Analysis of performance-limiting defects in *pn* junction GaAs solar cells grown by water-mediated close-spaced vapor transport epitaxy

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Abstract

Precursor and substrate costs currently limit the adoption of III-V photovoltaics for large scale manufacturing. Here, we use water-mediated close-spaced vapor transport (CSVST) to produce homojunction GaAs devices with pressed GaAs powder as an alternative to expensive gas-phase precursors. These unpassivated devices reach $V_{oc} > 910$ mV, demonstrating the plausibility of CSVST as an alternative method for growth of III-V epitaxial films for photovoltaic devices. We find that Zn-doping of the absorber films decreases after a number of growths cycles using a single source, which suggests an alternative transport agent should be investigated for *p*-type doping. Performance of these solar cells is largely limited by formation of macroscopic surface defects which we find to be caused by particulate transfer from the source material and the formation of oxide phases during growth. We present strategies for mitigating these defects and improving device performance.

Keywords – GaAs solar cell, close-spaced vapor transport, epitaxy, homojunction

1. Introduction

Currently, crystalline Si-wafer based photovoltaics (PV) dominate the market for terrestrial solar power generation, accounting for 92% of PV production in 2014 [1]. One-sun efficiency for a laboratory Si PV device has reached a record 25.6%, with a record module efficiency of 24.1% [2]. Further gains in efficiency for Si cells have become increasingly challenging, and a practical limit of around 26% is likely [3,4]. In contrast, III-V PV devices have a record one-sun efficiency of 28.8% for a single junction GaAs cell and 38.8% for multiple junction cells [5] so there is considerable interest in developing these technologies for large-scale production. However, due to the high cost of manufacturing, III-V PV devices are used only in niche applications such as concentrating solar cells or in the aerospace industry where high efficiency is of utmost importance. The largest costs are associated with the use of single-crystal substrates and current commercialized deposition techniques. For III-Vs to be cost-competitive, both must be substantially reduced.

Metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) are the most common techniques used for epitaxial growth of III-Vs, though only MOCVD is used commercially. The gas-phase precursors used for MOCVD are a source of significant expense. A recent analysis by Woodhouse and Goodrich reported that trimethylgallium costs around \$2.50/g and is expected to have ~30% utilization with current MOCVD reactor designs, while arsine is \$0.44/g and has an expected ~20% utilization [6]. Additionally, capital expenses are significant as MOCVD is a batch process with low throughput and requires considerable safety infrastructure. Alternative techniques that have been considered to address deposition costs include thin-film vapor-liquid-solid (TF-VLS) growth [7] and

hydride vapor phase epitaxy (HVPE) [8], which both use the metallic form of the more expensive group III element but still use gas-phase precursors for the group V element. HVPE in particular can attain high growth rates and multi-layer growth has recently been demonstrated for GaAs solar cells with GaInP cladding layers in a dual-chamber reactor [9]. Radically different approaches have also been proposed, such as a method in which nanowires might be fabricated without a substrate using a continuous gas phase synthesis (aerotaxy) [10]. Such an approach is supported by the recent result of a GaAs nanowire array solar cell with 15.3% efficiency (fabricated by imprint lithography and MOCVD growth) [11]. Each of these approaches faces substantial challenges.

Close-spaced vapor transport (CSVT) is an alternative deposition technique using only solid precursors, which has been demonstrated for a number of semiconductor materials relevant to PV production [12–17]. CSVT can achieve growth rates up to $\sim 1 \mu\text{m}/\text{min}$ [18], but with the potential for better material utilization than MOCVD or HVPE (approaching 100%) because the solid source is placed in close proximity to the substrate with growth rate and material losses determined by diffusion of the *in situ* generated gas-phase reactants. For many III-V materials, CSVT epitaxy is possible using an H_2 ambient at atmospheric pressure with low concentrations ($<10,000$ ppm) of H_2O , HCl , or I_2 added as a transport agent for the group III element, thus avoiding the use of toxic or pyrophoric gas precursors. In comparison with other growth techniques, however, doping and precursor preparation techniques are not well established for CSVT. In particular, past studies have not considered the effect of using powder source material (which should be more cost-effective than single-crystal wafer sources) or reusing the same source material multiple times. Demonstration of consistent film and device properties over many growth cycles is necessary before CSVT can be considered as a viable alternative for manufacturing III-V materials and devices.

We have reported that the electronic properties of GaAs grown by CSVT using H_2O transport are satisfactory for high-efficiency PV devices, and have demonstrated the first working homojunction GaAs solar cells [19–22]. Here, we report on progress towards high-efficiency CSVT GaAs solar cells. Device results suggest that performance of these cells is currently limited by the presence of macroscopic surface defects rather than intrinsic material quality. These appear to originate from either particulates due to the use of powder source material, or condensed Ga oxide phases. We also find that the absorber Zn-doping decreases over several growth cycles from the same source material, which may also be due to a reaction of Zn with water vapor.

2. Experimental Details

The reactor used for growth of GaAs is a quartz tube chamber that operates under ambient pressure of H_2 , and has been described in detail elsewhere [19,21]. Growth occurs between two graphite resistive heaters, where the solid source and substrate are separated by ~ 1 mm using a quartz ring which is cut and polished by hand. The H_2O is introduced by mixing dry H_2 with H_2 bubbled through H_2O held at a constant temperature.

Junctions were grown over two separate depositions, with samples exposed to atmosphere between *p*-type and *n*-type growths since the reactor consists of only a single stage. Solid GaAs source material was prepared by grinding wafers in an agate mortar and pestle, followed by hydraulic pressing at ~ 4000 psi to form pellets [19]. *N*-type sources were used for the emitter films and were Te-doped at $\sim 2 \times 10^{18} \text{ cm}^{-3}$. *P*-type sources were used for the absorber films and were Zn-doped by the wafer manufacturer at $\sim 2 \times 10^{19} \text{ cm}^{-3}$, with the exception of one pellet which was prepared by adding Zn powder to undoped GaAs powder followed by annealing in a vacuum-sealed ampoule. Resulting films are expected to be doped with [Te] $\sim$

$2 \times 10^{18} \text{ cm}^{-3}$ and $[\text{Zn}] \sim 2 \times 10^{17} \text{ cm}^{-3}$ due to the reported transport efficiencies of the dopants [19,23]. Control films used to measure carrier type and concentration were grown on undoped substrates and measured on a custom-built room-temperature Hall effect system at 10 kG with In contacts applied at the edges of the circular films. Film thicknesses were determined using a Zygo NewView 7300 optical profilometer.

Immediately prior to loading into the reactor, the undoped or Zn-doped ($>10^{19} \text{ cm}^{-3}$), nominally exact (100)-GaAs substrates were etched in 10:1:0.5 $\text{H}_2\text{O}:\text{NH}_4\text{OH}:\text{H}_2\text{O}_2$ for 30 s, rinsed in H_2O and isopropyl alcohol (IPA), then spun dry. Absorber films were grown at a substrate temperature of 820 °C while emitter films were grown at a substrate temperature of 760 °C to minimize cross diffusion of dopants. H_2O concentration was varied from ~1500 to ~5000 ppm for different film depositions, as measured by a hygrometer (Panametrics Moisture Target Series 5) mounted upstream of the reaction zone. Each film was observed under an optical microscope using differential interference contrast (DIC) imaging and the surface defect density was counted from these images.

Front contacts to the *pn* junction devices were prepared by thermal evaporation of Ni/AuGe through a photolithographically-patterned mask. Device mesas with areas of 0.04 cm^2 were then patterned by photolithography and etched in an aqueous citric acid / hydrogen peroxide solution (prepared by mixing 50 wt% citric acid solution and 30 wt% H_2O_2 solution in a 5:1 ratio [24]) to electrically isolate 10 devices on each substrate. Back contacts were prepared by thermal evaporation of Au/Zn/Au. In some cases, contacts were subsequently annealed at 450 °C under 5% H_2 in N_2 to improve contact resistance.

Current-voltage (IV) measurements on the completed devices were collected using a Keithley 2400 sourcemeter unit while capacitance-voltage measurements were collected on a Biologic potentiostat and fit to the typical circuit model as described in Ref. [19] to extract absorber carrier concentration. Illuminated IV curves were collected under a simulated AM1.5G solar spectrum using a Newport Oriel Sol3A Class AAA solar simulator calibrated to 100 mW/cm^2 using a thermopile. External quantum efficiency (EQE) curves were collected using a Bentham PVE300 spectral response system, and normalized using reflectance data collected on an integrating sphere [21] to produce internal quantum efficiency (IQE). The illuminated spot size for the measurement was approximately 0.1 mm, smaller than the size of the mesas, so the spot position was adjusted to produce the maximum responsivity at a wavelength 500 nm such that the effect of grid shading was consistent between measurements. The EQE measurement is also therefore less affected by grid shading than the IV curves.

Two *pn* junctions with fully fabricated devices were chosen for further study of surface defects. Several characteristic surface defects were selected from each device and time-of-flight secondary ion mass spectroscopy (ToF-SIMS) was performed using an Ion-ToF mass spectrometer with Cs^+ sputter source and Bi^+ analysis source in negative ion mode. We then analyzed the elemental composition of the sputtered regions in three dimensions to correlate the position of detected impurities with the positions of the defects in DIC and scanning electron microscope (SEM) images. SEM imaging, energy dispersive spectroscopy (EDS) measurements, and focused ion beam (FIB) milling (for creating defect cross-sections) was carried out in an FEI Helios Dual-Beam. Transmission electron microscopy (TEM) and EDS linescans were performed using an FEI Titan 80-300.

3. Results and Discussion

3.1 Device properties

The devices fabricated are homojunction n^+p -type solar cells without passivation or antireflective coatings. Such devices are simple to fabricate and as a benchmark can be readily compared with results from other deposition techniques. The IV curve and IQE of the highest-efficiency (unpassivated) GaAs homojunction cell we have produced by CSVT is shown in Figure 1 (measured prior to contact annealing, as discussed below). Integration of the EQE curve predicts $J_{sc} = 14.6 \text{ mA/cm}^2$ for the AM 1.5G spectrum, which is in good agreement with the IV measurement of 13.9 mA/cm^2 , given the effect of grid shading. This J_{sc} compares favorably with HVPE homojunction devices fabricated at NREL which reach 14.2 mA/cm^2 for similar structures [8,25]. However, since the devices in the study are unpassivated (and therefore have poor short-wavelength response) and lack antireflective coating, the primary figure of merit is the open-circuit voltage (V_{oc}) which reflects the overall quality of the junction and should not depend strongly on J_{sc} . This also minimizes the impact of emitter thickness (which typically varies between 50 – 200 nm) in interpreting our results. Thickness uniformity could be improved by substituting machined graphite for the quartz spacers which are not precisely cut; it may also be influenced by temperature variations across the heaters as the uniformity of the heaters has not been evaluated. The maximum V_{oc} produced for CSVT devices is 916 mV, compared to 936 mV reported for an unpassivated HVPE cell [25] and 960 mV reported for an unpassivated HVPE cell with antireflective coating [3]. Further improvement is needed to compete with standards set by MBE and MOCVD, for which cells can attain $V_{oc} > 1 \text{ V}$.

Figure 1: (A) JV curve for record efficiency device with unannealed contacts under one-sun simulated illumination. (B) Internal quantum efficiency for the same device.

The ToF-SIMS depth profile of a pn junction is shown in Figure 2. The emitter/absorber interface can be distinguished by the decrease in Te and S as well as an interfacial O spike which arises from the exposure to atmosphere between growths. Te concentration decreases by a factor of 10 over ~20 nm, similar to the junction abruptness reported for recent Si-doped HVPE pn -GaAs structures with a growth interruption step between layers [8]. The elevated S concentration in the emitter is due to the use of a different graphite heater assembly and quartz tube; cleaning or replacing these parts decreases the unintentional n -type background to $\sim 10^{16} \text{ cm}^{-3}$ based on Hall effect measurements of undoped films. The detection of O by SIMS is not surprising given H_2O is used as a transport agent, though its concentration could not be determined since a relative sensitivity factor was not available for the conditions used to collect this depth profile. Oxygen is known to be related to a defect level near the middle of the GaAs bandgap. However, while O has been detected in CSVT films at a concentration $\sim 10^{16} \text{ cm}^{-3}$ by SIMS [26], the midgap state has only been detected by deep-level transient spectroscopy (DLTS) when O_2 was intentionally introduced into the reactor [27]. Increasing water vapor concentrations during growth have

also been correlated with degraded photoluminescence [28][4], although in our own work with electrochemical cells J_{sc} was only degraded at very high water concentrations (>4000 ppm) [20]. The influence of oxygen on device performance merits further study.

In our experience, specular films are produced by CSVT rarely and unpredictably when using commercial GaAs wafers as source material. Smooth film morphology in CSVT has previously been attributed to a reaction of water vapor with the substrate surface just prior to growth [29], suggesting that small variations in the growth atmosphere during temperature ramping can have a large impact on surface roughness. Since we have found that pressed powder sources almost always produce specular films, all of the solid-state devices here have been grown from powder sources rather than a wafer. However, these typically have a higher density of surface defects, often with an oval or circular aspect. Oval defects have not been observed in the specular films we grow from wafer sources. The source of these defects could therefore be GaAs particulates or a contaminant in the powder.

Figure 2: SIMS depth profile of a CSVT pn junction, smoothed by adjacent averaging 25 data points (with a resolution of ~ 1 nm). The interface between the emitter and absorber is indicated as a dashed vertical line at 180 nm depth.

Due to the difficulty in growing multiple layers in our simple research reactor, devices in this study do not use a highly-doped (typically $>10^{19} \text{ cm}^{-3}$) contact layer which is common in III-V devices, though we have shown that these carrier concentrations are achievable using Zn and Te [19]. The lowest possible contact resistance to the $N_D \approx 10^{18} \text{ cm}^{-3}$ emitter layers could only be obtained with an annealing step to form a tunneling contact. The device shown in Figure 1 was subsequently annealed but this degraded the V_{oc} . On other devices annealed under the same conditions pits were observed at the edges of contact grids after annealing (shown in Figure S3), consistent with contact spiking, which is known to occur at these temperatures due to formation of AuGa alloys [30,31]. Since the contact resistance or presence of a contact barrier do not significantly affect V_{oc} , we focus on the characterization of unannealed devices in this study. In a more-advanced CSVT reactor design with multiple sources, passivation and contact layers could be developed more readily to optimize these aspects of device performance.

Figure 3 shows the variation of V_{oc} with surface defect density for 9 different samples and 90 individual mesa-etched devices with absorber films grown from three separately-prepared source pellets, all grown with the same substrate temperatures but with varied water vapor concentration (details are given in the Supporting Information). It is clear that surface defects have a major impact on V_{oc} . There is also a strong relationship between the source pellet preparation and the surface defect density N_{SD} . Film morphology and V_{oc} was best for the later growths when unannealed source powders were used. For the

two films with highest V_{oc} , the source had been prepared by addition of Zn metal to undoped GaAs and was annealed in pellet form at 1200 °C in an evacuated quartz ampoule. These results are evidence that a majority of the defects observed are due to particulate transfer from the source. Small particulates are likely consumed by vapor transport, sintering during annealing, or the repeated thermal cycling during multiple film depositions, thereby improving the film quality. Reduction in surface defects with source pellet reuse was also observed in investigations of GaAs_{1-x}P_x growth by CSVT [15].

Figure 3: Effect of surface defects on V_{oc} . Different colors/symbol shapes represent different absorber source pellets, while the numbers indicate the order in which the samples were grown from that source. Averages are for the 10 mesa-isolated devices for each pn junction and error bars represent a single standard deviation. The single open square was collected on a device with annealed contacts.

It is interesting to note that the best performing devices were grown from a pellet annealed in an evacuated ampoule with no As overpressure. The resulting source material is therefore somewhat Ga-rich, yet still produces films with high minority carrier diffusion lengths as evidenced by IQE and J_{sc} measurements. This is interesting since the concentration of intrinsic defects such as the EL2 defect (which is related to an As_{Ga} antisite point defect) would be expected to vary with source stoichiometry. The effect of substrate temperature on EL2 in CSVT GaAs has previously been studied using DLTS [32], but no studies have investigated the effect of changes in source composition which might occur over time due to incongruent loss of As and Ga from the source material. Such an effect could be minimized in a carefully engineered reactor where gas leakage from within the reaction zone would be small. In the current reactor the quartz ring separating source and substrate must have small gaps to allow infiltration of the transport agent since there is no mechanical mechanism to separate the source and substrate *in-situ*.

Capacitance-voltage (CV) measurements were performed to determine the hole concentration in the absorbers (Figure 4). The water vapor concentration was not identical for all growths but did not appear to have an effect on dopant density. Pellet A is the annealed source referenced above, which was doped by addition of Zn powder to undoped GaAs powder, while the other two pellets were prepared by grinding wafers which were doped by the wafer manufacturer. For each source, the first deposition was a control film on an undoped substrate which was characterized by Hall effect. Both Hall effect and capacitance measurements show a trend of decreasing hole concentration as a pellet is reused for multiple growths, to the point that the last two films from pellet B had an *n*-type Hall effect response. One possible explanation for the decreased doping efficiency is that water vapor reacts with Zn to form oxides which are less volatile [33] and that over several growth cycles oxygen diffuses throughout the source material. The lack of volatility of ZnO makes Zn doping by this method less feasible, especially in a manufacturing context. In contrast to Zn, Te has been reported to transport with unity efficiency [23], likely due to the higher volatility of its oxides, and we have not observed a decrease in the Te doping with source reuse.

Consistent Zn doping is probably achievable using HCl as a transport agent because zinc chloride species have high vapor pressures at the growth temperatures, and thus would be expected to have high utilization.

Figure 4: Carrier concentration over sequential growths from a given source pellet. Open symbols represent Hall effect measurements performed on control samples deposited on undoped substrates. For some growths carrier concentrations could not be determined and are omitted from the figure.

3.2 Origin of surface defects

Oval defects have been extensively studied in films grown by MBE, and are often associated with the Ga source due to spitting or oxide formation, but can also arise from substrate contamination or particulate transfer [34–39]. Oval defects have been previously reported in CSVT GaAs grown from single-crystal wafer sources and were attributed to surface contamination of the substrate prior to growth [29]. We have observed that residue left after surface preparation can lead to the formation of elongated polyhedral pits originating at the substrate interface these are easily distinguishable from the defects studied here which are surrounded by hillocks and can form far from the substrate/film interface. In the CSVT reactor used here, particulates are a likely source of these defects due to the use of powder sources in close proximity to the substrate. Oxide-related defects are also possible due to the use of H₂O as a transport agent.

In order to better understand the origin of the performance-limiting surface defects, we chose two samples with relatively high N_{SD} for detailed study. Sample A was a device with both absorber and emitter grown by CSVT, and with $N_{SD} = 3 \times 10^5 \text{ cm}^{-2}$. Sample B was an *n*-type emitter film grown by CSVT on a commercial *p*-type wafer which was Zn-doped to $5 \times 10^{17} \text{ cm}^{-3}$ and with $N_{SD} = 8 \times 10^4 \text{ cm}^{-2}$. For Sample A, the H₂O concentration was measured to be 2400 ppm and 1900 ppm for the absorber and emitter films, respectively, while Sample B was grown with a concentration of 4000 ppm. Processing of these cells was identical except that the contacts for Sample B were annealed and therefore some of the devices from Sample B have better fill factors due to a lower series resistance. The IV characteristics for the mesa-etched cells fabricated on these films are shown in Figure 5. The large scatter in V_{oc} is attributed to shunting through differing numbers of surface defects. The best devices for the wafer absorber sample in Figure 5B have higher V_{oc} than the best CSVT absorber devices in Figure 5A due to the lower number of surface defects in that sample, and therefore a lower likelihood of shunting. Devices with CSVT absorbers have a higher current since the minority carrier diffusion lengths are higher in CSVT material than in the wafer substrates (which are produced by the vertical gradient freeze technique) [19,20].

Figure 5: IV curves for all of the mesa-etched cells chosen for surface defect characterization. (A) emitter and absorber films grown on a wafer substrate, (B) emitter film grown by CSVT using wafer substrate as the absorber layer.

Optical images of two defect sites analyzed by ToF-SIMS are shown in Figure 6. The defects which are mostly present on the Sample A have large pits with irregularly-shaped spikes near the center of the hillocks, including some which are present underneath the front contact (Figure S4) and can contribute to device shunting. The difference in morphology between Sample A and B is at least partially attributable to the thickness of the CSVT absorber film ($\sim 7\ \mu\text{m}$) which has probably grown around sites of contamination. We refer to defects such as those in Figure 6A as particulate-related defects based on morphology and the SIMS, SEM, and TEM analyses of similar defects. For Sample B, most of the defects are morphologically similar those in Figure 6B; that is, consistently-shaped hillocks with relatively small central cores just visible by optical microscopy. We refer to these as oxide-related defects based on EDS analysis below.

Figure 6: Differential interference contrast images of the film surfaces prior to SIMS measurement. A) Defects with irregular cores found on Sample A. B) Defects found on Sample B with more regular morphology. The white boxes indicate the approximate SIMS analysis regions.

A comparison of the SIMS spectra for a number of defect sites and defect-free regions revealed that Si is present only in the particulate-related defects (Figure 7), while both defect types had elevated concentrations of oxygen and hydrocarbon species compared to defect-free regions. The mass spectrum in Figure 7 is constructed from a $75 \times 75\ \mu\text{m}$ total area with 300 nm sputter depth but excludes data from the first 25 nm to avoid detection of adventitious surface species. In our experiments, we have never detected Si in defect-free regions of CSVT-grown GaAs films even when both Si and fused quartz are present in the hot zone of the reactor, or when intentionally Si-doped source material was utilized [19]. Si

is only likely to transport as SiO at very low rates in very dry H₂ [40]. Si has a vapor pressure several orders of magnitude lower than ZnO at 900 °C [41], so the transport efficiency of Si should be substantially lower than Zn (which is < 1%). The Si detected in defective regions is thus very likely transported in the solid phase as a particulate. The origin of Si in the source material might be contamination during grinding in the agate mortar and pestle.

Figure 7: DIC image, Si XY map, and Si mass spectrum peak for a region on the CSVT sample collected from the bulk of the emitter. The mass spectra indicate that Si counts within the clean region are attributable to background noise.

Composition and morphology of the two types of defects were compared under SEM by creating cross-sections using FIB milling. In addition, the particulate-caused defect was thinned and lifted out for TEM analysis. A comparison of the SEM images and EDS maps is shown in Figure 8. For the defects believed to be caused by particulates (i.e. those defects that reduce in density with source pellet annealing), the defective region has very little contrast compared to the epitaxial film in the SEM image and the composition is identical to the film within detection limits of the EDS. In contrast the oxide-related defects (as in the optical image in Figure 6B) on Sample B have increased oxygen concentration and arsenic deficiency, indicating that the central portion is likely a GaO_x phase. The higher water concentration during deposition for Sample B (~4000 ppm) as compared to Sample A (~2000 ppm) may account for the higher proportion of oxide-related defects. The small number of particulate-related defects in Sample B is probably due to the limited deposition time as well as the variability of the source pellet properties.

Figure 8: SEM images and EDS mapping of the central core of A) a particulate-related defect and B) an oxide-related defect and EDS intensity maps of O, Ga, and As for cross sections prepared by FIB. The SEM image and the EDS elemental maps are of identical regions and the scale is the same.

Figure 9 shows the bright-field TEM image of the same particulate-caused defect as shown in Figure 8A. There is a clear grain boundary between the defect and the epitaxial film, and at least three grains are apparent within the defect. This might indicate that the particulate consisted of several sintered crystallites which grew into a polycrystalline mass during film deposition. EDS linescans performed on the TEM across the grain boundary again showed no compositional difference between the epitaxial film and the defect.

Figure 9: Bright-field TEM image of a particulate-caused defect.

3.3 Strategies for defect mitigation in CSVT materials and devices

Elimination of particulate-caused surface defects will require either an alternative source preparation technique or a method to block particulates from transferring in the growth chamber. The latter strategy may be possible by integrating a thin ceramic membrane between source and substrate, but may decrease growth rate which is driven by diffusion in CSVT. Particulate-free source material might be prepared cheaply through a hot-pressing technique. The fact that specular films can be grown more easily from powder sources than from wafer sources merits further investigation but is likely related to the increased surface area of the powder since the powder is produced by grinding sections of the same wafers. For instance, the transport rate of Ga at the start of growth from a pellet might be higher due to the increased surface available for oxidation.

Oxide-related defects appeared in high density only in the emitter film grown directly on a wafer, and so their formation may be related to the higher water concentration used for that growth. This suggests that, while increasing water vapor concentration increases growth rate, the water concentration must be kept below some threshold value to prevent formation of these defects (at least at substrate temperatures used for the emitter depositions). Thus, the high growth rates desired for a high-throughput CSVT process are best achieved by minimizing source/substrate spacing or by increasing the temperature gradient between source and substrate. Alternatively, replacing H_2O with HCl should eliminate oxide-related defects, at the cost of more stringent requirements on reactor components to avoid corrosion and film contamination. The use of HCl for transport is still an attractive option since the chlorides of metals of interest for III-V growth have much higher vapor pressures than their corresponding oxides. Zn doping efficiency, for example, should be improved in an HCl system, and growth might be achieved at lower substrate temperatures typical of MOCVD or HVPE.

4. Conclusions

We have demonstrated simple small-area unpassivated CSVT *pn* junctions with good junction properties and promising photovoltaic performance ($V_{oc} > 910$ mV). By analyzing a large number of devices we discovered that V_{oc} is most strongly impacted by the formation of surface defects rather than intrinsic material properties. It should be possible to minimize the formation of both particulate-caused surface defects and oxide-related defects with suitable source material preparation and choice of growth conditions.

Using HCl as an alternative to H₂O as a transport agent could eliminate oxide-related defects as well increase the volatility of elements which transport inefficiently as oxides. We are currently designing and building such a system in our laboratory. A theoretical analysis of GaAs halogen transport in a closed-tube is given by Fergusson and Gabor [42] and experimental results for GaAs and GaP have been described by Moest and Shupp [43]. In the latter study, epitaxial growth was reported with $T_{src} = 700 - 800$ °C and $T_{sub} = 500 - 640$ °C indicating lower deposition temperatures can be used with HCl. Close-spaced reactors using HCl, however, have only been described for the growth of II-VI compounds such as ZnSe [44]. The growth mechanism in CSVT is the same as for a long closed-tube vapor transport system, in principle differing only in reactant diffusion path length. Deposition of Al_xGa_{1-x}As cladding layers or AlAs epitaxial release layers may also be possible, though due to the reactivity of HCl and Al-containing compounds, the reactor design will need to avoid the use of fused quartz parts typical in III-V deposition systems. The preliminary reactor design uses graphite parts for the hot zone to avoid unintentional introduction of impurities, as well as multiple growth stages such that different layers can be deposited without exposing source material to atmosphere that may result in oxygen contamination.

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