Determination of the order parameter of CuPt-*B* ordered $GaInP_2$ films by x-ray diffraction

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We present quantitative characterization of atomic ordering in semiconductor alloy films by x-ray diffractometry. In particular, we show that the order parameter of CuPt-*B* ordered $GaInP_2$ films can be determined without measuring the fundamental reflections or examining structural details of the ordered domains. Our method is based on the fact that the ordering peak is modulated by statistical displacements of atom planes, which is a function of the degree of ordering. Therefore, by comparing two or more ordering peaks in an x-ray spectrum, the order parameter of an ordered film can be extracted solely for those regions that are, in fact, ordered. The method can straightforwardly be extended to other ordered alloys.
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INTRODUCTION

The band structures and optical properties of long-range ordered semiconductor alloys depend on the degree of atomic ordering,[1–5] which is usually specified by an order parameter. Determination of the order parameter is thus essential for understanding the physical properties of the alloys and performing "band-gap engineering." However, until very recently, in most structural studies only a qualitative measure of the ordering information using words such as "strong," "medium," and "weak" was reported.[6–10] Attempts to obtain quantitative ordering information have, however, been made lately by employing sophisticated electron and x-ray diffraction techniques,[5,11,12] largely based on a 40-year old principle given, e.g., by Warren.[13] These methods require either knowledge of fundamental reflections[5,11] or structural details of the ordered domains.[11,12] This makes the analysis complicated and less accurate, because the required information is often not readily accessible. For example, the fundamental reflections of an ordered film often overlap the substrate reflections because the film is usually designed to be lattice matched with the substrate. In our most recent work,[12,14] a method was developed to take into account the statistical displacements of atom planes due to ordering in determining the correct intensities of the ordering reflections. It requires, however, theoretical fittings of x-ray reciprocal space maps in order to obtain structural details. This is quite time consuming (for both experimental measurements and theoretical fitting) and is not readily applicable to all cases.

CuPt-*B* ordering is the most commonly observed type of ordering in III–V ternary alloy films, in which the mixed group III or V atoms preferably stay on alternative {111} lattice planes and form an atomic layer superlattice structure. The films may be ordered with a single variant or with double variants with a large number of antiphase boundaries.[15] In the case of a double variant, it is known that a layered structure with alternating variants may form. In this article, an x-ray method, which requires neither fundamental reflections nor complicated reciprocal space map analysis, is proposed to determine the order parameters of CuPt-*B* ordered $GaInP_2$ films grown on GaAs substrates. We determine the order parameter by comparing two x-ray ordering peaks from the same variant. The basic idea is that ordering reflections are modulated by statistical displacements of the atom planes, and these displacements are functions of the order parameter. Our method thereby yields an average order parameter of the ordered domains that contribute to these reflections and avoids the ambiguity inherent in averaging over the entire film, which may either contain well-ordered domains or be a more poorly, but uniformly, ordered structure.

EXPERIMENTAL METHODS

Our $GaInP_2$ samples were prepared by metalorganic vapor phase epitaxy (MOVPE) on GaAs substrates with exact [001] orientation (sample S1, 2 μm thick), 6° miscut towards (111)*A* plane (sample S2, 1 μm thick), and 6° miscut towards (111)*B* plane (samples S3 and S4, 1 μm thick), respectively. The substrate miscut was introduced to control the ordered structure, which results in a double-variant layered structure in samples S1 and S2 and a single variant structure in samples S3 and S4. The growth of the films was described in Refs. 2 and 4. X-ray measurements were performed on a standard four-circle diffractometer at beamline X14A of the National Synchrotron Light Source (NSLS) with an x-ray energy of 8.0478 keV. Skew diffraction geom-

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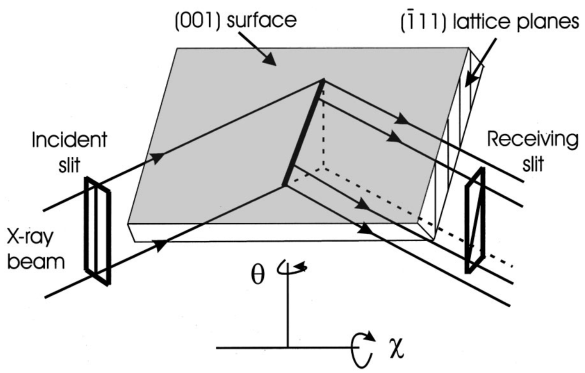

FIG. 1. Schematic diagram of the skew, symmetric x-ray diffraction geometry used in this work with the sample surface tilted using the χ axis, so that the ordered {111} lattice planes are perpendicular to the plane of diffraction that contains the incident and diffracted beam vectors.

etry was used so that a symmetrical (*hhh*) reflection from the ordered {111} lattice planes could be realized (Fig. 1). The slits used in the experiment are $0.15\times 1\ \mathrm{mm}^2$. Radial (*hhh*) reflections were used in order to avoid any possible effect from defects, such as stacking faults or microtwins.[16] In general, integrated intensity of the ordering reflections needs to be measured for the purpose of evaluating the order parameter, but the height of the ordering reflections could also be used if the widths of these reflections in reciprocal space are the same (see Fig. 3 and Ref. 12).

RESULTS AND DISCUSSION

The x-ray structure factor of an atomically ordered alloy crystal can be written as[12]

$$F=\sum_i [\overline{f}_i+f(\mathbf{r_i})]e^{2\pi i\mathbf{Q}\cdot(\mathbf{r_i}+\boldsymbol{\delta}_i)}, \tag{1}$$

where, $\overline{f}_i$ is the mean atomic form factor of a disordered alloy crystal at lattice site $\mathbf{r_i}$ in a virtual crystal approximation in which each atom in the crystal is assumed to be on the ideal zinc blende lattice site exactly. $f(\mathbf{r_i})$ is the deviation of the atomic form factor from $\overline{f}_i$ at $\mathbf{r_i}$ due to atomic ordering. $\mathbf{Q}$ is the scattering vector. δ_i is the displacement of the atom at $\mathbf{r_i}$, which, in a ternary semiconductor alloy crystal, is caused by the difference in bond length between the constitutive binaries. Since this displacement is much less than the bond length itself, we can use a first-order approximation which leads to

$$\begin{aligned}
&F(s)=F_0+F_r(s)+F_d(s),\\
&F_0=\sum_i \overline{f}_i e^{2\pi i\mathbf{Q}\mathbf{r_i}},\\
&F_r=\sum_i f(\mathbf{r_i})e^{2\pi i\mathbf{Q}\mathbf{r_i}},\\
&F_d=2\pi i\sum_i \mathbf{Q}\cdot\langle\boldsymbol{\delta}_i\rangle(\overline{f}_i+\langle f(\mathbf{r_i})\rangle)e^{2\pi i\mathbf{Q}\cdot\mathbf{r_i}},
\end{aligned} \tag{2}$$

where F_0 is the contribution by the virtual crystal, which results in fundamental reflections. F_r and F_d are contributions by atomic ordering and statistical displacements of the atomic planes. Both F_r and F_d are functions of the order parameter, *s*, and they both contribute to the ordering reflections. F_r is known to be linear in *s*,[13] whereas F_d depends on $\boldsymbol{\delta}_\mathbf{i}$. $\boldsymbol{\delta}_\mathbf{i}$ is a complex function of *s* and can be obtained independently from a valence force field (VFF) model calculation.[12,14] For CuPt-*B* ordered $\mathrm{GaInP_2}$, we found that the difference in length between the In–P and the Ga–P bonds is mainly accommodated by the displacement of P atoms. The displacement of In and Ga atoms is significantly smaller. The average displacement of P atom planes is in the [111] ordering direction. The magnitude of this displacement, in fractions of the unit cell dimension, is[12]

$$\langle\delta\rangle=\frac{s}{2}(1+s^2)d_1+\frac{s}{4}(1-s^2)d_2, \tag{3}$$

where $d_1=0.014$ and $d_2=0.05$ are dimensionless parameters obtained from the VFF calculations.

If only ordering reflections are considered, we have

$$F_{\mathrm{order}}(s)=F_r(s)+F_d(s). \tag{4}$$

Further information on the calculation of $F_{\mathrm{order}}(s)$ can be found in Ref. 12. The x-ray intensity of an ordering peak is then calculated as

$$\begin{aligned}I_{\mathrm{order}}(s)=&L(\theta)G(\theta,\chi,w)P\\ &\times\exp(-2\mu t/\sin\theta/\cos\chi)|F_{\mathrm{order}}(s)|^2,\end{aligned} \tag{5}$$

where θ is the Bragg angle and χ is the angle between the {111} lattice planes and the (001) surface. *w* is the width of the detector window and *t* the layer thickness. $L=1/\sin(2\theta)$ is the Lorentz factor for the polarized synchrotron beam. *G* is a geometrical correction taking into consideration the skew geometry in Fig. 1. This is necessary because the footprint of the incident x-ray beam on the sample surface is inclined. Therefore, part of the diffracted beam may not be collected by a finite detector window. *P* is a factor arising from the phase relation between different domains of the same variant for double-variant ordered layer structures. As was shown in Ref. 12, *P* is determined by the geometrical structure of the ordered film and is the same for all ordering reflections. In addition, antiphase domains are known to have no effect on the intensity of ordering reflections.[13] Debye–Waller factors, which were deduced from the Debye temperatures of GaP and InP, were included in the atomic form factors.[12]

The intensity of the ordering peaks increases as the order parameter increases. On the other hand, the relative intensity of the ordering peaks is modulated by atomic displacements. Figure 2 shows a comparison of the relative intensity of several ordering peaks with and without taking into account the atomic displacements for a 1 μm thick $\mathrm{GaInP_2}$ film with $s=0.5$. We see that the intensity modulation of the ordering peaks due to atomic displacements is strong enough to turn the (−5/2 5/2 5/2) peak from weaker to stronger compared with the (−3/2 3/2 3/2) peak.

Figure 3 shows the measured (−5/2 5/2 5/2) and (−3/2 3/2 3/2) peaks for sample S1. We see that the (−5/2 5/2 5/2) peak is indeed stronger than the (−3/2 3/2 3/2) one. This is also true for the other three samples. The solid lines in Figs.

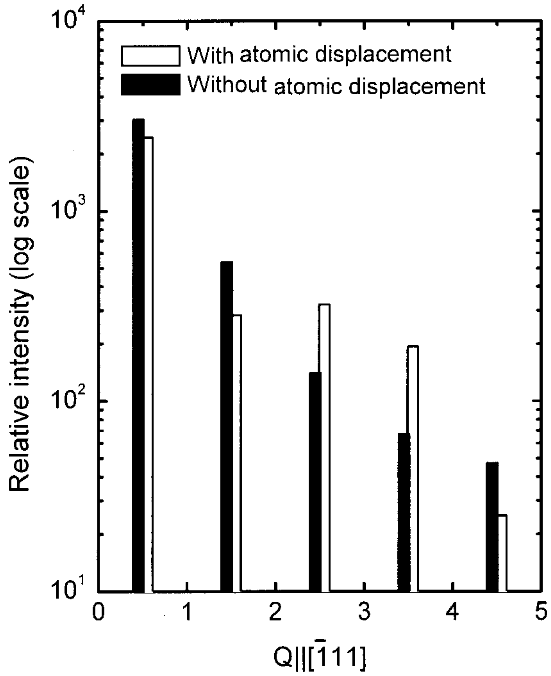

FIG. 2. Calculated relative intensities of several ordering peaks with and without taking into account atomic displacement for a 1 μm thick $GaInP_2$ film with $s=0.5$. The height of the black columns represents the intensities of the ordering reflections without considering atomic displacement. The height of the white columns represents the intensities of these ordering reflections after taking into account atomic displacement.

4(a) and 4(b) show the calculated intensity ratios of the (−5/2 5/2 5/2) peak over the (−3/2 3/2 3/2) peak, as a function of s, for both the 1 and 2 μm thick films. The thick horizontal bars represent the experimental intensity ratios, with the error range being taken into account (indicated by the height of the shaded areas). A cross section of the experimental data and the calculated curves gives the order parameters of the corresponding samples directly. From Fig. 4, we extracted the mean order parameters of samples S1–S4 as being 0.60, 0.41, 0.43, and 0.55, respectively. The calculated intensity ratios shown in Fig. 4 are film thickness dependent

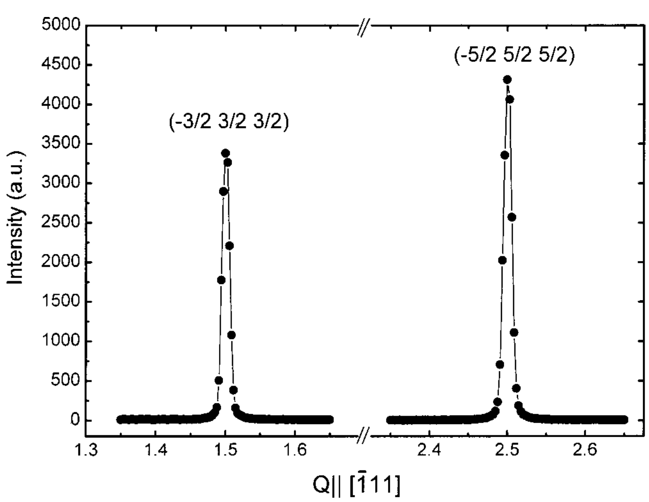

FIG. 3. Experimental (−3/2 3/2 3/2) and (−5/2 5/2 5/2) x-ray diffraction peaks of sample S1.

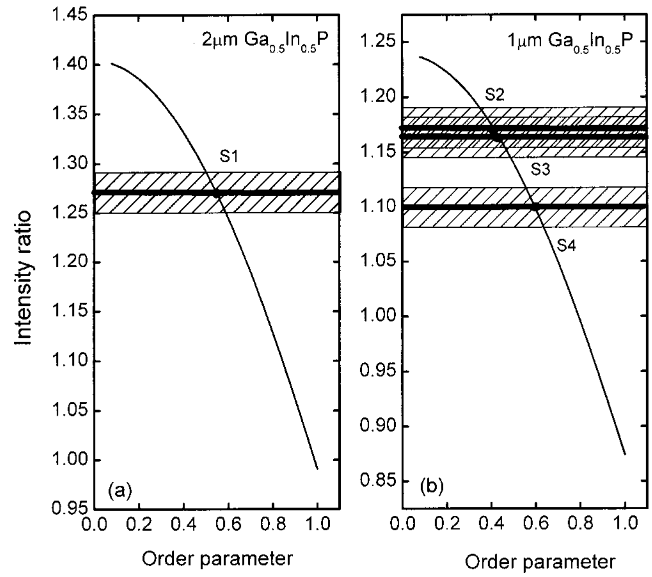

FIG. 4. Calculated intensity ratio of the (−5/2 5/2 5/2) peak over the (−3/2 3/2 3/2) peak vs the order parameter (solid curves) and the measured intensity ratios of the four samples, S1–S4 (solid horizontal bars). The shaded areas represent the range of experimental error. The panel on the left is for the 2 μm thick $GaInP_2$ films and the panel on the right is for the 1 μm thick films.

primarily because of x-ray absorption. If the film becomes very thick (e.g., >5 μm), this dependence becomes negligible. It is also worth pointing out that the order parameters we obtained are in good agreement with those deduced indirectly by comparing the measured band-gap reductions and theoretical band-gap calculations.[17]

The two major sources of error of the order parameter obtained this way are (1) inaccurate sample parameters, such as film thickness, composition, and composition nonuniformity and (2) inaccurate experimental peak intensity. Accurate film thickness may be obtained with the assistance of other techniques such as x-ray reflectometry or cross-sectional transmission electron microscopy (TEM). If the alloys composition deviates from that of $GaInP_2$, even locally, the alloy will never become perfectly ordered, and this will result in an error in the assessment of atomic displacements. It should be noted that the range of the intensity ratios in Fig. 4 from $s=0.1$ to 1.0 is limited, so that any mistake in the experimental intensity measurement, e.g., due to sample misalignment, may also contribute considerable error in the order parameter. Therefore, very careful alignment and repeated scans are necessary in the experiment to assure that correct peak intensities are obtained.

Finally, it should be emphasized that our method gives the order parameter of the ordered domains instead of that averaged over the entire film. The latter has in the past come from comparing the ordering and fundamental reflections.[5]

SUMMARY

We have demonstrated an x-ray diffraction-based method for quantitative measurement of the order parameter of CuPt-*B* ordered semiconductor alloy films. The method is relatively simple and requires no information about x-ray fundamental reflections and structural details of the ordered domains. The method can be extended to other types of ordering in semiconductor alloys, e.g., triple-and quadruple-period ordered systems where modulation of the peak intensity due to atomic displacements has been observed by both x-ray diffraction[14,16] and electron diffraction.[18]

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