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Influence of Ga Concentration on the Ordering Process of $\text{Ga}_x\text{In}_{1-x}\text{P}$ Grown on GaAs

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We study the ordering process of $\text{Ga}_x\text{In}_{1-x}\text{P}/\text{GaAs}$, for lattice matched and non-lattice matched samples in the Ga concentration range $0.51 < x < 0.57$. The valence band splitting and the band gap reduction are calculated for partially ordered samples as a function of the Ga concentration and of the long range order (LRO) parameter. Using polarized photoluminescence, we compare the effect of growth temperature and that of Ga concentration on the LRO parameter. The degree of ordering depends strongly on growth temperature, in the range 600°C to 725°C. On the other hand, the change in alloy composition has a minor effect.

KEYWORDS: long range order parameter, $\text{Ga}_x\text{In}_{1-x}\text{P}/\text{GaAs}$, valence band splitting, ordering process

1. Introduction

Vapor phase growth of $\text{Ga}_x\text{In}_{1-x}\text{P}/\text{GaAs}$ (001) is now known to produce spontaneous ordering of the form $(\text{GaP})_1/(\text{InP})_1$ (111) superlattice (the "CuPt_B" structure).¹ Concomitant with ordering one finds a reduction in the band gap^{1,2} and a splitting of the valence band maximum,^{1,3} both reflecting folding of the L point onto the center of the Brillouin zone.⁴

Recently,⁵ measurements of band gap reduction ΔE_g and valence band splitting ΔE_{12} were used along with the theory of Laks *et al.*⁶ to predict the degree of long range order vs. growth temperature. In this work we extend the scope of such previous efforts to study the effect of the composition change on (i) the ordering process, and (ii) on ΔE_g and ΔE_{12} .

2. Theory

The states near the valence band maximum in ordered CuPt structure can be described as⁴

$$E_{1,2,3} = \begin{cases} \frac{1}{3} (\Delta_0 + \Delta_{\text{CF}}) \\ -\frac{1}{6} (\Delta_0 + \Delta_{\text{CF}}) \pm \frac{1}{2} \left[(\Delta_0 + \Delta_{\text{CF}})^2 - \frac{8}{3} \Delta_0 \Delta_{\text{CF}} \right]^{1/2} \end{cases} \quad (1)$$

Where Δ_0 is the spin orbit splitting in a cubic crystal and Δ_{CF} is the crystal field splitting in the absence of spin orbit coupling. Loosely speaking, levels $|1\rangle$, $|2\rangle$ and $|3\rangle$ are heavy-hole, light-hole and split-off band, respectively. In general Δ_0 and Δ_{CF} depend on composition and on the degree η of long range order (LRO), the latter ranging between ideal randomness ($\eta=0$), and perfect CuPt order ($\eta=1$). It has recently been shown^{5,6} that any lattice property $P(x, \eta)$ for $0 < \eta < 1$ can be expressed, to within a reasonable approximation, by the properties of

the random alloy $P(x, 0)$ and those of the perfectly ordered structure $P(X, 1)$ at composition X as:

$$P(x, \eta) = P(x, 0) + \eta^2 [P(X, 1) - P(x, 0)] \quad (2)$$

For ideal CuPt ordering $X=1/2$. The value of η in eq. (2) is bound by $\eta = \min [2x, 2(1-x)]$. Applying eq. (2) to Δ_0 and Δ_{CF} gives:

$$\begin{aligned} \Delta_0(x, \eta) &= \Delta_0(x, 0) + \eta^2 \left[\Delta_0\left(\frac{1}{2}, 1\right) - \Delta_0\left(\frac{1}{2}, 0\right) \right] \\ \Delta_{\text{CF}}(x, \eta) &= \eta^2 \Delta_{\text{CF}}\left(\frac{1}{2}, 1\right) \end{aligned} \quad (3)$$

(Since $\Delta_{\text{CF}}=0$ for the $\eta=0$ random alloy), whereas application to the band gap reduction with respect to the random alloy gives:

$$\begin{aligned} \Delta E_g(x, \eta) &\equiv E_g(x, \eta) - E_g(x, 0) \\ &= \eta^2 \left[E_g\left(\frac{1}{2}, 1\right) - E_g\left(\frac{1}{2}, 0\right) \right] \end{aligned} \quad (4)$$

Substituting eq. (3) into eq. (1) gives the x and η dependent valence band splitting:

$$\begin{aligned} \Delta E_{12}(x, \eta) &= \frac{1}{2} \left\{ [\Delta_0(x, \eta) + \Delta_{\text{CF}}(\eta)] \right. \\ &\quad \left. \times \sqrt{[\Delta_0(x, \eta) + \Delta_{\text{CF}}(\eta)]^2 - \frac{8}{3} \Delta_0(x, \eta) \Delta_{\text{CF}}(\eta)} \right\} \end{aligned} \quad (5)$$

To evaluate eqs. (4) and (5) one needs first to determine its main variables. The band gap $E_g(x, 0)$ of the random alloy can be written as:

$$E_g(x, 0) = x E_g^{\text{GaP}} + (1-x) E_g^{\text{InP}} - b_g x(1-x) \quad (6)$$

While for the spin-orbit (SO) splitting of eq. (3):

$$\Delta_g(x, 0) = x \Delta_0^{\text{GaP}} + (1-x) \Delta_0^{\text{InP}} - b_{\text{SO}} x(1-x) \quad (7)$$

Where b_g and b_{SO} are the bowing parameter for the

direct band gap and of the SO splitting, respectively. We use the room temperature values $E_g^{\text{GaP}}=2.78$ eV, $E_g^{\text{InP}}=1.35$ eV and $b_g \approx 0.76$ eV,⁷⁾ and $\Delta_0^{\text{GaP}}=0.08$ eV,⁸⁾ $\Delta_0^{\text{InP}}=0.110$ eV⁸⁾ and $b_{\text{SO}}=-0.02$ eV.⁴⁾

$\Delta E_g(x, \eta)$ and $\Delta E_{12}(x, \eta)$ are determined by $\Delta_{\text{CF}}(1/2, 1)$, $\Delta_0(1/2, 1)$ and $E_g(1/2, 1)$, all pertaining to the fully ordered CuPt structure. Since such $\eta=1$ samples are unavailable we use the calculated⁵⁾ values $\Delta_{\text{CF}}(1/2, 1)=0.20$ eV (for the cubically constrained film), $\Delta_0(1/2, 1)=0.105$ eV, and $E_g(1/2, 1)-E_g(1/2, 0)=-0.32$ eV. One can measure $\Delta E_g(x, \eta)$ and $\Delta E_{12}(x, \eta)$ at different growth temperatures and compositions, and deduce $\eta(x, T_g)$ from fitting to eqs. (4) and (5).

This theory shows that if (a) the film is cubic for all composition (i.e. $c/a=1$) and (b) dislocations at the film/substrate interface (8000 Å from the sample surface) do not affect the optical properties over the penetration depth of the probing beam (1000 Å from the sample surface), and (c) the film is compositionally uniform (i.e. no ‘‘composition pinning’’⁹⁾), then:

(i) The $\Delta E_{12}(x, \eta)$ valence band splitting depends weakly on composition (Fig. 1(a)) but strongly on the degree of LRO (Fig. 1(b)).

(ii) The band gap reduction $\Delta E_g(\eta)$ is composition independent but depends strongly on η [eq. (4)].

(iii) Items (i) and (ii) indicate that the functional relation between $\Delta E_{12}(x, \eta)$ and $\Delta E_g(\eta)$ depends weakly on x (Solid line in Fig. 2).

3. Experiments

Most samples were grown by MOCVD at the Tech-

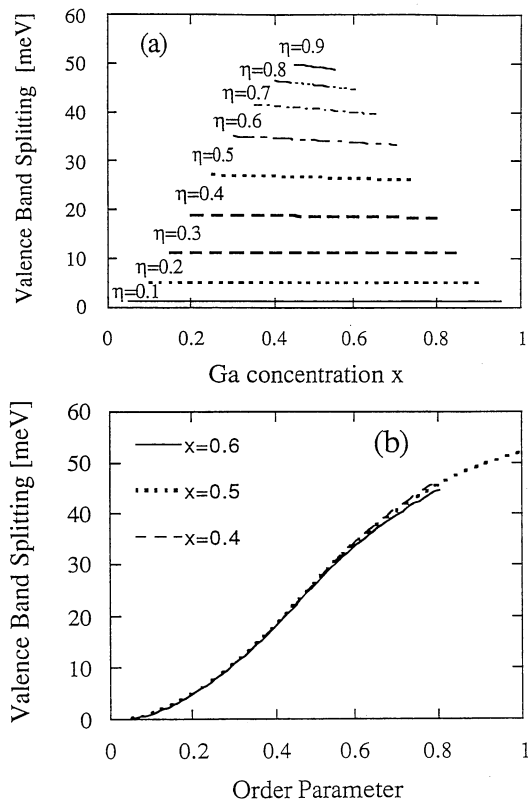


Fig. 1. Predicted dependence of ΔE_{12} on composition x and LRO parameter η . From eqs. (3), (5) and (6).

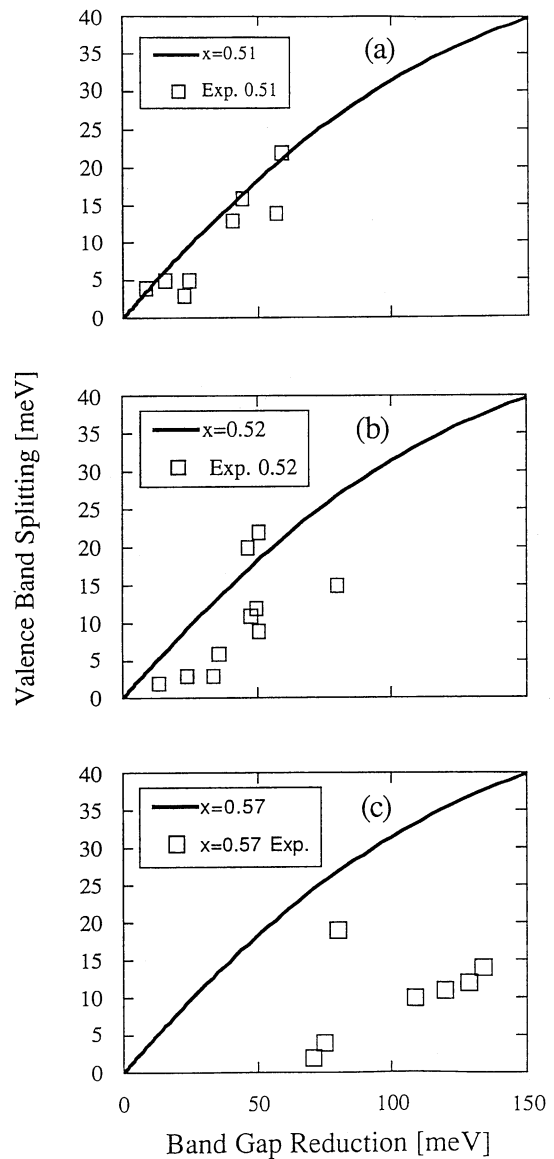


Fig. 2. The solid lines depicts the theoretical dependence of the valence band splitting $\Delta E_{12}(x, \eta)$ on the band gap reduction $\Delta E_g(x, \eta)$ [from eqs. (4) and (5)]. Open squares give measured values.

nion-Institute of Technology, in the Ga concentration range $0.51 < x < 0.57$, and in the temperature range $670^\circ\text{C} < T_g < 725^\circ\text{C}$ at a growth rate of $\approx 2-3$ $\mu\text{m}/\text{h}$. The samples grown at $T_g=600^\circ\text{C}$ were grown in Aachen by low pressure Metal Organic vapor phase epitaxy.¹⁰⁾ All the films were grown perpendicular to the [001] direction of the GaAs substrate.

Two sets of experiments were performed: Raman scattering, which measures Ga concentration, and polarized PL with outgoing polarization vector either parallel or perpendicular to the [110] direction. The outgoing polarization parallel to the $\langle 100 \rangle$ crystal axis corresponds mainly to the conduction band minimum to heavy hole $|1\rangle$ transition, and the perpendicular polarization corresponds mainly to the conduction band minimum to light $|2\rangle$ transition.¹¹⁾ The energy difference between the two polarizations peaks gives ΔE_{12} and the parallel polarization gives $E_g(x, \eta)$.

All Raman and PL measurements were taken at room

temperature using the Ar⁺ 5145 Å line with 15 mW power as an exciting source and analyzed using Dilor's micro-Raman spectrograph with an accuracy of $\cong 1.0$ meV on the value of ΔE_{12} . The concentration x was determined from Raman scattering with an accuracy $\Delta x \cong 1\%$.

4. Results and Conclusion

Figure (3) displays the LRO parameter η vs growth temperature where η was extracted by fitting the measured ΔE_{12} to eq. (5) [Fig. 3(a)], and the measured $\Delta E_g(\eta)$ to eq. (4) [Fig. 3(b)]. We observe the usual²⁾ nonmonotonic behavior of η vs T_g in both cases. Composition variations have a small effect on ΔE_{12} and ΔE_g , as predicted by the theory of Wei *et al.*^{4,5)} (Fig. 1 and eq. (4)).

The symbols of Fig. 2 gives the experimental dependence of $\Delta E_{12}(x, \eta)$ on $|\Delta E_g(\eta)|$ for $x=0.51$ (part a) $x=0.52$ (part b) and $x=0.57$ (part c). In all cases, the solid curve gives the theoretical prediction. We see a good fit for $x=0.51$ and $x=0.52$, indicating that in these cases band gap reduction and valence band splitting share a common physical origin, namely ordering. For $x=0.57$ our samples exhibit a larger ΔE_g than granted by ordering alone. A similarly large ΔE_g (≈ 150 meV) was found by Kondow *et al.*¹²⁾ for Ga-rich ordered alloys Ga_{0.70}In_{0.30}P relative to the disordered alloy of the same composition.

Equations (4) and (5) assume that the film is cubic ($c/a_s=1$). If however, the film is coherent with the (001) substrate then, away from the lattice matched composition the film will have a tetragonal deformation:

$$\frac{\Delta a_{\perp}}{a_s} = \frac{c(x)}{a_s} - 1 = \left(1 + 2 \frac{C_{12}}{C_{11}}\right) \varepsilon(x) \quad (8)$$

Where $\varepsilon(x) = [a(x) - a_s]/a_s$ is the misfit strain, a_s is the substrate lattice constant, C_{ij} are elastic constant, and $a(x)$ is the lattice parameter of the unstrained film. This deformation leads to $\Delta_{CF}(x, 0) \neq 0$ even for $\eta=0$.

Kuo *et al.*¹³⁾ measured the effect of (001) strain on the fully random ($\eta=0$) alloy, finding that this leads to $\Delta E_{12}(x, 0) = 5.7\varepsilon$ eV and $\Delta E_g(x, 0) = 11.7\varepsilon$ eV. Assuming 100% coherence at $x=0.57$, eq. (8) gives $(c/a_s) - 1 = -7.92 \times 10^{-3}$ and $\varepsilon = -3.98 \times 10^{-3}$, so from Kuo *et al.* this leads to a 47 meV reduction in $\Delta E_g(x, 0)$, and 23 meV increase in $\Delta E_{12}(x, 0)$. Our results differ from this case in two ways: First, using our measured deviation of the (004) X-ray diffraction line we find $(c/a_s) - 1 = -2.45 \times 10^{-3}$ rather than the fully coherent value of -7.92×10^{-3} . Second, since our samples show $\eta \neq 0$, they have an ordering-induced crystal field splitting $\Delta_{CF}^{(111)}(x, \eta)$ even without strain. The (001) strain splitting $\Delta_{CF}^{(001)}$ interacts with the (111) ordering induced splitting $\Delta_{CF}^{(111)}$ so that the simple relation used by Kuo *et al.*¹³⁾ are no longer valid. We have solved the 6×6 generalized quasicubic model¹⁴⁾ for $x=0.57$, $\eta=1/2$ and our measured ε . We find that relative to $\varepsilon=0$, strain increases ΔE_{12} by ≈ 1 meV and reduces ΔE_g by 10 meV. These changes are (a) small on the scale of Fig. 2(c), and (b) in the wrong direction (the measured points have to be moved to smaller ΔE_{12} and larger ΔE_g). We conclude that misfit strain is not the reason for the discrepancy of Fig. 2(c), so this

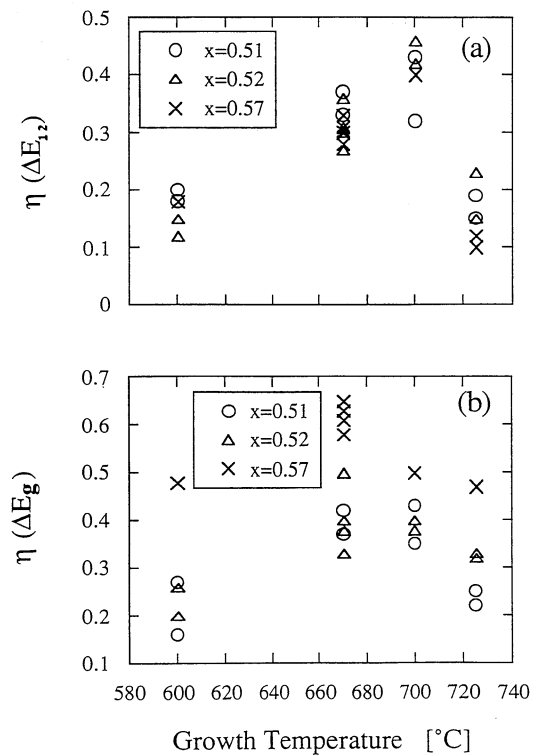


Fig. 3. LRO parameter from (a) fitting the data to the valence band splitting $\Delta E_{12}(x, \eta)$ [eq. (5)], and (b) fitting to band gap reduction $\Delta E_g(x, \eta)$ [eq. (4)].

result is not understood.

The following possibilities exist: (i) If the film exhibits local phase-separation (i.e. short range clustering), recent calculation¹⁶⁾ predict a large reduction in ΔE_g without a concomitant valence band splitting, in qualitative agreement with Fig. 2(c). Direct measurements of clustering, of the sort reported in similar alloys¹⁷⁾ are needed here. (ii) "composition pinning"⁹⁾ could eventually increase ΔE_g . This could be examined by X-ray microanalysis and by electron diffraction.

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