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Growth of GaInTIAs layers on InP by molecular beam epitaxy

F. Sánchez-Almazán, M. Gendry, P. Regreny, E. Bergignat, G. Grenet, and G. Hollinger^{a)}

Ecole Centrale de Lyon, LEOM, (UMR CNRS 5512), 69131 Ecully Cedex, France

J. Olivares and G. Bremond

INSA de Lyon, LPM, (UMR CNRS 5511), 69621 Villeurbanne Cedex, France

O. Marty and M. Pitaval

Université Lyon 1, LENAC, 69621 Villeurbanne Cedex, France

B. Canut

Université Lyon 1, DPM, (UMR CNRS 5586), 69621 Villeurbanne Cedex, France

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Growth of GaInTIAs alloys on InP(001) has been attempted by solid source molecular beam epitaxy. Thallium incorporation into $\text{Ga}_{1-x}\text{In}_x\text{As}$ matrices was studied as a function of substrate temperature, arsenic overpressure, matrix composition, and growth rate. At high temperatures ($>350^\circ\text{C}$) thallium evaporates, whereas at intermediary temperatures ($270\text{--}350^\circ\text{C}$) thallium segregates into droplets on the surface. Only in the low temperature range ($180\text{--}260^\circ\text{C}$) can thallium be incorporated in some conditions, leading to mirror-like surfaces. Up to 18% Tl content was incorporated into a $\text{Ga}_{0.70}\text{In}_{0.30}\text{As}$ matrix and up to 40% Tl into a GaAs matrix. For these high Tl concentrations, Tl droplets are avoided and Tl incorporation is achieved only when using high arsenic pressures. However, this limits surface adatom diffusion and leads to amorphous, polycrystalline, or twinned materials. Finally, a narrow window for single-crystal growth has been found for low Tl contents (4%) using optimized growth conditions with low V/III pressure ratios and high growth rates. © 2001 American Vacuum Society. [DOI: 10.1116/1.1359530]

I. INTRODUCTION

As and P based ternary or quaternary thallium alloys have been recently proposed as new infrared materials for long wavelength operation. According to theoretical predictions, TIP and TIAs have a negative band gap and a marginally stable zinc-blende structure with lattice parameters close to those of InP and InAs, respectively.¹ Consequently, low band gap GaInTIP and GaInTIAs alloys can theoretically be prepared lattice matched to InP or GaAs. As an example, it is expected to reach operation wavelengths of about $2.7\ \mu\text{m}$ with 26% Tl in $\text{Ga}_{0.54}\text{In}_{0.20}\text{Tl}_{0.26}\text{As}$ layers, lattice matched to InP.

These predictions have stimulated several experimental studies. Growth of P and As based Tl alloys has been tried on GaAs, InP, and InAs substrates using solid source molecular beam epitaxy (SSMBE), gas source MBE (GSMBE) and metalorganic chemical vapor deposition (MOCVD).^{2–13} Thallium is more volatile than Ga and In with a vapor pressure of 10^{-7} and 10^{-6} Torr around 320 and 360°C , respectively, whereas the corresponding temperatures for indium are around 540 and 600°C . Consequently, the standard growth temperature for GaInTIAs alloys should be around 350°C (i.e., the highest temperatures for which the thallium sticking coefficient should be equal or near equal to 1), to compare with $500\text{--}550^\circ\text{C}$ for GaInAs alloys. When using standard growth temperatures, most authors found that thallium accumulates on the surface in the form of metallic drop-

lets. This encouraged studies either at higher temperatures ($400\text{--}450^\circ\text{C}$) or at lower temperatures ($<250^\circ\text{C}$).

For growths performed at high temperatures, contradictory conclusions have been reached and the situation is presently rather confusing. Using GSMBE, Asahi and co-workers^{2–5} claimed successful growth of TIP, InTIP, GaTIP, GaInTIP, and GaInTIAs alloys in the growth temperature range of $400\text{--}450^\circ\text{C}$. In these works, experimental evidence for Tl incorporation is only based on x-ray and electro-optical (photoluminescence and photoconductance) results which are only indirect characterizations. Hübener *et al.*⁶ claimed the successful fabrication by SSMBE of a GaTIP light emitting diode (LED) grown on GaAs and emitting at $1.3\ \mu\text{m}$. Razeghi *et al.*⁷ also claimed the growth by low pressure MOCVD of $(\text{InP})_{1-x}(\text{TIP}_3)_x$ with Tl content of $x=0.6$, an evaluation exclusively based on photoconductance measurements. However, none of these authors gave clear evidence of Tl incorporation since they did not measure the thallium concentration using analytical techniques. By contrast, Antonell *et al.*,⁸ Wei *et al.*,⁹ and Sánchez *et al.*,^{12,13} who measured Tl concentrations using analytical techniques, did not succeed in incorporating Tl into InP, GaInAs, and InAs matrices using GSMBE⁸ or SSMBE.^{9,12,13} They reported that, for substrate temperatures higher than $350\text{--}400^\circ\text{C}$, thallium atoms evaporate and consequently are not incorporated.

Results for growth performed at low temperature are less contradictory. Antonell *et al.*⁸ described the formation of an “InTIAs” phase at low temperature (275°C) together with metallic droplets. Lubyshev *et al.*¹⁰ reported MBE growth at

^{a)}Electronic mail: Guy.Hollinger@ec-lyon.fr

200 °C of $\text{Tl}_x\text{Ga}_{1-x}\text{As}$ on GaAs with an estimated maximum Tl content of 5% but with metallic droplets on the surface. Sánchez *et al.*^{12,13} achieved the incorporation of up to 18% Tl in mirror-like InGaTIAs layers grown at 230 °C but these layers were not single crystalline.

The aim of this work is to clarify the incorporation behavior of Tl in III–V matrices in a wide range of substrate temperatures (150–500 °C) and to try to grow GaInTIAs alloys on InP by SSMBE. Our approach was, first to construct a phase diagram for the GaInAs:Tl system in order to define growth conditions for Tl incorporation, Tl surface segregation, and Tl evaporation, as a function of growth temperature and Tl flux. Then we looked (unsuccessfully) for incorporation in the high temperature regime and finally we found conditions, in the low temperature regime, for Tl incorporation and single-crystalline growth.

II. EXPERIMENT

The epitaxial layers were grown on epi-ready semi-insulating InP (001) substrates using a Riber 2300 reactor equipped with high capacity P and As cracking cells. High growth temperatures were measured with an optical pyrometer which was calibrated taking, as reference, the melting point of InSb at 525 °C. Low temperatures were estimated using a combination of thermocouple temperatures, values of the power delivered to the heater filament, and indium melt measurements. Before growth, InP substrates were deoxidized under a P_2 flux with a beam equivalent pressure (BEP) of 10^{-5} Torr at 530 °C. For all grown structures, an 0.2 μm thick InP buffer layer was grown at 480 °C using a P_2 cracking temperature of 800 °C, the optimum temperature to obtain the minimal incorporation of nonintentional impurities. We have explored a wide range of growth conditions for GaInAs:Tl materials by varying four main parameters: the growth temperature ranging from 450 to 150 °C, the Tl flux, the arsenic pressure, the composition of the $\text{Ga}_{1-x}\text{In}_x\text{As}$ host matrix, and in some cases the growth rate. The surface morphology of the layers was observed using Nomarski optical microscopy and scanning electronic microscopy (SEM). The incorporation of thallium was systematically investigated using secondary ion mass spectrometry (SIMS) profile measurements. Rutherford backscattering spectrometry (RBS) was utilized to determine the absolute Tl concentration and also to calibrate SIMS data. X-ray photoelectron spectroscopy (XPS) measurements were performed to evaluate Tl concentrations on the surface and into the bulk. Energy dispersive x-ray analysis (EDX) performed in SEM equipment was applied to characterize layers with droplets on the surface. The surface structural properties of the layers were studied during growth using reflection high energy electron diffraction (RHEED) and after growth using Nomarski microscopy and atomic force microscopy (AFM). Double crystal x-ray diffraction (DCXRD) and transmission electron microscopy (TEM) were employed to investigate the bulk structural properties.

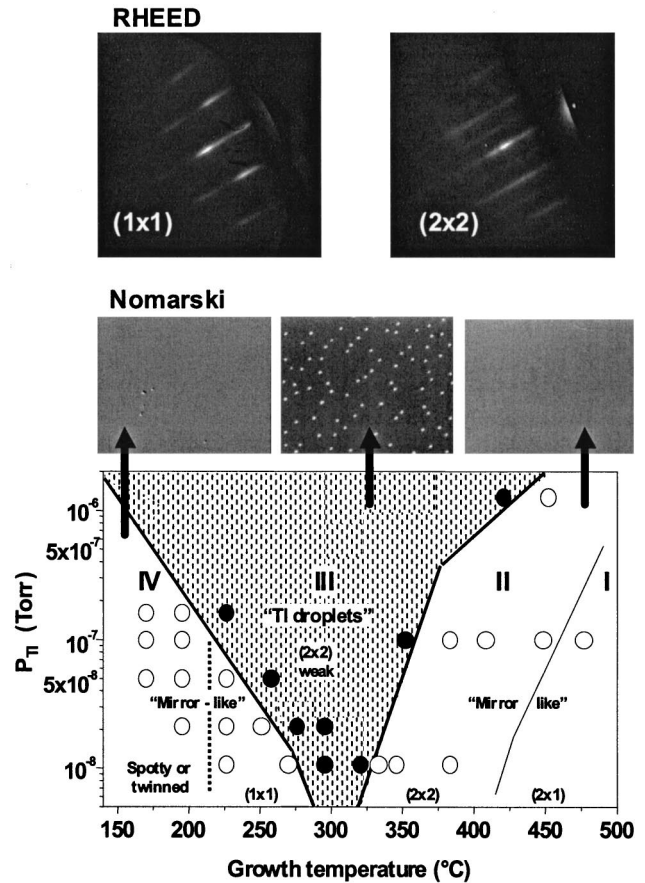


Fig. 1. Phase diagram for GaInAs:Tl showing four growth regimes for thallium incorporation when Tl pressure and growth temperature are varied. Regions I and II are associated with Tl evaporation and Tl surface segregation, respectively. Region III is associated with Tl surface segregation and formation of metallic Tl surface droplets. Tl incorporation occurs for region IV. Surfaces in region II are covered by ~ 0.1 – 0.2 ML of Tl atoms which leads to a (2×2) surface reconstruction. The phase diagram was constructed mainly for $\text{Ga}_{1-x}\text{In}_x\text{As}$ tensively strained matrices grown at $1 \mu\text{m/h}$. The V/III ratio was in the 5–11 range. Also shown are the corresponding Nomarski photographs of surface morphologies and RHEED patterns taken in the $[110]$ azimuth.

III. PHASE DIAGRAM FOR THE GaInAs–Tl SYSTEM

Our preliminary objective was to construct a “phase diagram” for the GaInAs:Tl system in order to look for a Tl incorporation window between the “droplet” regime and the “mirror-like” regime, when varying the thallium flux and the growth temperature but keeping Ga, In, and As fluxes constant. A careful study of the RHEED patterns during growth and an examination of the surface morphology of the corresponding samples have allowed us to define four regions as shown in Fig. 1.

When decreasing the substrate temperature, the following regions have been found in sequence:

- (1) Region I: mirror-like surfaces and RHEED patterns with (2×1) bulk streaks (similar to $\text{Ga}_{1-x}\text{In}_x\text{As}$ patterns),
- (2) Region II: mirror like surfaces and (2×2) surface reconstruction,
- (3) Region III: surface droplets and weak RHEED diagrams, and

(4) Region IV: mirror-like surfaces and no single-crystal RHEED pattern.

Region I corresponds to TI-free GaInAs because the TI sticking coefficient is almost equal to 0. Region II is characterized by a (2×2) surface reconstruction induced by surface TI atoms. Such a reconstruction has been already reported by others^{3,4,10} for TI exposed InP, GaAs, InAs, and GaInAs. Using XPS, we found that the (2×2) surface reconstruction in region II is associated to the presence of about 0.1–0.2 thallium monolayer on the surface. In regions III and IV, it is believed that the TI sticking coefficient Θ_{TI} is equal or close to 1 since the onset for significant TI desorption is around 320–360 °C. When traveling in Fig. 1 from right to left through regions I, II, and III, the whole process can be roughly understood as an effect of the TI sticking coefficient increasing from 0 to 1 when the growth temperature is decreasing. When the number of TI atoms increases on surface, TI atoms first form a surface overstructure and then when the coverage becomes sufficient for metallic TI–TI interaction to emanate, metallic droplets appear. The abrupt phase boundary between regions III and IV is more astonishing and will thus be in the following the subject of a special study. However, it may be thought as the result of the surface atom mobility decreasing as temperature decreases, while the sticking coefficient being equal to 1.

A. Growth at high temperatures (regions I, II, and III)

First we grew a set of GaInAs: TI layers covering a wide variety of conditions in the “high temperature” (350–480 °C) regions I, II, and III. TI pressures (BEP) were varied from 10^{-8} to 10^{-6} Torr. The arsenic pressure was 4×10^{-6} Torr and the temperature of the As cracker cell was fixed at 800 °C. After growing a 0.2 μm thick InP buffer layer and then a 0.4 μm Ga_{0.47}In_{0.53}As buffer layer at 480 °C, 0.4 μm «GaInTIAs» layers were grown at various temperatures from 350 to 480 °C. The growth rate of the layers was 1.2 $\mu\text{m}/\text{h}$. Some of these growth conditions were very similar to those used by Asahi and co-workers.^{4,5} Four compositions for the host tensilely strained matrices have been tried: GaAs, Ga_{0.70}In_{0.30}As, Ga_{0.58}In_{0.42}As, and Ga_{0.52}In_{0.48}As which correspond to 3.6%, 1.6%, 0.77%, and 0.36% lattice mismatch to InP, respectively. Special attention was paid to find an incorporation window just at the boundary between

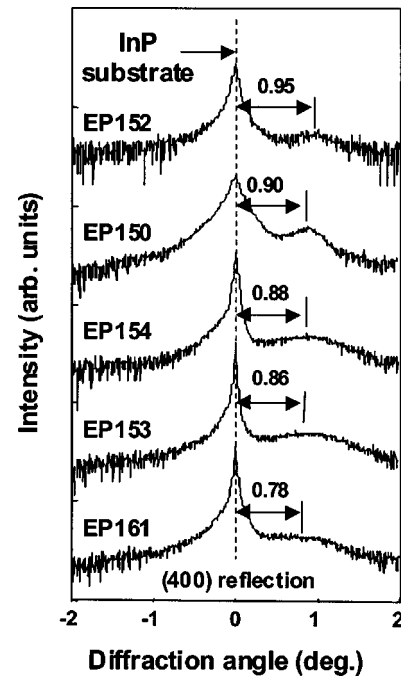


Fig. 2. Double crystal x-ray diffraction curves for different Ga_{0.70}In_{0.30}As:TI samples compared to that of a reference TI free sample. Shifts are attributed to variations in the relaxation degree of the layers and not to TI incorporation.

the droplet regime (region III) and the evaporation regime (region II). The idea was to use the tensile matrix effect to stabilize TI–As bonds and thus to favor TI incorporation in regions where the sticking coefficient is normally equal to zero on lattice-matched materials. No significant TI incorporation was found by SIMS in all the samples which show either TI droplets, TI surface segregation, or TI evaporation. The highest TI concentration levels detected by SIMS were always lower than 0.01%. Some SIMS profiles showed, in some cases, an incorporation enhancement (by a factor of 2) from one sample to another but this was always far below a significant incorporation level. EDX measurements performed on the samples exhibiting droplets on surface revealed TI only in the droplet areas and no TI between the droplets. Figure 2 shows a set of DCXRD rocking curves of (400) reflection for some Ga_{0.70}In_{0.30}As: TI layers (EP150, EP154, EP153, and EP161) compared to that of a TI free Ga_{0.70}In_{0.30}As sample (EP152). The corresponding growth

TABLE I. Growth conditions for a set of Ga_{0.70}In_{0.30}As:TI layers presenting the same Ga_{0.70}In_{0.30}As matrix composition and the same thickness (2000 Å). Only the thallium flux and the growth temperature are changed. Also given is the hypothetical TI content, calculated assuming the same strain relaxation degree for all layers.

Sample	T_c (°C)	P_{TI} (Torr)	P_{In} (Torr)	P_{Ga} (Torr)	DCXRD hypothetical \times TI content	Surface morphology	Droplets per cm^2
EP152 (ref)	450	0	1.5×10^{-7}	2.31×10^{-7}	0	mirror like	0
EP150	450	10^{-7}	1.5×10^{-7}	2.31×10^{-7}	0.06	mirror like	0
EP154	425	10^{-7}	1.5×10^{-7}	2.31×10^{-7}	0.04	mirror like	0
EP153	450	10^{-6}	1.5×10^{-7}	2.31×10^{-7}	0.03	droplets	9×10^2
EP161	425	10^{-6}	1.5×10^{-7}	2.31×10^{-7}	0.1	droplets	8×10^4

conditions are given in Table I. The epilayer–substrate peak separation, decreasing from EP152 (taken as reference) to EP161 could be interpreted as an indication of a possible TI incorporation. For example, assuming a lattice parameter of 6.18 Å for TIAs¹ and assuming the same degree of strain relaxation (20%) found in the reference layer (EP152), we would predict a thallium content ranging from 3% to 10%. Since we know from SIMS and EDX measurements that there is no TI incorporation, these shifts have to be actually related to a variation of the growth dependent degree of strain relaxation. Photoluminescence measurements at 4 K confirmed that there is no reduction in the band gap of the layers and thus no thallium incorporation achieved. Note that such x-ray diffraction shifts have been interpreted by some authors as an indication of TI incorporation.⁴ Our results show that isolated data from indirect characterization techniques are not reliable enough for claiming TI incorporation.¹⁴

B. Growth at low temperatures (region IV)

1. Growth of defective GaInTIAs layers at low temperature

As no incorporation was achieved at high temperatures and as droplets are formed at intermediary temperatures, only the low temperature domain appears suitable for the incorporation of thallium atoms during growth. The GaInAs:TI system was further explored in the temperature range of 180–370 °C. Besides this parameter, TI incorporation in the Ga_{1-x}In_xAs matrix was also studied by varying the thallium pressures (BEP range of 10⁻⁸–10⁻⁶ Torr), the arsenic pressures (10⁻⁷–2×10⁻⁵ Torr range, which corresponds to V/III BEP ratios varying from 1 to 50), and the indium compositions of the Ga_{1-x}In_xAs matrices (x=0.3, 0.42, 0.48, and 0.53). Growth rates were varied from 0.35 to 1.4 μm/h. Before the GaInAs:TI layers were grown in the temperature range of 180–370 °C, a 200 Å thick GaInAs LM buffer layer was grown at 500 °C, and cooled to the growth temperature GaInAs:TI layer while maintaining a (3×4) RHEED reconstruction indicative of a good surface structural quality. The TI, In, and Ga relative fluxes were chosen in order to achieve a GaInTIAs compound lattice matched to InP or slightly tensile strained.

In some conditions, below 340 °C, TI incorporation was achieved without any droplet formation leading to mirror-like surfaces. A set of growth conditions leading to TI incorporation and mirror-like surfaces is collected in Table II. At these low temperatures, the sticking coefficient of TI atoms is 1 and a first-order composition of the mirror-like layers can be estimated from Ga, In, and TI fluxes, as given in Table II. The absolute concentration of thallium was more precisely evaluated using RBS (Fig. 3), EDX and XPS (Fig. 4) measurements confirming these estimations. SIMS profiles measured for several samples showed that the TI concentration was homogeneous in depth and proportional to the incoming TI flux (Fig. 5). As shown in Table II, the highest TI concentration was found equal to 40% for a GaAs host matrix and a growth temperature of 180 °C (EP414). It was

TABLE II. Growth conditions and atomic composition for several (Ga_{1-y}In_y)_{1-x}Tl_xAs samples. The expected compositions were calculated from Ga, In, and TI beam pressures assuming an incorporation coefficient equal to 1. The experimental compositions were evaluated by RBS.

Sample	T_c (°C)	P_{As} (Torr)	P_{TI}/P_{In}	y % In	1-y % Ga	x % TI expected	x % TI RBS
EP306	230	1.5×10^{-6}	0.18	42	58	4.2	3.5
EP304	180	1.5×10^{-6}	0.35	42	58	8.2	8
EP329	180	1.5×10^{-6}	0.59	42	58	13	14
EP386	200	10 ⁻⁵	0.60	30	70	15	18
EP398	180	10 ⁻⁵	1.6	0	100	41	32
EP414	180	10 ⁻⁵	2.25	0	100	49	40

also incorporated up to 18% TI into Ga_{0.70}In_{0.30}As at 200 °C (EP386). TI concentrations of 3.5%, 8%, and 14% were also obtained in Ga_{0.58}In_{0.42}As matrices for growths at 180, 180, and 230 °C, respectively (EP306, EP304, EP329).

At this point, it is important to note that TI atoms are not systematically incorporated whatever the growth conditions are. A variation of some growth parameters, especially the growth temperature and the V/III ratio, can allow the shift towards an incorporation behavior (leading to mirror-like surfaces) or towards no incorporation behavior (TI atoms remaining segregated on the surface and giving droplets). As an example, when growth conditions are achieved at 200 °C in order to produce TI incorporation [Fig. 6(a)], decreasing the V/III pressure ratio from 20 to 4 leads to the appearance of TI droplets [Fig. 6(b)]. Finally, increasing the TI flux

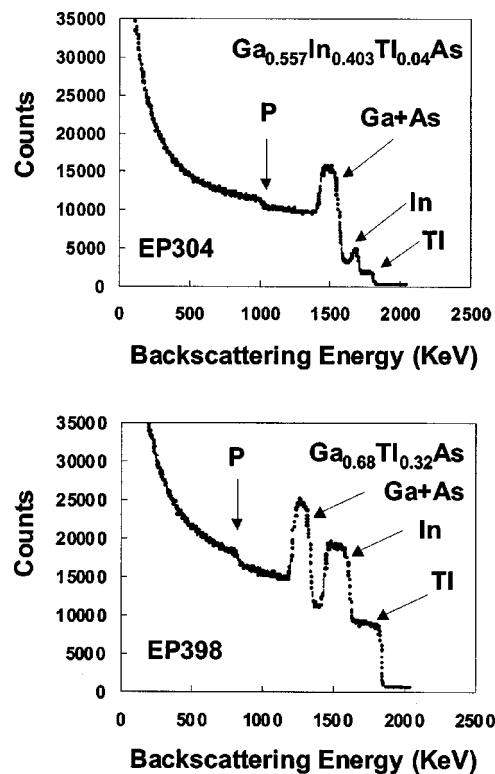


Fig. 3. RBS spectra of GaInTIAs showing incorporation of thallium into the bulk. Analysis conditions: ⁴He⁺ ions of 2 MeV energy; detection angle = 150°.

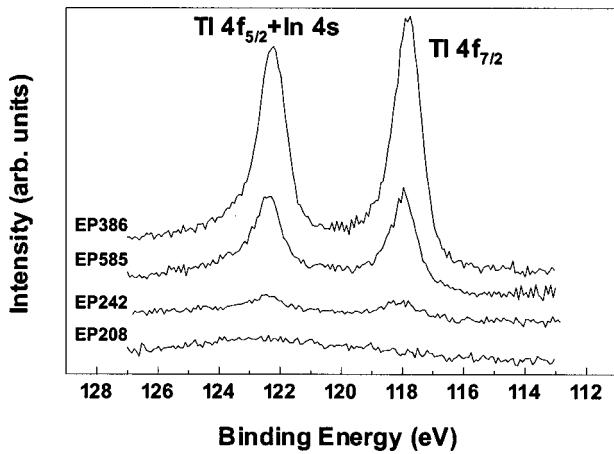


FIG. 4. XPS spectra taken at normal emission for the Tl 4f region of three samples with increasing Tl content: EP242: 1%, EP585: 4%, EP386: 15%. The samples have been deoxidized before introduction into vacuum in order to limit surface contribution effects.

when keeping all the other growth parameters constant can also lead to a transition from Tl incorporation to Tl surface coalescence (see Fig. 1). This has to be associated to an As overpressure not high enough.

RHEED pattern observations during growth show that, generally, the GaInTIAs alloys are defective and cannot be grown as a thick single crystal. At 180 °C, the layers are polycrystalline or amorphous. At 230 °C, the GaInTIAs layers grow first epitaxially (1×1 RHEED pattern) but rapidly become twinned and then polycrystalline (see Fig. 7). This is illustrated by the cross section TEM image shown also in Fig. 10. About 80 Å of single-crystalline GaInTIAs was grown before twins were formed. The twinning character lead to a final polycrystalline phase. The poor structural quality of the layers was confirmed by high resolution x-ray diffraction measurements which did not show any peak associated to the GaInTIAs layers.

This behavior was mainly attributed to limitation of surface mobility of group III and V species due to the low growth temperature and to the high arsenic fluxes. It is well known that low temperature epitaxy and high arsenic fluxes limit surface mobility and allow arsenic incorporation¹⁵ leading to an arsenic excess incorporation within the layers. In fact, RBS (As/Ga ratio) and XPS (elemental As/As bonded to group III elements ratio) measurements have shown, for layers grown at 180 °C, a huge elemental arsenic incorporation up to several tens of percents. In contrast, at 230 °C we did not detect any As incorporation within RBS and XPS sensitivity (a few percent). However it is expected, on the basis of the literature, that the amount of excess arsenic incorporated at 230 °C could be less than 1% or 2%.^{16,17} As such highly defective materials are of no interest for applications, we tried to find conditions such that a single crystal growth process can be performed in the low temperature range .

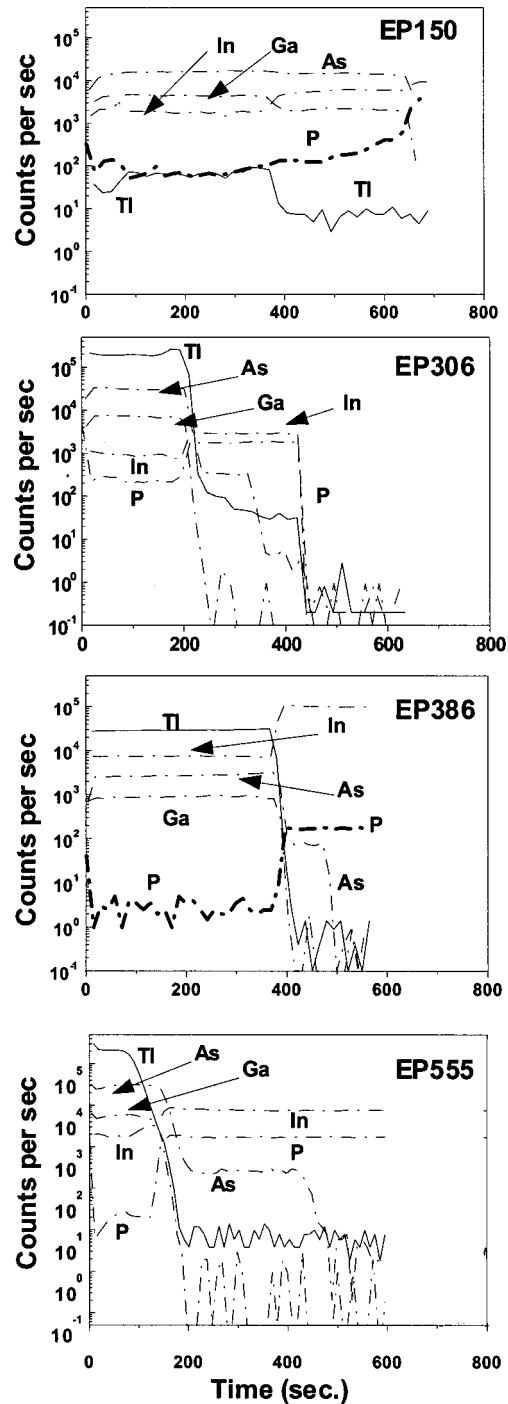


FIG. 5. SIMS profiles for four samples prepared in various conditions. Sample EP150 prepared at high temperature displays only Tl incorporation at the doping level. Samples EP306 (polycrystalline), EP386 (single crystalline/polycrystalline), and EP555 (single crystalline) prepared at low temperature show a thallium signal about 400 times higher than that of the high temperature sample.

2. Growth of single-crystalline GaInTIAs at low temperature

Low temperature MBE in semiconductors has been widely studied for both fundamental and application reasons.¹⁵ As an example, GaAs has been grown epitaxially at 75 °C while maintaining a high crystalline perfection.¹⁸

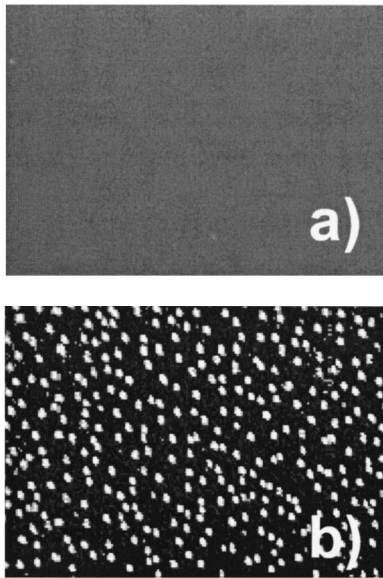


FIG. 6. Nomarski photographs of surface morphologies for two $\text{Ga}_{0.58}\text{In}_{0.42}\text{As}:\text{Tl}$ samples grown at 200°C with V/III pressure ratios of 20 (a) and 4 (b), respectively. Keeping other growth conditions identical, incorporation of Tl is favored when using high arsenic fluxes rather than low arsenic fluxes. At these temperatures a mirror-like surface is indicative of Tl incorporation whereas droplets reveal Tl surface segregation and no incorporation.

This was achieved by controlling the incorporation of excess arsenic using low V/III ratio and using migration enhanced epitaxy techniques. Using more conventional MBE techniques, Kunzel *et al.*¹⁷ were able to grow single-crystalline $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}$ layers on InP down to 125°C .

As Tl incorporation necessitates the highest possible As overpressure, we first defined the substrate temperature—As

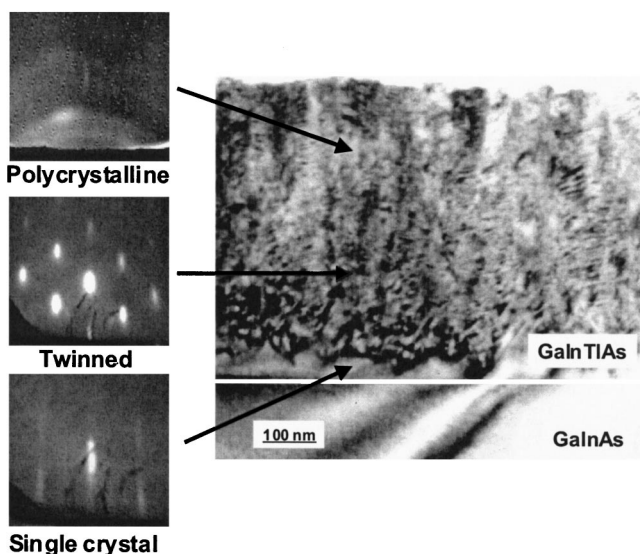


FIG. 7. Plan-view TEM image (right hand side) of $\text{Ga}_{0.56}\text{In}_{0.40}\text{Tl}_{0.04}\text{As}$ sample EP353 grown at 230°C showing, successively from the interface, single crystal, twinning, and polycrystalline growth. The corresponding RHEED patterns taken during growth are also presented (left hand side).

overpressure domain where $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}$ layers can be grown epitaxially. The single crystallinity was checked by the presence of the reciprocal lattice rods in the RHEED patterns and by the existence of a peak in the DCXRD rocking curves. Figure 8(a) shows the growth conditions for lattice-matched GaInAs single-crystalline layers, twinned materials, and amorphous layers. It appears that single-crystalline layers can be obtained in a wide range of V/III ratios in the $200\text{--}260^\circ\text{C}$ temperature range. Similar results have been obtained for two growth rates, 0.35 and $1\ \mu\text{m/h}$. The single crystal domain for strained lattice-mismatched layers was not explored but it is expected that it could be slightly reduced.

On the basis of the results shown in Fig. 9(a), it is clear that we could expect to grow a single crystal material at 200°C only for V/III ratios much lower (<15) than those previously used to achieve high Tl content (i.e., V/III of 26 for 18% Tl in $\text{Ga}_{0.70}\text{In}_{0.30}\text{As}$). However these ratios should be compatible with the growth of GaInTIAs containing Tl less than 10%. Consequently, we explored a wide range of V/III ratios—substrate temperatures conditions, for two growth rates, 0.35 and $1\ \mu\text{m/h}$ and for nominal Tl concentrations from 1% to 12% in tensilely strained $\text{Ga}_{0.58}\text{In}_{0.42}\text{As}$ matrices, staying in the vicinity of the “droplet formation”/“Tl incorporation” boundary. The thickness of the GaInTIAs layers were $500\ \text{\AA}$. In most cases the GaInTIAs layer was grown on a $200\ \text{\AA}$ GaInAs lattice-matched layer. We checked that growing the GaInTIAs layer directly on the InP buffer layer gives similar results. Some characteristic growth conditions are given in Table III for a set of representative GaInTIAs and reference GaInAs layers.

First, we explored growth conditions at low growth rate ($0.35\ \mu\text{m/h}$). The results are reported in Fig. 8(b). A comparison of Figs. 8(a) and 8(b) indicates that adding a Tl flux (4% nominal composition) during growth of a GaInAs single-crystalline layer leads automatically to a twinned material for the highest V/III ratios or to Tl droplets for the lowest V/III ratios, with no window for single crystal growth.

Increasing the growth rate from 0.35 to $1\ \mu\text{m/h}$ modifies completely the phase diagram [Fig. 8(c)]. As an example, for a 230°C growth temperature, the droplet region appears at a much lower V/III ratio, 3, than it was (~ 10) for $0.35\ \mu\text{m/h}$. Interestingly, a single crystalline window appears now between the “droplet” and the “twinning” regions. This window exists only for low Tl contents (1%–4%). For Tl concentrations from 4% to 12%, no single-crystalline growth conditions have been found yet. The single crystallinity of the $\text{Ga}_{0.56}\text{In}_{0.40}\text{Tl}_{0.04}\text{As}$ layers was shown by a (1×1) RHEED pattern during growth and by a peak in the (004) DCXRD rocking curves. It was confirmed by plan-view TEM [Fig. 9(a)]. The corresponding electron diffraction pattern [Fig. 9(b)] does not show any additional spot when compared with a single crystal $\text{Ga}_{0.58}\text{In}_{0.42}\text{As}$ substrate taken as reference. However, these layers are characterized by a high density ($\sim 10^9\ \text{cm}^{-2}$) of structural defects. The same density of defects is found by AFM on the surface of the layers

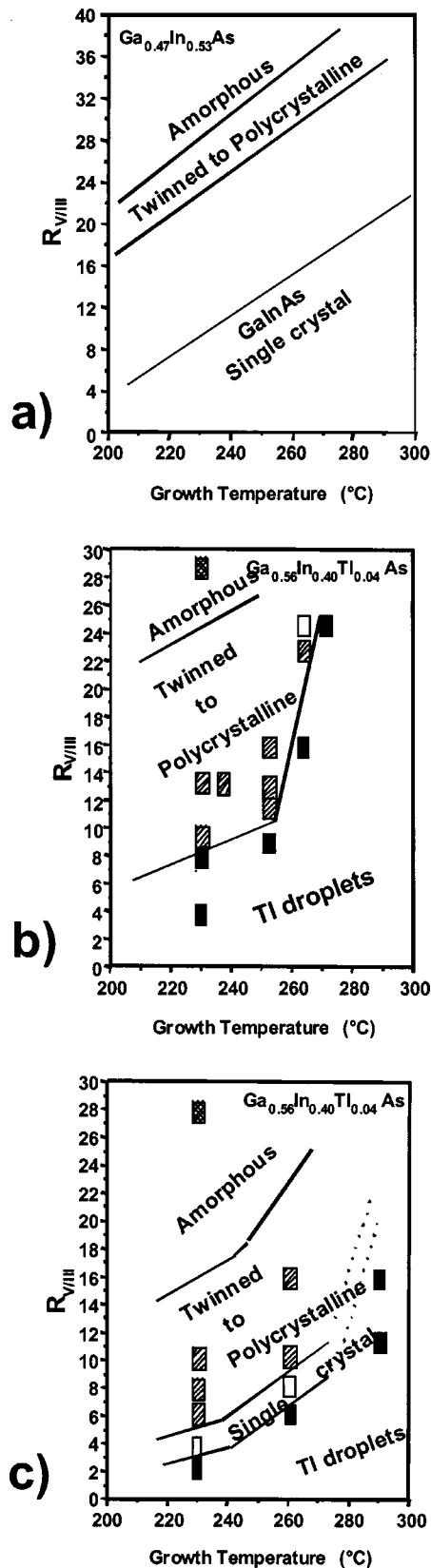


FIG. 8. Growth conditions at low temperature for single crystalline, twinned, polycrystalline, and amorphous layers. (a) $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}$, (b) $\text{Ga}_{0.56}\text{In}_{0.40}\text{Tl}_{0.04}\text{As}$ grown at $0.35 \mu\text{m/h}$, and (c) $\text{Ga}_{0.56}\text{In}_{0.40}\text{Tl}_{0.04}\text{As}$ grown at $1 \mu\text{m/h}$.

where round and convex holes with a diameter of about 70 nm and a height of 2 nm are observed. The origin of these defects has been related to stacking faults and twins by cross section TEM. Figure 10 shows a cross sectional TEM image showing single crystal areas and isolated twins. An interesting point is that twinning appears only after 150–200 Å growth. Twinning is believed to arise from roughening of the growth front due to low surface mobility of adatoms and from the development of {111} facets. It is also clearly associated to thallium atoms since, using identical growth conditions, thick single crystal GaInAs layers can be grown without any twinning. For the single-crystalline layers, x-ray chemical analysis associated to TEM measurements showed that thallium is incorporated homogeneously in the layers.

Using the same growth conditions, 4% Tl was also successfully incorporated into $\text{Ga}_{0.47}\text{In}_{0.53}\text{As}$ lattice-matched matrices and into $\text{Ga}_{0.35}\text{In}_{0.65}\text{As}$ compressively strained matrices, leading to single-crystalline layers. We explored more deeply growth conditions for lattice-matched host matrices (see Table III). Again, single crystal growth was achieved for Tl contents equal to or less than 4% and twinning occurred for Tl content of 8% and 12%.

Figure 11 shows a set of DCXRD rocking curves taken for a nominal $\text{Ga}_{0.53}\text{In}_{0.43}\text{Tl}_{0.04}\text{As}$ layer and for a reference $\text{Ga}_{0.55}\text{In}_{0.45}\text{As}$ layer. The two layers have been grown one after another while keeping all growth conditions and flux parameters identical. It appears that both layers are single crystalline and that thallium incorporation is associated to an increase of the lattice parameter. This behavior is in agreement with the 6.18 Å theoretical lattice parameter expected for TIAs¹ but differs from a recent result where it was observed, in III antimonides, a lattice contraction of InTISb layers upon Tl incorporation.¹⁹ The observed shift would correspond to 2.2% Tl, assuming that the GaInTIAs layer is fully strained and to 6.9%, assuming it is fully relaxed. These values are in reasonable agreement with the expected 4% actual Tl concentration. Note that in our calculations we supposed the same concentration of interstitial elemental arsenic in both GaInTIAs and GaInAs layers.

The corresponding TEM cross section image shows that the initial growth is defect free and {111} twinning and stacking faults begin to appear after about 300 Å growth. This is in agreement with RHEED observations during growth. One can conclude that Tl incorporation seems not to be influenced by the composition of the host matrix, at least for low Tl contents. Kinetic effects associated to the behavior of thallium atoms on the surface growth front appear to prevent growing high quality materials with high Tl contents.

IV. DISCUSSION

At high temperatures, no thallium incorporation in arsenides was found whatever the conditions used (low/high sticking coefficients, low/high Tl pressures, tensilely or lattice-matched matrices, low/high arsenic overpressures...). This is in agreement with the thermodynamical predictions of Berding *et al.*²⁰ At intermediate temperatures ($\sim 350 \text{ }^\circ\text{C}$) where the sticking coefficient is equal to 1, thallium atoms

TABLE III. Growth conditions for a set of representative $(\text{Ga}_{1-y}\text{In}_y)_{1-x}\text{Tl}_x\text{As}$ layers and reference samples showing either single crystal growth, surface droplets, or twinning when varying some parameters.

Sample	Growth temperature (°C)	As pressure (Torr)	V/III BEP ratio	Growth rate ($\mu\text{m/h}$)	Composition $(\text{Ga}_{1-y}\text{In}_y\text{As})_{1-x}(\text{TlAs})_x$		Crystallinity	Surface morphology
					y% In	x% Tl		
EP353	230	7.1×10^{-6}	14	1	42	4	polycrystalline	mirror like
EP555	230	2.3×10^{-6}	4	1	42	4	single crystal	mirror like
EP579	230	1.6×10^{-6}	3	1	42	4	single crystal	droplets
EP553	230	3.45×10^{-6}	6	1	42	4	twinning	mirror like
EP469	230	1.6×10^{-6}	8	0.35	42	4	single crystal	droplets
EP697	230	2.3×10^{-6}	4	1	55	Ref. 0	single crystal	mirror like
EP698	230	2.4×10^{-6}	4.2	1	55	4	single crystal	mirror like
EP689	230	2.3×10^{-6}	4	1	55	4	single crystal	droplets
EP690	230	2.4×10^{-6}	4.2	1	55	8	twinning	mirror like
EP691	230	2.75×10^{-6}	4.8	1	55	12	twinning	mirror like
EP593	230	2.3×10^{-6}	4	1	65	4	twinning	mirror like

segregate on the surface and behave like a surfactant giving a specific 2×2 surface reconstruction. This conclusion is in agreement with Antonell *et al.*⁸ and Wei *et al.*⁹ results but is in contradiction with Asahi and co-workers' claims.³⁻⁵ Note that Asahi *et al.* did not actually use a direct analytical technique to demonstrate the Tl incorporation in the layers.

We have shown that thallium can be incorporated at low temperature (180–260 °C) but with a high enough arsenic overpressure. In such conditions the Tl–As bond can be stabilized. However, the so-obtained layers are generally either amorphous, polycrystalline, or twinned. Nevertheless, for the lowest arsenic pressures, high growth rates and low Tl contents, a single crystal growth can be achieved even if after a few hundred angstrom growth, the surface roughening induces some structural defects. This behavior can be under-

stood by considering a competition on the growth front between the formation of Tl–As bonds and Tl–Tl bonds.

As found experimentally, Tl atoms behave as surfactants and segregate on surface in standard growth conditions. Tl–As bonds can be achieved at low growth temperature, only if enough As_2 molecules are dissociated and if the vapor pressure above the weak Tl–As bonds is high enough to prevent dissociation.²⁰ As the dissociation rate of As_2 molecules is low at such low temperatures, it is expected that Tl–As bonds can be stabilized only for relatively high arsenic overpressures. Unfortunately, high arsenic overpressures at low growth temperature prevents high quality growth and leads to the breakdown of crystallinity above a characteristic thickness, a behavior which is well known in low temperature epitaxy.¹⁵

Decreasing the As pressure, favors group III adatom mobility which could help to maintain epitaxial growth. However, it limits Tl–As bond formation for the thermodynamical reasons given above and permits more time for the Tl atoms to move on the surface and reach other Tl atoms. Consequently Tl–Tl bonds are favored and droplet formation could occur. To limit droplet formation, the average diffusion distance of Tl atoms has to be limited and this can be achieved by increasing the growth rate, as observed experimentally. Consequently, optimal growth can be achieved when different conditions are satisfied: (1) enough As pres-

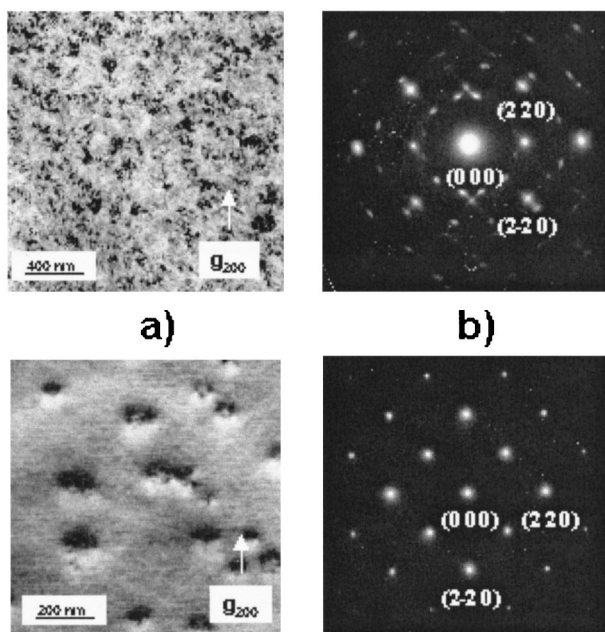


FIG. 9. Plan-view TEM images of (a) twinned and (b) single-crystalline $\text{Ga}_{0.56}\text{In}_{0.40}\text{Tl}_{0.04}\text{As}$ (EP555) layers grown at 230 °C. The corresponding electron diffraction patterns are also shown.

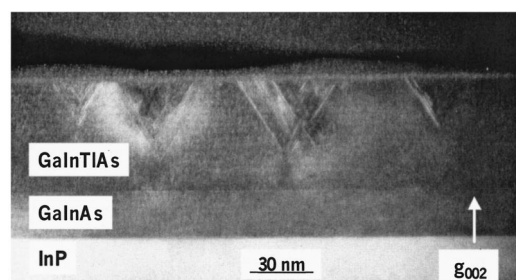


FIG. 10. $[1\bar{1}0]$ directional cross sectional TEM bright field micrograph of single-crystalline $\text{Ga}_{0.56}\text{In}_{0.40}\text{Tl}_{0.04}\text{As}$ (EP555) showing perfect single crystal areas with isolated twins.

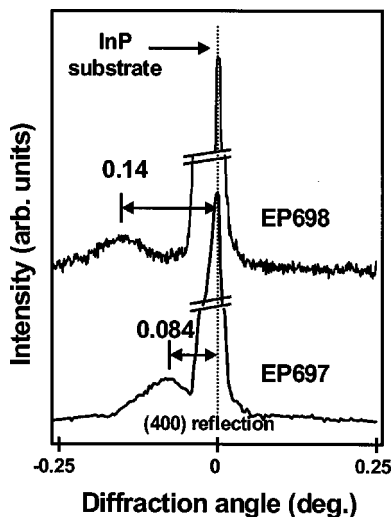


FIG. 11. (004) DCXRD curves for a single-crystalline $\text{Ga}_{0.43}\text{In}_{0.53}\text{Tl}_{0.04}\text{As}$ layer grown at 230°C (V/III BEP ratio=4) and of a reference sample, showing lattice expansion upon Tl incorporation.

sure to help formation of sufficient Tl–As bonds, (2) enough growth rate to limit Tl–Tl bond formation, and (3) enough adatom mobility (temperature, V/III ratio) to allow single crystal growth. We found a set of critical parameters for $\text{Ga}_{0.53}\text{In}_{0.43}\text{Tl}_{0.04}\text{As}$ layers grown at 230°C which lead to epitaxial growth but without reaching perfect structural properties. For most other conditions (higher Tl content, higher As pressure, ...), the growth starts epitaxially and then turns to twinning, a behavior already observed in low temperature epitaxy. Breakdown of crystallinity for GaAs or GaInAs was previously considered to be due to surface roughness built during the early stages of growth.¹⁵ Roughening was associated to low adatom mobility and to some arsenic incorporation which adds additional compressive strain in the epilayer. As for similar conditions used at 230°C , perfect crystal growth is obtained for GaInAs and twinning for GaInTIAs, it appears that thallium atoms favor surface roughening at low growth temperature and help to break down epitaxy. The origin of Tl induced roughening and twinning is not clear yet. It may be related to any of three possible mechanisms: (1) the surfactant behavior of thallium atoms which would decrease the surface mobility of other adatoms, (2) the formation of small Tl clusters, and (3) the alloy demixing into Tl rich and Ga rich areas on the growth front.

In all three cases, the roughening effect is expected to be stronger as the Tl content is increasing.

Finally, we think that the way to decrease surface roughening and achieve single-crystalline layers containing a greater Tl percentage and of better structural quality, would be either to enhance the surface mobility of adatoms (while maintaining enough arsenic overpressure) using for example, mobility enhanced epitaxy or to enhance arsenic reactivity using plasma enhanced epitaxy. Work is in progress in these directions.

V. CONCLUSION

To summarize, we have shown that thallium can be incorporated in GaInAs matrices for low substrate temperatures ($180\text{--}260^\circ\text{C}$) and sufficiently high enough V/III ratios. The higher the expected Tl concentration is, the higher the V/III ratio should be. For high Tl contents, the high arsenic overpressure prevents to achieve single crystal growth and the layers are either amorphous, polycrystalline, or twinned. However a narrow window for single crystal growth has been found for low Tl contents (4%) using optimized growth conditions with low V/III pressure ratios and high growth rates.

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