The use of a surfactant (Sb) to induce triple period ordering in GaInP

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(Received 23 November 1999; accepted for publication 18 January 2000)

A surfactant is used to induce an ordered structure in an epitaxial layer. The addition of small amounts of triethylantimony during the organometallic vapor phase epitaxy growth of GaInP on (001) GaAs substrates is shown to remove CuPt ordering with a resultant increase in band gap energy. Increasing the concentration of Sb in the vapor beyond a critical Sb to P ratio [Sb/P(v)] of 4×10^{-4} gives a reversal of this behavior. The band gap energy is observed to decrease by 50 meV at a concentration of Sb/P(v)$=1.6\times10^{-3}$, coincident with the formation of an ordered phase with a period triple the normal lattice spacing along the [111] and [$\bar{1}\bar{1}1$] directions. The formation of this new ordered structure is believed to be related to high concentrations of Sb on the surface, which leads to a change in the surface reconstruction from (2×4)-like to (2×3)-like, as indicated by surface photoabsorption performed *in situ*. © *2000 American Institute of Physics.* [S0003-6951(00)02011-8]

Ordering on an atomic scale in ternary III–V alloy semiconductors grown by organometallic vapor phase epitaxy (OMVPE) has been widely observed.[1,2] Ordering may take many forms, including CuPt[1,2] and triple period ordering.[3,4] In $Ga_{0.52}In_{0.48}P$ (GaInP) grown by OMVPE on (001)-oriented GaAs substrates, the only reported form of ordering is CuPt–B with ordering on the ($\bar{1}11$) and ($1\bar{1}1$) planes.[1,2] This structure, unstable in the bulk, is made thermodynamically stable at the surface by the alternating stresses generated by rows of [$\bar{1}10$]-oriented phosphorous dimers in the (2×4)-like surface reconstruction.[5]

Since ordering is stabilized by the surface, it provides a powerful method to investigate the surface during epitaxy.[6] One way that ordering is proving useful in studying the surface during growth is in the study of the effects of surfactants. The addition of the dopant Sb in the growth of SiGe alloys has been shown to eliminate ordering by eliminating the ⟨110⟩ Si dimers.[7] More recently, the addition of Sb as an isoelectronic surfactant during the growth of GaInP has been demonstrated to alter the surface bonding, by replacing the P dimers with Sb, and to eliminate ordering.[8,9] Similarly, Bi, also an isoelectronic surfactant, has been added to GaInP to eliminate ordering by changing the surface structure.[10]

This letter discusses the use of a surfactant to produce a change in ordered structure. The surfactant Sb has been used to produce a triple-period {111} ordered structure that has never before been observed in GaInP or in any material grown by OMVPE. Moreover, the surfactant, Sb, is isoelectronic with P, so produces no first order changes in either the solid composition or Fermi level, unlike dopant surfactants studied previously.[7,11,12]

Growth of the GaInP epilayers was carried out in a horizontal flow atmospheric pressure OMVPE system[13] on semi-insulating GaAs substrates at 620 °C. The substrates used were (001) oriented GaAs, either with 0° intentional miscut (singular) or 3° misorented to the (111) B direction (vicinal). Details of the growth process are reported elsewhere.[8] Three representative, singular samples, labeled A, B, and C, grown at low, moderate, and high Sb to P ratios in the vapor [Sb/P(v)], respectively, were selected for special attention in this study. All are nearly lattice matched, $\Delta a/a \leqslant 0.1\%$, as determined by x-ray diffraction. Optical characterization was performed *ex situ* by photoluminescence (PL) and *in situ* by surface photoabsorption (SPA). Details of the setups are given elsewhere.[8,14] In SPA, a reflectivity difference spectrum is generated by subtracting the reflectivity of a group V terminated surface from that of a group III terminated surface, normalized to the reflectivity of the group III surface. The spectra were taken with tertiarybutylphosphine (TBP) flowing to produce the group V terminated surface. Reflec-

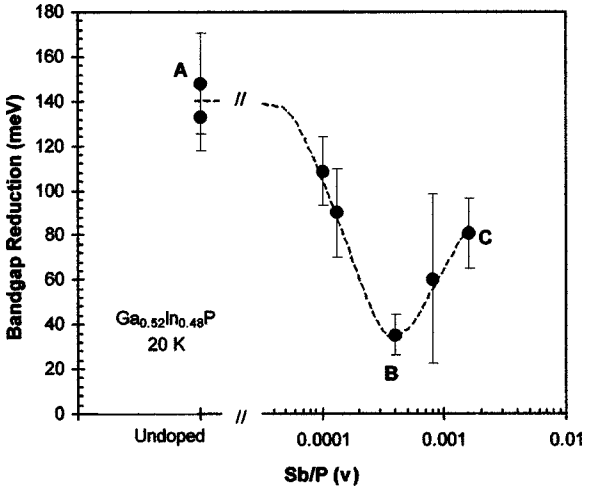

FIG. 1. Band gap reduction as determined by 20 K PL spectra in GaInP grown with various partial pressures of TESb. The data represent an average between multiple samples grown on both singular and vicinal GaAs (001) substrates. Three are marked A, B, and C for comparison with the data presented in the other figures. The line is meant as a guide to the eye. The band gap of disordered GaInP under these conditions is taken as 2.005 eV.

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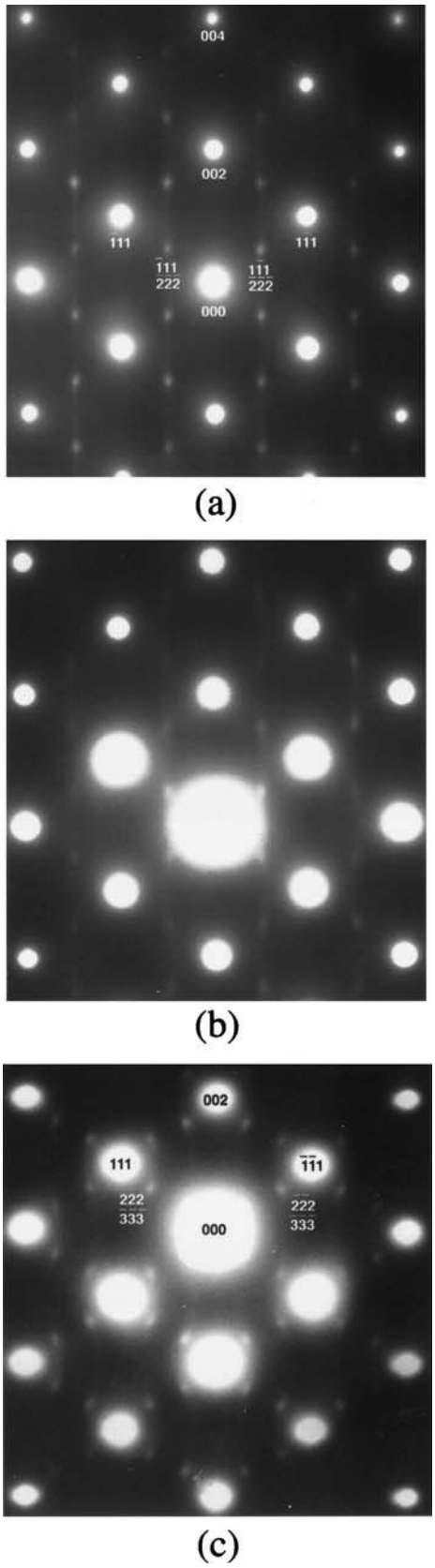

FIG. 2. TED patterns taken for the samples A, B, and C from Fig. 1. For samples A and B the [110]-zone image is shown and for sample C is the $[\bar{1}10]$-zone image is reported. Sample A shows strong $\frac{1}{2}\{111\}$ superspots, indicative of strong CuPt ordering. Sample B is similar, with a reduction in the relative intensity of the superspots. Sample C clearly shows two sets of superspots at 1/3 and 2/3 along the [111] and $[\bar{1}\bar{1}1]$ directions. The central spot is intense enough to partially mask the nearer superspots. Satellite zinc blende spots clearly show both superlattice spots. The superspots indicate a tripling of the lattice periodicity along the [111] and $[\bar{1}\bar{1}1]$ directions and hence triple period ordering.

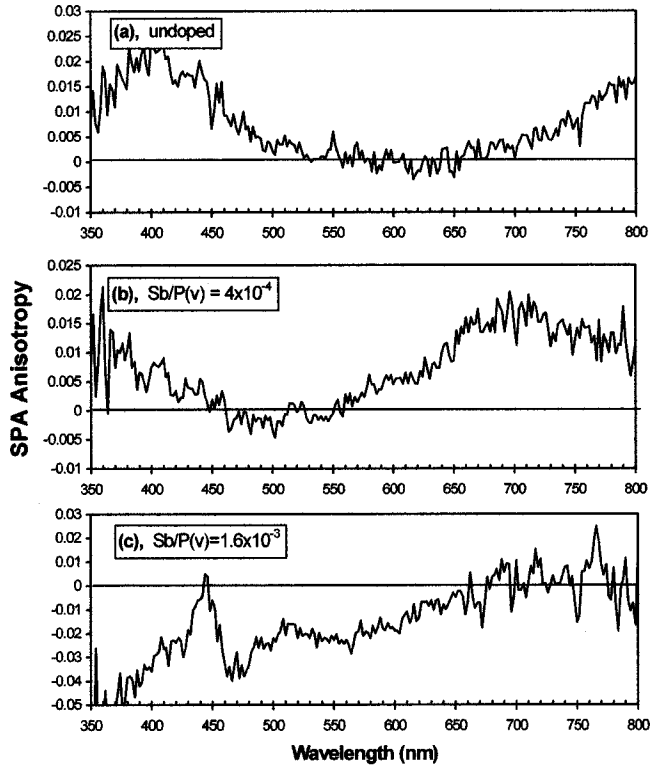

FIG. 3. SPA anisotropy spectra taken *in situ* for several partial pressures of TESb during growth. Sample A, with no TESb, shows a clear positive peak centered near 400 nm. Sample B grown with $\mathrm{Sb/P}(v)=4\times10^{-4}$, shows a decrease in this 400 nm peak and a new positive peak centered near 650 nm. For $\mathrm{Sb/P}(v)=1.6\times10^{-3}$, the signal at 400 nm has become negative, new features near 470–560 nm appear as negative peaks, and the positive feature at 650 nm appears to be weaker and to have moved to longer wavelengths.

tivity of the group III terminated surface was taken at the same temperature but 2 min after TBP was removed from the system. SPA anisotropy spectra are derived by subtracting the reflectivity difference spectrum along the [110] azimuth from that along the $[\bar{1}10]$ azimuth. Transmission electron diffraction (TED) was performed by taking patterns along the [110] and $[\bar{1}10]$ zones using a JEM 2010 scanning TEM operated at 200 kV.

Figure 1 shows the band gap reduction as determined from 20 K PL measurements. The peak energy is assumed to be the band gap energy. The band gap reduction is the energy reduction from an expected value of 2.005 eV for completely disordered GaInP.[15] The data represent an average of multiple samples both singular and vicinal. The behavior of samples A and B has been reported previously.[8,9] Sample A, for undoped GaInP, is highly ordered and shows a 140 meV reduction in the band gap energy. For a Sb/P ratio in the vapor of 4×10^{-4}, sample B shows a small band gap reduction of 35 meV, indicating that the material is nearly disordered. Above this critical concentration, the behavior changes. Sample C, at a Sb/P vapor ratio of 1.6×10^{-3} shows that the PL peak energy has been reduced relative to the disordered material by over 80 meV. While the change in band gap energy from sample A to B is easily explained by the loss of CuPt order, the change from sample B to C may be due to another phenomenon.

The TED results allow a clear explanation of the PL observations. Figure 2 shows the TED patterns from the three samples. Samples A and B are the [110]-zone diffrac-

tion patterns. In sample A, clear superspots from the {111} lattice period doubling due to CuPt–B variants are visible between the regular zincblende spots along the $[\bar{1}11]$ and $[1\bar{1}1]$ directions. In sample B, a clear reduction of the intensity of the superspots relative to the zincblende spots is observed (much larger due to an increased exposure time necessary to allow the superspots to be observed) as compared to sample A. This behavior correlates well with the observed increase in the PL peak energy. Sample C showed a very different behavior. The [110]-zone TED pattern showed no superspots. However, in the $[\bar{1}10]$-zone image a new type of superspot is clearly formed. The superspots are no longer at the midpoint between the zinc blende spots; but are located at position 1/3 and 2/3 of the way from the origin to the zinc blende spots along the $[\bar{1}\bar{1}1]$ and [111] directions. This type of pattern has been reported for AlInAs and GaInAs grown by gas source molecular beam epitaxy (GSMBE) at temperatures of 460 and 445 °C, respectively.[3,4,16,17] A triple period superlattice in GaInP is reported by Liu *et al.*[18] However, their observation was made on a 150 Å scale and was categorized as a statistical fluctuation in the CuPt ordering, not a long-range structure as presently observed. To our knowledge, there is no other report of this type of ordering (i) in GaInP, (ii) in material grown by OMVPE, and (iii) in material grown at temperatures normally used for growth of high quality epilayers. Since the ordering is along the *L* direction in *k* space, as for CuPt ordering, folding of those states into the Γ states results in a band gap energy reduction much like that due to CuPt ordering.[3–5] Thus, the observation of triple period ordering (TPO) explains the band gap reduction observed in PL.

The TPO structure observed in AlInAs was found to be caused by the surface reconstruction during growth.[3,4,16,17] Using reflection high energy electron diffraction (RHEED) in the GSMBE system, Gomyo *et al.* found a surface with a (2×3) periodicity for the growth conditions resulting in layers with TPO. A (2×3) reconstructed (001) surface contains both [110] group V dimers bonded to subsurface group V atoms and $[\bar{1}10]$ oriented group V dimers bonded to subsurface group III atoms. The two different types of dimers are arranged with a periodicity triple that of the unreconstructed surface along the $[\bar{1}10]$ direction. The resultant subsurface strains cause the A variants of ordering [ordering on the (111) and $(\bar{1}\bar{1}1)$ planes].[3,5]

The SPA spectra for samples A, B, and C, Fig. 3, clearly show that sample C has a different surface reconstruction. Samples A and B have SPA spectra typical of the (2×4)-like reconstruction, with positive spectral features near the 400 and 650 nm. These feature have been previously attributed to $[\bar{1}10]$ P dimers and $[\bar{1}10]$ Sb dimers, respectively.[8,9,18,19] The reduction in CuPt ordering induced by Sb is attributed to a reduction in the surface strain, due to larger Sb dimer spacing. Sample C has a completely different SPA spectrum. The SPA anisotropy spectrum is negative in the 400 nm region and nearly zero at 650 nm. The SPA anisotropy spectra cannot reveal the periodicity of the surface, since this technique probes the surface electron states. Also, there are no published SPA anisotropy spectra for a (2×3)-like reconstructed surface. The change in reconstruction is attributed solely to an increase in Sb concentration on the surface.

In summary, an isoelectronic surfactant has been used to control the surface reconstruction during OMVPE growth to induce a new ordered phase. Above a critical vapor Sb/P ratio of 4×10^{-4} the SPA anisotropy spectrum changes dramatically. This new surface reconstruction induces the A variants of a TPO structure with TED patterns having superspots at the 1/3 and 2/3 positions along the [111] and $[\bar{1}\bar{1}1]$ directions. This TPO has never before been observed in OMVPE grown material or in the GaInP alloy system. It is shown to produce a reduction in band gap energy.

The authors wish to thank the NSF (surface photoabsorption) and the DOE (sample growth and photoluminescence) for their financial support of this work.

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