Dynamic Hydride Vapor Phase Epitaxy (D-HVPE) as a route to inexpensive, high-performance III-V materials and devices

John Simon, Kevin L. Schulte, Wondwosen Metaferia, Alessandro Cavalli, and Aaron J. Ptak

National Renewable Energy Laboratory, 15013 Denver West Parkway, Golden, CO 80401-3305

Keywords: Hydride Vapor Phase Epitaxy, III-V materials, III-V devices, high throughput, low cost

Abstract

This work describes the recent development of Dynamic Hydride Vapor Phase Epitaxy (D-HVPE), which extends the standard HVPE process to allow for the deposition of relatively complex heterostructures and devices at growth rates in excess of 300 µm/h. This process uses low-cost elemental metal precursors, and uses all of the reactants efficiently to create high-performance devices. D-HVPE also lends itself to potential in-line growth, which when combined with the low-cost precursors and extremely fast growth rates for high-quality III-V materials, can lead to significantly lower epitaxial growth costs. Here, we focus on the growth of high-efficiency photovoltaics as an example device to show the capabilities of the D-HVPE growth process.

INTRODUCTION

III-V materials such as GaAs and GaInP have some of the best electronic and optical properties of any semiconductors, including high electron mobilities that enable high-frequency transistors for wireless communication applications, and direct bandgaps, which permit exceptionally efficient absorption and emission of light. For example, III-V photovoltaic (PV) devices hold record conversion efficiencies for both single and multijunction solar cell devices [1]. III-V PV can also be 1-2 orders of magnitude thinner than industry-dominant Si due to their direct bandgaps, yielding the highest power-to-mass (W/kg) and power-to-area (W/m^2) ratios, while also maintaining high conversion efficiency in flexible form factors. III-Vs are readily integrated into more complex multijunction solar cell structures that increase efficiency far beyond single junction limits, increasing their value.

Despite these advantages, the cost of III-V materials and devices remains high compared to other prevalent semiconductors, particularly Si. III-Vs have historically focused on performance with less regard to costs, and their pervasiveness in the space industry did not provide a driving force to drastically lower costs in the same way as the development of CMOS did for Si. PV potentially provides a sizeable market for III-Vs that could apply significant opportunity to reduce epitaxy costs, and it is possible that other devices, including the power amplifiers used in cell phones, as well as light-emitting diodes (LEDs), lasers, and other devices, could benefit from the cost reductions that would come with increasing III-V PV deployment.

Much of the cost of a finished III-V device, especially in PV, is in the deposition process where high-value molecules such as trimethylgallium and trimethylaluminum are used as precursors during semiconductor growth using metalorganic vapor phase epitaxy (MOVPE) [2]. The typically low growth rates for III-V materials and the low throughput of today's batch growth systems also contribute to the relatively high cost of III-V devices. Hydride vapor phase epitaxy (HVPE) is a decades-old technique that is well-known for producing low-defect III-V materials at extremely fast rates, due in large part to the low kinetic barrier of the growth process. HVPE uses elemental metal precursors, e.g. Ga and In, which are approximately an order of magnitude less expensive than the metalorganic molecules that they replace. HVPE also demonstrated GaAs growth rates up to 300 µm/h [3]. Historically, however, the ability of HVPE to produce relatively complex devices with clean, defect-free, abrupt heterointerfaces paled in comparison to other growth techniques such as MOVPE and molecular-beam epitaxy (MBE).

Here, we describe the recent enhancement of the HVPE process, called *Dynamic*-HVPE (D-HVPE) that allows the HVPE process to finally fulfill its promise of the production of high-performance devices with complex structures at extremely high growth rates, all while using low-cost precursors. We describe recent progress showing high-efficiency solar cells using D-HVPE, and show that the growth platform is appropriate for a wide range of devices. This indicates that D-HVPE can potentially be useful to reduce the cost of any application that relies on defect-free, epitaxially grown III-V materials

DEVELOPMENT OF D-HVPE FOR III-V DEVICES

Traditional HVPE suffers from the fact that the *in situ* generation of reactants inside a hot wall reactor contains some inertia, meaning that reactant flows cannot be changed quickly enough to obtain abrupt heterointerfaces. For example, the formation of a GaAs/GaInP heterointerface first requires generation of GaCl from elemental Ga and anhydrous HCl to form the GaAs side of the heterointerface. Deposition of GaInP requires both GaCl and InCl, but the delay in the time between turn on of HCl flow to the In source

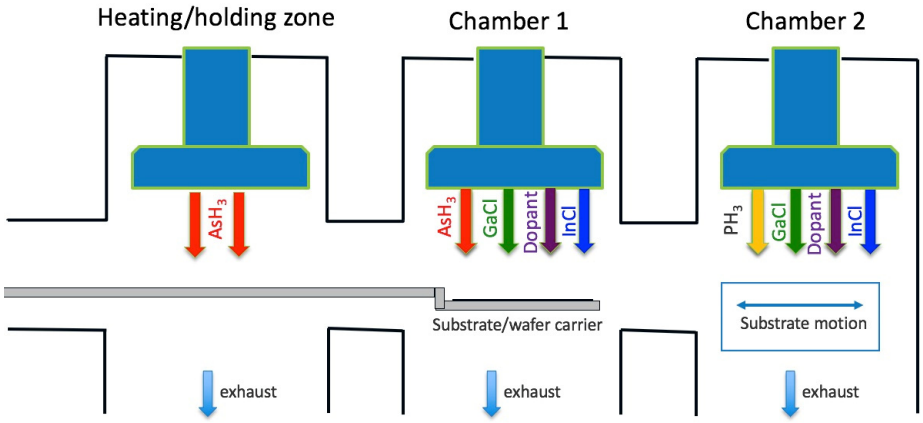

Fig. 1. Schematic representation of the D-HVPE process. The substrate moves horizontally between independent growth chambers that are each have an established steady-state reaction for the material of interest, e.g. GaAs or GaInP. The wafer moves from one chamber to the next in approximately 1-2 sec to create abrupt and defect-free heterointerfaces.

and the time that a steady-state flow of InCl out of the source occurs results in grading of the heterointerface, which is significantly exacerbated at high growth rates. These graded interfaces are detrimental to device performance for solar cells and other III-V devices [4]. In traditional HVPE, switching between the growth of two different materials requires a "growth interrupt", during which impurities can accumulate on the surface of the wafer leading to defective and ineffective interfaces. The recent development of D-HVPE, which uses substrate motion at high temperature between different growth chambers, as depicted in Fig. 1, obviates this problem and leads to the successful growth of abrupt and defect-free interfaces, enabling high-efficiency devices [5-7]. D-HVPE combines the ability of traditional HVPE to deposit many III-V alloys at high rate with low bulk defect densities, with the ability to form abrupt, defect-free interfaces, all without sacrificing throughput or quality. The general idea of substrate motion through different growth chambers depicted in Fig. 1 is clearly extendable to a fully in-line system, similar to the version shown in Fig. 2. Here, the thickness of any particular device layer can be tuned either by regulating the growth rate in any of the independent growth chambers, or by adjusting the length of that chamber. A recent roadmap for lowering the costs of III-V PV showed that the D-HVPE process could potentially allow for significant penetration of III-Vs into terrestrial markets [8], something they are currently unable to do with today's more established growth techniques. This concept is also agnostic to the type of device grown. For example, each individual chamber could be capable of growing a range of alloys from the (Al, Ga, In)(N, P, As, Sb) family of materials, thereby providing flexibility in the growth process and allowing for the realization of many important III-V device structures.

Material and Device Development using D-HVPE

Growth rate is an area where HVPE excels. Increasing the growth rate leads to lower costs by increasing the amount of material produced by a single production tool [8, 9], so long as there is no degradation in material quality. Previously, HVPE was used to demonstrate GaAs epilayer growth rates of 300 µm/h [3], although the limitations of traditional HVPE did not allow for the demonstration of high-efficiency devices.

The D-HVPE process, however, allows for the production of devices with the heterointerface quality necessary to support high-performance. In the case of PV, the open-circuit voltage (V_{OC}) represents an excellent proxy for "high

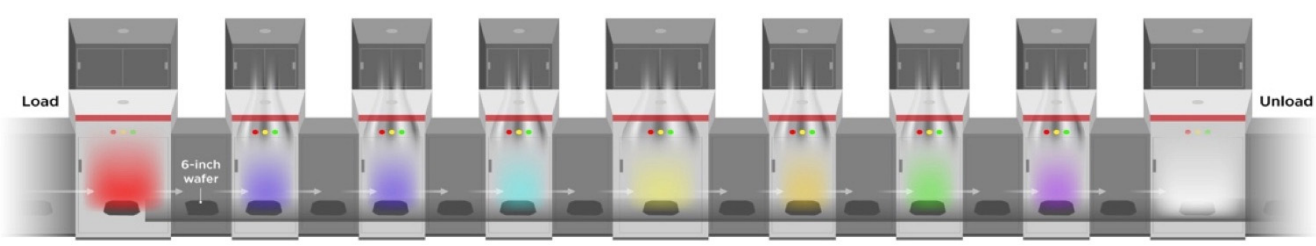

Fig. 2. Schematic representation of a fully in-line D-HVPE reactor with modular, independent chambers for the growth of each layer in a device. The throughput of a single in-line reactor is expected to be ~70x higher than a current, batch-style MOVPE reactor.

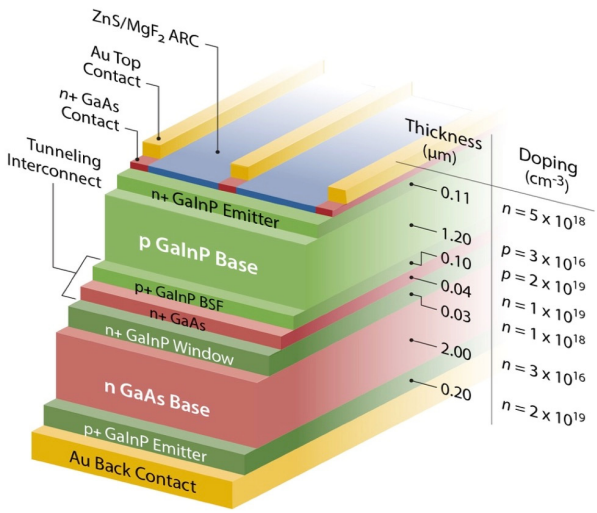

Fig. 3. Schematic of the device structure for a D-HVPE-grown two-junction solar cell. One can envision altering the alloys and/or doping to create other familiar III-V devices.

performance." In the particular case of GaAs solar cells, a V_{OC} > 1.01 V is considered the threshold for a high-efficiency device that can support > 25% conversion efficiency. D-HVPE-grown GaAs solar cells recently demonstrated V_{OC} > 1.02 V for growth rates up to 110 µm/h [10], and this was more recently extended to V_{OC} > 1.04 V at rates exceeding 300 µm/h (5 µm/min) [11]. At these rates, the growth of a typical 2-µm-thick GaAs base layer would take 24 s, compared to 20 min or more using today's standard growth techniques. We also developed GaInP that acts as an effective heterobarrier in GaAs-based devices with growth rates in excess of 100 µm/h, showing for the first time that the growth of other alloys that constitute III-V devices does not need to hamper total production throughput at very high rates.

In addition to GaAs solar cells, D-HVPE also produced the world's first GaInP [7] and GaInAsP [12] devices using any HVPE technique, as well as the first tunnel junction interconnects [13] and GaInP/GaAs two-junction solar cells [14], establishing the capabilities of this growth platform to produce a wide range of III-V materials and devices. The growth of tunnel junctions, in particular, speaks to the ability of D-HVPE to produce not only the high quality interfaces these interconnects require, but also the high doping range and very thin layers needed by so many devices. Indeed, the back-and-forth nature of the pseudo-in-line D-HVPE reactor shown in Fig. 1 is ideal for the formation of many types of structures, including DBRs containing many periods of materials with different indices of refraction, multi-quantum well regions consiting of wells and barriers, or metamorphic compositionally-graded buffer layers that change the lattice constant from that of the substrate to a lattice constant of more technical interest through the deposition of step-graded alloys. The fully in-line reactor depicted in Fig. 2 is more appropriate for devices with distinct and non-repeating layers, e.g. solar cells, HBTs, or power amplifiers. Fig. 3 shows the structure of a two-junction GaInP/GaAs solar cell grown by D-HVPE. This schematic provides an example of the complexity of devices that can be achieved. Simply switching the alloy composition or the doping type of some of these layers would lead to familiar device configurations beyond solar cells. The potential low cost, flexibility, high throughput, and quality possible in D-HVPE could be very beneficial for the production of a wide range of III-V devices.

Conclusions

We describe the beneficial attributes of the HVPE growth technique, as well as our development of D-HVPE for the production of high-efficiency devices with abrupt and defect-free heterointerfaces. We specifically discuss D-HVPE-grown single-junction GaAs solar cells with V_{OC} capable of supporting conversion efficiencies > 25% with extremely high growth rates in excess of 300 µm/h, but also show that the D-HVPE process is agnostic to device type and design. We believe that the D-HVPE process can be used to cost-effectively produce devices with very thick or very thin layers, with high dynamic doping range, with quality that rivals today's current production techniques. The potential cost benefit of D-HVPE - without the need to sacrifice material and device quality - will be important to future attempts to reduce the costs associated with III-V epitaxy.

Acknowledgements

This work was authored by the Alliance for Sustainable Energy, LLC, the manager and operator of the National Renewable Energy Laboratory for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. This material is based upon work supported by the U.S. Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) under Solar Energy Technologies Office (SETO) Agreement Number 30290. The views expressed in the article do not necessarily represent the views of the DOE or the U.S. Government. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid-up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

References

[1] Green, M. A., Hishikawa, Y., Dunlop, E. D., Levi, D. H., Hohl-Ebinger, J., and Ho-Baillie, A. W. Y., 2018, "Solar cell efficiency tables (version 52)," Progress in Photovoltaics: Research and Applications, 26(7), pp. 427-436.
[2] Woodhouse, M., and Goodrich, A., 2013, "A Manufacturing Cost Analysis Relevant to Single- and Dual-Junction Photovoltaic Cells Fabricated with III-Vs and III-

Vs Grown on Czochralski Silicon," No. NREL/PR-6A20-60126.
[3] Deschler, M., GrÜter, K., Schlegel, A., Beccard, R., Jürgensen, H., and Balk, P., 1988, "VERY RAPID GROWTH OF HIGH QUALITY GaAs, InP AND RELATED III-V COMPOUNDS," Journal de Physique Colloques, 49(C4), pp. C4-689-C684-692.
[4] Schulte, K. L., Rance, W. L., Reedy, R. C., Ptak, A. J., Young, D. L., and Kuech, T. F., 2012, "Controlled formation of GaAs pn junctions during hydride vapor phase epitaxy of GaAs," J Cryst Growth, 352(1), pp. 253-257.
[5] Simon, J., Schulte, K. L., Young, D. L., Haegel, N. M., and Ptak, A. J., 2016, "GaAs Solar Cells Grown by Hydride Vapor-Phase Epitaxy and the Development of GaInP Cladding Layers," IEEE Journal of Photovoltaics, 6(1), pp. 191-195.
[6] Simon, J., Schulte, K. L., Jain, N., Johnston, S., Young, M., Young, M. R., Young, D. L., and Ptak, A. J., 2017, "Upright and Inverted Single-Junction GaAs Solar Cells Grown by Hydride Vapor Phase Epitaxy," IEEE Journal of Photovoltaics, 7(1), pp. 157-161.
[7] Schulte, K. L., Simon, J., Mangum, J., Packard, C. E., Gorman, B. P., Jain, N., and Ptak, A. J., 2017, "Development of GaInP Solar Cells Grown by Hydride Vapor Phase Epitaxy," IEEE Journal of Photovoltaics, 7(4), pp. 1153-1158.
[8] Horowitz, K. A., Remo, T. W., Smith, B., and Ptak, A. J., 2018, "A Techno-Economic Analysis and Cost Reduction Roadmap for III-V Solar Cells," No. NREL/TP-6A20-72103 United States 10.2172/1484349 NREL English, ; National Renewable Energy Lab. (NREL), Golden, CO (United States).
[9] Schmieder, K. J., Armour, E. A., Lumb, M. P., Yakes, M. K., Pulwin, Z., Frantz, J., and Walters, R. J., 2017, "Effect of Growth Temperature on GaAs Solar Cells at High MOCVD Growth Rates," IEEE Journal of Photovoltaics, 7(1), pp. 340-346.
[10] Schulte, K. L., Braun, A., Simon, J., and Ptak, A. J., 2018, "High growth rate hydride vapor phase epitaxy at low temperature through use of uncracked hydrides," Applied Physics Letters, 112(4), p. 042101.
[11] Metaferia, W., Schulte, K. L., Simon, J., and Ptak, A. J., 2019, "GaAs Solar Cells Grown at Rates > 300 µm/h by Atmospheric-Pressure Dynamic Hydride Vapor Phase Epitaxy," Nature Communications.
[12] Jain, N., Simon, J., Schulte, K. L., Friedman, D. J., Diercks, D. R., Packard, C. E., Young, D. L., and Ptak, A. J., 2018, "Tunable Bandgap GaInAsP Solar Cells with 18.7% Photoconversion Efficiency Synthesized by Low-Cost & High-Growth Rate Hydride Vapor Phase Epitaxy," accpted for publication in J. Photovoltaics.
[13] Ptak, A. J., Simon, J., Schulte, K. L., and Jain, N., 2018, "Tunnel Junction Development Using Hydride Vapor Phase Epitaxy," IEEE Journal of Photovoltaics, 8(1), pp. 322-326.
[14] Schulte, K. L., Simon, J., and Ptak, A. J., 2018, "Multijunction Ga0.5In0.5P/GaAs Solar Cells Grown by Dynamic Hydride Vapor Phase Epitaxy," accepted for publication in Progress in Photovoltaics.

ACRONYMS

CMOS: Complementary Metal-Oxide Semiconductor
DBR: Distributed Bragg Reflector
D-HVPE: Dynamic Hydride Vapor Phase Epitaxy
HBT: Heterojunction Bipolar Transistor
HVPE: Hydride Vapor Phase Epitaxy
LED: Light Emitting Diode
MBE: Molecular-Beam Epitaxy
MOVPE: Metal-Organic Vapor Phase Epitaxy
V_{OC}: Open-Circuit Voltage