SINGLE AND DOUBLE VARIANT CUPT-B ORDERED GaInAs

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ABSTRACT

Nominally lattice-matched GaInAs layers grown by metal organic vapor phase epitaxy on InP substrates have been studied using high-resolution x-ray diffraction (HRXRD) to determine the growth conditions under which ordering is introduced. HRXRD provides an independent means to quantify the order parameter of semiconductor heterostructures as well as the ordering on different {111} planes, i.e., double variant ordering. This independent means to determine ordering provides for a better understanding of the effects of ordering on the electronic and optical properties. Double variant ordering was observed for epitaxial layers grown on exact (001) InP substrates, with an order parameter of about 0.1 in both variants. For substrates that were miscut by 6 degrees, single variant ordering was detected. In these cases, an order parameter as high as 0.66 was measured for certain growth conditions. The layers grown on vicinal substrates are all of high crystalline quality, those on (001) substrates exhibit some mosaic spread.

INTRODUCTION

It has been well established that atomic ordering, which is commonly observed in epitaxially grown III-V alloys, effects the alloys' electronic and optical properties.[1] Ordering reduces the band gap with respect to the random alloy, changes the band structure, and establishes optical polarization. These effects are of considerable interest to the semiconductor community for the development of high-quality, band gap engineered materials. Many studies of atomic ordering have been reported, particularly in GaInP, including analyses of the electronic effects using photoluminescence (PL)[2], and structural analyses using transmission electron microscopy (TEM)[3], scanning tunneling microscopy[4], and x-ray diffraction (XRD).[5,6] Recent works have reported on $CuPt_B$ in technologically important $Ga_xIn_{1-x}As$ grown on InP using photocurrent spectroscopy[7], TEM[8], and ultrahigh frequency photoconductive decay measurements[9]. The current paper presents a direct, quantitative measurement of the degree of order in $Ga_xIn_{1-x}As$ samples using high-resolution XRD (HRXRD).

CuPt is the most commonly observed type of ordering in ternary III-V epilayers grown on [001] oriented substrates. It consists of (111) planes rich in alternating group-III constituents. Group-V rich surface reconstructions typically lead to ordering of the $(\bar{1}11)$ and/or $(1\bar{1}1)$ planes, referred to as the $CuPt_B$ variants. Epilayers grown on exact [001] substrates typically contain approximately equal amounts of the two B variants. Epilayers grown on substrates tilted 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 $CuPt_B$ ordering.[10]

EXPERIMENT

Eight $Ga_xIn_{1-x}As$ samples were studied with HRXRD. The samples were grown by low pressure metal organic vapor phase epitaxy at a total pressure of 75 Torr on InP substrates. The precursors were arsine (AsH_3), phosphine, triethylgallium and trimethylindium. The carrier gas was hydrogen for sample 3, with a growth rate of 32 nm/min, and nitrogen for all others, with a

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growth rate of 20 nm/min. The AsH$_3$ partial pressure was 1.6 Torr for the GaInAs layer in each sample. The GaInAs was grown on an InP buffer layer and then capped with InP deposited at 620 °C. The growth temperatures and V/III ratios are given in Table I. Three sets of samples were grown in order to compare double and single variant ordering; samples 1 "a" and "b", 2 "a" and "b", and 3 "a" and "b". In each set, samples "a" and "b" were grown simultaneously with identical growth conditions, sample "a" on a (001) substrate (leading to double variant ordering) and sample "b" on a substrate miscut by 6° towards the [1$\bar{1}$1] (leading to single variant ordering). Samples 2b, 4 and 5 were grown in order to investigate the effects of growth temperature on ordering, they were grown at the same V/III flux ratio (V/III = 235), but with growth temperatures ranging from 550° to 600° C.

Table I. Summary of GaInAs growth conditions.

Sample	Growth temperature (° C)	V/III flux ratio	Nominal GaInAs thickness (μm)	Substrate miscut
1a	550	235	0.5	0
1b	550	235	0.5	6° B
2a	550	235	1.8	0
2b	550	235	1.8	6° B
3a	550	284	2.9	0
3b	550	284	2.9	6° B
4	575	235	1.8	6° B
5	600	235	1.8	6° B

X-ray diffraction analysis was done on a Bede D^3 diffractometer with a sealed tube source, using Cu K$_\alpha$ radiation (λ = 1.54051Å). The diffractometer axes ω and 2θ are position encoded, providing an angular precision of 0.07 arc sec and an absolute accuracy of 2 arc sec over 360°. Initial x-ray beam optics consist of a Si (111) channel cut collimator and a Si (111) monochrometer, all in (+, -, -) geometry. In triple axis diffraction (TAD) mode, the diffracted beam from the sample is conditioned by a four bounce (+, -, +, -) Si (220) analyzer crystal. In double axis diffraction (DAD) mode, the diffracted beam is defined by slits.

The composition and crystalline quality of the samples were determined from TAD measurements of their (004) peaks. The order parameter (S) was calculated from integrated intensities measured by DAD (see below). Off-axis peaks were accessed in the skew geometry, in which the angle between the diffracting planes and the sample surface (Φ) is accommodated along χ (in the plane perpendicular to the diffraction plane). This allows skew symmetric reflections to be accessed where the incident angle of the x-ray beam equals that of the exit beam.

The degree of order is described by the order parameter, S. We use the generalized Bragg-Williams order parameter for CuPt ordered Ga$_{1-x}$In$_x$As. S varies from 0, for the random alloy, to 1, for the perfectly ordered alloy. The generalized order parameter accounts for composition, so that only Ga$_{0.5}$In$_{0.5}$As can result in S = 1.[5,11]

Ordering results in diffraction peaks not produced by the random alloy (non-fundamental peaks), called superstructure peaks. Each [111] CuPt variant results in a unique set of superstructure reflections, and it is therefore straightforward to distinguish among them with diffraction techniques. The integrated intensity (I, the total intensity diffracted at a diffraction peak) is proportional to either the square of the crystal structure factor ($|F_T|^2$), or to the absolute

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value of the structure factor ($|F_T|$), depending on whether the peak diffracts kinematically or dynamically. (The subscript T indicates inclusion of thermal Debye-Waller factors in the structure factor.) F_T for a superstructure reflection can be written in terms of the order parameter S. Thus, for a kinematically diffracting superstructure peak, S^2 is proportional to the integrated intensity of the superstructure reflection. This results in a straightforward experimental method of measuring S, by taking the ratio of the integrated intensities of a superstructure and fundamental reflection set. This is described in greater detail in Forrest, et al.[5]

The integrated intensity from "perfect" crystals is described by dynamical diffraction theory ($I \frown |F_T|$). The integrated intensity from "imperfect" crystals, or from weak reflections, is described by kinematical diffraction theory ($I \frown |F_T|^2$).[11] With our samples, the superstructure reflections are weak and therefore diffract kinematically. Then for the ($\frac{1}{2} \frac{1}{2} \frac{3}{2}$) and (113) reflection set, for example, the order parameter is given by

$$S = \left\{ \frac{I_{\frac{1}{2}\frac{1}{2}\frac{3}{2}}}{I_{113}} \left(\frac{8}{3\pi} \frac{V_a}{\lambda} \right) \left(\frac{mc^2}{e^2} \right) \frac{[|F_T| \times (\text{Lorentz Polarization})]_{113}}{[|F_T|^2 \times (\text{Lorentz Polarization}) \times (\text{absorption})]_{\frac{1}{2}\frac{1}{2}\frac{3}{2}}} \right\}^{\frac{1}{2}}, \quad (1)$$

if the fundamental peak diffracts dynamically, or by

$$S = \left\{ \frac{I_{\frac{1}{2}\frac{1}{2}\frac{3}{2}}}{I_{113}} \frac{[|F_T|^2 \times (\text{Lorentz Polarization}) \times (\text{absorption})]_{113}}{[|F_T|^2 \times (\text{Lorentz Polarization}) \times (\text{absorption})]_{\frac{1}{2}\frac{1}{2}\frac{3}{2}}} \right\}^{\frac{1}{2}}, \quad (2)$$

if the fundamental peak diffracts kinematically. In equation 1, V_a is the volume of the unit cell, λ is the x-ray wavelength, c is the speed of light, and e and m are the charge and mass of the electron. Atomic scattering factors were obtained from Ref. 12 and using standard dispersion corrections. The Debye-Waller factors were included, and were calculated from the estimated Debye temperatures, usign the Debye model, resulting in $B_{GaAs} = 0.3628$, and $B_{InAs} = 0.4341$.[13, 14] The individual values of B_{Ga}, B_{In}, and B_{As} were not available for the GaInAs structure.

RESULTS

Figure 1 depicts x-ray scans for sample 1b for the (004), ($\bar{1}$ 13) and ($\frac{\bar{1}}{2} \frac{1}{2} \frac{3}{2}$) peaks. The high crystalline quality of the thin GaInAs epilayer is evident from the obvious thickness fringes. The results of the HRXRD analysis for all samples are listed in Table II. It lists the compositions, measured by TAD analysis of the (004) peaks, the (004) ω full widths at half-maximum (fwhm), and the order parameters. All of the $Ga_{1-x}In_xAs$ epilayers are nearly lattice matched to the InP substrate, and are assumed to be fully strained. The lattice mismatches with respect to the InP substrate ($a_{InP} = 5.8687$ Å), were calculated from the relaxed lattice constants corresponding to the measured composition, and ranged from 0.04% to 0.1%. Samples 2 and 3 have compositional grading in the bottom third of the GaInAs layers, the listed composition corresponds to that of the top 2/3 of the layer.
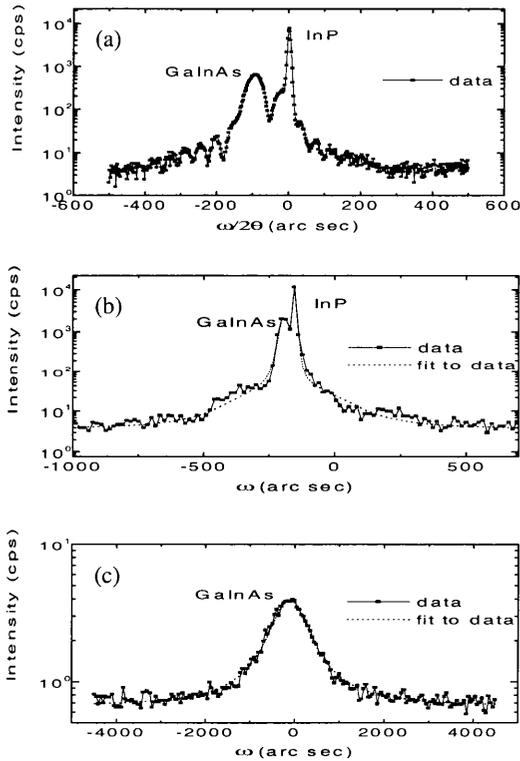
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Figure 1. X-ray diffraction scans for sample 1b; (a) $\omega/2\theta$ TAD scan of the (004) peak, and ω DAD scans of the (b) ($\bar{1}$ 13) peak and (c) ($\frac{\bar{1}}{2}\ \frac{1}{2}\ \frac{3}{2}$) superstructure peak. Squares represent experimental data points, dashed lines in (b) and (c) represent fits to the data.

Table II. Summary of x-ray diffraction data. The composition was calculated from TAD measurements of the (004) peaks, the TAD (004) ω fwhm values give a measure of the crystalline quality. The order parameters for both $CuPt_B$ variants are listed.

Sample	x_{In}	$a_{relaxed}$ (Å)	InP ω fwhm (arc sec)	GaInAs ω fwhm (arc sec)	S [1 $\bar{1}$ 1]	S [$\bar{1}$ 11]
1a	0.5380	5.8712	5.7	4.9	0.00 ± 0.05	0.00 ± 0.05
1b	0.5375	5.8711	5.3	4.7	0.66 ± 0.008	0.00
2a	0.5387	5.8715	13.2	26.2	0.11 ± 0.01	0.10 ± 0.01
2b	0.5390	5.8717	6.7	6.6	0.27 ± 0.003	0.00
3a	0.5350	5.8702	11.0	67.4	0.12 ± 0.01	0.11 ± 0.01
3b	0.5375	5.8710	13.8	14.8	0.22 ± 0.003	0.00
4	0.5379	5.8712	8.5	9.6	0.18 ± 0.002	0.00
5	0.5477	5.8752	7.1	6.7	0.00	0.00

The ω fwhm of the peaks can be used to estimate the crystalline quality of the GaInAs. As shown in Table II, most of the GaInAs epilayers have narrow (004) peaks, indicating high crystalline perfection. This includes the samples grown on miscut substrates, and the thin sample 1a. Samples 2a and 3a, grown on (001) substrates, have broader (004) peaks, indicating higher mosaic spread. Based on these results, the fundamental peaks of samples 2a and 3a were modeled using kinematical diffraction theory, while the others were modeled using dynamical theory.

The order parameters are also listed in Table II. They were calculated from DAD measurements of the integrated intensities of the appropriate ($\frac{1}{2}$ $\frac{1}{2}$ $\frac{3}{2}$) and (113) reflection sets, i.e. for S [1$\bar{1}$1] the ($\frac{\bar{1}}{2}$ $\frac{1}{2}$ $\frac{3}{2}$) and ($\bar{1}$13) reflections were used. The order parameter was calculated using eqn. 1 for all samples except 2a and 3a, for which eqn. 2 was used.

The order parameter is plotted as a function of growth temperature in Figure 2. The order parameter increases with decreasing temperature, consistent with previous TEM results.[8] For these growth conditions, ordering is maximized at or below 550° C.
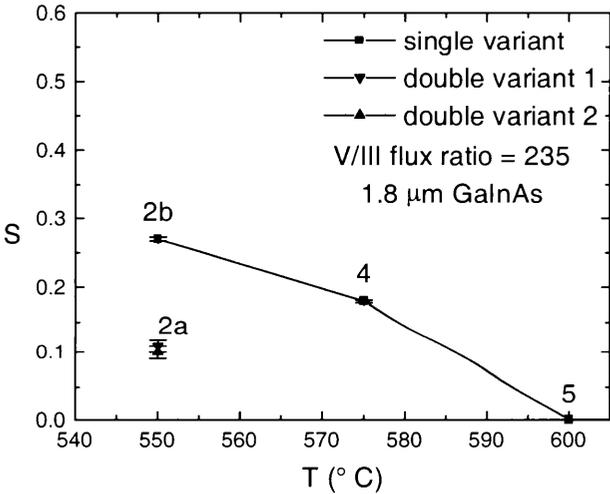

Figure 2. Order parameter versus growth temperature for single variant samples 2b, 4, and 5, and double variant sample 2a

The ω fwhm of the ($\frac{\bar{1}}{2}$ $\frac{1}{2}$ $\frac{3}{2}$) superstructure peaks decreased with increasing epilayer thickness. The ω fwhm for samples 1b, 2b, and 3b were 865 ± 18, 229 ± 9, and 213 ± 4, respectively. Since no domain orientation differences are expected between these samples[3, 15], this fwhm trend can be interpreted as increasing ordered domain size with layer thickness. This is consistent with previous GaInP results.[16]

For sample set 3, the order parameter for the single variant sample (3b) is approximately equal to the sum of the two double variant order parameters (sample 3a). Surprisingly, this is not the case, for sample sets 1 and 2. The difference is most striking for sample set 1, where the

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single variant sample (1a) has S = 0.66, one of the highest values ever measured in III-V alloys, and sample 1b contains no measurable ordering. This surprising result bears further investigation.

CONCLUSIONS

The order parameter (S) has been measured for single and double variant $CuPt_B$ ordered GaInAs using x-ray diffraction. The S in the single variant samples increases with decreasing growth temperature, and the ordered domain size increases with increasing layer thickness, consistent with previous GaInP results. For all double variant samples, S for the two variants is the same within measurement error. Surprisingly, however, only for sample set 3 is the single variant S twice the individual double variant S values.

ACKNOWLEDGEMENTS

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