



# Time-resolved reflectance difference spectroscopy of InAs growth under alternating flow conditions

R. Arès<sup>\*,1</sup>, J. Hu, P. Yeo, S.P. Watkins

*Department of Physics, Simon Fraser University, Burnaby, BC, Canada*

---

## Abstract

We report a time-resolved reflectance difference spectroscopy (RDS) study of the growth of InAs during alternating flow conditions typical of atomic layer epitaxy (ALE). The precursors used were trimethylindium (TMIn) and tertiarybutylarsine (TBAs). For ALE growth we observe that the InAs surface remains As-rich for an appreciable fraction of the 1 monolayer (ML) TMIn pulse. This is similar to results obtained for the growth of GaAs by ALE using trimethylgallium. Three distinct RDS spectra are observed, two corresponding to As-rich phases, and one which is In-rich. In both InAs and GaAs the extra As layer appears to play a key role in maintaining self-limiting behaviour. © 1998 Elsevier Science B.V. All rights reserved.

*PACS:* 78.40.Fy; 78.66.Fd; 81.15.Gh; 82.20.Pm

*Keywords:* Atomic layer epitaxy; InAs; Adsorbates; Surface; MOCVD; Growth mechanisms

---

## 1. Introduction

Surface processes in ALE have generated debate for several years. The main focus has been placed on two distinct phenomena: understanding how the surface regulates the incorporation of the different chemical species under self-limiting growth conditions [1–3], and finding the source and mechanisms

of carbon incorporation [4,5]. Most of the previous work has been performed on GaAs but InAs has also been successfully grown by ALE with a high level of purity using TMIn and TBAs as precursors [6].

In a recent publication we proposed a model for the chemical processes governing ALE of GaAs using RDS as the main analytical technique [7]. Since the known surface reconstructions of GaAs following As-exposure under ALE conditions are known to involve more than one ML of As, it has been difficult to explain how self-limiting growth rates of 1 ML per cycle could be obtained under ALE conditions. We proposed a simple model in

---

\* Corresponding author.

<sup>1</sup> Present address: Nortel Technology, Ottawa, ON, Canada K1Y 4H7. Fax: +1 613 763 4147; e-mail: ares@nortel.ca.

which the excess As is actually required to achieve single ML/cycle growth. In this model the extra outer layer As protects the inner complete As layer from desorption and facilitates the reaction of the incoming group III source in an epitaxial fashion. As evidence for this model we showed by time resolved RDS measurements that an As-rich surface remains As rich despite the addition of over 0.5 ML of trimethylgallium.

In a similar fashion, it has previously been proposed that methyl radicals stabilize the surface coverage of Ga terminated surfaces under ALE conditions [8]. In the absence of methyl radicals, all known Ga-rich surfaces of GaAs consists of less than 1 ML of Ga. In our model both mechanisms are required to give the observed growth rate of 1 ML/cycle. In this work we point out the significant similarities between the growth mechanisms in InAs and GaAs ALE.

## 2. Experimental procedure

The InAs samples were grown in a MOCVD stainless steel 1" vertical reactor manufactured by Thomas Swan. The growths were performed at low pressure (50 Torr) using TMIIn and TBAs as precursors. The hydrogen carrier flow was adjusted in order to maintain a gas velocity through the chamber of 50 cm/s, which allowed switching of precursors and purging of the chamber for less than 0.5 s. The precursor partial pressure in the growth chamber was adjusted at 1.8 mTorr for TMIIn and at 180 mTorr for TBAs. The wafers were (0 0 1)InAs. The chamber is equipped with an optical port and a quartz window for normal incidence measurements. The substrate was heated by a resistive graphite heater on the back of the susceptor. The substrate temperature was monitored using an optical pyrometer looking at the back of the susceptor through a quartz light pipe. A thermocouple in contact with a test sample's surface was used to calibrate the pyrometer reading. The RDS setup is very similar to the one developed by Aspnes et al [9]. It uses front surface optics, quartz and MgF Rochon polarizers, and a 0.1 m grating spectrometer coupled to a photomultiplier tube. The system can either be used in a single wavelength mode

which has an acquisition rate of up to 8 measurements per second, or in energy mode to obtain energy spectra of stable surface reconstructions. The first mode is also used to produce time-resolved RDS spectra of the surface during a dynamic cycle. Since the RDS signal is observed to be highly reproducible during an ALE growth cycle, it is possible to obtain a full energy spectrum of the surface as a function of time by growing a series of ALE cycles and monitoring RDS transients at different wavelength during each cycle. A software triggering system linked to the switching of valves in the system assures the simultaneity of corresponding time points between cycles. After enough cycles have been monitored to cover the energy range, the energy spectra are reconstructed by plotting corresponding time points from each individual cycle.

Growth rate measurements were obtained by growing a few angstroms thick InP marker layer followed by a number (usually 200) of InAs cycles. The cap layer thickness was measured using X-ray diffraction (XRD) by measuring the Pendellösung fringe spacing [10]. The growth rate was then obtained by dividing the thickness by the number of cycles grown.

## 3. Results and discussion

Reflection high energy electron diffraction (RHEED) is normally used to identify the symmetry of surface reconstructions under high vacuum conditions and the corresponding RDS energy spectrum for these structures can be obtained if the appropriate optical setup is available. Several groups have published direct identification of a number of surface structures. For InAs, two reconstructions have been correlated with RDS spectra: the In-terminated ( $4 \times 2$ ) and the As-terminated ( $2 \times 4$ ) structures. We were able to produce surfaces that exhibited the same RDS signature in our system. The ( $4 \times 2$ ) surface was obtained by exposing the surface to a short TMIIn pulse at 390°C. This spectrum, which is shown in Fig. 1, has a strong negative minimum at 1.8 eV, which we attribute to In dimers by analogy to a similar structure in Ga-rich GaAs. The ( $2 \times 4$ ) RDS spectrum

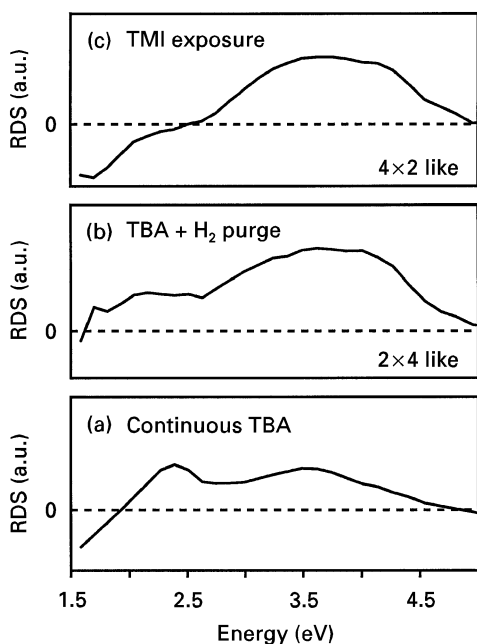


Fig. 1. RDS spectra of stable surface of InAs under typical ALE conditions.

appears after the surface has been exposed to TBAs and then purged with hydrogen for 30 s at 390°C. This spectrum shows a positive feature at 2.4 eV which is presumably due to As dimers as in the case of a similar feature for the  $(2 \times 4)$  GaAs surface. We have also observed a third RDS spectrum when the surface is exposed continuously to TBAs, and which has a different form than the one associated with the  $(2 \times 4)$  reconstruction. In a previous work we labeled this the “As super-rich” spectrum to distinguish it from the  $(2 \times 4)$  [7]. As indicated in Fig. 1, both the ASR and  $(2 \times 4)$  spectra show two positive features corresponding to electronic transitions in the As dimers but the ASR surface has sharper and slightly shifted peaks. The exact dimer structure for these three surface reconstructions is not known at this time. It is important to point out that both the  $(2 \times 4)$  and the  $(4 \times 2)$  spectra are stable for several minutes in our system at 390°C under pure  $H_2$ .

Similar behavior is observed in the RDS spectra of GaAs. During continuous As exposure of GaAs under MOCVD conditions, a  $d(4 \times 4)$  reconstruction is observed. Subsequent purging then results in

a  $c(4 \times 4)$  reconstruction which is believed to consist of approximately 1.75 ML of As. Further purging of this surface results in a  $(2 \times 4)$  reconstruction which is stable for several minutes and which is believed to incorporate somewhat less than 1 ML of As.

### 3.1. Description of As

In order to investigate further the difference between the two As-terminated InAs surfaces observed at 390°C we performed time resolved RDS during the hydrogen purge following TBA exposure. The results are shown in Fig. 2. The top panel shows the RDS signal measured at 2.4 eV as a function of time. The surface is first stabilized under TBAs flow and the RDS signal is constant. At 0 s the TBAs flow is interrupted and the RDS signal quickly drops towards zero (dotted line), at which point it slowly goes back up and eventually stabilizes at a different level after about one minute. The original signal quickly returns when TBAs is introduced in the chamber again. The lower panels show the RDS energy spectra corresponding to different instants of the experiment as indicated by the labels. Spectrum (i) shows the ASR signature typical of the TBAs exposed surface. Spectrum (ii) corresponds to the instant at which the RDS signal is halfway along its course towards zero. The main difference in the RDS response at that point is the reduction in the intensity of the lower energy peak. The higher energy peak is also observed to weaken and spread. It is important to note that although the low energy peak is weaker, it is still not shifted in energy compared to its position in the ASR spectrum. This trend is maintained until the instant of spectrum (iii) where the low energy feature has completely disappeared. Since the anisotropy related to that feature is thought to be related to the presence of As dimers, it is likely that at this point in the process, the dimer structure of the surface is severely disrupted. Spectrum (iv) shows the stable surface under hydrogen purge and corresponds to a  $(2 \times 4)$  As-terminated reconstruction. The low energy feature is observed to grow back, but at a lower energy. Our results show that, like GaAs, the  $(2 \times 4)$  InAs As-terminated surface is stable under hydrogen purge at ALE growth temperatures.

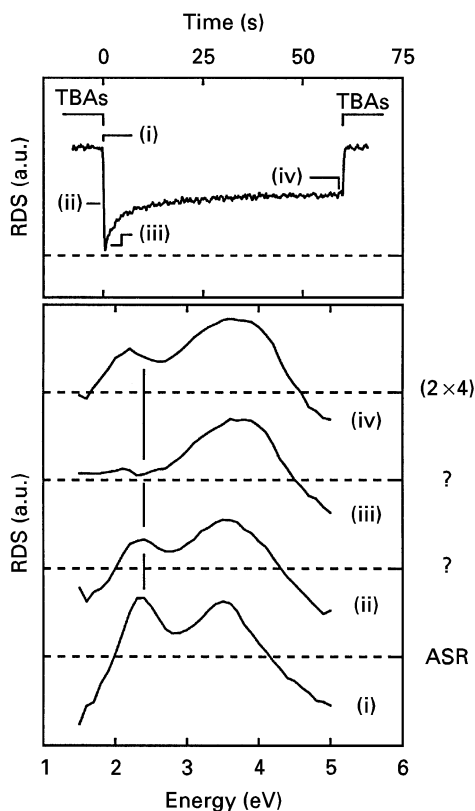


Fig. 2. Time-resolved RDS during As desorption in InAs. The top panel shows the RDS trace at 2.4 eV. Spectra in the lower panel correspond to instants as identified in the top panel.

As we have just shown, the ASR surface transforms in two distinct steps. The first step happens quickly and is characterized by the disappearance of the low energy RDS feature. The second step then slowly takes place as the feature appears again at a lower energy. The difference in rate between the two steps suggests a multiple desorption mechanism. The first, rapid, step takes place as weakly bonded As dimers are broken by the desorption of one or both As atoms. These weak dimers most likely come from the top of a double As layer structure suggesting that the ASR structure consists of a double As layer with a total As coverage of more than 1 ML, in analogy to the  $c/d(4 \times 4)$  surface of GaAs. The second, slower, step happens as the stronger, first layer dimers are created on the surface as the structure forms the  $(2 \times 4)$  reconstruction. The changes following  $H_2$  purging are sugges-

tive of those that occur during similar conditions for GaAs. In that case the  $d(4 \times 4)$  surface for TBAs exposure rapidly changes to the very similar  $c(4 \times 4)$  surface spectrum. In the case of InAs, the ASR spectrum rapidly changes to a surface with little anisotropy at 2.4 eV, suggesting a disruption of the dimer arrangement immediately following TBAs exposure.

We have studied the dynamic properties of the two processes by measuring the temperature dependence of the slope of the RDS signal in the first instants of the process. An Arrhenius plot of this dependence is given in Fig. 3. The activation energies are 49.6 and 58.5 kcal/mol for the “fast” and “slow” mechanisms respectively. Both values are close to the reported energy of formation of  $As_2$  (52.5 kcal/mol) [11], and  $As_4$  (54.2 kcal/mol) [12]. A similar experiment was done on GaAs and the corresponding activation energies were measured to be 59 and 63 kcal/mol [13]. The lower activation energy measured on InAs is consistent with the weaker bond strength in that material.

### 3.2. The ALE cycle

We applied the time-resolved RDS technique to the complete ALE cycle in order to study the evolution of the surface during the process. The cycles were executed at 390°C which was previously determined as the optimal temperature for self-limiting growth in InAs [6]. The flows were also adjusted to their optimal values. In order to allow the surface to stabilize at every step of the cycle, the growth interruptions were made longer. The cycle that was used is: 20 s TBAs, 2 s  $H_2$  purge, 2.5 s TMIIn, 10 s  $H_2$  purge. Only the TMIIn exposure time was kept at the normal ALE value to prevent any loss of morphology which would influence the RDS background. Careful monitoring of the surface roughness during the course of the experiment was performed to ensure that no roughness component was introduced in the RDS spectra. The results are illustrated in Fig. 4.

The top panel shows the RDS trace at 2.4 and 1.8 eV which, based on similarities to the GaAs spectra, likely correspond to As and In dimers, respectively. The two lower panels represent the RDS energy spectra at instants identified by a letter

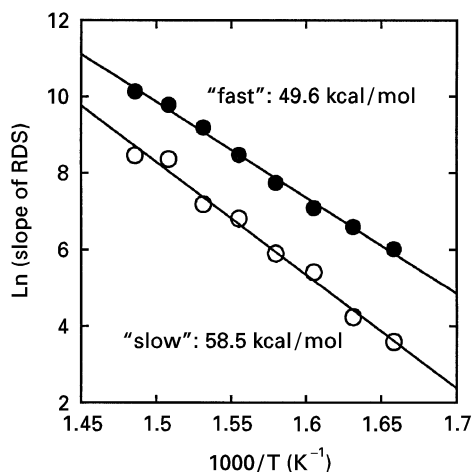


Fig. 3. Arrhenius plot of the two transients observed in the RDS trace of Fig. 2.

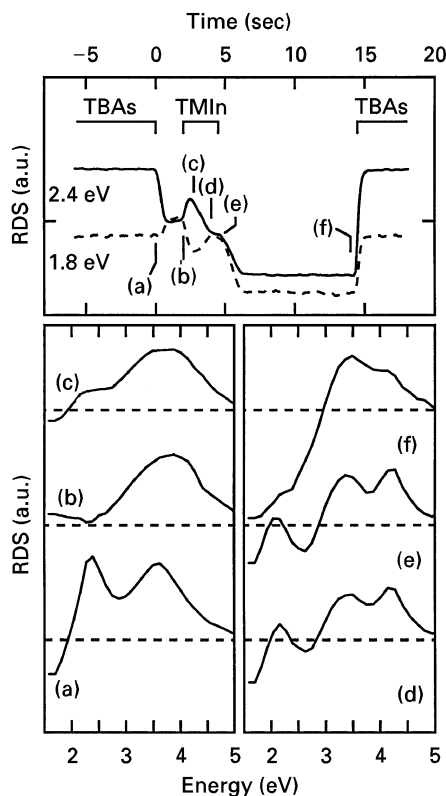


Fig. 4. Time-resolved RDS during an ALE cycle. The spectra in the lower panel correspond to instants as identified on the RDS trace in the top panel.

on the time trace. Initially, under TBAs flow, the surface is stable with an RDS signature corresponding to the ASR structure. Spectrum (a) shows the state of the surface immediately before the TBAs flow is turned off. During the subsequent hydrogen purge the surface goes through the same transformations we discussed earlier with respect to Fig. 2. Spectrum (b) shows the surface just before the TMIn flow is turned on. The RDS spectrum has then completed its fast transformation process and is just starting the slow mechanism. During the first 0.5 s of the TMIn exposure, the 2.4 eV RDS signal becomes positive and reaches a maximum. Spectrum (c) shows the RDS response of the surface at that moment. The shape of the spectrum is close to that of the  $(2 \times 4)$  reconstruction indicating the surface is still terminated with As atoms even though a significant amount of In has already been incorporated into the crystal. This observation was also made in GaAs and we will discuss it further later in this report. At instant (d), XRD measurements of the growth rates of ALE samples under identical TMIn exposure times show that the surface is saturated with In. The RDS spectrum then shows a surface with an undetermined structure. The saturation of the surface is confirmed by the preservation of the spectrum shape until the end of the TMIn pulse at instant (e). This spectrum does not correspond to any reported surface reconstruction. Since the TMIn molecule is expected to decompose via a homolytic fission mechanism, methyl radicals are likely to be present on the surface. The presence of such radicals disrupts the formation of dimers and therefore affects the shape of the RDS spectrum. This effect is discussed later in the report. The presence of methyl radicals on the surface has also been suggested as a regulating force in the self-limiting behavior of the growth by preventing the formation of Ga droplets [7]. When the surface is subsequently purged with hydrogen, the In terminated  $(4 \times 2)$  surface rapidly appears as shown by spectrum (f). The sequence of surface reconstructions for InAs ALE has several similarities with the one observed during GaAs ALE. Both materials have a stable As terminated surface at growth temperature. They do not reach a completely reconstructed group III terminated state until the surface has been purged for some time, and the surface

remains As terminated even after a significant amount of group III source has been incorporated on the surface. These three facts have been identified as critical to the GaAs ALE mechanism [7] and seem to play just as important a role in the growth of InAs by the same technique.

### 3.3. TMI<sub>n</sub> exposure of the surface

The time resolved results have shown that the RDS energy spectrum of the surface remains As terminated for almost half of the exposure time necessary to saturate the surface with In. During an actual RDS cycle however, the surface is in a dynamic state and the observed RDS spectra do not always correspond to known steady state surface spectra. In order to investigate the surface coverage as a function of TMI<sub>n</sub> exposure, we performed the following steps, as was performed in a recent work on GaAs ALE [7]. The surface was first stabilized under TBAs and purged for 2 s as in a typical ALE cycle. A TMI<sub>n</sub> pulse of a given duration was then introduced in the chamber and the surface was purged with H<sub>2</sub> until the RDS signal became stable. In the absence of TMI<sub>n</sub> (duration of 0 s) the resulting surface spectrum after purging is that of the (2 × 4) As rich surface as previously discussed. For finite values of the TMI<sub>n</sub> exposure time however, we observe a spectrum which is a linear combination of the (2 × 4) and (4 × 2) surface spectra depending on the exact exposure time. The RDS spectrum was fitted using the following relation:

$$\text{RDS}_{\text{mixed}} = \alpha \text{RDS}_{(4 \times 2)} + (1 - \alpha) \text{RDS}_{(2 \times 4)}$$

where  $\alpha$  is the fraction of (4 × 2) character.

In Fig. 5 we plot the fraction of (4 × 2) character for the resulting RDS spectra as a function of TMI<sub>n</sub> exposure time. The thin solid line shows the RDS signal at 2.4 eV during the TMI<sub>n</sub> exposure and the thick line represents an interpolation of the growth rate measurements, obtained by XRD, in ML/cycle for ALE samples grown with the same TMI<sub>n</sub> exposure time (from 0 to 4.5 s in 0.25 s intervals).

We observe that the purged surface retains its (2 × 4) character even with a TMI exposure of 0.5 ML/cycle. The surface can therefore incorporate up to 0.5 atomic layer of In and remain As terminated. After 1 s of TMI<sub>n</sub> exposure the purged

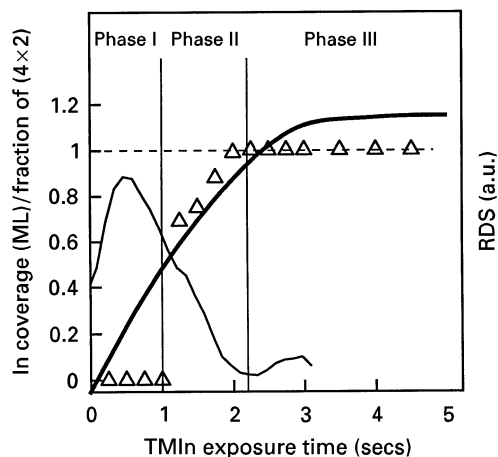


Fig. 5. Overlay of the In incorporated in the layer as measured by XRD (thick solid line) and the (4 × 2) fraction  $\alpha$  of the fit (triangles). The RDS transient at 2.4 eV (thin solid line) is given for comparison.

surface becomes mixed with increasing fractions of (4 × 2) structure. Finally, after 1 ML of TMI<sub>n</sub> exposure the surface spectrum consists of a pure (4 × 2) signature.

These results are very similar to purging experiments performed on the GaAs surface. In that case, the surface was also found to remain As-rich for roughly 0.5 ML of group III incorporation. The data indicate that no In dimers are formed until the surface has incorporated 0.5 ML of In. The TMI<sub>n</sub> molecules arriving at the surface stimulate the desorption of As atoms from the top layer through the liberation of methyl arsenic. The In is then incorporated in the surface as a methylindium group. The methyl group is subsequently desorbed during H<sub>2</sub> purge but the In is not observed to form a dimer. Since no evidence whatsoever of the In rich (4 × 2) surface is seen for the first 0.5 ML, we must invoke a rearrangement mechanism of the surface As whereby the remaining As is uniformly distributed over the surface following purging in order to achieve the observed uniform (2 × 4) surface. Creighton has proposed a mechanism for the rearrangement of the surface As which relies on the presence of step edges [14]. We assume that a similar mechanism could be used to explain the present results.

For exposures greater than 0.5 ML, the surface changes smoothly over to the  $(4 \times 2)$  surface as the coverage of As becomes insufficient to inhibit the formation of the In surface dimers which we assume to be responsible for the  $(4 \times 2)$  surface. Since the surface is observed to saturate at 1 ML of As per cycle under similar ALE conditions, we must assume that all of the excess As is desorbed by the time one ML of In has been deposited.

In the previous picture, the excess As of the ASR surface protects the inner As layer, and ensures that it is complete. In a similar way, methyl radicals have been invoked to explain how a Ga rich surface can be stabilized at 1 ML total coverage while adsorbate free GaAs surfaces with the characteristic  $(4 \times 2)$  surface have only partially complete Ga layers [8]. We assume that a similar mechanism operates in InAs. As evidence of methyl radical desorption, we show in Fig. 6 a plot of the initial slope of the RDS transients at 2.4 eV following purging of the TMIn exposed surface by  $H_2$  at various temperatures. An example of such a signal is shown in the inset along with the corresponding fitted straight line. After  $H_2$  purging, the RDS signal changes towards the level corresponding to the  $(4 \times 2)$  surface. This behaviour is similar to that

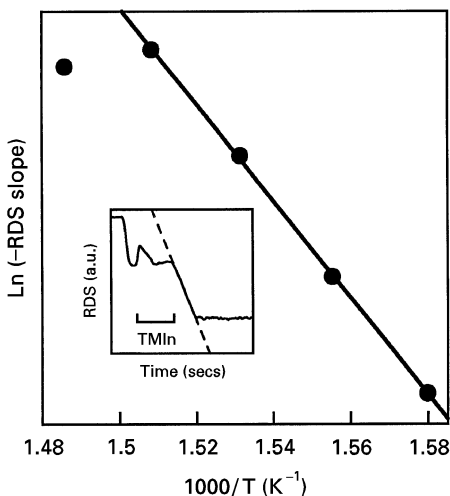


Fig. 6. Arrhenius plot of the RDS transient at 2.4 eV, during the hydrogen purge following TMIn exposure. The inset show a typical fit of the slope of the RDS signal. The corresponding activation energy is 51 kcal/mol.

observed in GaAs for the precursors TMGa and trisneopentylgallium, both of which result in high levels of methyl radicals [15]. In contrast, exposure to triethylgallium followed by  $H_2$  purging was found to produce a very rapid recovery to the  $(4 \times 2)$  surface, with no evidence for radical desorption. The similarity with GaAs growth is an indication that adsorbates, most likely methyl groups, are present on the surface during TMIn exposure. The observed activation energy for this process is 51 kcal/mol. A similar measurement for GaAs produced an activation energy of 59 kcal/mol. The lower energy, measured for InAs, is consistent with a weaker In–methyl bond compared to the Ga–methyl bond.

#### 4. Conclusions

We have reported a study of the growth mechanisms present in ALE of InAs. RDS measurements showed that the state of the TBAs stabilized surface is different from the previously reported  $(2 \times 4)$  surface. The evolution of the TBA stabilized surface during a hydrogen purge proceeds in two steps which have activation energies of 49.6 and 58.5 kcal/mol and ending with a  $(2 \times 4)$ -like surface spectrum. RDS was also used in a time-resolved manner to obtain the energy spectra of the surface during an ALE-like growth cycle. It was shown that the surface remains As-terminated during TMIn flow for almost half of the exposure time. Our results are very similar to our recent model for GaAs in which the group III and group V surface are both stabilized by the presence of weakly bonded adsorbates. The group V surface is apparently stabilized by an extra layer of As. In the case of the group III surface the adsorbate is likely to be methyl radicals as has been proposed for the case of GaAs ALE. This stabilization by adsorbates is responsible for the self-limiting, single ML per cycle growth mechanism in both GaAs and InAs.

#### References

- [1] B.Y. Maa, P.D. Dapkus, *J. Electron. Mater.* 19 (1990) 289.
- [2] P.D. Dapkus, B.Y. Maa, Q. Chen, W.G. Jeong, S. P. DenBaars, *J. Crystal Growth* 107 (1991) 73.

- [3] M.L. Yu, N.I. Buchan, R. Souda, T.F. Kuech, *Mater. Res. Soc. Symp. Proc.* 222 (1991) 3.
- [4] M. Ozeki, *Mater. Sci. Rep.* 8 (1992) 97.
- [5] E. Colas, R. Bhat, B.J. Skromme, G.C. Nihous, *Appl. Phys. Lett.* 55 (1989) 2769.
- [6] C.A. Tran, R. Arès, S.P. Watkins, *J. Electron. Mater.* 24 (1995) 1597.
- [7] R. Arès, S.P. Watkins, P. Yeo, G.A. Horley, P. O'Brien, A.C. Jones, *J. Appl. Phys.* 83 (1998) 3390.
- [8] J.R. Creighton, *Surf. Sci.* 234 (1990) 287.
- [9] D.E. Aspnes, J.P. Harbison, A.A. Studna, L.T. Florez, *J. Vac. Sci. Technol. A* 6 (1988) 1327.
- [10] L. Tafter, M. Ospelt, H. von Känel, *J. Appl. Phys.* 67 (1990) 1298.
- [11] J. Drowart, S. Smoes, Vanderauwera-Mahieu, *J. Chem. Thermodyn.* 10 (1978) 453.
- [12] E.N. Vigdorovich, V.V. Popov, M.M. Artamonov, V.M. Andreev, *Izv. Akad. Nauk. SSSR Neorg. Mater.* 9 (1973) 771.
- [13] Y. Yamaguchi, K. Uwai, N. Kobayashi, *Jpn. J. Appl. Phys.* 32 (1993) 3363.
- [14] J.R. Creighton, *Appl. Surf. Sci.* 82/83 (1994) 171.
- [15] P. Yeo, R. Arès, S.P. Watkins, *J. Electron. Mater.* 26 (1997) 1174.