# Band-gap control of GaInP using Sb as a surfactant

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The use of surfactants to control specific aspects of the vapor-phase epitaxial growth process is beginning to be studied for both the elemental and III/V semiconductors. To date, most reported surfactant effects for semiconductors relate to the morphology of the growing films. However, semiconductor alloys with CuPt ordering exhibit much more dramatic effects. The change in the CuPt order parameter induced by the surfactant translates into a marked change in the band-gap energy. Previous work concentrated on the effects of the donor tellurium. Te is less than ideal as a surfactant, since the change in band-gap energy is coupled to a large change in the conductivity. This letter presents the results of a study of the effects of an isoelectronic surfactant on the ordering process in GaInP. Sb has been found to act as a surfactant during organometallic vapor-phase epitaxial growth. At an estimated Sb concentration in the solid of $1\times10^{-4}$, order is eliminated, as indicated by the band-gap energy. Surface photoabsorption (SPA) data indicate that the effect is due to a change in the surface reconstruction. Adding Sb leads to attenuation of the peak at 400 nm in the SPA spectrum associated with $[\bar{1}10]$ P dimers. The addition of Sb during the growth cycle has been used to produce a heterostructure with a 135 meV band-gap difference between two layers with the same solid composition. © *1999 American Institute of Physics.* [S0003-6951(99)03539-1]

Atomic-scale ordering to produce the CuPt structure frequently occurs in $Ga_{0.52}In_{0.48}P$ layers grown by organometallic vapor-phase epitaxy (OMVPE) on (001)-oriented GaAs substrates.[1,2] The alternating surface stresses resulting from the formation of rows of $[\bar{1}10]$-oriented phosphorous dimers on the $(2\times n)$-reconstructed (001) surface thermodynamically stabilize the variants of the CuPt structure with ordering on the $(\bar{1}11)$ and $(1\bar{1}1)$ planes.[1–3]

One of the factors having a strong effect on ordering is doping. Several studies in GaInP have demonstrated a connection between ordering and doping as the electron (or hole) concentration is varied.[4–7] For Si and Zn, the effect has been attributed to diffusion in the bulk.[4] On the other hand, Te added during OMVPE growth of GaInP was observed to act as a surfactant, dramatically increasing the $[\bar{1}10]$ step velocity, which resulted in the growth of disordered material.[5–7] This is one of the rare examples of surfactant effects during OMVPE growth resulting in a major change in the semiconducting properties of the epilayer.

Somewhat different surfactant effects related to the morphology of highly strained layers have been the object of study in both elemental[8,9] and III/V semiconductors.[10,11] The addition of dopants during molecular beam epitaxy (MBE) growth has been shown to affect both adatom attachment at step edges[12,13] and surface reconstruction.[14] The addition of the isoelectronic surfactant As has been shown to modify the surface reconstruction of cubic GaN grown by MBE.[15]

The ordering phenomenon in semiconductor alloys is of considerable practical interest, because CuPt ordering has a large effect on the materials properties, e.g., the band-gap energy is found to be 160 meV lower in partially ordered $Ga_{0.52}In_{0.48}P$ than in disordered material of the same composition.[16] The effect of the surfactant Te on the order parameter, and hence, the band-gap energy, raises the possibility of producing heterostructures and elaborate multilayer structures required for the most advanced devices by simply modulating the concentration of a surfactant during growth. This would be particularly powerful if the surfactant did not result in the loss of control of the Fermi-level position in the structure.

The purpose of this work is to demonstrate that the isoelectronic element Sb has a dramatic effect on the order parameter and, hence, the band-gap energy in GaInP grown by OMVPE. The elimination of CuPt ordering for a tiny Sb concentration is correlated with the loss of $[\bar{1}10]$ P dimers on the surface, as indicated by surface photoabsorption (SPA) measurements. Disorder-on-order heterostructures were grown by simply modulating the flow rate of the Sb precursor during growth. Since Sb is isoelectronic with P, this surfactant enables the independent control of the band gap and the conductivity of the individual layers in complex structures.

$Ga_{0.52}In_{0.48}P$ layers were grown in a horizontal, atmospheric pressure OMVPE system[17] directly on semi-insulating GaAs substrates without GaAs buffer layers. Both singular (001) and vicinal $3^{\circ}_{B}$ [3° toward the $(111)B$ direction] orientations of the substrates were used. The substrates were prepared by standard degreasing followed by a 1 min etch in a $12H_2O$:$2NH_4OH$:$1H_2O_2$ solution. They were rinsed for 5 min in deionized water, and blown dry with filtered $N_2$ before being loaded directly into the reactor. Trimethylgallium at 7 °C and ethyldimethylindium at 15.9 °C were used as the group III precursors. Tertiarybutylphosphine (TBP) at −7 °C was used as the group V precursor. Triethylantimony (TESb) at −7 °C was used as the surfactant precursor. Pd-diffused hydrogen was used as the carrier gas. All of the layers were grown at a temperature of 620 °C with a V/III ratio of 40 and a total flow rate of 5500 ml/min. The growth

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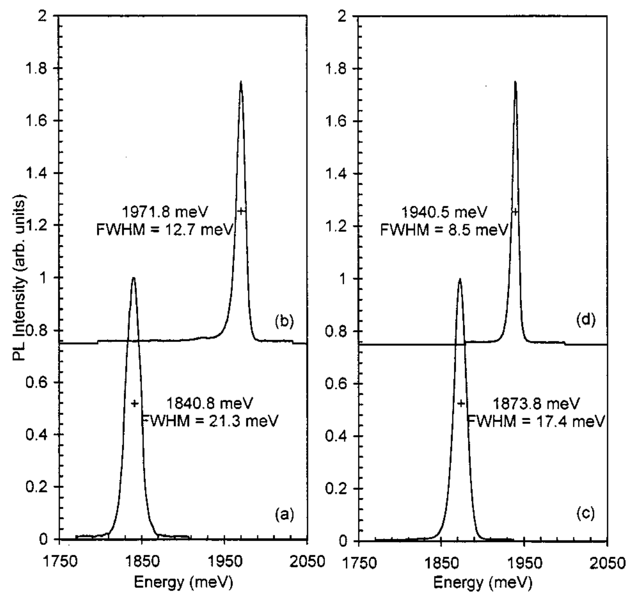


FIG. 1. 20 K PL spectra for undoped, ordered $Ga_{0.52}In_{0.48}P$ layers (a) and disordered layers grown with the addition of TESb (b) on vicinal $(3_B)$ GaAs substrates and layers grown without (c) and with TESb (d) on singular (001) GaAs substrates.

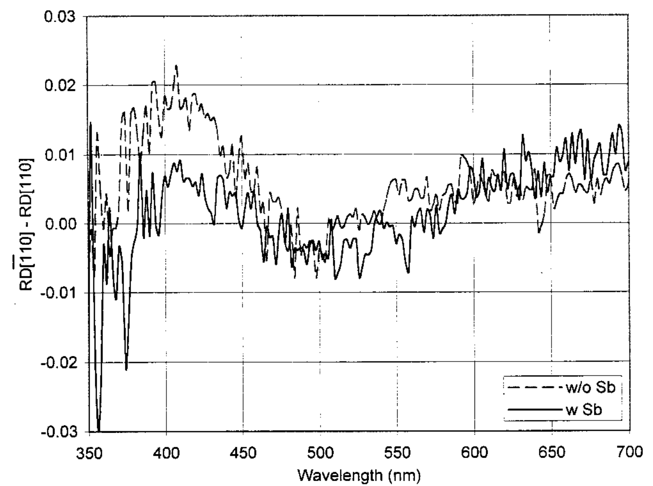


FIG. 2. SPA anisotropy spectra for $Ga_{0.52}In_{0.48}P$ layers grown with and without Sb.

rate was approximately 0.6 $\mu$m/h. In order to obtain lattice-matched samples, with a mismatch of $<0.1\%$ as confirmed by x-ray diffraction measurements, the Ga-to-In ratio had to be changed from 1.22 for undoped $Ga_{0.52}In_{0.48}P$ layers to 1.44 for layers with Sb. The surface morphologies of the layers were mirror like as determined by Nomarski phase contrast optical microscopy. Photoluminescence (PL) measurements were done at 19 K. The 488 nm line of an $Ar^+$ laser with a power of 10 mW focused to a 0.5 $mm^2$ spot was used to excite the samples. The PL signal was dispersed with a SPEX monochromator and detected with a photomultiplier tube using standard lock-in amplifier techniques. A SPA system attached to the OMVPE reactor was used to make *in situ* measurements of bonding on the GaInP surface.[18] Chopped, *p*-polarized light from a 150 W Xe lamp irradiated the surface in the direction of the gas flow at an incident angle 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 following procedure was used for the SPA measurements. After deposition of the GaInP layer, the temperature of the sample was reduced to 520 °C. With TBP flowing through the reactor, the reflectivity of the group V-terminated surface was then measured in 2 nm steps with a 1 s integration time at each step. The TBP flow was then stopped and the surface was allowed to stabilize for 7 min. The reflectivity of the group III-terminated surface was then measured over the same wavelength range. This procedure was performed with the incident light parallel to the $[\bar{1}10]$ and $[110]$ directions for both undoped layers and layers with Sb. The difference in the reflectivity between the group V- and group III-terminated surfaces, normalized by the group III surface, is termed the SPA difference spectrum. The SPA anisotropy spectrum is the difference between the $[\bar{1}10]$ and $[110]$ SPA difference spectra.

Figure 1(a) shows the PL spectrum for an ordered $Ga_{0.52}In_{0.48}P$ layer grown on a vicinal $(3^{\circ}_B)$ substrate without Sb. Figure 1(b) shows the PL spectra for a layer grown with the addition of a small amount of Sb. The peak energies for the undoped layer and the layer with Sb are 1841 and 1972 meV, respectively, indicating that the layers without Sb are highly ordered, but the layers are essentially disordered when grown with Sb present. The 132 meV difference in the bandgap energies indicates the large difference in degree of CuPt ordering between the two layers. The PL spectra for $Ga_{0.52}In_{0.48}P$ layers grown with and without Sb on singular substrates are shown in Figs. 1(c) and 1(d), respectively. Clearly, the addition of a small quantity of Sb during growth, estimated to be $1\times10^{-4}$ from the vapor-phase composition and the Sb distribution coefficient in GaInPSb alloys,[19] was sufficient to disorder the $Ga_{0.52}In_{0.48}P$ layers.

Sb as a donor, when added during the MBE growth of Si and Si/Ge alloys, is known to accumulate at the surface.[8,9,12,13] A similar effect is expected for Sb added during the OMVPE growth of GaInP. The large size of Sb relative to P gives rise to a large positive deviation from ideal mixing behavior, yielding a small solubility in GaInP.[20,21] In addition, the volatility of Sb is much less than that of P. These two factors suggest that Sb is likely to accumulate at the surface during growth.[22]

Figure 2 shows the SPA anisotropy spectra for undoped layers and layers grown with Sb. The results indicate a dramatic change in the surface reconstruction induced by the addition of Sb to the system. Previous SPA studies showed that the intensity of the peak at 400 nm in SPA anisotropy spectra directly correlates to the concentration of $[\bar{1}10]$ P dimers on the surface.[17,18,23] Comparison of the spectra for the undoped $Ga_{0.52}In_{0.48}P$ layers and layers with Sb clearly indicates that the P dimer concentration on the surface of the samples grown with Sb present has been significantly reduced. This is experimental evidence that an isoelectronic element, such as Sb, can act as a surfactant to change the surface reconstruction of a III/V semiconductor layer during OMVPE growth.

Since the $[\bar{1}10]$ P dimers produce the surface thermodynamic driving force for formation of the CuPt structure during growth, it is not surprising that the removal of $[\bar{1}10]$ P dimers by the addition of Sb also eliminates ordering. These

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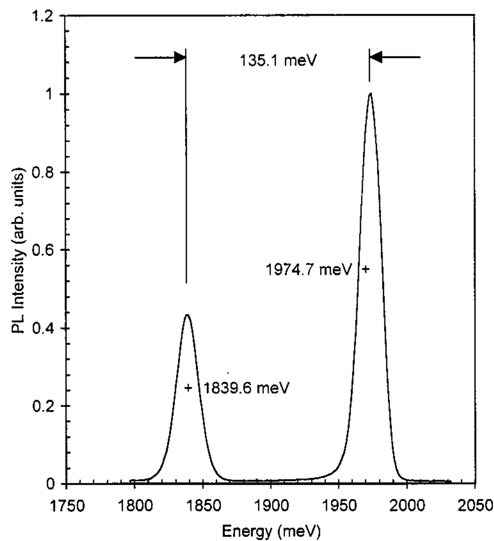


FIG. 3. 20 K PL spectrum for a GaInP disorder-on-order heterostructure grown by modulating the TESb flow during growth.

results confirm previous observations that the degree of order in $Ga_{0.52}In_{0.48}P$ layers is directly related to the P dimer concentration.[4–7,23] The lower volatility of Sb, relative to P, and the rejection of Sb from the solid lead to the accumulation of Sb at the surface. The elimination of $[\bar{1}10]$ P dimers may be due to the formation of a second layer of Sb at these temperatures.

The ability to control the ordering and, thus, the band-gap energy of GaInP layers by the addition of Sb during growth suggests the possibility of producing heterostructures and quantum wells. To grow a disorder-on-order heterostructure, the surface of the undoped, ordered $Ga_{0.52}In_{0.48}P$ layer grown first was exposed to TBP and TESb for 5 min, without growth, to allow Sb to accumulate. The disordered layer containing Sb was then grown. Figure 3 shows the PL spectrum for a disorder-on-order heterostructure grown by this procedure. A remarkable difference in the band-gap energy between the two layers of 135 meV was achieved. This is a demonstration of a potentially powerful method for the production of atomically engineered structures for advanced electronic and photonic devices. The ability to independently modulate the band gap and the Fermi-level position is the key to the potential usefulness of this technique. The 135 meV band-gap discontinuity is more than 5 kT at room temperature, which should be sufficient for many devices.

The addition of Sb, from the pyrolysis of TESb, during the OMVPE growth of $Ga_{0.52}In_{0.48}P$ essentially eliminates the CuPt ordering observed in layers grown without Sb. The loss of ordering leads to a 132 meV increase in the band-gap energy, as judged from the 20 K PL peak positions. The results of *in situ* SPA analysis of the surface indicate that this is due to a change in the surface reconstruction induced by the Sb. The results indicate that modulation of the TESb flow rate can be used to control the GaInP band-gap energy. A single heterostructure gives PL peaks from the two layers, grown with and without Sb present, that differ by 135 meV. This demonstrates the use of an isoelectronic surfactant to modulate the band-gap energy of a material grown by OMVPE. Since Sb is isoelectronic with P and is present at small concentrations, the modulation in band-gap energy is accomplished with no effect on either the solid composition or the Fermi-level position. It is anticipated that surfactant Sb can also be used to produce more complex structures, such as quantum wells.

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