**X-ray Diffraction Evidence for Transient Composition Effects in MOVPE Multilayer Growth for Ga_{1-x}Al_xAs Alloys**

BY S. BENSOUSSAN, C. MALGRANGE AND M. SAUVAGE-SIMKIN*

Laboratoire de Minéralogie-Cristallographie, Universités P. et M. Curie et Paris VII, associé au CNRS, 4 place Jussieu, 75252 Paris CEDEX 05, France

AND K. N’GUESSAN AND P. GIBART

Laboratoire de Physique des Solides et d’Energie Solaire, CNRS, Sophia-Antipolis, 06560 Valbonne, France

(Received 23 July 1986; accepted 27 January 1987)

**Abstract**

X-ray rocking-curve analysis is applied to the detection of artifacts in multilayer epitactic growth of III–V ternary compounds by metal–organic vapour-phase epitaxy (MOVPE). Transient spikes in the composition result in unwanted additional thin layers whose presence disturbs the interference pattern expected from the designed heterostructures, thus modifying the oscillating part of the reflection profile. X-ray methods and secondary-ion mass spectroscopy (SIMS) lead to descriptions of the actual layer stacking in good agreement with each other.

**Introduction**

In the previous paper (Bensoussan, Malgrange & Sauvage-Simkin, 1987) the correlation between the fine structures of simple-heterojunction rocking curves and the depth profiling of the strain was established. A numerical procedure was presented to simulate the rocking curve of continuously graded heterostructures, whereas abrupt junction profiles could be obtained by a fully analytical treatment. The extension of this procedure to any number of perfect layers in a multiple stacking was developed. This last approach will now be applied to the study of a nominally double heterojunction intended to be one step in a research programme dedicated to the elaboration of multispectral solar-cells (Beaumont, Contour, Gibart, Guillaume & Verie, 1984), (Ga, Al)As/GaAs materials being used for the conversion of the high-energy side of the solar spectrum. A major problem is that of n-dopant incorporation in the ternary alloy. In pure GaAs, X-ray characterization and Mössbauer experiments (Bensoussan et al., 1987; N’Guessan, 1986; Williamson, Gibart, El Jani & N’Guessan, 1987) have shown that tin was incorporated not only on substitutional sites as a donor but also in more complex defects.

The same type of X-ray characterization was attempted for ternary alloys and a bilayer sequence, Ga_{1-x}Al_xAs:Sn/Ga_{1-x}Al_xAs/GaAs, was grown by metal–organic vapour-phase epitaxy (MOVPE) for this purpose.

As a rule, multilayer rocking curves cannot be interpreted in a straightforward manner owing to the numerous subpeaks visible in the reflection profile. Interference effects become predominant in the building of the intensity output, and computer simulation following well established procedures (Halliwell, Lyons & Hill, 1984; Hill, Tanner, Halliwell & Lyons, 1985; Bensoussan et al., 1987) has to be used. Since in the present case the introduction of the design parameters in the calculation did not lead to a satisfactory match between experimental and simulated curves, a more general procedure has been thought of and some guidelines are proposed which use the reflectivity ratios and possible periodicities apparent in the reflection profile.

**Sample growth**

Fig. 1 is a schematic of the design sample. The aim was to grow two ternary layers with identical Al content, Ga_{0.5}Al_{0.5}As, and individual thicknesses in the micrometre range, the outermost layer being tin-doped.

---

*And LURE, CNRS, CEA, MEN, bâtiment 209d, UPS, 91405 Orsay, France.
The growth process was therefore continuous for the gallium and aluminium supply with a constant flow of trimethylgallium (TMG) and trimethylaluminium (TMA), whereas the tin supply was set on at a given time under a fairly high partial pressure of tetramethyltin (TMSn) of $3 \times 10^{-2}$ Pa, needed to achieve an n-doping level of a few times $10^{17}$ cm$^{-3}$, by instantaneously switching the dilute TMSn flow.

After growth completion, a rough estimate of the total overgrowth thickness was around 3 $\mu$m.

**X-ray characterization**

X-ray rocking curves have been recorded on the laboratory high-resolution double-crystal spectrometer described elsewhere (Bensoussan et al., 1987). Measurements have been performed with a narrow slit (200 $\mu$m) at different locations on the sample. An experimental profile is shown in Fig. 2(c); obviously, the overlayer region of the rocking curve shows a single main maximum, with complex side structures of much lower intensity. The derivation of the tin-induced mismatch $(\Delta a/a)^2_{\text{tin}}$ between the two layers is thus not possible from direct inspection. However, information can still be obtained from the experiments to orient the computer simulation:

(i) The Bragg-angle shift corresponding to the actual $(\Delta a/a)^2_{\text{tin}}$ must be smaller than the individual layer reflexion widths. To put figures on this remark it should be noted that the reflexion width for a 1.5 $\mu$m Ga$_{0.5}$Al$_{0.5}$As layer is 12.3" (400 reflexion, Cu K$_{\alpha 1}$ radiation) and the Bragg-angle shift corresponding to $(\Delta a/a)^2_{\text{substrate}} = 10^{-4}$ is 14.5".

(ii) The overall layer reflectivity, compared with the substrate peak, and full width at half maximum (10.5") are compatible with a total thickness in the 3 $\mu$m range if the broadening effect due to the mismatch is considered.

A first computer simulation has been tried with the following starting values:

- undoped layer $t_1 = 1.5$ $\mu$m,
- doped layer $t_2 = 1.5$ $\mu$m,
- mismatch between substrate and layer 1 $(\Delta a/a)^2_{\text{substrate}} = 14.5 \times 10^{-4}$,
- interlayer mismatch $(\Delta a/a)^2_{\text{interlayer}} = 0.5 \times 10^{-4}$.

The resulting profile, somewhat too symmetrical, shown in Fig. 2(a) does not reproduce the overall shape of the epilayer peak. A change of $t_1/t_2$ to 1.5 and reduction of $(\Delta a/a)^2_{\text{interlayer}}$ to 0.45 $\times 10^{-4}$ led to a better agreement but a further scaling was necessary to adjust the peak reflectivity ratio between layer and substrate. In order to preserve the layer peak overall shape, scaling is performed by letting the total thickness $t$ vary while keeping constant the ratio $t_1/t_2$ and the product $t(\Delta a/a)^2$. However, in this thickness range ($nt/\Lambda \sim 1$, $\Lambda$ being the extinction length) such a scaling is not perfect and a final adjustment of $(\Delta a/a)^2_{\text{interlayer}}$ is still necessary to obtain the optimized fit, shown in Fig. 2(b) where $t_1 = 1.55$, $t_2 = 1.03$ $\mu$m, $(\Delta a/a)^2_{\text{substrate}} = 0.58 \times 10^{-4}$.

However, the experimental and computed rocking curves are still significantly different in the inter-

Fig. 2. Computed convolved profiles for several trial models compared with the experimental data. (a) $t_1 = t_2 = 1.5$ $\mu$m; $(\Delta a/a)^2_{\text{substrate}} = 0.5 \times 10^{-4}$; $(\Delta a/a)^2_{\text{interlayer}} = 14.5 \times 10^{-4}$. (b) $t_1 = 1.55$, $t_2 = 1.03$ $\mu$m; $(\Delta a/a)^2_{\text{substrate}} = 0.58 \times 10^{-4}$; $(\Delta a/a)^2_{\text{interlayer}} = 14.5 \times 10^{-4}$. (c) Experimental rocking curve. 400 reflexion, $l(Cu K_{\alpha 1})$; laboratory double-crystal spectrometer with an asymmetric Ge 400 monochromator where the (100) planes make an angle of 31.8° with the crystal surface (Bragg angle = 33.0°). Angular scale referred to an angle $\theta_0$ depending on the relative monochromator and sample setting. (d) Enlargement of the intermediate region: discrepancy between experimental (upper curve) and computed (lower curve) profiles.
mediate region between the epilayer and substrate peaks, as shown in Fig. 2(d). While the computer simulation produces an oscillating curve very similar to what would be obtained with a single layer of total thickness \( t = t_1 + t_2 \), the experimental curves show structures of much larger amplitude, quasiperiodic in some angular regions but with a period corresponding more nearly to a layer thickness in the micrometre range, and aperiodic in other parts of the profile. The whole system seems to behave as if an angle-dependent phase shift were present between the two epilayers. Indeed, a computer simulation where a constant phase shift was introduced between layers 1 and 2 produced the expected effect on the intermediate-region oscillating pattern, although it was not possible to reproduce the whole profile with this single additional parameter.

At this stage it was clear that a two-layer model was not sufficient and more information was needed to select a realistic physical perturbation able to induce the required angle-dependent phase discontinuity.

**Secondary-ion mass spectroscopy (SIMS)**

A previous study of tin doping in MOVPE growth (Bensoussan et al., 1987) has shown a delayed and graded incorporation of the dopant in the epilayer, further confirmed by a SIMS analysis. It was thus decided to submit also the present double heterostructure to this characterization technique in order to detect possible anomalies in the layer composition: the measurements, presented in Fig. 3, have been performed by Mrs S. Asher.* Two important features have to be outlined: first, the tin distribution in the outermost layer is graded, and, secondly, a severe accident in the Al/Ga ratio is observed at the opening on the TMSn inlet valve (arrow in Fig. 3). Such compositional transients had already been observed by Thrush, Whiteaway, Wale-Evans, Wight & Cullis (1984) in heterojunction MOVPE growth. These transients are believed to be due to perturbations in the flow regime when adding an extra 200 ml min\(^{-1}\) flow in the inlet manifold.

On the basis of this additional information, a new description of the sample in terms of a multilayer stacking has been introduced in the calculation.

**Model refinement**

The sample has been considered as a four-layer stacking on a GaAs substrate (Fig. 4). The individual layer thickness \( t_i \) and aluminium content \( x_i \) are allowed to vary with constraints compatible with the SIMS and preliminary X-ray data: the total thickness \( t \) remains close to 2.5 \( \mu \)m, the Al contents in layers 1 and 4 are identical, the central perturbation extends over about 2000 \( \AA \). The tin-induced dilation in layer 4 has been introduced optionally either through a constant additional mismatch with respect to layer 1 or through a step-like dilation taking into account the grading. Since the effect on the rocking curve was small in either case, the first solution was preferred for the sake of simplicity. Owing to the fairly large number of parameters it has not been possible to reach a complete match between the experimental and computed profiles. However, a quite satisfactory fit has been obtained with the values listed in Table 1, where \((\Delta a/a)_i^L\) is the relative lattice-parameter difference between the substrate and the ith layer. Layer 1 and layer 4 differ by the tin content which has been

![Table 1. Sample parameters leading to an optimal fit](image-url)

<table>
<thead>
<tr>
<th>Layer</th>
<th>( t_i (\mu m) )</th>
<th>( x_i )</th>
<th>((\Delta a/a)_i^L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0.53</td>
<td>( 1.48 \times 10^{-4} )</td>
</tr>
<tr>
<td>2</td>
<td>0.12</td>
<td>0.33</td>
<td>( 3.93 \times 10^{-4} )</td>
</tr>
<tr>
<td>3</td>
<td>0.12</td>
<td>0.67</td>
<td>( 1.87 \times 10^{-4} )</td>
</tr>
<tr>
<td>4</td>
<td>1.30</td>
<td>0.53</td>
<td>( 1.50 \times 10^{-4} )</td>
</tr>
</tbody>
</table>

*Solar Energy Research Institute, Golden, Colorado, USA.

![Fig. 3. SIMS data. Arrow points to the anomalies in the Al/Ga ratio.](image-url)

![Fig. 4. Schematic of a multilayer model.](image-url)
accounted for by a \(0.2 \times 10^{-4}\) relative dilation. As can be seen in Fig. 5, apart from the left wing of the epilayer peak which appears somewhat too low in reflectivity, the rest of the experimental curve is remarkably well reproduced. The same set of parameters has been used to simulate an 800 reflexion profile, experimentally recorded on the two-axis spectrometer of the LURE-DCI synchrotron radiation facility in quasi-plane-wave conditions (\(\lambda = 1.2378\) Å). This high-order reflexion provides an improved strain sensitivity since the ratio \(\Delta \theta / \delta\) of the strain-induced peak shift to the intrinsic reflexion width is multiplied by a factor of seven with respect to the 400 K\(\alpha\) rocking curve. The agreement between the experimental and computed profiles shown in Fig. 6 is quite satisfactory. For both reflexions minor changes in the individual layer thicknesses and compositions would provide an equally good fit, as a whole, where the best coincidence area would take place in different angular regions of the profile. With this restriction in mind, it can be said that the parameters listed in Table 1 are close enough to the actual ones to convey the necessary physical information on this sample. The accuracy of the values lies around 5\% for the individual thicknesses and is better than 1\% for the average strains in the main layers 1 and 4.

**Concluding remarks**

The main results can be summarized as follows: the design double heterostructure has not been obtained owing to a severe perturbation introduced in the constituent-element ratio by the opening of the dopant supply. The aluminium concentration is rapidly decreasing and increasing over more than 2000 Å. Such a transition bilayer, still coherent with the surrounding crystal, may very well behave as the angle-dependent phase object mentioned above. Although the best fit, presented in Fig. 5, has been calculated with a non-zero tin-induced mismatch (here \(2 \times 10^{-5}\)), the numerical value itself should be taken with some caution. Indeed rocking curves computed with a zero mismatch led also to a fair agreement with the experimental data. In the present sample, the profile features are primarily influenced by the existence of the unwanted bilayer and the effects of the tin incorporation are thus smeared out. A temporary conclusion could be that such effects are probably smaller than in pure GaAs (Bensoussan et al., 1987). A confirmation of this assumption will be obtained in the near future with newly grown samples since a modified MOVPE procedure is expected to suppress composition transients.

It should be pointed out that the X-ray diffraction experiments have enabled the detection of the presence of a strong disturbance between the two main layers of the overgrowth in a nondestructive way. However, the exact assessment of the sample parameters would not have been possible without the additional SIMS information.

**References**

