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X-Ray High-Resolution Diffraction and Transmission Topography Study of InGaAs Grown by Liquid Encapsulated Czochralski Technique

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New results on ternary InGaAs crystals grown using liquid encapsulated Czochralski technique with constant liquid composition are reported. X-ray high-resolution diffractometry (rocking curves and reciprocal space maps) as well as X-ray topography using the transmission Lang setup were used. Growth history of the bulk ingots was revealed.

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1. Introduction

Laser diodes, solar cells, photodetector structures and other optoelectronic applications of InGaAs ternary bulk crystals and layers stimulate constant interest in the improvement of growth methods for this material. Growth of bulk ternary crystals based on III–V compounds with chemical compositions given by formula $A^{III}_{1-x}B^{III}_{x}C^{V}$ is a difficult task due to the thermodynamical properties of their solutions. Most of the techniques to obtain ternary crystals are focused on layer growing on the relevant substrates. Techniques like metalorganic chemical vapor deposition (MOCVD) [1, 2], metalorganic vapor phase epitaxy (MOVPE) [3, 4] and molecular beam epitaxy (MBE) [5, 6] are often used. Growth of quantum wells and quantum wires is also focused on ternary crystals. Some theoretical discussions about bulk growth of ternaries can be found in [7]. Recently rotational Bridgman method [8], liquid phase electroepitaxy [9] and zone growth [10] were used.

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Liquid encapsulated Czochralski (LEC) technique was also used for this type of material [11, 12]. This particular method, although producing large bulk crystals, is very difficult to control while growing ternary crystals. Standard procedure for growth of such crystals is to cool down the growth melt without replenishing the constituents. Since the melt is a mixture of GaAs and InAs binaries and GaAs has a higher melting point of the two constituents, it is crystallized before InAs, leading to depletion of the latter in the growth melt. As a result, single crystals with a composition variation are produced. An improvement of the homogeneity of the bulk samples may be achieved by controlling their growth through supersaturation of the liquid solution (addition of GaAs during growth) while maintaining a constant temperature [11, 12].

X-ray diffraction methods of characterization of crystals grown by various techniques, including LEC, is a source of invaluable information on their quality and distribution of defects. High-resolution X-ray diffractometry [13] can supply overall information about the quality of the samples while X-ray topography [14] provides both direct evidence of the absence or presence of single defects and visualization of their distribution. In the present paper we report results of the standard LEC procedure where the growth melt is cooled down to achieve crystallization. Growth history of the bulk ingots is revealed and investigated.

2. Samples

Our first batch of samples was grown using the standard LEC setup with arsenic pressure compensation and control via argon overpressure (1.4 atm) in the growth chamber. It consisted of six samples: three two-wafer sets cut from three different bulk crystals. We investigated samples which were cut from two opposite parts of the ingots (top and bottom). The crystals were grown intentionally along [111] crystallographic direction with growth velocity around 1–1.5 mm/h. The intentional In content (x) was 0.02–0.04.

General growth parameters, including the weights of the constituents, the final weights of the crystal, their length and crystallographic characteristics of the final bulk material together with some standard electrical parameters and data from In content measurements are shown in Table I.

3. Results

X-ray diffraction rocking curves and reciprocal space maps were measured using a multi-crystal, multi-bounce high-resolution X-ray diffractometer with the Bartels–Hart monochromator and a standard laboratory X-ray source [15]. We used {333} reflections with the Cu K_{α_1} radiation either in symmetric or asymmetric mode, in accordance with the particular orientation of the sample. Prior to measurements, back-reflection lauegrams of the samples were taken in order to establish their possible departure from the intentional [111] direction. The samples and their orientations are listed in Table II.

TABLE I

Pre-growth and after-growth parameters of the samples. Common parameters for all three crystals: constituents — 1029 g GaAs (undoped) + 71 g InAs (undoped), concentration of In atoms in the liquid — 5%. SC — single crystalline, PP — partially polycrystalline, PL — photoluminescence measurements, EDS — energy-dispersive X-ray spectroscopy.

	Weight [g]	Length [mm]	Resistivity [Ω cm]	Mobility [cm^2/(V s)]	Carrier conc. [cm^{-3}]	In content [%] (PL)	(EDS)	
A	946	115	3.73×10^{-1}	3741	4.48×10^{15}	1.1	0.9	SC
			2.70×10^{-1}	157	1.47×10^{-1}	2.05	2	PP
B	561*	205	2.98×10^{-2}	4236	4.94×10^{16}	1.15	1	SC
C	760*	182	1.27×10^{-1}	3537	1.38×10^{16}	1.25	1	PP

*Including the seed.

TABLE II

Position in the bulk crystal and crystallographic orientation of the samples.

Bulk crystal	Sample	Position	Orientation
A	A1	top	0.7° off [111] direction
	A2	bottom	0.7° off [111] direction
B	B1	top	[221]
	B2	bottom	[221]
C	C1	top	[411]
	C2	bottom	[411]

3.1. High-resolution diffraction

The rocking curves (RC's) shown here were obtained in the Omega scan mode. For wafers A1 and A2 it was very difficult to record any clear peak, since they showed distinct signs of polycrystalline state. As an example, Fig. 1a shows two separate peaks evidencing adjoining blocks of slightly different orientation in the crystal lattice. However, a careful search over the surfaces of the samples allowed to measure some RC's with reasonable widths (Fig. 1b).

For the rest of the samples (B1, B2, C1, C2) we recorded RC's of basically standard shape and reasonable width (see Fig. 1c as an example), with exception of area 2 in sample C2 (Fig. 1d). This particular RC shows clearly that in the area where it was recorded the crystal lattice was heavily strained and distorted.

The reciprocal-space intensity maps (Fig. 2) clearly confirm that wafers A1

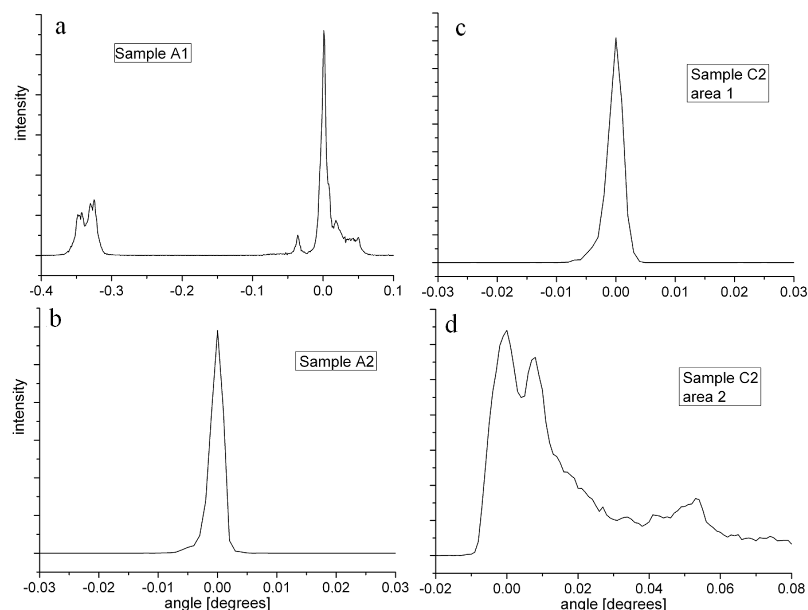

Fig. 1. The rocking curves recorded in the Omega scan mode, Cu K_{α_1} radiation, {333} reflections; (a) sample A1, (b) sample A2, (c) area 1 in sample C2, (d) area 2 in sample C2.

and A2 were cut from a very distorted bulk crystal. The map is either very wide in all directions (Fig. 2a) which means a big change of lattice parameter together with a large lattice bending, or has a much lower intensity (Fig. 2b), suggesting a small area of the crystal taking part in the diffraction (significantly smaller than the X-ray beam area). For wafers B1, B2 and C1 as well as for area 1 in wafer C2 we recorded reasonably perfect intensity maps (Fig. 2c–f). The observed streaks across them are due to the analyzer crystal.

Area 2 in wafer C2 shows a large spread of intensity in the vertical direction on the map (Fig. 2g). Such a spread is usually interpreted as due to a large bending of the lattice planes or to a misoriented adjoining crystal volume. It should be pointed out that all the measurements reported in this section were performed in randomly chosen regions of the sample.

3.2. Topography

Our experiment was performed using the transmission Lang topography [16]. We used Mo K_{α_1} radiation from an X-ray laboratory source. Since the intentional crystallographic orientation of the samples was around the [111] direction, we chose {220} reflections in the symmetric geometry. Using our lauegrams we were able to set all the samples for this geometry despite their misorientations (Table II). Careful angular positioning allowed to record topographs for all our samples. Most difficult in this respect were wafers A1 and A2 where the intensity of the reflection

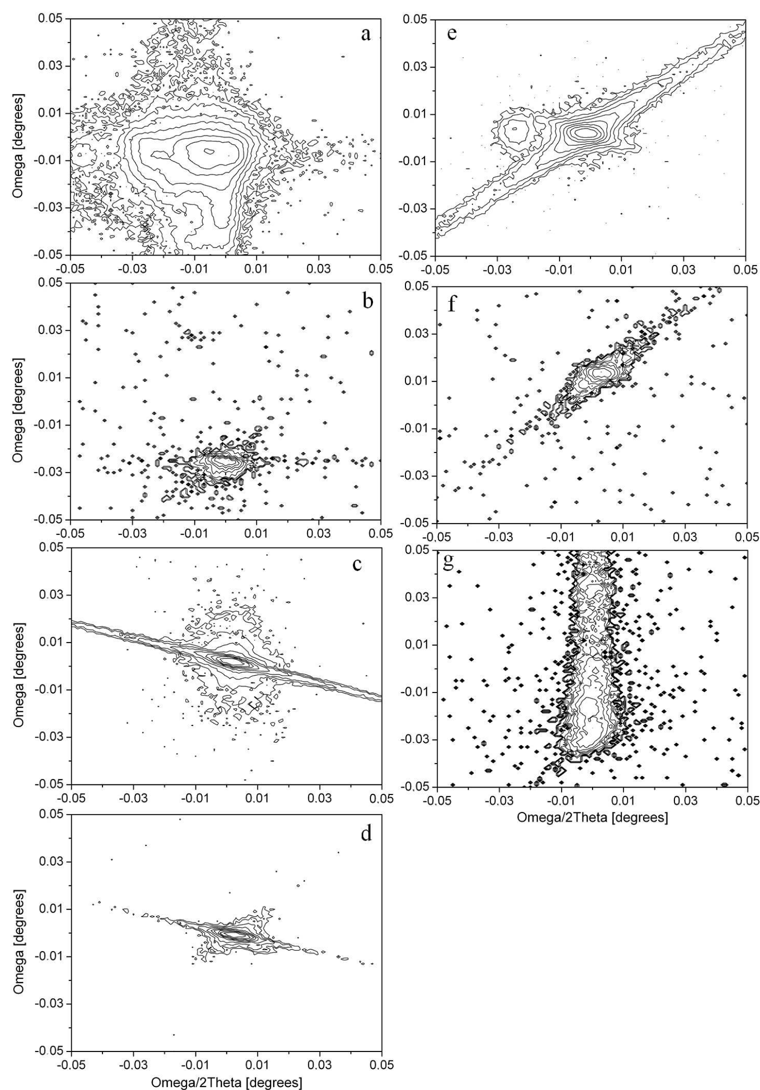

Fig. 2. Intensity maps recorded in the Omega–Omega/2Theta scan mode, Cu K_{α_1} radiation, {333} reflection; (a) sample A1, (b) sample A2, (c) sample B1, (d) sample B2, (e) sample C1, (f) area 1 in sample C2, (g) area 2 in sample C2.

was very low. Imaged areas were almost the same for all samples and were limited by our slit and scan range system to about 15 mm by 15 mm.

The topographs of the samples from bulk crystal A are shown in Fig. 3a,b. One can easily see that both of them show small volumes of the crystal reflecting strongly (black areas) with the rest of the recorded volume of the crystal almost non-reflecting. It means that within the imaged volume of the sample we had

only small pieces of the crystal lattice properly oriented along the [111] direction. There are not many details to be seen of any specific lattice defects for these two wafers.

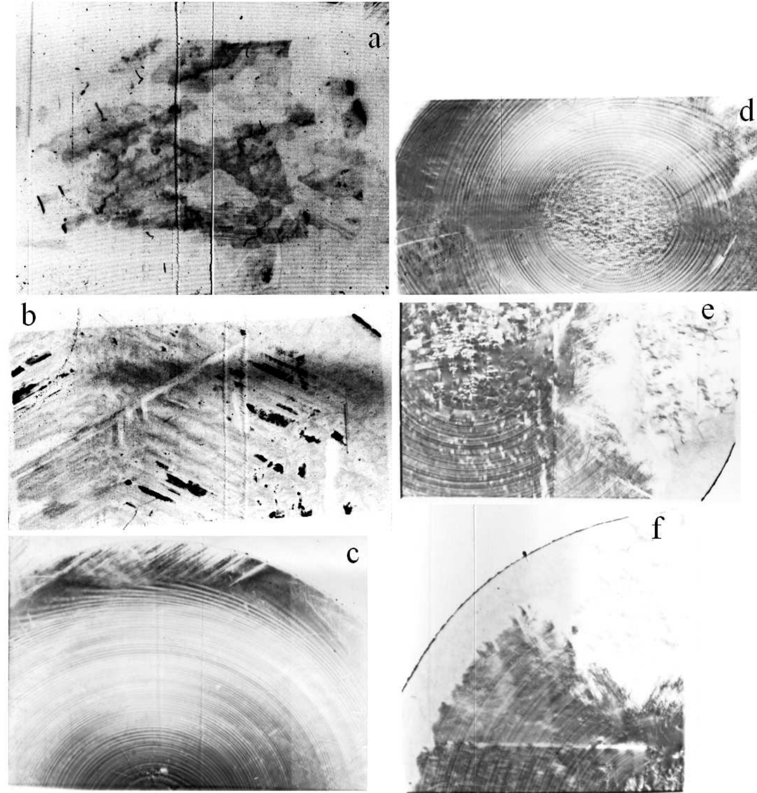

Fig. 3. Lang transmission topographs, {220} reflections, Mo K_{α_1} radiation; (a) sample A1, (b) sample A2, (c) sample B1, (d) sample B2, (e) sample C1, (f) sample C2.

Crystal B was the most structurally uniform one and it showed very interesting defect contrasts on both topographs (Fig. 3c,d). The main feature on both wafers was a strong striation pattern seen as circular bands covering almost the whole of the image. It is a growth pattern typical of the rotational LEC technique. The main factor responsible for it was most probably the segregation of the constituents and the resulting lattice parameter changes. Besides, both images show typical patterns of threading dislocations. For sample B1 there are dislocation bands spreading from the outer edge of the sample which is the usual pattern for bulk crystals being cooled after growth. In the center of the topograph of sample B2 (Fig. 3d) one can see an array of dislocation patterns with the main direction along the growth direction (perpendicular to the sample surface). The source of this system might be the seed which precipitated the formation of grown-in dis-

locations in the crystal. We can see the initial phase of the dislocation system in the center of the image of sample B1 which was much closer to the seed.

Crystal C represented by wafers C1 and C2 shows similar features (Fig. 3e,f). A significant exception for this crystal are regions where the crystal is not reflecting at all (white areas). It means that large parts of the wafer are misoriented with respect to the [111] direction. The rest of the features, like the central grown-in dislocation system and circular banding, are quite similar to those in both B samples.

4. Discussion

The main objective of the present work could be summarized in a simple question: can we grow sufficiently perfect bulk InGaAs crystals by the usual LEC technique? Our results show that generally in all investigated crystals there are reasonably good lattice volumes, but there is also a lack of continuity in the composition and crystallographic properties (orientation) within the ingot from where both samples were cut (crystal A). For the whole set of the GaInAs crystals we had to deal with changes of the orientation of the relevant parts of the samples investigated (Table II).

In one case we recorded data for the same sample (C2) but in two different areas. They showed that even though in a place the crystal was of good quality and uniformity, it was largely non-uniform in another area. Besides, samples from ingot A contradicted the simple pattern where the top of the ingot is better than the bottom — it was exactly opposite in this case.

Our results also demonstrate that investigations based on one randomly chosen area may be misleading. For instance, wafers A2 and C1 show evidence of a reasonable quality but samples A1 and C2 did not confirm this observation since the recorded RC's and maps showed highly distorted areas. It should be stressed in this respect that X-ray topography gives comprehensive information on the crystal quality and uniformity. Few results of this type had been reported for ternary crystals grown by LEC technique, topography being used mostly to investigate layer-type systems of growth [17]. Our results confirm the validity of this method of investigation.

The three bulk crystals investigated in this work constitute the first part of a wider research into LEC technique as used for ternary crystal growth. The results presented in this paper show that the unmodified arrangement is not well suited for this purpose. Although the intentional In content as well as growth conditions were the same for all samples, we had three examples of completely different results of the crystal growth. Ranging from almost completely distorted lattice of ingot A, ingot C was partially polycrystalline and ingot B presented a reasonable good-quality crystal lattice. However, even B samples showed a large amount of lattice defects and segregation of the constituents (the circular pattern of striations) made whole crystal largely non-uniform as far as In content was concerned.

It is known from InAs–GaAs pseudo-binary phase diagram [18] that the slope of the solid–liquid line becomes flatter with lowered temperature, resulting in composition changes. In order to control such fluctuations it is necessary to stabilize the temperature which in turn requires stabilization of the composition of the growth melt. Such a system of modified LEC technique with constant temperature and melt replenishment (via GaAs addition) was already reported in [12]. We will report our own investigations on the samples obtained from this type of growth in a second, incoming paper.

Acknowledgments

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