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In situ study of GaAs growth mechanisms using tri-methyl gallium and tri-ethyl gallium precursors in metal-organic vapour phase epitaxy

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Abstract

A comparative study of GaAs (0 0 1) growth from tri-methyl gallium (TMGa) and tri-ethyl gallium (TEGa) was performed in metal-organic vapour phase epitaxy. The growth surfaces were characterised by reflectance anisotropy spectroscopy (RAS). Three distinct shapes of the RAS spectra typical for certain growth parameter regions were observed for both precursors. The RAS spectra typical for the growth at low temperatures correspond to kinetic limited growth and the surface is covered by adsorbates. At slightly higher temperatures in mass transport limited growth mode, a more gallium-rich surface appears with both precursors. In the case of TEGa, the lack of arsenic on the surface below 500°C is simply due to the lack of decomposed AsH_3. However, using TMGa gallium-rich surfaces are already found below 600°C. We propose steric hindrance of As diffusion by methyl groups around the incorporation sites and forced arsenic desorption by the formation of methyl arsine as the cause. At typical buffer growth temperatures above 600°C, the surfaces during growth are identical to the AsH_3 stabilised arsenic-rich pre-growth surfaces for both gallium precursors.

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1. Introduction

The growth of gallium arsenide in metal-organic vapour phase epitaxy (MOVPE) has been investigated for more than 30 years. Even in the first publication on crystal growth in MOVPE tri-methyl gallium (TMGa) and tri-ethyl gallium (TEGa) were used [1], and both have been used ever since. The choice of the precursor is mostly

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related to the desired growth task, e.g. TMGa is dominant for (Al)GaAs, while TEGa often is used for InP-based GaInAsP. However, for standard tasks like buffer growth both precursors are equally qualified.

There are many studies on the decomposition mechanism of the different precursors (overview, e.g. Ref. [2]). The consent is that TMGa decomposes in the vapour phase by the formation of methyl radicals ($\cdot CH_3$) up to mono-methyl gallium ($GaCH_3$) [3], which arrives at the surface:

$$\begin{aligned} &Ga((CH)_3)_3 + R\cdot \rightarrow \cdot Ga((CH_3)_2 + R{-}CH_3,\\ &\cdot Ga((CH_3)_2 + R\cdot \rightarrow : GaCH_3 + R{-}CH_3 \end{aligned} \quad (1)$$

The 50% decomposition temperature is at about 450°C using hydrogen as carrier gas. Using helium or nitrogen instead, the decomposition temperature is 20–30°C higher [4–6]. Thus, using TMGa many methyl groups are present on the surface during growth, especially at lower temperatures. The carbon originating from these methyl groups is easily incorporated, and can cause intrinsic p-doping up to about $5\times10^{19}\,cm^{-3}$ at low V/III ratios, depending on the surface conditions (e.g. Ref. [7] and references therein).

TEGa on the other hand decomposes via β-elimination

$$(CH_3{-}CH_2) - Ga{-}R \rightarrow CH_2 = CH_2 + H{-}Ga{-}R, \quad (2)$$

forming GaH_3 and three ethylene (C_2H_4). The temperature of 50% decomposition is about 300°C [4,5,8,9] which is much lower than typical growth temperatures. Thus, only very little carbon reaches the surface during growth.

However, most studies have been focussing on the decomposition in the vapour phase. The mechanisms on the surface are less well understood, even though in situ reflectance anisotropy spectroscopy (RAS) has been used for more than 10 years to successfully compare surface under well-controlled ultra-high vacuum conditions [10] with surfaces during MOVPE [11]. Therefore, we were especially interested in the direct comparison of the surfaces during growth using TMGa or TEGa, which has not been made so far by in situ RAS.

2. Experimental procedure

The experiments were performed in a double-wall horizontal quartz reactor (Aix 200/4) equipped with a purged strain-reduced window allowing in situ measurements. The RAS system used is an EpiRAS 200 with the ability to measure also on rotating samples. The difference of the thermocouple reading to the surface temperature was verified by an SiAl eutecticum to be less than 10°C [12]. The carrier gas was hydrogen (11 l/min) at a total pressure of 15 kPa, the AsH_3 (arsine) partial pressure was 120 Pa. The gallium source for buffer growth was always TMGa.

We used two TMGa lines and one TEGa line in the growth system. A TMGa partial pressure of 0.75 Pa resulted in a growth rate of 670 nm/h at 600°C using the TMGa line for higher flows. All other partial pressures were normalised to this growth rate. This was especially important for TEGa growth and comparison with literature data.

The substrates were Si-doped (0 0 1) epi-ready GaAs wafers with a miscut of 2° towards [0 0 1], since these substrates are widely used for device production. An earlier study using TMGa and AsH_3 found no significant differences for miscut angles up to 2° [13], so that the results presented here should also be valid for exact orientation.

3. Surface types during growth

For the characterisation of the surfaces during growth the respective RAS spectra were classified by their typical shape and assigned to a group of typical spectra or as intermediate spectra. During growth using TMGa and a constant AsH_3 partial pressure three typical RAS spectra—called phases—have been observed [7,13–16]. Only at reduced AsH_3 partial pressures and using V/III ratios near to unity, another fourth phase was observed [7]. From our measurements with TEGa we found also three distinct phases. Fig. 1 compares the RAS spectra of these phases for TMGa and TEGa. Despite the different decomposition pathways for the two precursors the

typical spectra are very similar. The resulting phase diagram is shown in Fig. 2.

Phase I corresponds to growth near equilibrium, i.e. all precursor-related processes are fast compared to the growth rate. The AsH_3 stabilised surface RAS spectrum and the RAS spectra during growth for a given temperature are very similar. Thus, the surfaces during growth are comparable to the pre-growth surfaces. All those surfaces are relatively arsenic-rich with the actual As coverage strongly depending on temperature and substrate misorientation. At the elevated temperatures in phase I, AsH_3 decomposition is nearly complete, so As desorption from step-edges limits the actual surface arsenic coverage [13]. On a singular GaAs substrate below 600°C the surfaces typically are c(4 × 4)-like reconstructed, but with increasing miscut the surfaces get less arsenic-rich due to increasing As desorption from the step-edges [13].

For phase II, the minimum of the RAS spectrum is at lower energies around 2 eV (Fig. 1). Such spectra can be modelled by a linear combination of RAS spectra of $(n \times 6)$ and $d(4 \times 4)$ surface reconstructions [21]. This indicates the presence of gallium dimers during growth. On vicinal surfaces the effect is even more pronounced: on a 6° misoriented surface the spectrum under phase II conditions resembles entirely that of an $(n \times 6)$ surface reconstruction [13].

Finally, at low temperatures a third phase (phase III) can be found. The corresponding spectrum is similar to that of the very arsenic-rich pre-growth $d(4 \times 4)$ surface reconstruction, but the peak at around 2.6 eV is a little sharper while the peak in the UV region is shifted by about 0.4 eV to higher energies. In phase III, the growth rate depends strongly on temperature, due to steric hindrance of adsorbates from the incomplete Ga precursor decomposition. In Fig. 2, crossed diamonds indicate values from literature for the transition from the mass flow limited mode to the kinetic limited growth mode (reduced growth rate) [12,17–20] which corresponds nicely to the border to phase III. In the case of TMGa, the surface during growth was identified as an arsenic and methyl-rich (1×2)-CH_3 surface structure by

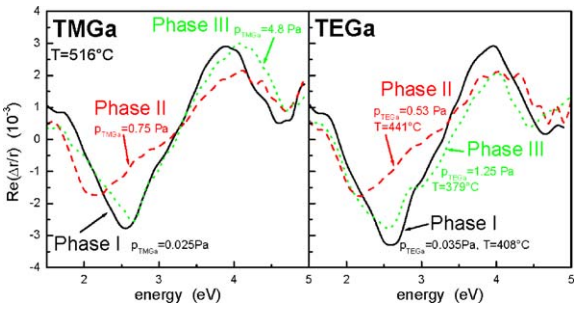

Fig. 1. Typical RAS spectra measured during growth on a GaAs (0 0 1) 2° AB substrate using either TMGa (left) or TEGa (right).

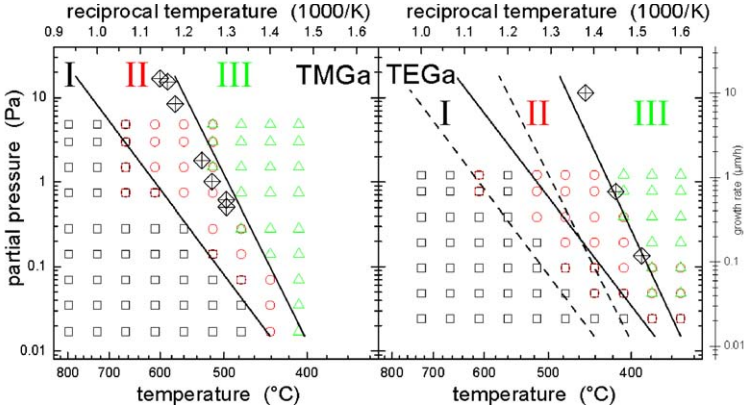

Fig. 2. Phase diagram during growth using TMGa (left) and TEGa (right) on a GaAs (0 0 1) 2°AB substrate. The crossed diamonds in the diagrams mark transition points from mass flow to kinetic limited growth (from Refs. [12,17–20] and own data). The lines mark the phase boundaries (dotted lines for TMGa boundaries in the right figure).

comparing RAS spectra during growth and spectra of well prepared surfaces in an UHV chamber [15].

4. Comparing growth using TMGa or TEGa

The main difference between the phase diagrams in Fig. 2 using TMGa (left) and TEGa (right) are the different temperature regions for the three phases. Using TEGa instead of TMGa seems to shift the phase boundaries to about 100–150°C lower temperatures. On the other hand, the RAS spectra in Fig. 1 are surprisingly similar, which points to similar surface structures on these surface even though at different temperature regimes.

In the case of phase I, i.e. the fast kinetic regime, similar spectra for both precursors are expected. Since the spectra are identical to the ones of an AsH_3-stabilised surface, the choice of precursor does not affect the surface. Precursor decomposition and surface processes are much faster than the growth rate.

In phase II at lower temperatures, but still in the mass transport limited regime, the minimum in the RAS spectra is at 2 eV. As said above, parts of the surface are covered by a relatively gallium-rich $(n \times 6)$-like reconstruction, and overall the surface is less arsenic-rich compared to phase I. In other words, the incorporated gallium is not covered by arsenic immediately. A simple explanation would be that at these temperatures the decomposition of AsH_3 is not sufficient. The mean temperature for 50% decomposition of AsH_3 is 575 ± 50°C (e.g. Refs. [2,5]). Since typical V/III ratios are higher than 100, probably the temperature for 10% decomposition (about 520°C) is more important to sustain an arsenic-rich surface. This temperature corresponds indeed to the appearance of phase II for the case of TEGa. With TMGa, the surfaces become gallium-rich at even higher temperatures.

Therefore, another explanation is needed for the TMGa case. As noted before, the main difference between TMGa and TEGa are their decomposition pathways. Using TMGa mono-methyl gallium (MMGa, CH_3Ga) is the main surface species at higher temperatures (above 470°C) [20]. TEGa undergoes mainly a β-elimination, the resulting species is in principle GaH_3, a much more volatile species. Thus, the main difference must originate from the methyl groups. Normally, it is assumed that the methyl groups are still present on the surface after incorporation of the gallium by the formation of one or two covalent bond. The methyl groups desorb only after reaction to methane with hydrogen from AsH_3 decomposition. Atomic hydrogen on a GaAs surface has a very short lifetime at these elevated temperatures. The desorption temperature on a (2×4) reconstruction in vacuum was less than 300°C [22]. Since the methyl groups have a small probability of meeting hydrogen, they may rest long enough on the surface to act in many ways, e.g. they could block further adsorption of AsH_3 on the surface, although a selective blocking of the smaller AsH_3 (compared to Ga precursors) only would be quite unexpected. (The methyl group are certainly blocking further attachment in phase III, when the growth rate drops.)

Another way would be blocking the AsH_x species diffusion towards the just incorporated gallium. Since the gallium is preferably incorporated at the step-edges (due to tighter binding there) around the step-edges a higher concentration of methyl groups is expected. These methyl groups may prevent surface diffusion of AsH_x to the step-edges, and around the steps larger gallium-rich areas would form. Instead of blocking, the methyl groups could enhance As species desorption, by the formation of volatile methyl arsine which has been actually measured [5,6,23]. By this way, arsenic would be removed from the surface before it can reach to the gallium-rich regions at the step-edges.

Fig. 3 shows the temperature dependence of the formation of methyl arsine from literature data. It is mainly observed between 400°C and 600°C with a peak around 500°C. The peak concentration corresponds nicely with the appearance of phase II in our experiments (black arrow bar in Fig. 3). The limit at high temperatures is the stability of the methyl arsine itself: tri-methyl arsine has a decomposition temperature of about 600°C. The significance of methyl arsine for the growth

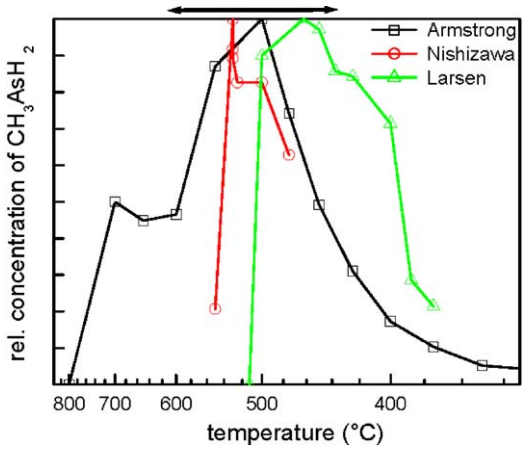

Fig. 3. Production of mono- or di-methyl arsine ($(CH_3)_xAsH_{3-x}$) during MOVPE growth using TMGa and AsH_3 measured by IR-adsorption and mass spectroscopy (Nishizawa (IR) [23], Armstrong (IR + MS) [5], Larsen (MS) [6]). The black arrow bar marks the phase II temperature region in our experiments.

process has been discussed at the beginning of the 1990s [5,6,23]. Due to its very small concentrations (about 1% or less) it was judged as being not important for the actual decomposition in the vapour phase. However, this does not exclude an important role at the substrate surface, since the substrate area is small compared to the total reactor or susceptor area.

Thus, we propose the following model for the origin of the gallium-rich surfaces in phase II. Using TMGa many methyl groups reach the surface as mono-methyl gallium. Since these methyl groups are released, when the gallium is incorporated—mostly along step-edges—a high concentration of methyl is present near the incorporation sites. However, this is only a small part of the surface and does not influence the RAS spectrum. But to cover the gallium by arsenic, the arsenic species must diffuse through this methyl-rich region. Therefore, these methyl groups can prevent diffusion of AsH_x to the steps and can also remove AsH_x by forming volatile methyl arsine which desorbs. Thus the surface becomes less arsenic-rich, even at higher temperatures. Using TEGa, the As-deficient phase II simply occurs due to the decreased AsH_3 decomposition, while the TEGa decomposition still is 100%.

Contrary to phase II, phase III has the same origin either using TMGa or TEGa. Phase III is clearly correlated to kinetic limited growth, indicated by a drop of the growth rate. The different temperatures for the appearance of phase III with TMGa and TEGa simply reflect the different activation energies for precursor decomposition. In phase III adsorbates from undecomposed precursor are present on the surface, hindering further attachment or incorporation and increasing the carbon incorporation. Intrinsic carbon doping from partly decomposed precursor adsorbates has been well studied for TMGa (i.e. Refs. [7,15]) and is used for the growth of devices. However, also with TEGa high carbon concentrations can be reached, e.g. for growth at 400°C with $p_{TEGa} = 1.7$ Pa we measured a hole concentration higher than 10^{19} cm^{-3}.

The similar spectra during growth in phase III from both precursors might indicate that the adsorbate covered surfaces are similar for both precursors. In the case of TMGa the underlying structure was an (1×2)-CH_3 reconstruction [15]. For TEGa, the ethyl groups of the TEGa may partly split into methyl groups, or analogue to TMGa [15] a (1×2)-C_2H_5 reconstruction is also quite possible. The RAS spectra for methyl or ethyl adsorbates on the same (1×2) surface structure would be expected to be similar, because the adsorbate bond is mostly facing upwards, and thus is not anisotropic.

5. Conclusion

We present the first in situ comparison of growth with TMGa or TEGa using RAS. During growth with a constant AsH_3 partial pressure three different phases can be found. At high temperatures, growth and pre-growth surfaces are nearly the same and all processes on the surfaces are fast compared to the time for the growth of one monolayer. At very low temperatures, corresponding to kinetic limited growth (phase III), the surfaces are covered by adsorbates from undecomposed precursors which prevent attachment and thus lower the growth rate and increase carbon incorporation. At intermediate

temperatures in the mass transport limited regime (phase II) the surfaces becomes gallium-rich during growth. Using TEGa the gallium-rich surfaces are found for temperatures between 400°C and 500°C, a region where TEGa decomposition is nearly complete, while AsH_3 decomposition is less than 10%. However, with TMGa these gallium-rich surfaces appear at 100°C higher temperatures when most of the AsH_3 is decomposed. To explain the difference, we propose methyl groups around the incorporation sites which are hindering As surface diffusion and promote methyl-induced arsenic desorption.

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