X-ray diffraction and excitation photoluminescence analysis of ordered GaInP

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X-ray diffraction is shown to provide a direct, quantitative, structural measurement of the degree of spontaneous ordering in GaInP. In this paper we combine x-ray diffraction and excitation photoluminescence analyses of CuPt-ordered GaInP, and comparing the results to theoretical predictions for the dependence of the band structure on order parameter, determine the values of the band-gap reduction and crystal-field splitting parameters for the perfectly ordered alloy. [S0163-1829(98)06447-9]

Atomic ordering is frequently observed in epitaxially grown ternary and quaternary III-V semiconductor alloys. It has received a great deal of attention because it affects the electro-optical properties of the alloy and reveals interesting surface-controlled epitaxial growth processes.[1–13] Although many techniques, such as excitation photoluminescence (PLE), are well suited to measuring the effects of ordering on electro-optical properties, they can only estimate the degree of ordering in a sample by relying on theoretical calculations modeling the effects of ordering on the electronic band structure.[4,5] Recently, nuclear magnetic resonance spin echo measurements have been applied to the evaluation of the order parameter.[6] Measurement of the quadrapole interactions between nuclei and the local electric field gradient (EFG) were made, and a simple point charge model was used to theoretically calculate the EFG at the cation sites and deduce an order parameter. This technique of determining the order parameter, however, is also based on theoretical estimates, in this case of the EFG using the point-ion model or the local-density-functional formalism method.[6,7] A technique is therefore needed that directly determines the order parameter without relying on the results of electronic structure calculations.

X-ray diffraction can provide a direct, quantitative measure of the order parameter. It has previously been used to qualitatively study ordering in these materials.[8] We present a quantitative analysis of CuPt-ordered GAInP samples using x-ray diffraction to directly measure the order parameter. By comparing x-ray results with those obtained using PLE, we test of the accuracy of the theoretical band-structure calculations and give the first independent determination of the band-gap reduction and crystal-field splitting parameters for the perfectly ordered alloy.

CuPt ordering is the most commonly observed and studied ordering in ternary III-V alloys grown epitaxially on approximately [001] oriented substrates.[1–13] Only partial ordering has been achieved in these samples. In a III$_a$-III$_b$-V zincblende alloy with perfect [111] CuPt ordering, the III$_a$ and III$_b$ atoms occupy alternate (111) planes. The $[\bar{1}11]$ and $[1\bar{1}1]$ (hereafter referred to as [111]B) CuPt ordering variants are almost exclusively observed in these alloys. Epilayers grown on exact [001] substrates typically contain approximately equal amounts of the two [111]B variants. Epilayers grown on substrates tilted a few degrees from [001] towards a (111)B plane contain more of that [111]B variant than the other. A substrate tilt of 6° has been shown to produce nearly single variant [111]B CuPt ordering.[9,10]

Six Ga$_x$In$_{1-x}$P samples were studied. All were grown by metalorganic vapor phase epitaxy (MOVPE) on GaAs substrates cut 6° off of [001] towards the (111) plane. All GaInP epilayers were nominally 2 μm thick. The growth is described in more detail in Refs. 4 and 5.

For PLE, a dye laser with a DCM dye was used for excitation at a power level of approximately 1 mW. The valence-band splitting (ΔE_{VBS}) was measured with an accuracy of ± 0.4 meV. The band-gap reduction (ΔE_g) was measured with an accuracy of ± 5 meV, the uncertainty being mainly due to the uncertainty in the value used for the band gap of a random sample (we used $E_g = 2.006$ eV for random Ga$_{0.52}$In$_{0.48}$P). The band gap for each sample was determined with an accuracy of ± 0.5 meV. The ΔE_{VBS} and ΔE_g measured values have been corrected for composition variations referenced to a composition of $x = 0.52$. The PLE measurements are described in more detail in Ref. 4.

Each sample was characterized using high-resolution x-ray diffraction. Measurements were made on a 12-kW rotating anode x-ray generator, with a standard four-circle diffractometer, and a Cu $K_{\alpha 1}$ radiation ($\lambda = 1.54051$ Å) produced by a Ge(111) monochromator with slits. This monochromator, combined with a pulse height analyzer, eliminates the $\lambda/2$ radiation, which is essential for these experiments. The resolution of the diffractometer was determined from the full width at half-maximum (FWHM) of the GaAs substrate peaks and was used to correct the measured data. Typical detector slits used for determining peak positions were 0.15 by 1 mm, corresponding to a radial (θ–2θ) resolution of 0.0174°. Detector slits used to measure integrated intensities in rocking (θ) scans were 3 by 5 mm.

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The $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$ compositions were evaluated from the positions of the (004) fundamental peaks. The degree of order was calculated by comparing the four $\{\frac{1}{2},\frac{1}{2},\frac{3}{2}\}$ superstructure peaks to the corresponding {113} fundamental peaks (see below). These off-axis reflections were accessed using the χ circle so that the incident and exit angles of the x-rays were approximately equal ($\omega \cong 2\theta/2$), and absorption in the thin sample was a function of θ and χ, determined by the traverse of the incident and exit beams, as described below.

The integrated Bragg intensity from a periodic crystal is proportional to the complex product of the crystal structure factor, $I \propto |F_T|^2$. The structure factor F_T for CuPt-ordered $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$ includes both fundamental zinc-blende reflections and superstructure reflections resulting from the CuPt-type long-range order. The T indicates the inclusion of thermal factors (see below). Each [111] CuPt variant results in a unique set of superstructure reflections, and it is therefore a simple matter to distinguish among them with diffraction techniques.

We define the order parameter for CuPt ordered $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$ as $S=2(r_{\mathrm{Ga}}-x_{\mathrm{Ga}})=2(r_{\mathrm{In}}-x_{\mathrm{In}})$, where $x_{\mathrm{Ga(In)}}$ is the fraction of type-III atoms that are Ga (In) atoms, and $r_{\mathrm{Ga(In)}}$ is the fraction of Ga (In) sites that are ''rightly'' occupied by Ga (In) atoms. S varies from 0, for completely random $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$, to 1 for the perfectly ordered structure. According to this definition, only $\mathrm{Ga}_{0.5}\mathrm{In}_{0.5}\mathrm{P}$ can result in $S=1$.[14]

The structure factor at a superstructure reflection can be written in terms of the order parameter S. This results in a straightforward experimental technique for quantitatively measuring the order parameter for each order variant, from the integrated intensities of a superstructure and a fundamental reflection set. For example, S can be calculated from the ratio of the integrated intensities of the $(\frac{1}{2},\frac{1}{2},\frac{3}{2})$ and (113) peaks, by

$$S=\left\{\frac{I_{(1/2)(1/2)(3/2)}}{I_{113}}\,\frac{4\left[[|f_{\mathrm{P}}|^2+|x_{\mathrm{Ga}}f_{\mathrm{Ga}}+x_{\mathrm{In}}f_{\mathrm{In}}|^2]\left(\frac{1+\cos^2 2\theta}{\sin 2\theta}\right)(1-e^{-2\mu L/\sin\theta})\right]_{113}}{\left[|f_{\mathrm{Ga}}-f_{\mathrm{In}}|^2\left(\frac{1+\cos^2 2\theta}{\sin 2\theta}\right)(1-e^{-2\mu L/\sin\theta})\right]_{(1/2)(1/2)(3/2)}}\right\}^{1/2}, \qquad (1)$$

where θ is one-half the angle between forward incident and scattered beam directions, f_i is the atomic scattering factor for atom i, $(L/\sin\theta)$ is the x-ray path length inside the sample, and μ is the linear absorption coefficient of the sample.[14]

The atomic scattering factors were obtained from Ref. 15 and standard corrections for dispersion and thermal vibrations (using Debye–Waller factors) were used. The Debye–Waller factors were calculated from the estimated Debye temperatures, using the Debye model, resulting in $B_{\mathrm{GaP}}=0.3001$ and $B_{\mathrm{InP}}=0.2799$.[16,17] The individual values of B_{P}, B_{In}, and B_{Ga} for the GaInP structure were not available.

CuPt ordering in ternary III-V alloys reduces the band gap and causes a splitting of the valence band. Theoretical predictions for the dependence of the band gap reduction relative to a random alloy (ΔE_g) and the valence band splitting (ΔE_{VBS}) on the order parameter S are given by[11]

$$\Delta E_g(S)=E_g(S)-E_g(0)=\Delta E_g(1)S^2, \qquad (2)$$

$$\Delta E_{\mathrm{VBS}}(S)=E_1(S)-E_2(S).$$

Using the quasicubic model, the valence-band maxima $E_1(S)$ and $E_2(S)$ are given in terms of the spin orbit splitting (Δ_{SO}) and the crystal-field splitting (Δ_{CF}) by[11]

$$E_1(S)=\tfrac{1}{2}[\Delta_{\mathrm{SO}}+\Delta_{\mathrm{CF}}(S)],$$

$$E_2(S)=\tfrac{1}{2}\{[\Delta_{\mathrm{SO}}+\Delta_{\mathrm{CF}}(S)]^2-\tfrac{8}{3}\Delta_{\mathrm{SO}}\Delta_{\mathrm{CF}}(S)\}^{1/2},$$

where $\Delta_{\mathrm{CF}}(S)$ also depends quadratically on S, $\Delta_{\mathrm{CF}}(S)=\Delta_{\mathrm{CF}}(1)S^2$. Δ_{SO} has been assumed to be independent of S, based on experimental observations. Experiment gives $\Delta_{\mathrm{SO}}=102.6\pm0.2$ meV for $0\leqslant S\leqslant 0.55$.[5] We can relate $\Delta E_{\mathrm{VBS}}(S)$ to $\Delta_{\mathrm{CF}}(S)$, and therefore to S^2, as

$$\frac{\Delta E_{\mathrm{VBS}}^2(S)-\Delta E_{\mathrm{VBS}}(S)\Delta_{\mathrm{SO}}}{\Delta E_{\mathrm{VBS}}(S)-\frac{2}{3}\Delta_{\mathrm{SO}}}=\Delta_{\mathrm{CF}}(1)S^2. \qquad (3)$$

PLE can be used to measure $\Delta E_{\mathrm{VBS}}(S)$ and $\Delta E_g(S)$. Without an independent measurement of S, these PLE measurements can only give a value for the ratio of the parameters $\Delta E_g(1)$ and $\Delta_{\mathrm{CF}}(1)$. In order to extract a value for the order parameter, PLE measurements must be combined with theoretical calculations of $\Delta E_g(1)$ or $\Delta_{\mathrm{CF}}(1)$. By combining PLE measurements with independent x-ray diffraction measurements of the order parameter, we are able to verify the form of the above equations, and, if valid, individually fit the parameters $\Delta E_g(1)$ and $\Delta_{\mathrm{CF}}(1)$.

The composition of the six $\mathrm{Ga}_x\mathrm{In}_{1-x}\mathrm{P}$ samples ranged from $x=0.515$ to 0.528, corresponding to lattice mismatches with respect to GaAs of 0 to 0.094%. Although quite well latticed matched, even a small difference will result in some inhomogeneous strain in the film. Both {113} and {333} fundamental peak sets were measured, as were the $\{\frac{1}{2},\frac{1}{2},\frac{3}{2}\}$ and $\{\frac{3}{2},\frac{3}{2},\frac{3}{2}\}$ superstructure peak sets. The θ FWHM of the $(\bar{1}\bar{1}3)$ peaks measured in the integrated intensity scans ranged from 1.3 to 2.9 times that of the GaAs substrate peaks. In addition, most samples showed some mosaic structure in the tails of the GaInP peaks measured, again, in the θ scans. Based on these observations we have used standard kinematic diffraction theory to model the integrated intensity because the strain is sufficient to eliminate extinction.[14] We have chosen

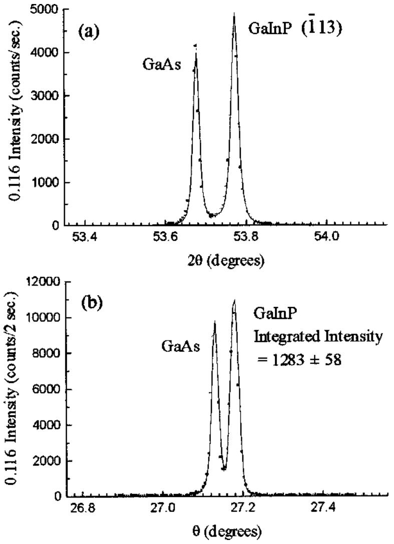

FIG. 1. (a) Radial (θ–2θ) and (b) rocking (θ) scans of the $(\bar{1}13)$ fundamental peak from a typical sample. Points represent experimental data, solid lines represent fits to the data.

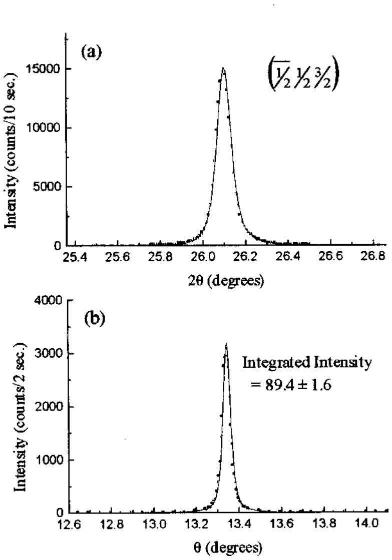

FIG. 2. (a) Radial (θ–2θ) and (b) rocking (θ) scans of the $(\bar{\frac{1}{2}}, \frac{1}{2}, \frac{3}{2})$ superstructure peak from a typical sample. Points represent experimental data, solid lines represent fits to the data.

to use the {113} and $\{\frac{1}{2},\frac{1}{2},\frac{3}{2}\}$ peaks to measure the order parameter, since the {333} peaks are broader and cannot be fit as accurately.

All samples contained primarily $[\bar{1}11]$ CuPt ordering, as indicated by strong $(\bar{\frac{1}{2}},\frac{1}{2},\frac{3}{2})$ peaks. Figures 1 and 2 show typical radial and rocking scans of the $(\bar{1}13)$ and $(\bar{\frac{1}{2}},\frac{1}{2},\frac{3}{2})$ peaks. The correlation length of the crystalline domains [calculated from the radial FWHM of the (113) peaks corrected for resolution], the correlation length of the [111] ordered domains [calculated from the radial FWHM of the $(\bar{\frac{1}{2}},\frac{1}{2},\frac{3}{2})$ peaks], the mosaic spread of these peaks (given by the θ FWHM), and the [111] order parameters are given in Table I. The results indicate large, high-quality crystalline domains, and somewhat smaller ordered domains.

A small amount of the [111] variant was also present in four samples, resulting in weak $(\frac{1}{2},\frac{1}{2},\frac{3}{2})$ peaks. The $[\bar{1}11]$ order parameters in these samples ranged from 0.012±0.001 to 0.044±0.002. These values are 10% or less of the measured [111] order parameters. The correlation lengths of these ordered domains, 48 Å±5 to 126 Å±35, are much smaller than those of the $[\bar{1}11]$ ordered domains. This indicates that relatively poor [111] ordering is forming in small areas within the GaInP epilayer.

There are two simplified models for the structure of a partially ordered material; either perfectly ordered domains exist within an otherwise disordered film, or the entire film has homogeneous partial order. In the first model, the order parameter would equal the fraction of the volume that is ordered. Based on the measured correlation lengths, this model would result in smaller [111] order parameters than those that were measured for these samples, except perhaps for sample number 1642. The homogeneous model seems to fit these samples better, with the smaller ordered domains explained by the occurrence of antiphase boundaries, which do not affect the magnitude of S. This is a simplified model; since x-ray diffraction averages over the entire irradiated volume, it will give an average order parameter if any inhomogeneity exists.

The measured order parameters are plotted versus PLE-measured ΔE_{VBS} and ΔE_g values in Figs. 3 and 4. The circles represent the measured data. The solid lines represent

TABLE I. X-ray diffraction results for GaInP samples. Correlation length is calculated from the resolution corrected radial FWHM of the peaks; the mosaic spread is given by the θ FWHM in rocking scans. The order parameter is calculated from the integrated intensities, taken in the rocking (θ-scan) mode, using Eq. (1).

Sample No.	Correlation Length (Å)		Mosaic spread (degrees)		$[\bar{1}11]$ order parameter
	Crystalline domains	$[\bar{1}11]$ order domains	Crystalline domains	$[\bar{1}11]$ order domains	
396	3685±165	1103±19	0.026	0.038	0.468±0.010
407	7351±283	1038±6	0.018	0.032	0.437±0.001
1639	2451±49	797±9	0.025	0.057	0.503±0.019
1642	8424±358	1038±5	0.018	0.040	0.282±0.008
1643	10037±305	1175±9	0.024	0.042	0.443±0.017
1650	5513±123	197±1	0.024	0.274	0.516±0.014

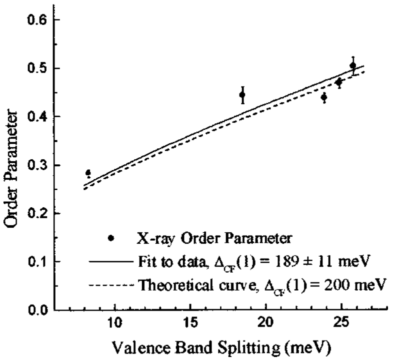

FIG. 3. Order parameter vs $\Delta E_{\mathrm{VBS}}(S)$. Circles represent experimental data, the solid line represents a fit to the data using Eq. (3), the dashed line represents theoretical predictions using LAPW-LDA (Ref. 11) calculations.

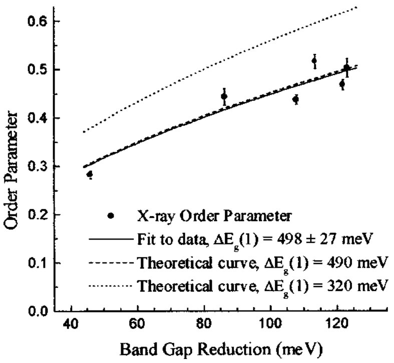

FIG. 4. Order parameter vs $\Delta E_g(S)$. Circles represent experimental data, the solid line represents a fit to the data using Eq. (2), the dashed and dotted lines represent theoretical predictions using pseudopotential-LDA (Ref. 12) and LAPW-LDA (Ref. 11) calculations.

fits to our data using Eqs. (2) and (3), and fitting the values of $\Delta_{\mathrm{CF}}(1)$ and $\Delta E_g(1)$. The dashed line in Fig. 3 represents theoretical predictions using linearized augmented plane wave local density approximation (LAPW-LDA) (Ref. 11) calculations. The dotted and dashed lines in Fig. 4 represent theoretical predictions using LAPW-LDA[11] and pseudopotential-LDA (Ref. 12) calculations.

Our data are consistent with the proposed quadratic dependence of the band structure on S. Our fits result in $\Delta E_g(1) = 498 \pm 27$ meV and $\Delta_{\mathrm{CF}}(1) = 189 \pm 11$ meV. LAPW-LDA yields calculated values of $\Delta E_g(1) = 320$ meV and $\Delta_{\mathrm{CF}}(1) = 200$ meV. This theory is expected to be a good estimate for the ground states, and hence the valence-band splitting (Δ_{CF}), but less accurate for the excited states (ΔE_g), which it is expected to underestimate for GaInP.[13] The LAPW-LDA value for $\Delta_{\mathrm{CF}}(1)$ is quite close to our experimental fit (dashed curve in Fig. 3), while the pseudopotential-LDA calculation results in the closest theoretical $\Delta E_g(1)$ to our value (dashed curve in Fig. 4). This is reasonable, since the pseudopotential-LDA calculation included an LDA correction intended to improve the estimate of the band gap.

PLE and absorption studies have given values for $\Delta E_g(1)/\Delta_{\mathrm{CF}}(1)$ of 2.36 ± 0.06 (Ref. 4) and 2.66 ± 0.15.[5] The LAPW-LDA theoretical prediction for this ratio is 1.6.[11] Our results give 2.63 ± 0.2, which agrees well with the experimental result of Ref. 5. All of these experimental values are higher than the theoretical LAPW-LDA result.

In conclusion, we have presented the first quantitative measurement of the average order parameter in CuPt-ordered GaInP using x-ray diffraction. By combining this data with PLE band structure measurements we have confirmed the quadratic dependence of the band structure on the order parameter and independently determined the two important parameters $\Delta E_g(1)$ and $\Delta_{\mathrm{CF}}(1)$ for GaInP. X-ray diffraction has traditionally been used to study structure and ordering in materials, and proves here to be a powerful tool for studying these phenomena in III-V semiconductor alloys.

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