unity). Finally, the SIMS depth profile suggests that the incorporation constant of Sb in GaInP is very small.

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References

[1] M. Copel, M. C. Reuter, Efthimios Kaxiras, and R. M. Tromp, Phys. Rev. Lett., **63**(6), 632 (1989).

[2] J. Massies, N. Grandjean, and V. H. Etgens, Appl. Phys. Lett. **61**(1), 99 (1992).
[3] R. Yakimova, T. Paskova, I. Ivanov, J. Crystal Growth, **129**, 143 (1993).
[4] E. Tournie and K. H. Ploog, Thin Solid Films, **231**, 43 (1993).
[5] J.E. Cunningham, K.W. Goossen, W. Jan, and M.D. Williams, J. Vac. Sci. Technol., B, **13**(2) 646 (1994).
[6] R. Kaspi, D.C. Reynolds, K.R. Evans and E.N. Taylor, Inst. Phys. Conf. Ser. **141**(2), 57 (1995). B.R.A. Neves, M.S. Andrade, W.N. Rodrigues, G.A.M. Safar, M.V.B. Moreira, and A.G. de Oliveira, Appl. Phys. Lett., **72**, 1712 (1998). D. Reinking, M. Kammier, M. Horn-von Hoegen, and K.R. Hofmann, Appl. Phys. Lett. **71**, 924 (1997).
[7] J.K. Shurtleff, R.T. Lee, C.M. Fetzer, and G.B. Stringfellow, Appl. Phys. Lett., **75**, 1914 (1999).
[8] R.T. Lee, C.M. Fetzer, J.K. Shurtleff, and G.B. Stringfellow, J. Appl. Phys.
[9] C.M. Fetzer
[10] G. B. Stringfellow, in *Common Themes and Mechanisms of Epitaxial Growth*, edited by P. Fuoss, J. Tsao, D. W. Kisker, A. Zangwill, and T. Kuech (Materials Research Society, Pittsburgh, 1993), pp. 35-46.
[11] G. B. Stringfellow, Ordering in III/V Semiconductor Alloys, in *Thin Films: Heteroepitaxial Systems*, ed. M. Santos and W.K. Liu (World Scientific Publishing, 1998).
[12] See several papers in "Compositional Modulation and Ordering in Semiconductors", ed. T.P. Pearsall and G.B. Stringfellow, MRS Bulleting, **22**(7) (1997).
[13] S.B. Zhang, S. Froyen, and A. Zunger, Appl. Phys. Lett. **67**, 3141 (1995).
[14] L.C. Su, I.H. Ho, N. Kobayashi, and G.B. Stringfellow, J. Crystal Growth, **145**, 140 (1994).
[15] K.A. Bertness, S.R. Kurtz, D.J. Friedman, A.E. Kibbler, C. Kramer, and J.M. Olson, Appl. Phys. Lett. 65, **989** (1994); T. Takamoto, E. Ikeda, H. Kurita, and M. Ohmori, Appl. Phys. Lett. **70**, 381 (1987).
[16] G.B. Stringfellow, in *High Brightness Light Emitting Diodes*, ed. G.B. Stringfellow and M.G. Craford (Academic Press, Boston, 1997).
[17] Y. Ueno et al., Jpn. J. Appl. Phys. **29**, L1666 (1990); K. Itaya, M. Ishikawa, G. Hatakoshi, and U. Uematsu, IEEE J. Quantum Electron. **27**, 1496 (1991).
[18] Y. W.A. Harrison, *Electronic Structure and the Properties of Solides: Physics of the Chemical Bond* (Freeman, New Yourk, 1980).
[19] I. Langmuir, *J. Am. Chem. Soc.* **40** 1361 (1918).