High Growth Rate Hydride Vapor Phase Epitaxy at Low Temperature through Use of Uncracked Hydrides

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We demonstrate hydride vapor phase epitaxy (HVPE) of GaAs with unusually high growth rates (R_G) at low temperature and atmospheric pressure by employing a hydride-enhanced growth mechanism. Under traditional HVPE growth conditions that involve growth from As_x species, R_G exhibits a strong temperature dependence due to slow kinetics at the surface, and growth temperatures >750 °C are required to obtain R_G >60 µm/h. We demonstrate that when the group V element reaches the surface in a hydride the kinetic barrier is dramatically reduced and surface kinetics no longer limit the R_G. In this regime, R_G is dependent on mass transport of uncracked AsH_3 to the surface. By controlling the AsH_3 velocity and temperature profile of the reactor, which both affect the degree of AsH_3 decomposition, we demonstrate tuning of R_G. We achieve R_G above 60 µm/h at temperatures as low as 560 °C, and up to 110 µm/h at 650 °C. We incorporate high-R_G GaAs into solar cell devices to verify that the electronic quality does not deteriorate as R_G is increased. The open circuit voltage (V_{OC}), which is a strong function of non-radiative recombination in the bulk material, exhibits negligible variance in a series of devices grown at 650 °C with R_G = 55-110 µm/h. The implications of low temperature growth for the formation of complex heterostructure devices by HVPE are discussed.

Hydride vapor phase epitaxy (HVPE) is a III-V growth technique regarded for its high growth rates (R_G), relatively low cost inputs, and high utilization. R_G for (100)-oriented GaAs in excess of 150 µm/h have been achieved in atmospheric-pressure, hot-wall reactors,[1] and these high rates are an important driver for lowering the cost of device growth. R_G is the strongest lever for cost reduction in large area III-V growth for applications such as photovoltaics[2,3] up to at least 60 µm/h,[4] so we regard this as a minimum desirable rate. Unfortunately, the rate-limiting step under typical growth conditions has a large kinetic barrier of ~200 kJ/mol,[5] so growth temperatures >750 °C are required to achieve R_G above 60 µm/h on (100)-oriented susbtrates.[6] Many devices, including high efficiency III-V solar cells, commonly include $Ga_{0.5}In_{0.5}P$ layers, but high growth temperatures are generally incompatible with the growth of In-containing alloys by HVPE because thermodynamics dictates that In incorporation becomes more difficult as temperature is increased.[7] $Ga_{0.5}In_{0.5}P$ growth at high temperature requires onerously high InCl/GaCl ratios that can be difficult to control.[7] This presents a dilemma: either a lower temperature must be chosen to permit deposition of $Ga_xIn_{1-x}P$, compromising the GaAs R_G and hence system throughput, or a growth pause must be employed while the temperature is ramped between layers with incompatible growth temperatures. Temperature ramping requires multiple minutes in a hot wall reactor, which would also create a drag on throughput, and more importantly can lead to contaminated interfaces.[8]

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Hence, the ability to grow GaAs at lower temperatures while maintaining the high R_G that makes HVPE attractive would enable cost effective manufacture of heterostructure devices.

In HVPE, group V atoms can be input in multiple forms: a hydride such as AsH_3[9], an elemental source (As_4),[6] or a halide-containing molecule such as $AsCl_3$.[10] Above ~400 °C, well below typical growth temperatures, AsH_3 rapidly decomposes to form As_2 and As_4 inside hot wall reactors,[9,11,12] with growth kinetics indistinguishable from growth using As_2 or As_4 as inputs. In these cases, the reduction of AsGaCl surface complexes by hydrogen to form GaAs and HCl is the rate-limiting step, resulting in the high kinetic barrier to growth.[13]

Despite this limitation, high-growth-rate III-Vs have been demonstrated previously by HVPE, typically by using non-standard conditions that modify the kinetic barrier. Hollan *et al.*, for example, demonstrated orders of magnitude increases in GaAs R_G up to over 100 of µm/h at 720 °C in the $AsCl_3$-Ga-H_2 system by sending extremely high $AsCl_3$ flows to the Ga source to generate a high concentration of GaCl in the reactor.[1,14] The authors attributed the high R_G to activation of a disproportionation mechanism in which $GaCl_3$ generated at the surface consumes surface Cl at a faster rate than the hydrogen reduction mechanism.[15,16] Growth was demonstrated at temperatures as low as 630 °C,[15] but R_G of only ~25 µm/h could be achieved on vicinal (100) substrates at these temperatures. Grüter *et al*.[17] demonstrated extremely high R_G with the AsH_3-HCl-Ga-H_2 system at 700 °C without the extremely high GaCl partial pressures by using reactor pressures below 8 Torr. Their high rates were attributed to a 'hydride-enhanced' growth mechanism, where growth occurs from uncracked AsH_3, rather than As_x.[17] Low pressure HVPE is a potential path to high R_G at low temperatures, but requires a significant vacuum to access the desired R_G (much lower than typical metalorganic vapor phase epitaxy reactors, which use pressures ~100 Torr or higher), limiting potential reactor materials and geometries. Goodridge and Hasdell showed high-R_G InP at one atmosphere (atm), up to 140 µm/h at 650 °C, by injecting PH_3 near the relatively cool substrate rather than upstream near the high temperature source.[18] Enstrom *et al*. noted a similar effect during GaInP growth using PH_3.[19] Karlicek *et al*. demonstrated that R_G was directly dependent on the degree of decomposition of PH_3 to P_2 and P_4, with higher R_G achieved when PH_3 decomposition is lower.[20] Hydride decomposition accelerates at high temperature in the presence of quartz;[11] thus by injecting PH_3 closer to the substrate, Goodridge and Enstrom obtained higher R_G by limiting PH_3 decomposition.

A similar effect might be expected for the growth of GaAs from AsH_3, but so far the only R_G demonstrations of hydride-enhanced, high R_G growth at one atm involve phosphide materials, likely due to the fact that PH_3 is much more resistant to decomposition than AsH_3.[12] Here we show that by controlling the decomposition of AsH_3 we can change the rate-limiting step and greatly lower the kinetic barrier to GaAs growth. We demonstrate R_G >60 µm/h at temperatures as low as 560 °C, and over 110 µm/h at 650 °C. The ability to grow GaAs in this temperature range allows us to deposit GaAs solar cells passivated with lattice-matched GaInP in our dynamic-HVPE (D-HVPE) reactor[21] at a single growth temperature, without growth interrupts. We demonstrate that the device open circuit

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voltage (V_{OC}), which is sensitive to the defect density in the material, is high, and independent of R_G.

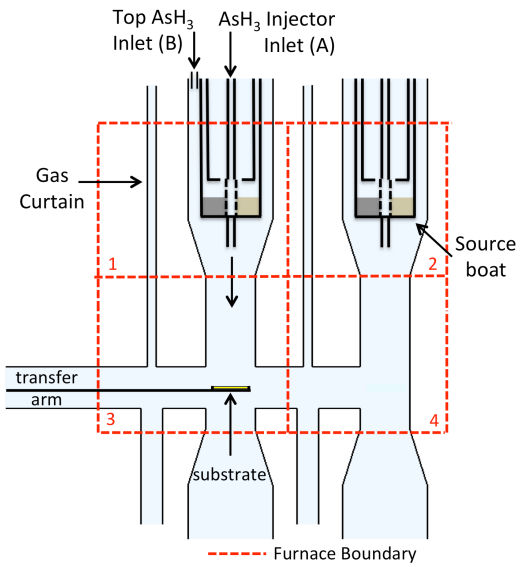

Fig. 1 – Schematic of the dynamic HVPE reactor used in this study.

All materials were grown in our dual chamber reactor, shown schematically in Fig. 1. Complete details of the reactor design can be found in ref. [22]. Metal chlorides were generated *in situ* through the reaction of HCl with elemental Ga and In metal sources contained in quartz source boats located within each chamber. AsH_3 and PH_3 were supplied as group V transport agents. Heterostructures were formed by setting up conditions for GaAs growth in one chamber, and $Ga_{0.5}In_{0.5}P$ in the other chamber, then rapidly transferring the substrate between chambers.[23] The transfer occurs in under 2s. Substrates were (100) GaAs offcut 4° towards (111)B. R_G was determined by selectively etching a step into a GaAs layer grown on a $Ga_{0.5}In_{0.5}P$ etch stop and measuring the thickness with stylus profilometry. The reactor has four independently controlled temperature zones, outlined by the broken line in Fig. 1. Zones 1 and 2 contain the metal sources and are referred to as the 'source zones', while zones 3 and 4 are referred to as the 'deposition zones'. The source zone temperatures (T_S) were 800 °C unless noted otherwise.

Solar cell devices were grown and characterized as a means to evaluate the electronic quality of the material. We grew cells in an inverted configuration using dynamic transfer between chambers to grow a GaAs base clad with $Ga_{0.5}In_{0.5}P$ window and back surface field (BSF) layers. Growth and processing details are in ref. 3. H_2Se and dimethylzinc were used as dopants. We employed a rear heterojunction design in contrast to the cells in ref. 3, with a 2 µm thick n-GaAs absorber layer, and the p-n junction formed at the back of the cell between the n-GaAs and the p+ $Ga_{0.5}In_{0.5}P$ BSF. The deposition temperature (T_D) was constant at 650 °C for all layers during cell growth. External quantum efficiency was measured on a custom instrument and used to calibrate a solar simulator to the air mass 1.5G spectrum, under which current density-voltage (J-V) characteristics of the devices were measured.

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The delivery of uncracked AsH_3 to the substrate is critical to our ability to achieve high R_G. For the majority of growths in this study, the AsH_3 is input at high velocity through a 4 mm inner diameter injector tube that outlets just before the end of the source zone, 17 cm above the substrate (Inlet A in Fig. 1). In one experiment, however, the AsH_3 was input into the main reactor chamber through Inlet B. Each reactor chamber is 12.5 cm across at its widest point, tapering to 7.5 cm across just before the deposition zone. Typically 9.5 SLM of H_2 carrier flow was supplied to the reactor during GaAs growth, divided as 2.5 SLM through the Ga section of the boat, 2.5 SLM through the In section, 2.5 SLM through Inlet A, and 2 SLM through Inlet B. Under these growth conditions, the velocity is 340 cm/s through Inlet A, and only 0.26 cm/s through Inlet B. Reactant partial pressures (P_i), equivalent to the molar fraction of a given gas in the reactant vapor, are calculated by invoking the ideal gas law at one atm and are nominal.

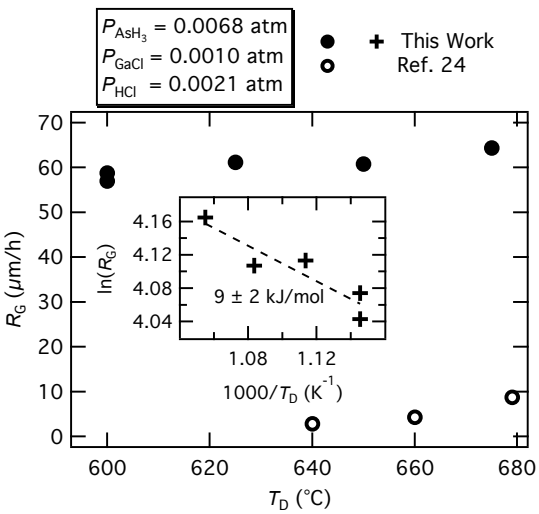

Fig. 2 – (closed circles) GaAs R_G as a function of T_D, grown under listed conditions. (open circles) Data from Kobayashi *et al.*[24], grown using P_{AsCl_3} = 0.001 atm. (inset) Arrhenius plot of the data from the closed circles.

We performed an initial set of GaAs growth rate calibrations in which T_D varied from 600 to 675 °C to establish R_G in a temperature range that is much lower than typical for HVPE growth of GaAs. Fig. 2 shows that R_G varied from 58 to 64 μm/h and was much higher than reported in the literature for samples grown under similar conditions.[6,24] The apparent activation energy for the temperature dependent growths was 9 ± 2 kJ/mol, drastically lower than the typical kinetic barrier of ~200 kJ/mol observed for HVPE-grown GaAs.[25] The absence of a strong temperature dependence implies that the rate-limiting step is not reduction of Cl at the surface. Indeed, the magnitude of the activation energy is more similar to that expected for diffusion of AsH_3 in H_2 (~13 kJ/mol),[26] implying that diffusion through the stagnant boundary layer that forms above the substrate surface is rate limiting instead of surface kinetics.

We also measured the effect of P_{GaCl} and P_{AsH_3} on R_G at low growth temperature. Data were acquired at two different H_2 carrier flow rates through Inlet A (Q_A). Fig. 3 shows that R_G exhibited a strong, roughly linear dependence on P_{GaCl}, increasing from 42 to 108 μm/h in the range P_{GaCl} = 0.8 to 1.7 x 10^{-3} atm. R_G was again significantly higher than

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expected for these low-temperature conditions because this range of P_{GaCl} is well below the partial pressures necessary to activate the disproportionation mechanism of Hollan.[15] The linear dependence agrees with previous results showing $R_G \propto P_{GaCl}$ at low relative P_{GaCl}.[27,28] R_G also increased linearly with P_{AsH3}, in agreement with Gruter's results at low pressure,[17] and in contrast to the results of other groups that observed a sub-linear dependence of R_G on P_{AsH_3} (or P_{As4} for decomposed AsH_3) at one atmosphere.[6,28,29] A linear dependence implies that growth proceeds from AsH_3 rather than As_x, which complements the above discussion on previous work showing high R_G in phosphide-based materials using PH_3. Importantly, we achieved GaAs R_G well above 60 µm/h, even for T_D as low as 560 °C.

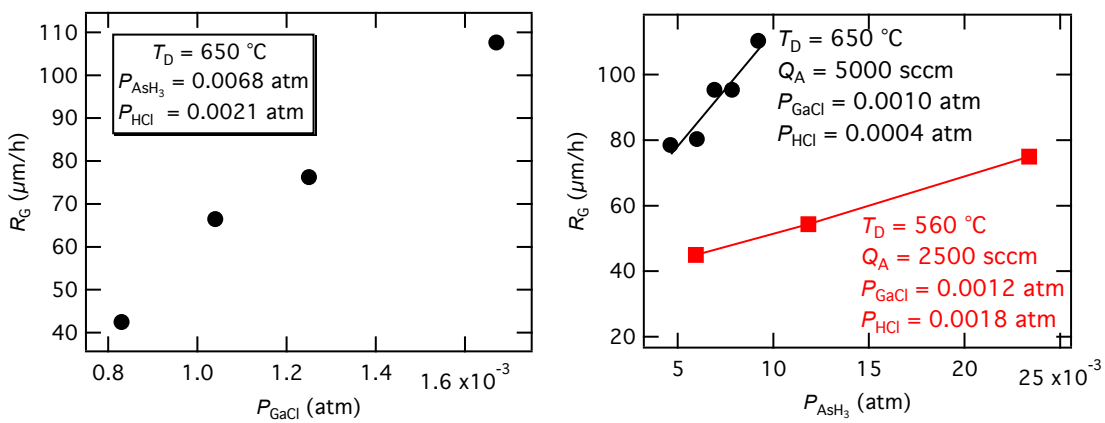

Fig. 3 - (left) R_G as a function of P_{GaCl}, (right) R_G as a function P_{AsH3} for two different T_D and Q_A.

If diffusion through the stagnant boundary layer is limiting R_G, as postulated above, R_G should depend on the gas velocity employed in the reactor. Fig. 4 shows the effect of varying the H_2 carrier flow through Inlet A while adjusting the flow through Inlet B such that the total carrier flow remained at 9.5 SLM. We note that the velocity through Inlet A is quite high, and varies strongly with carrier flow rate, from 140 to 300 cm/s in the given range. R_G increased strongly with increasing carrier flow, from 17 to 63 µm/h. It is possible that the higher local gas velocity, which decreases the boundary layer thickness and increases the transport rate of reactants to the surface, is solely responsible for increasing R_G. However, when the AsH_3 was input through Inlet B rather than Inlet A, with all reactant partial pressures held constant and while maintaining a high gas velocity through Inlet A, R_G *was nearly zero*. This result implies that the path the hydride takes to the surface is important to maintaining high R_G, similar to what Goodridge *et al*. found for InP growth.[18] The gas velocity though Inlet B is orders of magnitude lower than through Inlet A, resulting in the AsH_3 spending much more time in the hot part of the reactor and likely leading to complete decomposition.[12]

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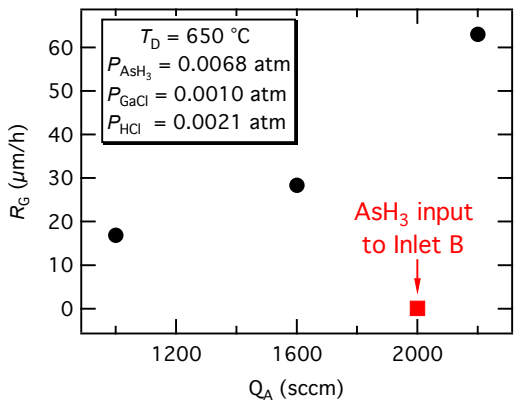

Fig. 4 – GaAs R_G as a function of Q_A. (circles) AsH_3 input through Inlet A. (square) AsH_3 input through Inlet B.

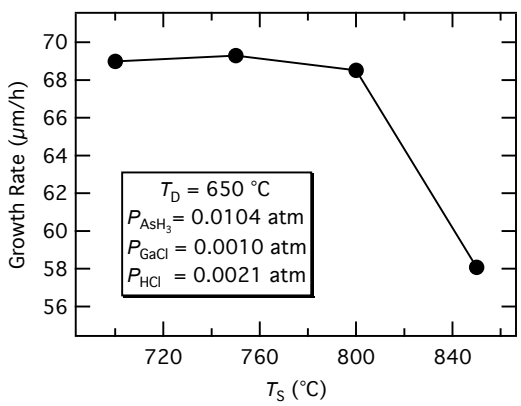

Fig. 5 – Effect of the source zone temperature (T_S) on R_G, with all other parameters held constant.

Fig. 5 shows further evidence that the R_G increase is related to AsH_3 decomposition. We grew a series of samples under constant T_D and reactant partial pressures, while varying only T_S. T_S controls the conversion efficiency (CE) of HCl to GaCl at the Ga source, and CE should increase at higher T_S, up to the equilibrium limit of Ga conversion.[12] If CE is below that limit, increasing the source temperature should *increase* R_G, by increasing P_{GaCl} in the reactor, similar to Fig. 3, and reducing the amount of free HCl that drives the reverse reaction,[21] while if CE is already at its equilibrium limit, raising T_S should have little effect on R_G. Fig. 5 shows that R_G stays relatively constant and then begins to drop sharply for T_S above 800 °C. The observation of *decreasing* R_G with increasing T_S is most easily explained by AsH_3 decomposition kinetics because higher quartz surface temperatures in the reactor increase the decomposition rate.[11]

Our results build on those of Gruter *et al*., who obtained high-R_G GaAs at low pressure in their vacuum HVPE system.[17] They theorized that the high AsH_3 velocities left a significant portion of the AsH_3 uncracked until it reached the substrate surface, leading to increased R_G. Indeed, they obtained lower R_G when they pre-cracked some of their AsH_3.[17] We are able to deliver uncracked AsH_3 to the substrate surface in our atmospheric pressure reactor by injecting it with extremely high velocity, despite the fact that the overall velocity in our reactor is low relative to the vacuum system. The presence of uncracked AsH_3 at the surface eliminates the large kinetic barrier to growth, allowing us to obtain high R_G, even at low temperature. The exact mechanism for the increased R_G

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is still unclear. We note that the equilibrium constant for growth directly from AsH_3 is roughly 4 orders of magnitude higher than for growth from As_4,[17] meaning that there is a strong thermodynamic driving force for growth of GaAs from AsH_3. One possibility for the mechanism is that the cracking of AsH_3 on the surface leads to a large number of radicals that can rapidly reduce Cl with a low kinetic barrier.

The major advantage of the hydride-enhanced mechanism is that it enables the growth of heterointerfaces such as GaAs/GaInP by D-HVPE at a single temperature, without the need for growth interrupts that can contaminate interfaces[8] and limit throughput. There is also no need to compromise between high GaAs R_G and optimal GaInP growth conditions. We grew a series of single-junction GaAs solar cells with GaInP cladding layers to demonstrate the enabling nature of low temperature GaAs. We varied R_G of the GaAs absorber only by varying Q_A, as in Fig. 3. Fig. 6 shows V_{OC} as a function of R_G for this series of solar cells. V_{OC} is directly related to the degree of non-radiative recombination in the device, and is a sensitive measure of defect concentrations.[30] A bandgap-voltage offset ($W_{OC} = E_G/q - V_{OC}$, where q is the elemental charge) <0.40 V is regarded as the threshold for high quality solar cells.[31] The V_{OC} for these cells is in the range 1.02-1.03 V (W_{OC} = 0.38-0.39), which is high enough that we would expect small changes in defect concentrations to result in a measurable decrease in V_{OC}. V_{OC} does not vary with R_G in the range R_G =55-110 µm/h, however, verifying that the material quality does not deteriorate due to increased growth rate. The average short circuit current density (J_{SC}) for devices across each sample was in the range 19.6 ± 0.3 mA/cm^2 (no anti-reflective coating). This variance is within error for this measurement (~2-4%), indicating that collection efficiency does not vary with R_G either.

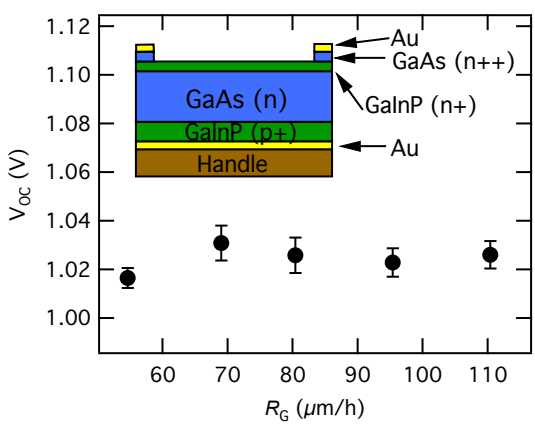

Fig. 6 – V_{OC} as a function of R_G for a series of GaAs solar cells with the illustrated structure. R_G was controlled by varying Q_A.

In summary, we demonstrated the deposition of high-R_G GaAs at low temperature in an HVPE system using a hydride-enhanced growth mechanism. We established that R_G dramatically increases when uncracked AsH_3 reaches the surface, and that this can be accomplished at one atmosphere by injecting the AsH_3 to the reactor with high velocity. We showed that the electronic material quality of a low temperature series of GaAs solar cells grown with GaInP passivation layers was constant in the tested range of R_G =55-110 µm/h. The low temperature GaAs enables the growth of heterostructure devices

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incorporating higher order materials (such as GaInP) that require $T_D < 700$ °C, without sacrificing the high R_G that makes HVPE desirable for lower cost applications.

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