Imperfections in \((\text{Ga}_1-x\text{Al}_x\text{As})n_1-(\text{GaAs})n_2/\text{GaAs}\) Superlattices as Observed by X-ray Diffraction Techniques

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Abstract

Growth imperfections in \((\text{Ga}_1-x\text{Al}_x\text{As})n_1-(\text{GaAs})n_2/\text{GaAs}\) superlattices, grown on GaAs(001) substrates, have been investigated by X-ray diffraction techniques coupling image and rocking-curve recording. The use of a synchrotron radiation source has enabled topographic images formed with very weak superlattice reflections to be obtained. The intensity distribution across the sample surface observed in such images has revealed two different types of superlattice defects: either overall gradients of both the average composition and period or islands showing different composition and period from the surrounding material. Since these parameters control the optoelectronic properties and particularly the gap value it is of primary importance to grow homogeneous samples and to have a technique able to detect inhomogeneities such as the ones described in the present work.

Introduction

Interest in designing III–V superlattices to tailor the transport and optoelectronic properties of semiconductor structures no longer needs to be demonstrated (Dingle, 1975). Modern epitaxic techniques like molecular beam epitaxy (MBE) and organometallic chemical vapor deposition (OMCVD) are now able to produce periodic stacking of a large number of alternate thin layers (thicknesses ranging from a few to a few hundred Ångströms). However, in order to control the exact composition with an accuracy of about 1% in the case of III–V ternary layers \(\text{Ga}_1-x\text{In}_x\text{As}\). Similar effects can be anticipated in superlattices involving ternary alloys. Since the layer composition has an influence on the growth rate, such gradients are likely to be associated with variations of the superlattice period.

By coupling a local diffractometric analysis with a topographic image of the whole sample, X-ray diffraction provides the necessary information to qualify non-destructively the homogeneity of the sample. On a different scale, high-resolution studies of the atomic arrangement at the interface performed by transmission electron microscopy bring local complementary information (Hetherington, Barry, Bi, Humphreys, Grange & Wood, 1985; Jeng, Wayman, Cole & Costrini, 1985; Yamamoto & Muto, 1984; Delamarre, Dubon, Laval, Guenais & Emery, 1985).

The two samples labelled \(A\) and \(B\) selected for presentation in this work provide the first examples of a three-dimensional characterization of faulted superlattices.

Experimental

Data have been collected on the LURE-DCI (Orsay, France) two-axis spectrometer using synchrotron radiation (SR). The samples were irradiated either by a quasi-plane wave (wavelength \(\lambda = 1.2378\ \text{Å}\), spectral width \(\Delta \lambda / \lambda \sim 7 \times 10^{-6}\), divergence \(\Delta \theta \sim 10^{-6}\ \text{rad}\).
delivered by a non-tunable triple-reflection monochromator (Petroff, Sauvage, Riglet & Hashizume, 1980) or by a broader angular and spectral band, selected from the continuous SR spectrum by a single-plane-crystal monochromator [InP(001), reflections 004 or 002; GaAs(001), reflection 004]. In the latter case, owing to the tunability of the monochromator, the value of the extracted wavelength had to be determined precisely. This was achieved by inserting a 9 μm thick zinc absorber in the beam path and adjusting the monochromator crystal under Bragg incidence for the zinc K absorption edge [λ = 1.2833 Å, according to Pettifer & Hermes (1985)]. The stability of the monochromator was easily controlled during the experiment by reinserting the Zn screen. At this wavelength, close to the one used for plane-wave studies, the contribution of the harmonics in any of the topographs presented in this work was calculated to be less than 5%. The sensitivity of the set-up depends on whether or not the monochromator–sample couple is adjusted in a non-dispersive geometry. As far as possible, a quasi-non-dispersive geometry was adopted for the experiments.

Although they have been extensively described in a previous work (Kervarec et al., 1984) some characteristic diffraction features of superlattices will be briefly recalled here. A heterostructure built with a moderately strained superlattice grown on a nearly matched substrate gives an X-ray diffraction pattern which can be described as follows:

(a) intense substrate Bragg peaks;
(b) main superlattice reflections, in the vicinity of the substrate reflections, hereafter referred to as zeroth-order satellites SL0 and corresponding to a virtual crystal with an average lattice parameter

\[ \bar{a} = \frac{n_1 a_1 + n_2 a_2}{n_1 + n_2}, \]

where \( n_1 \) and \( n_2 \) are the numbers of molecular III–V bilayers of each material within one period of the superlattice and \( a_1, a_2 \) are the lattice parameters normal to the interface;

(c) weak high-order satellite reflections, labelled \( SL_{\pm 1}, SL_{\pm 2} \) according to their position with respect to the \( SL_0 \) peak and whose intensity is several orders of magnitude lower than for the substrate and the \( SL_0 \) reflections. The angular spacing of the satellites is governed by the superlattice period \( C \), defined by

\[ C = \frac{n_1 a_1 + n_2 a_2}{2}, \]

since they occur at angular settings \( \theta_m \) satisfying Bragg’s law for a ‘crystal’ of parameter \( C \):

\[ 2C \sin \theta_m = m \lambda \]

and

\[ C = \lambda/2(\theta_{m+1} - \theta_m) \cos \theta_m. \]

A full characterization of a superlattice implies the determination of the four parameters \( a_1, a_2, n_1, n_2 \) across the whole sample. In the particular case of a ternary alloy, the parameter \( a_i (i = 1, 2) \) is a function of both the composition \( x_i \) and state of strain in the layer. An average composition \( \bar{x} \) can be defined:

\[ \bar{x} = \frac{n_1 x_1 + n_2 x_2}{n_1 + n_2} \]

in the example of a superlattice \((Ga_{1-x}Al_{x}As)n_1-(GaAs)n_2/GaAs\).

The advantage of the SR set-up over laboratory equipment lies first in the ability to work either in the diffractometric or in the imaging mode, even for superlattice reflections (Hill, Tanner & Halliwell, 1985), and secondly in the ability to provide both angular resolution and enough intensity to record in a simple \( \theta-2\theta \) scan the substrate, zeroth-order (SL0) and higher-order superlattice reflection peaks. Thus in a single experiment both the average strain in the superlattice, given by the angle shift between the substrate and SL0 peaks \( \Delta \theta_0 \sim \) a few tens of seconds, and the superlattice period \( C \), given by the angular spacing of the satellites, are obtained.

Samples A and B have been MBE grown, on laser-quality (001)-oriented GaAs substrates, at the CNET-Lannion (France) laboratory. The design parameters are listed in Table 1. Prior to the SR experiments, both samples had been studied by photoluminescence spectroscopy and were found to be of good quality. Laboratory double-crystal diffraction analysis had also been performed and some anomalies were revealed which required confirmation by SR experiments. In particular, different values of the periodicity were measured in sample A, whereas gradients in both the average composition \( \bar{x} \) and the period \( C \) were observed in sample B.

### Superlattice imaging data

Most X-ray work on superlattices is performed in reflection geometry since usually the back surface is not mechnochemically polished and, at least in MBE growth, is stained with indium patches.

An immediate result of plane-wave imaging was to reveal the parasitic distortions induced by these indium residues. Fig. 1 shows plane-wave topographs of sample A before and after removal of the back-surface damage and indium droplets. Because of the overall curvature of the sample, Bragg contours are observed on the photographic plate (Petroff et al., 1980). In Fig. 1(a) both the substrate and SL0 contours are visible together with the weaker thin-crystal oscillations (Bartels & Nijman, 1978). The distorted aspect of

<table>
<thead>
<tr>
<th>Sample</th>
<th>Period (Å)</th>
<th>Number of periods</th>
<th>Buffer layer</th>
<th>Encapsulation layer (GaAs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>1</td>
<td>60</td>
<td>150</td>
<td>+</td>
</tr>
<tr>
<td>Sample B</td>
<td>0.3 to 0.4</td>
<td>270</td>
<td>40</td>
<td>+</td>
</tr>
</tbody>
</table>
these contours is evidence of a severe and irregular curvature (Sauvage-Simkin & Petroff, 1984). By contrast, in Figs. 1(b) and (c) rather straight and parallel substrate and SL₀ reflection bands demonstrate the elimination of parasitic stress sources; only the elastic curvature induced by the misfit strain remains in the sample. Parallelism of the substrate and SL₀ contours is already an indication that the average composition is fairly constant over the sample. The improvement of the sample quality after etching was also checked by measuring the widths of the reflection profiles under plane-wave illumination for both the substrate and SL₀ peaks, together with their intensity ratio. The experimental values before and after indium removal are listed in Table 2 and compared with the theoretical ones.

As was mentioned before, two periodicities C₁ and C₂ had been found in this sample by previous measurements. This result was confirmed and in addition the spatial distribution of the different periods was established. θ–2θ scans recorded close to the substrate 004 peak with a narrow slit (1.3 x 0.4 mm) at two different locations on the sample gave the rocking curves presented in Fig. 2 showing the two values of the period: C₁ = 45.2 (curve a) and C₂ = 48.1 Å (curve b).

Reflection topographs taken on the +1 satellite with the sample adjusted successively for the two maxima gave the complementary images displayed in Figs. 3(a) and (b). (Typical exposure time was 15 min on Kodak dental film, when the DCI storage ring was operating at 1.72 GeV and 150 mA.) This accident shows that within a single growth run the local conditions may be perturbed enough to induce a different growth rate.

Since local measurements of Δθ₀ on the rocking curves have shown that the average composition, given in the present case by

\[ x = \left(1 + \frac{n_1}{n_2}\right)^{-1}, \]

was not changed, the growth rates of both constituents of the superlattice have to be equally affected (n₁/n₂ constant) leading to a modification of the total number (n₁ + n₂) of layers in each supercell.

The probable values of the sample parameters to replace those given in Table 1 are listed in Table 3 for both regions. The non-integer value in region 2 can be

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**Table 2. Sample A: influence of the back-surface state on the rocking-curve characteristics**

<table>
<thead>
<tr>
<th>004 reflection (FWHM)</th>
<th>SL₀ reflection (FWHM)</th>
<th>Ratio of 004 and SL₀ peak maxima</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before 22.5° 30°</td>
<td>20°</td>
<td>2.7</td>
</tr>
<tr>
<td>After 7.5° 19°</td>
<td>1.9</td>
<td>7.1</td>
</tr>
</tbody>
</table>

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**Fig. 1.** Plane-wave reflection topographs (λ = 1.2378 Å) of sample A (scale mark: 1 mm). (a) Before etching of the back surface: substrate 004 (arrow) and SL₀ contours. (b) After cleaning: substrate 004 contour. (c) After cleaning: SL₀ contour.

**Fig. 2.** θ–2θ scans, around the substrate 004 reflection, at two locations on sample A. Curve a: period C₁. Curve b: period C₂.
Table 3. Probable structural parameters for sample A as deduced from SR data

<table>
<thead>
<tr>
<th>Region 1</th>
<th>Period (Å)</th>
<th>n₁</th>
<th>n₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45.2</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>Region 2</td>
<td>48.1</td>
<td>8.5</td>
<td>8.5</td>
</tr>
</tbody>
</table>

interpreted in terms of fluctuations of $n_1$ and $n_2$ between the values 8 and 9, among the 150 periods. Incomplete cleaning of the substrate surface might be responsible for this growth anomaly.

The imaging data obtained with sample B are more difficult to interpret since the state of curvature is still rather complex even after indium removal. Through a careful examination of the substrate contour pattern across the sample, a schematic map of the local effective misorientation (projected on the plane of incidence) can be drawn (Fig. 4a).

Laboratory diffractometric measurements revealed the presence of gradients both in the average composition $\bar{x}$ and in the periodicity $C$. However, contrary to sample A, no discrete values of $C$ were observed.

Images recorded on the 002 reflection show parallel contours for the substrate and SL₀ reflected intensity, which means that the angular spacing between the substrate and average heterostructure reflection remains constant along the equiinclination lines (Fig. 4b). The mean concentration $\bar{x}$, which controls the average lattice parameter in the superlattice, must then be constant along those lines.

Topographs taken on the + 1 satellite in the vicinity of the substrate 004 reflection in the same sample region as in Fig. 4 are presented in Fig. 5 for three different angular settings of the sample labelled respectively $\theta_0$ (Fig. 5a), $\theta_0 + 15^\circ$ (Fig. 5b) and $\theta_0 + 47^\circ$ (Fig. 5c). The visibility of contours definitely not parallel to the equiinclination lines is evidence of a gradient in the superperiod $C$. The actual shape of the intensity pattern is a consequence of both the sample curvature and the period variation. Moreover, changes in the $\bar{x}$ value, displacing the angular position of the zeroth-order satellite and hence of the high orders as well, would also have an influence on the satellite intensity distribution. In the present case it was checked that this last effect was negligible, on the basis of the quantitative data presented in the next section and concerning local measurements of $\bar{x}$ and $C$, performed under the same conditions as the image recording.

**Rocking-curve analysis**

$\theta$–$2\theta$ scans have been recorded in a non-dispersive (+, -) parallel setting at selected positions on sample

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Fig. 3. Sample A: reflection topographs (scale mark: 0.5 mm) taken on both peaks of the split + 1 satellite in the vicinity of the 004 substrate reflection. Monochromator: GaAs(001), 004 reflection, $\lambda = 1.2833$ Å. (a) and (b) refer to curves a and b in Fig. 2.

Fig. 4. Sample B: (a) Equiinclination lines in the region of sample B under investigation. The angle of incidence increases by $20^\circ$ in the direction of the arrow between two full lines. (b) 002 reflection topograph (scale mark: 1 mm). Monochromator: GaAs (001), 004 reflection, $\lambda = 1.2833$ Å.
Fig. 5. Sample B: reflection topograph taken on the +1 satellite for three angular settings of the sample. (a) $\theta_0$; (b) $\theta_0 + 15^\circ$; (c) $\theta_0 + 47^\circ$. Labels 1, 2, 3, 4 in (c) refer to the rocking curves presented in Figs. 6 and 7 (scale mark: 1 mm). Monochromator: GaAs (001), 004 reflection, $\lambda = 1.2833 \text{ Å}$.

$B$ with a narrow incident beam ($1.3 \times 0.4 \text{ mm}$). Rocking curves are presented in two sets, where alternately $C$ and $\bar{x}$ are shown to vary (Figs. 6 and 7 respectively).

The $\bar{x}$ gradient, corresponding to an actual variation of the composition $x$ in the ternary layer $\text{Ga}_{1-x}\text{Al}_x\text{As}$ of about 0.009 mm$^{-1}$, is not surprising for a MBE layer grown on a static substrate. The existence of a gradient in $C$, implying that the number of molecular layers in individual slabs changes from 39 to 42, and its orientation with regard to the $\bar{x}$ gradient are also due to the geometrical characteristics of the MBE set-up; these values are confirmed by recent work of Talalaeff (1987) who calculated thickness and composition profiles of MBE-grown super-

Fig. 6. Sample B. (a) High-resolution rocking curves recorded at three different positions marked in Fig. 5(c): bottom curve, position 1; middle curve, position 2; top curve, position 3. $\bar{x}$ remains constant. (b) $\theta-2\theta$ scans recorded at the same positions on the sample. The period gradient is clearly visible. The curves have been set with the +1 satellites coincident to emphasize the effect.

Fig. 7. Sample B. (a) High-resolution rocking curves recorded at positions 3 (top curve) and 4 (bottom curve): a gradient of $\bar{x}$ is visible. (b) $\theta-2\theta$ scans recorded at the same positions, $C$ is constant.
lattices on the basis of the growth conditions of the samples described here.

**Concluding remarks**

Although these two samples, and especially sample A, may not be representative of the majority of MBE-grown superlattices, the type of defects which have been revealed are harmful enough for the device properties to justify a quasi-systematic control of the samples. Indeed, a continuous change in the superlattice period would lead to broadened optical emission lines and, in the present case, the compositional gradient in the ternary layer would result in a variable barrier height. The transport and optoelectronic properties would then be ill defined. A careful determination of the orientation of the gradients with respect to the geometrical arrangement of the MBE growth unit may help to minimize the defects introduced in the sample. By probing the material with the required sensitivity while still preserving the macroscopic information on the imperfection distributions, X-ray topography coupled to diffractometry is the most appropriate method to perform this control.

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**References**


