Comparison of Heterointerface Growth Procedures using High-Growth-Rate Hydride Vapor Phase Epitaxy

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Abstract

Hydride vapor phase epitaxy has several potential benefits over existing growth technologies for the deposition of high-quality III-V materials and devices. Amongst these is the ability to achieve extremely high growth rates. However, due to the *in situ* generation of group III reactants, it becomes difficult, if not impossible, to produce abrupt heterointerfaces in a single growth chamber as is done using other deposition techniques. Here, we show the impact of high growth rates on heterostructure formation, and the improvement achieved by using independent growth chambers. This approach also leads directly to the possibility of a fully inline deposition system for extremely high throughput of III-V devices.

INTRODUCTION

Hydride Vapor Phase Epitaxy (HVPE) recently reemerged as a viable growth technique for high quality III-V materials



Fig. 1. Drawing of the traditional HVPE process (top) and the D-HVPE technique (bottom) contrasting the achievable interface abruptness.

and devices [1], despite being largely supplanted by other growth technologies in the 1980s due to challenges with the technique. Recent developments led to critical advances that allowed HVPE to solve several key problems that plagued it in the past, including the effects of a large kinetic barrier to growth that created difficulties controlling growth rates and alloy compositions and a lack of viable precursors for the formation of Al-containing compounds. These challenges are largely solved [2-4]. However, the very high growth rates achievable with HVPE lead to additional difficulties. HVPE possesses significant chemical inertia due to the use of in situ generated precursors, which can lead to the growth of unintentional alloys, non-abrupt interfaces, and the formation of extended defects due to accumulated strain. Here, we show that the promise of HVPE relies largely on the use of multiple growth chambers to achieve excellent heterointerfaces at these high rates. This process has the additional benefit that it translates directly into the possibility of a high-throughput, inline production reactor design that can produce III-V devices at high rate with the same quality as other growth technologies.

HVPE'S HIGH GROWTH RATE "PROBLEM"

We previously used HVPE to achieve GaAs and GaInP growth rates $> 500 \mu$ m/h and $> 200 \mu$ m/h [2, 5], respectively, with high material quality, and it's clear that no fundamental limit has yet been reached. This allows us to deposit singleand multi-junction solar cell structures in minutes as opposed to hours. However, device structures requiring chemicallyand structurally-abrupt heterointerfaces, such as solar cells and most other III-V devices, cannot make use of highgrowth-rate HVPE in a single growth chamber like is currently done with batch-style molecular-beam epitaxy (MBE) or organometallic vapor phase epitaxy (OMVPE) systems. HVPE possesses significant chemical inertia due to the *in situ* generation of the volatile metal chlorides used as the group III growth species in this reaction. We form metal chlorides from the reaction of anhydrous HCl and an elemental metal such as Ga or In in an ampoule inside the growth chamber. HCl and a carrier gas enter the ampoule, the HCl reacts with the metal, and the generated volatile chloride is then transported to the substrate for growth. Switching to the growth of a different material requires that the gas in this interior volume be replaced with gas flows appropriate for the new alloy, which takes time. Contrast this with growth technologies like OMVPE or MBE. MBE uses shutters in an ultra-high vacuum environment to achieve exquisite control of interfaces, while OMVPE is mass-transport limited and uses precursors that do not typically intermix in the gas delivery plumbing, leading to the sequential deposition of materials. There is no analogous way to abruptly switch materials in an HVPE system because of the in situ precursor formation. The switching time in an HVPE system is design dependent but can be significant. We measured this switching time in our HVPE reactor, for typical total gas flows of ~8 SLM, to be in the range of 30 - 35 sec [6]. Even at a relatively modest (for HVPE) growth rate of 1 µm/min there will be a transition region from the growth of the first material to the second on the order of 0.5 µm thick. This is obviously untenable for devices that require abrupt interfaces but will also likely cause dislocation formation through the deposition of an unintentional, graded alloy that is unlikely to be lattice matched to the rest of the structure. The solution to this issue is not to change the precursor flows to deposit different alloys, but to move the wafer between adjacent growth chambers that each contain steady-state reaction conditions. Fig. 1 shows drawings of these two processes. The top panel in Fig. 1 shows the formation of an unintentional "purple" material at the interface between the desired red and blue materials. However, moving the wafer, depicted in the bottom panel, yields an abrupt heterointerface appropriate for high-quality device performance. The idea of moving a wafer between chambers is certainly not new [7-10], but HVPE's high growth rates require this approach to fully benefit from the technology. The use of multiple growth chambers allows for the deposition of arbitrarily complex device structures at high rate and overall throughput with excellent material and interface quality.

HETEROINTERFACE IMPROVEMENT VIA MULTIPLE GROWTH CHAMBERS

HVPE growth in our custom-built reactor proceeds by shuttling a 2" substrate between two adjacent growth chambers in a process we label Dynamic-HVPE (D-HVPE). Fig. 2 shows a schematic representation of our D-HVPE system. Moving the substrate between chambers, which in our system takes ~ 2 sec, leads to the chemically- and structurallyabrupt heterointerfaces represented in the bottom panel of Fig. 1. D-HVPE allows us to build up essentially any type of device stack by growing a material in one chamber while preparing for growth of another material in the other chamber.

To show why multiple chambers are required when using high deposition rates in HVPE, we grew and measured several double heterostructure (DH) samples using time-resolved photoluminescence (TRPL) to understand the changes in sample quality when using different procedures. These samples consist of a GaAs base layer clad with GaInP on both the top and bottom, as shown in the inset of Fig. 3. The GaAs



Fig. 2. Schematic representation of a D-HVPE reactor with two adjacent growth chambers.

and GaInP growth rates were ~ 1 μ m/min and 0.03 μ m/min, respectively. We grew two sets of samples. We also contemplated growing a third set of DH structures that would be produced all in one growth chamber by only switching the gases to produce the different materials. We expect, based on previous experience, that these samples would include the deposition of thick, graded (Ga,In)(As,P) material where the abrupt interfaces should be, much like that shown in the top panel of Fig. 1. Therefore, we did not expect that these would be appropriate for comparing different growth procedures on the formation of *abrupt* interfaces.

The first set of DH samples used the D-HVPE process, with the adjacent growth chambers set up with reactants for



Fig. 3. TRPL analysis of DH structures grown using either stop growths or the D-HVPE process. The sample structure used is inset in the figure.



Fig. 4. Raw TRPL decay curves for D-HVPE-grown DH structures (top) and stop-growth samples (bottom). Note the smaller x-axis range for the stop-growth structures.

GaAs in one and GaInP in the other. The substrate was moved between the growth chambers to create the DH structure.

The second set of DH samples was also grown using a single growth chamber, but this time stop growths were used to allow sufficient time for the chamber gases to reach steady state with the new growth chemistry before growth recommenced. That is, the substrate was protected under an arsine (phosphine) overpressure in a buffer chamber while the process gases switched from GaAs to GaInP (GaInP to GaAs) in the growth chamber. This sample set allowed for the formation of samples with abrupt interfaces, although we acknowledge that stop growths tend to be avoided in practice.

This was, however, the only available route to create samples with abrupt interfaces in a single growth chamber.

The TRPL analysis in Fig. 3 shows that both the bulk lifetime of the GaAs base layer and the interface recombination velocity (IRV) improve markedly by using the D-HVPE approach. Fig. 4 accentuates this finding by comparing the raw luminescence decay signals from the two sets of samples. Fig. 4 (top) shows the decay curves for samples with different base thicknesses grown using the D-HVPE method. These curves are close to single-exponential decays with long minority-carrier lifetimes. Fig. 4 (bottom) shows the decays for the stop-growth process. These are clearly not single-exponential and likely suffer from trap states at the interface. Interestingly, the bulk lifetime is also lower for these samples indicating that the degradation extends beyond the interface and into the base layer.

IMPACT OF FUTURE DEVICE PRODUCTION

Clearly, the D-HVPE process leads to higher material and interface quality compared to the need for stop growths, but it has additional benefits over today's batch growth methods. Indeed, it is trivial to consider the extension of the twochamber growth system shown in Fig. 2 to an arbitrary number of chambers comprising a fully-in-line deposition system. Fig. 5 shows a possible version of an in-line D-HVPE reactor that is configured for solar cell growth. However, many III-V devices, including solar cells, lasers, LEDs, rf components, etc., use the same materials in different combinations to achieve different goals. A modular D-HVPE system could be configured to deposit any arbitrary device structure with potential throughput measured in 100's of thousands to a million wafers per year, from just this one system, which will greatly increase the availability and lower the cost of III-V materials and devices.

CONCLUSIONS

The use of multiple growth chambers is virtually required to take advantage of the high-throughput capabilities of HVPE growth. The *in situ* generation of reactants leads to the



Fig. 5. Schematic of a fully-in-line production D-HVPE reactor set up for the growth of high-efficiency solar cells.

need to flush and reestablish gas flows when switching from the deposition of one material to another, which takes ~ 30 sec in our 2" wafer HVPE system. Stop growths can provide the necessary time for the system to equilibrate at new growth conditions and lead to abrupt interfaces, but TRPL measurements show both increased IRV and decreased bulk lifetime in DH samples grown in this way. Using multiple growth chambers set up with steady state flows for GaAs and GaInP led to DH structures with much better IRV and bulk lifetime. This process also leads to the vision of a fully in-line deposition system for very high throughput of III-V materials and devices.

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ACRONYMS

- HVPE: Hydride Vapor Phase Epitaxy MBE: Molecular Beam Epitaxy
- OMVPE: Organometallic Vapor Phase Epitaxy
- D-HVPE: Dynamic Hydride Vapor Phase Epitaxy
- DH: Double heterostructure
- TRPL: Time resolved photoluminescence
- IRV: Interface recombination velocity