

Surfactant Effects of Dopants on Ordering in GaInP

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The use of surfactants for control of specific aspects of the VPE growth process is beginning to be studied for both the elemental and III/V semiconductors. The objective is to change the characteristics of the material grown epitaxially by the addition of a surfactant during growth. Most reported surfactant effects for semiconductors relate to some detail of the morphology of the growing films. For ordered semiconductor alloys the effects can be much more dramatic, including major changes in the electrical and optical properties. Since the bandgap energy is dependent on the microscopic arrangement of the atoms in an alloy with a fixed composition, the change in order parameter induced by the surfactant translates into a marked change in the bandgap energy. This paper presents the results of a study of the effects of n-type (Te and Si), p-type (Zn), and isoelectronic (Sb) dopants on the ordering process in GaInP grown by OMVPE. All of the dopants studied were found to decrease or eliminate ordering; however, the mechanisms are quite different. The donor Te apparently affects the adatom attachment kinetics at steps on the (001) surface, a surfactant effect. On the other hand the donor Si was found to decrease the degree of order by an entirely different mechanism, attributed to an increase in the Ga and In diffusion coefficients in the bulk. It apparently does not involve the surface. Disorder due to the acceptor Zn was found to occur by the same mechanism. The isoelectronic impurity Sb is found to act as a surfactant and to decrease the order parameter by changing the surface reconstruction, eliminating the $[\bar{1}10]$ -P dimers that provide the thermodynamic driving force for formation of the CuPt structure during growth.

Key words: GaInP, surfactant effects, VPE growth

INTRODUCTION

Atomic-scale ordering to produce the CuPt structure frequently occurs in $\text{Ga}_{0.52}\text{In}_{0.48}\text{P}$ layers grown by organometallic vapor phase epitaxy (OMVPE) on (001)-oriented GaAs substrates.¹ The Ga and In atoms are spontaneously segregated into alternating {111} monolayers. For vapor phase epitaxy on (001)-oriented substrates, 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.^{1,2} The degree of CuPt order has been found to be reduced by decreasing the $[\bar{1}10]$ P dimer concentration on the

surface by increasing the temperature or decreasing the partial pressure of the group V precursor during OMVPE growth.^{3,4}

Although the driving force for ordering is understood, the mechanism remains unknown; however, several speculative models have been proposed.⁵ Besides the known role of surface reconstruction, surface steps may also be important factors in the ordering process. For example, $[110]$ steps are observed to assist the ordering process but $[\bar{1}10]$ steps retard ordering.⁶ Kinetic effects at step edges apparently affect the ordering process under certain growth conditions.

One of the factors having a strong effect on ordering is doping. Several studies in GaInP have demonstrated a connection between ordering and n-type⁷⁻¹¹ or p-type¹²⁻¹⁸ dopant concentration. The results show that a drastic decrease in ordering is caused by intro-

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ducing a high concentration of dopants during OMVPE growth. The effect has been attributed to diffusion in the bulk.^{14,17,18}

Recently, Te added during OMVPE growth of GaInP was observed to increase the $[\bar{1}10]$ step velocity dramatically, which resulted in the growth of disordered material.^{9–11} This is one of the few examples of surfactant effects during OMVPE growth. Somewhat different surfactant effects related to the morphology of highly strained layers have been the object of study in both elemental^{19,20} and III/V semiconductors.^{21,22} The addition of dopants during MBE growth has been shown to affect both adatom attachment at step edges^{23,24} and the surface reconstruction.²⁵ The addition of surfactant As has been shown to modify the surface reconstruction of cubic GaN grown by MBE.²⁶

The ordering phenomenon in semiconductor alloys is of considerable practical interest since CuPt ordering has a large effect on the materials properties, e.g., the bandgap energy is found to be 160 meV lower in partially ordered $\text{Ga}_{0.52}\text{In}_{0.48}\text{P}$ than in disordered material of the same composition.²⁷ The effect of the surfactant Te on the order parameter, and hence the bandgap energy, raises the possibility of producing heterostructures and the 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 prime motivation of this work is the elucidation of the mechanism by which the addition of surfactants during OMVPE growth leads to disordering. Another objective is the demonstration of a useful new technique for controlling the bandgap and other properties of semiconductor alloys by modifying the surface structure during growth. In particular, the effects of the n-type dopant Si will be compared with those of Te, previously reported. In addition, the effects of the p-type dopant Zn will be described. The preliminary results for the isoelectronic impurity Sb, expected to be a surfactant during the OMVPE growth of GaInP, will also be described.

EXPERIMENTAL

The $\text{Ga}_{0.52}\text{In}_{0.48}\text{P}$ epilayers were grown by OMVPE in a horizontal, infrared-heated, atmospheric-pressure reactor on semi-insulating GaAs substrates with both singular (001) and vicinal 3°_B (3° toward (111)B direction) orientations. Substrate preparation consisted of standard degreasing followed by a 1 min etch in a 2:12:1 solution of NH_4OH , H_2O , and H_2O_2 . The substrates were then rinsed in de-ionized water for 5 min. and blown dry with N_2 before loading into the reactor.

The experimental procedures for the growth of Te and Zn doped GaInP layers were described previously.^{9,28} For silicon doped GaInP epilayers, the sources were trimethylgallium (TMGa), ethyldimethylindium (EDMIn), and tertiarybutylphosphine (TBP) with disilane as the dopant precursor. The disilane was diluted to 5 ppm in H_2 . The carrier gas was Pd-

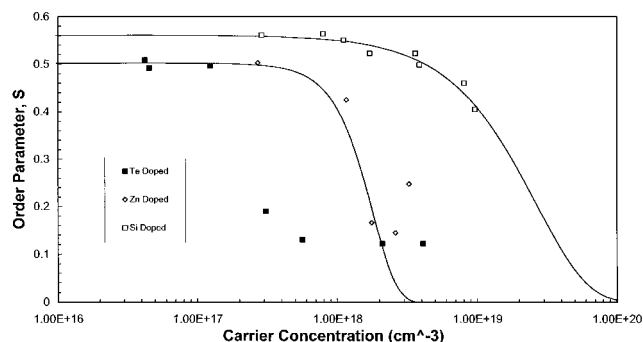


Fig. 1. Degree of order, deduced from the low temperature PL peak energy, versus doping level for Te (n-type), Si (n-type), or Zn (p-type). The lines through the data points for Si and Zn were deduced from a model where disordering is due to Ga and In interdiffusion in the bulk.³⁰

diffused hydrogen. The growth temperature and the V/III ratio were kept constant at 620°C and 30, respectively. The growth rate was $0.4 \mu\text{m/hr}$ and the GaInP layer thickness was approximately $0.2 \mu\text{m}$ for all Si doped samples.

For the Sb doped GaInP epilayers, triethylantimony (TESb) was used as the dopant precursor. The growth temperature was 620°C and the growth rate was $0.6 \mu\text{m/hr}$. The TESb molar flow rate was extremely low to avoid significant Sb incorporation into the solid. The molar ratio of Sb to P in the vapor was a maximum of approximately 4×10^{-4} .

The GaInP solid composition was measured by x-ray diffraction using CuK_α radiation. Only results for lattice matched layers, with values of GaP concentration in the solid of 0.515, are presented here. The free carrier concentration was measured at room temperature using the Hall effect with the van der Pauw geometry. Ohmic contacts were formed using indium dots alloyed for 10 min at 300°C in N_2 .

The 20K PL was excited using the 488 nm line of an Ar^+ laser with a power of 10 mw focused onto a 0.5 mm^2 spot. PL scans were performed with 5\AA steps. The emission was dispersed using a Spex model 1870 monochromator and detected using a Hamamatsu R1104 head-on photomultiplier. The characterization of the surface structure was carried out using a Nanoscope III atomic force microscope (AFM) in the tapping mode. Etched single-crystalline Si tips were used with an end radius of about 5 nm, and a side wall angle of about 35° . Scan rates of 1–2 lines per second were used and data were taken at 512 points/line and 512 lines per scan area. The samples were measured in air, so were covered by a thin, conformal oxide layer.

A surface photo-absorption (SPA) system was attached to the OMVPE reactor for in situ optical characterization of the bonding at the surface. P-polarized light from a 150 W Xe lamp was used to irradiate the surface of the GaInP 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 the gas flow in the reactor. The reflected light was monochromatized and detected by a Si PNN⁺ photodiode using standard lock-in amplification techniques.



Fig. 2. [110] transmission electron microscopy cross section of a sample where the lower layer was undoped and the upper layer was grown having a DETe flow rate consistent with a Te doping level of $4 \times 10^{17} \text{ cm}^{-3}$. A clear change in the APB spacing and angle is seen at the interface, where growth was interrupted for 10 sec while Te was added to the system.

RESULTS

Tellurium

The reduction in order parameter associated with the addition of Te (as DETe) to the system has been documented.⁹⁻¹¹ As seen in Fig. 1, for growth on a vicinal substrate, the reduction in order parameter associated with the addition of Te begins at a concentration of approximately 10^{17} cm^{-3} and the material is completely disordered for concentrations exceeding $5 \times 10^{17} \text{ cm}^{-3}$.⁹ The disordering effect of Te was verified by transmission electron diffraction results.⁹ It was attributed to the marked change in group III adatom

attachment kinetics at the step edge, due to a change in the step edge reconstruction and bond configuration. SPA results indicated no significant change in the surface reconstruction associated with the addition of Te.⁹

By changing the Te flow rate during the growth process, heterostructures can be produced. However, the adsorption/desorption kinetics dictate that the growth cycle be interrupted for several minutes in order to produce abrupt interfaces. An example of such a structure is shown in Fig. 2, the TEM image of a disorder/order heterostructure produced by adding Te to the system during the growth cycle. The bottom layer was grown without Te, followed by a 10 min interruption during which the group III precursors were removed from the system and DETe was added. After the 10 min interruption, growth of Te doped GaInP was initiated. The TEM image shows an abrupt decrease in the order parameter at the point where Te was added to the system. This also produced a marked change in the APB spacing and the propagation angle of the APBs. Order/disorder heterostructures were also produced, with PL consisting of two peaks, due to the undoped (highly ordered) and Te doped (less ordered) layers, with an energy separation of 60 meV. This is the first report of heterostructures with the change in bandgap energy produced by a modulation of the concentration of a surfactant. Similar techniques have also been used to produce quantum well structures with widths as small as 100 Å.²⁹

Silicon

As Si is added to the GaInP at levels exceeding 10^{18} cm^{-3} , the PL peak energy is observed to shift to higher energy, as seen in Fig. 1. The Si doping levels required to increase the PL peak energy are found to be much higher than for Te. In fact, at a Si doping level of 10^{19} cm^{-3} the material still has an order parameter of 0.4, as judged from the PL peak energy. These results are verified by the TED patterns obtained for samples with various Si doping levels. For example, Fig. 3 shows the TED patterns for undoped vicinal and singular samples for comparison with samples grown with a doping level of approximately 10^{19} cm^{-3} .

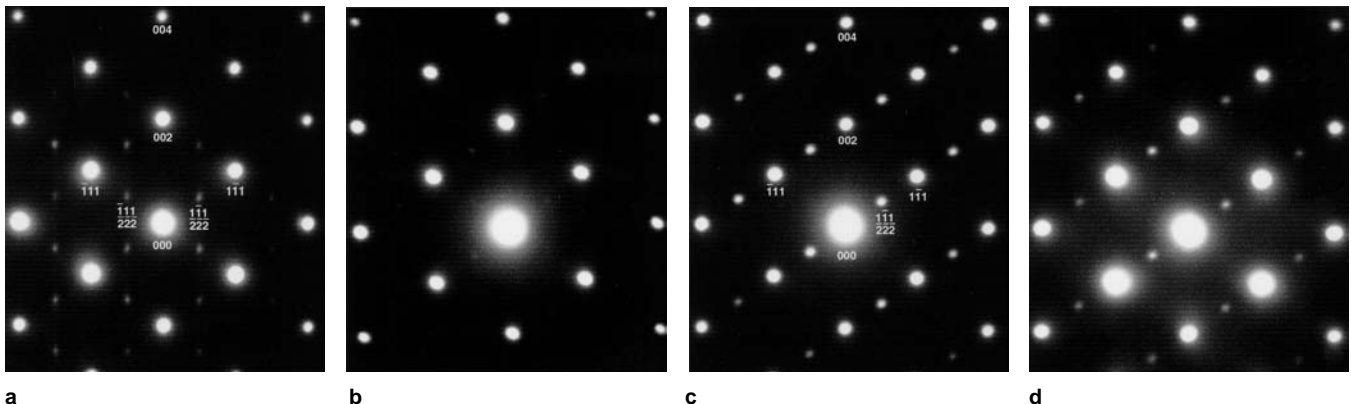


Fig. 3. TED patterns for undoped singular (a) and vicinal (c) layers and for Si doped GaInP layers with free electron concentrations due to Si doping of $7.2 \times 10^{18} \text{ cm}^{-3}$ (singular) (b), $9.6 \times 10^{18} \text{ cm}^{-3}$ (vicinal) (d).

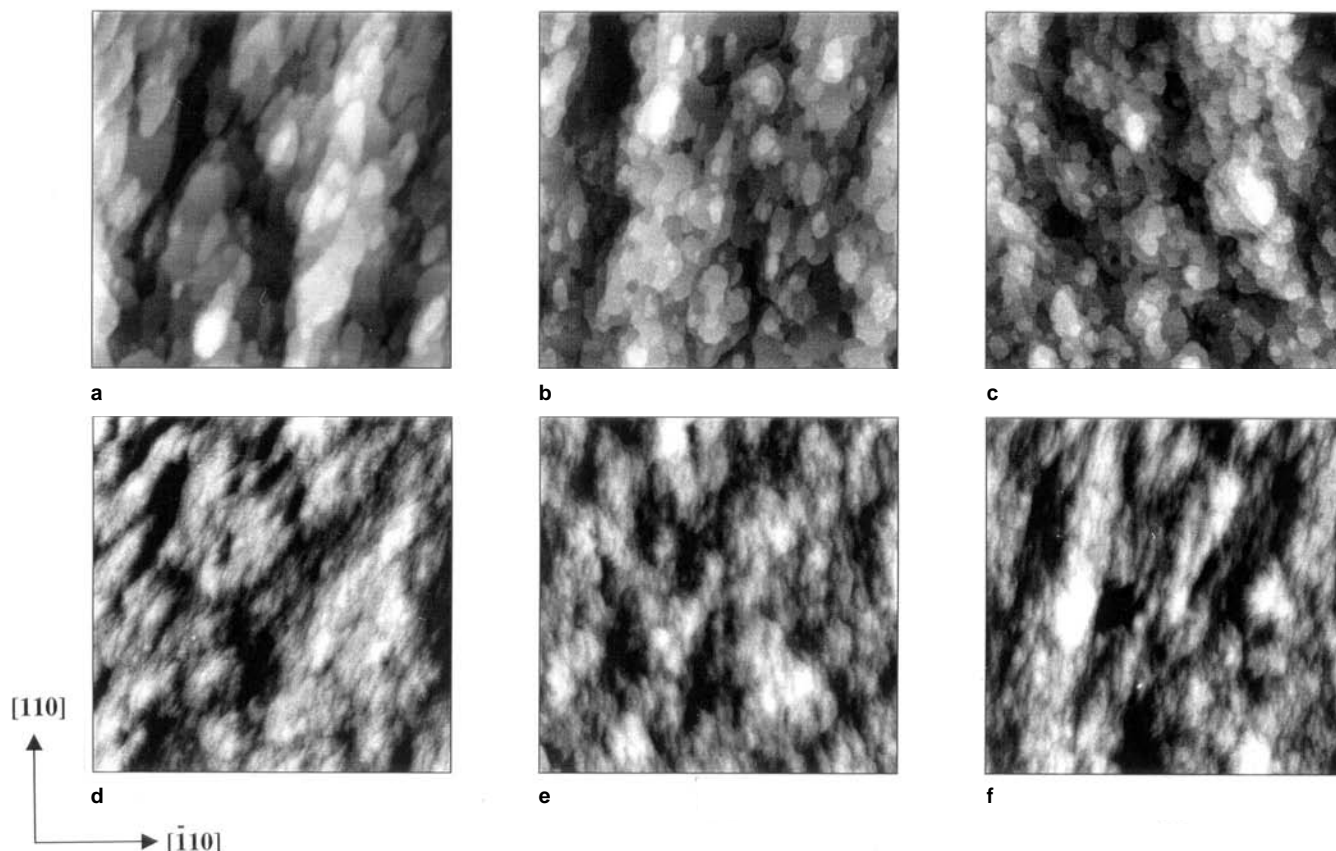


Fig. 4. AFM images of Si doped GaInP layers. (a), (b), and (c) are for singular samples with free electron concentrations (due to Si doping) of $2.8 \times 10^{17} \text{ cm}^{-3}$, $4.4 \times 10^{18} \text{ cm}^{-3}$, and $9.8 \times 10^{18} \text{ cm}^{-3}$, respectively. (d), (e), and (f) are for vicinal (3°B) samples with free electron concentrations (due to Si doping) of $2.2 \times 10^{17} \text{ cm}^{-3}$, $3.9 \times 10^{18} \text{ cm}^{-3}$, and $9.6 \times 10^{18} \text{ cm}^{-3}$, respectively. Each image shows a $1 \mu\text{m} \times 1 \mu\text{m}$ area of the surface.

Clearly, the intensities of the order spots are decreased for the high Si doping levels. However, the samples with electron concentrations of approximately 10^{19} cm^{-3} are still somewhat ordered. This contrasts sharply with the results for the Te doped samples, where a Te doping level of 10^{18} cm^{-3} yields completely disordered material. A comparison of surface photoabsorption spectra for the undoped and Si doped samples indicates that the decrease in order parameter due to Si doping is not due to a decrease in the $[\bar{1}10]$ P dimer concentration on the surface, which is known to provide the thermodynamic driving force for CuPt ordering, as discussed above.

AFM images of the Si doped samples grown on singular and vicinal substrates are shown in Fig. 4 for several doping levels. The average step height (measured from 20–1 μm surface profiles) for growth on a vicinal, 3°B , substrate, is plotted versus the electron concentration due to Si doping in Fig. 5. A slight decrease is seen over the range of doping giving the decrease in order parameter. For growth on singular (001) substrates, the islands are surrounded by a combination of monolayer and bilayer steps. In Fig. 6, the percentage of bilayer steps (averaged over 20–1 μm surface profiles) is seen to decrease with increasing Si concentration. As seen in Fig. 4, the islands are slightly elongated along the $[110]$ direction for the undoped layers with low electron concentrations.

However, the $[\bar{1}10]$ step spacing decreases slightly with increasing free electron concentration (due to Si doping), producing approximately isotropic islands for high Si doping levels. Clearly, the step structure is changed only slightly by the addition of Si at levels resulting in a significant decrease in the degree of order. Again, this contrasts sharply with the results for Te doped samples, where Te doping gives a marked smoothing of the interface and a 20x increase in the $[\bar{1}10]$ step spacing for growth on singular samples.

The line through the Si data points in Fig. 1 was calculated for disordering due to the increase in Ga and In diffusion coefficients due to the shift of the Fermi level with increasing doping level.³⁰ The good fit to the data suggests that the disordering mechanism for Si is simply diffusion in the bulk during the growth cycle. The Si disordering effect reported here is somewhat smaller than the results reported by Gomyo et al.⁷ The increased disordering caused by Si in that work is attributed to the higher growth temperature. Of course a higher temperature will increase the rate of disordering due to Ga and In diffusion in the solid.³¹

The data showing the degree of order versus p-type doping level for Zn doped GaInP is also included in Fig. 1. The disordering induced by Zn is verified by TEM results.²⁸ As reported previously, high Zn doping levels lead to the growth of disordered material.^{13,14,28}

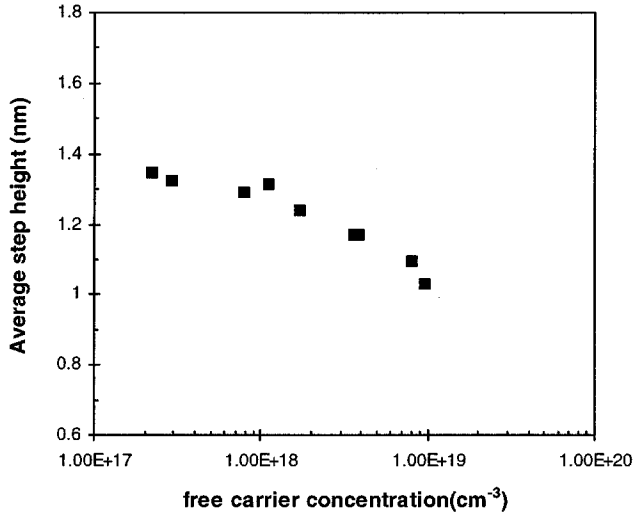


Fig. 5. Average step height measured from AFM cross section scans versus electron concentration due to Si doping of GaInP grown on vicinal substrates, misoriented by 3° to produce [110] steps on the surface.

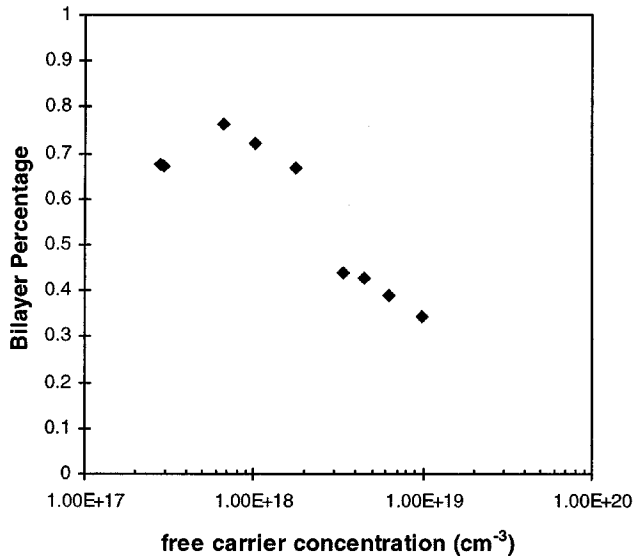


Fig. 6. Percentage of bilayer steps determined from AFM cross section scans versus electron concentration due to Si doping of GaInP grown on singular (001) substrates.

AFM results indicate that the Zn produces only a slight change in the step structure. As for the Si data, the line for Zn in Fig. 1 indicates the calculated disordering for a bulk disordering process.³⁰ The calculated effect of Zn on the Ga/In diffusion was obtained using data from a previous study of the effect of Zn on disordering in GaInP.¹⁴

The final dopant studied was Sb. It is isoelectronic with P so produces no significant change in the Fermi level position at the growth temperature, so should have essentially no effect on the Ga and In diffusion coefficients. Because it is much larger than P, the solubility is small.^{32,33} Thus, it is likely to accumulate at the surface during growth. The amount of TESb added to the system was insufficient to produce a measurable amount of Sb incorporation into the solid

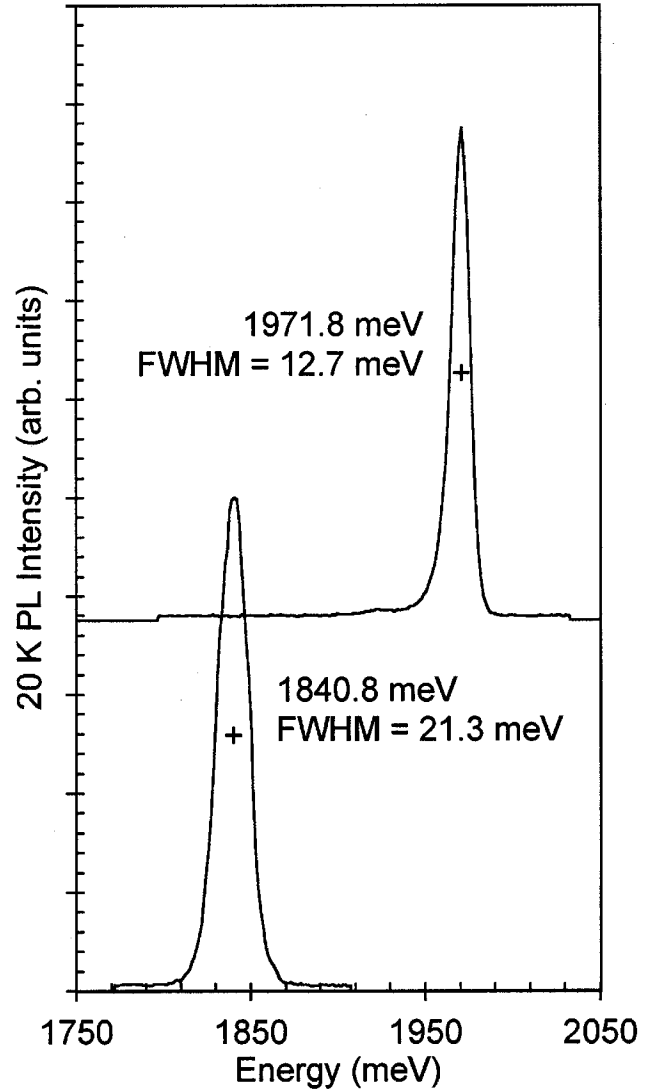


Fig. 7. 20-K PL spectra for an undoped GaInP sample and an Sb-doped layer with a ratio of $p_{\text{Sb}}/p_{\text{P}}$ in the vapor of approximately 4×10^{-4} . Very little (estimated to be 10 ppm) Sb is incorporated into the solid.

by x-ray diffraction. From previous studies,³³ the Sb concentration in the solid is expected to be approximately 10^{-4} . However, the addition of this tiny amount of Sb produces a marked increase in the low temperature PL peak energy, as shown in Fig. 7. The results indicate that the Sb leads to the growth of disordered GaInP. SPA analysis of the undoped and Sb doped surfaces indicates that the [110] P dimers are eliminated by the addition of Sb.³⁴ This indicates that Sb acts as a surfactant that changes the surface reconstruction with a resultant elimination of CuPt ordering during OMVPE growth. This is the first report of the use of Sb as a surfactant during the OMVPE growth of a III/V semiconductor. The effect is dramatic; it produces a 100-meV increase in the bandgap energy.

CONCLUSIONS

A number of dopants, including 2 donors (Te and Si), an acceptor (Zn) and an isoelectronic impurity (Sb) have been added to the system during the OMVPE

growth of GaInP. Te is found to act as a surfactant, causing disorder by changing the group III adatom attachment at steps during growth. The effect is clearly different than the disordering caused by Si. The latter occurs at much higher doping concentrations with little change in the step structure. It is caused by bulk Ga and In inter-diffusion to randomize the ordered structure during the remainder of the growth process. The disordering induced by Zn added during the growth process is similar to that observed for Si and is, again, interpreted in terms of bulk Ga and In diffusion. Perhaps the most dramatic effect is due to Sb. It does not change the Fermi level position, so produces no increase in the Ga/In bulk diffusion. Neither is the step structure changed markedly. However, SPA results indicate that the GaInP surface reconstruction is markedly changed by Sb addition. The [110] dimers responsible for the thermodynamic force for CuPt ordering are eliminated by Sb at concentrations sufficient to produce the growth of completely disordered GaInP. This is the first use of isoelectronic Sb as a surfactant during the OMVPE growth of III/V semiconductors. The use of surfactants to control the bandgap energy is expected to give rise to a new and powerful method for producing complex structures, such as heterostructures and quantum wells, during the OMVPE growth of III/V alloy semiconductors.

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