Flexible Perovskite-Perovskite PV for Mobile Power Applications: Final Technical Report

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National Renewable Energy Laboratory

NREL is a national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy
Operated by the Alliance for Sustainable Energy, LLC

Contract No. DE-AC36-08GO28308

Technical Report
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Suggested Citation

Moore, David. 2024. *Flexible Perovskite-Perovskite PV for Mobile Power Applications: Final Technical Report*. Golden, CO: National Renewable Energy Laboratory. NREL/TP-4B00-90983. https://www.nrel.gov/docs/fy25osti/90983.pdf.

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NOTICE

This work was authored by the National Renewable Energy Laboratory, operated by Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding provided by the U.S. Department of Energy Office of Energy Efficiency and Renewable Energy Solar Energy Technologies Office. The views expressed herein do not necessarily represent the views of the DOE or the U.S. Government.

Cover Photos by Dennis Schroeder: (clockwise, left to right) NREL 51934, NREL 45897, NREL 42160, NREL 45891, NREL 48097, NREL 46526.

Preface

a. Federal Agency	U.S. Department of Energy
b. Award Number	Agreement #35892
c. Project Title	Flexible perovskite-perovskite PV for mobile power applications
d. Recipient Organization	NREL; Swift Solar
e. Project Period	10/1/2019 – 12/31/2023
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Background & Introduction

This is the final report for the referenced TCF award which ran from Oct. 2019 through Jan. 2024 in conjunction with the industry partner Swift Solar. The long duration of the program was due to several factors including the pandemic and a technical work stoppage due to changes in the scope. Additionally, Swift's business focus shifted during the course of the program. As a result of these factors, this program underwent two distinct modifications that dramatically changed the work scope. The following report is organized into three separate sections, each of which addresses a distinct work scope. Those scope changes, what necessitated them, and any new tasks/milestones are given, briefly, at the top of each section.

The work performed was research on the hybrid halide perovskites (HHP), both the absorber material itself as well as other material layers that are required in a full device stack. At the start of the period of performance, there were two distinct challenges that we sought to address: (1) a wide band gap absorber (>1.6 eV), and (2) a recombination layer for tandem devices that provided good sequestration of the individual cell absorber materials in their respective device layers. NREL had previously published, and patented, advancements in both of these areas and they were the focus of much of the work throughout the program.

Initial Scope

The initial scope of work was based on the wide gap absorber and recombination layer technologies. Generally, the intent was to move both technologies to a higher TRL so that Swift could incorporate them into their prototype and pilot line processes. The second part of the initial scope was focused on scaling of those technologies to commercially relevant scales.

Tasks

There were 4 major tasks under the initial scope of work:

1. Understand the mechanism by which the wide gap alloy worked and use that understanding to improve the long term stability of the material. Once complete, translate the final formulation to vapor phase deposition.
2. Explore alternatives for high nucleation density of the recombination layer to decrease its thickness while maintaining the barrier properties.
3. Increase device size to >1cm2 and utilize vapor deposition techniques using Swift's equipment portfolio.
4. Construct multi-cell micro- and mini-modules, both rigid and flexible substrates.

Successes

During the first period of work, the following progress was made.

The wide gap material, denoted DMA10FA60Cs30 or simply DMA, includes a large organic cation in the formula. It was determined that the mechanism by which it works is the creation of 'hollow' perovskites whereby empty lattice positions create strain within the lattice.

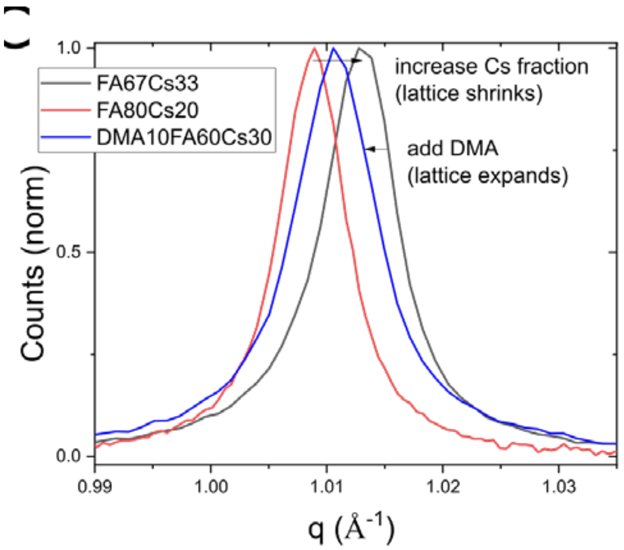


Figure 1: Density decreases from 4.368 (grey) to 4.336 g/cm3 (blue) when adding DMA. Given the lattice expansion and density decrease, the bandgap change is attributed to BX2 octahedral vacancies.

In the course of this work, we also noticed large standard deviations amongst different researchers and research locations. Several process controls were tested for their sensitivity to device yield and performance. At the start of the program we were using: one glovebox for all reagent storage, weighing all salts individually, antisolvent dousing during spin coating, using reagents as received. There were other controls in place as well, but these four were identified as the most sensitive. Figure 2 shows the impact of changing the overall process to include: separate gloveboxes for storage of wet and dry components, reagent purification prior to use, ball milling all salts together rather than weighing individually, and nitrogen quenching during spin coating.

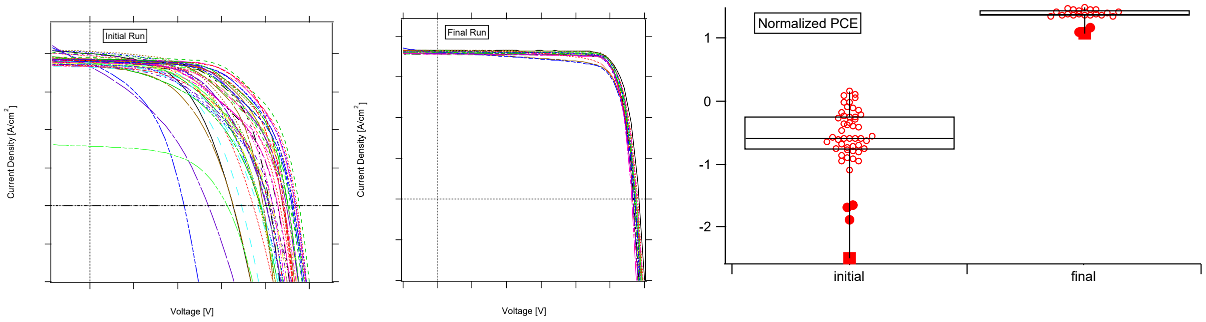


Figure 2: JV curves for initial process (left) and final process (middle). Right panel shows the statistical data for both. Overall device PCE improved from <16%> +/- 1.9% to just over <18%> +/- 0.3%; yield increased from 62% to 87%

The work on the wide gap material was published in ACS Energy Letters,
doi: 10.1021/acsenergylett.0c00872

The recombination layer was also improved. In its initial form, we had shown that use of a thin layer of PEIE helped increase the nucleation density of tin oxide or doped tin oxide interlayers. However, PEIE itself is an insulating molecule and we sought to replace that with something that maintained the high nucleation density without sacrificing the through plane conductivity of the layer. The recombination layer exists between the two separate devices in a tandem device stack and allows the charges from the individual cell to recombine. In the targeted architecture, this layer consists of C60 and SnO2. During this work, it was discovered that the SnO2 layers were somewhat porous and did not conformally coat the entire bottom device. The inclusion of PEIE between the C60 and SnO2 was used prior to the start of this program and resulted in better performing devices as well as more consistent device construction. Additionally, the more compact SnO2 layers proved more robust to penetration of the solvents used for processing the top device, as well as oxygen and water, which results in better long term durability.

In this work, the PEIE layer was replaced by a UVO treatment of the C60 layer prior to deposition of the SnO2. Figure 3 shows the final results of the UVO treatment, a more compact and thinner SnO2 layer, improved barrier properties, and better long term stability.

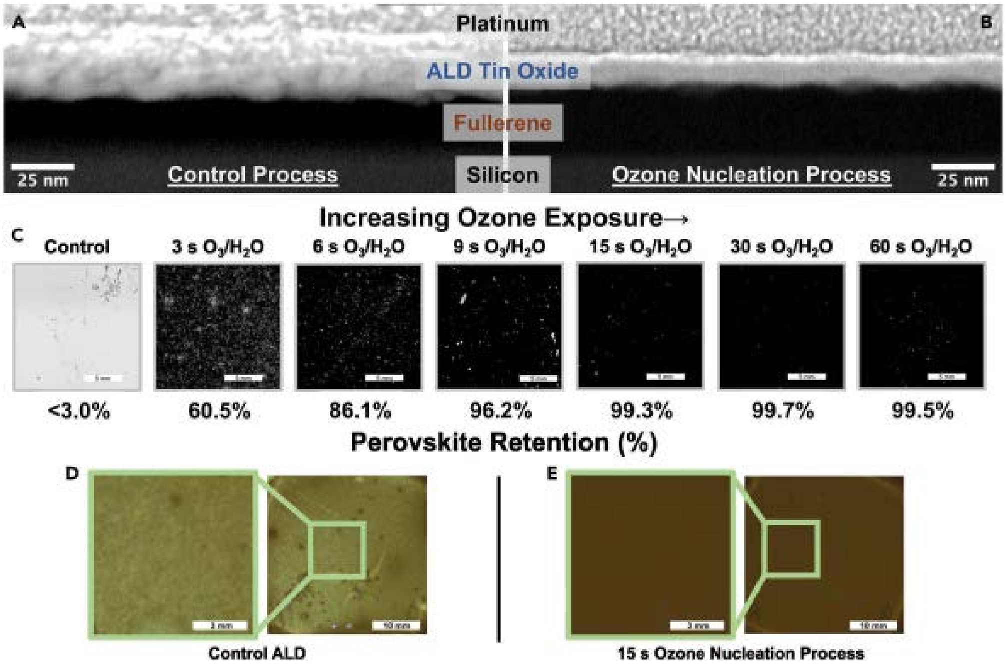


Figure 3: (A and B) Cross-sectional STEM images of Si/C60/SnOx/Pt substrates showing a comparison of (A) 125 cycles of control SnOx and (B) ozone-treated (15 s) SnOx. (C) Perovskite film retention after a 10 s dimethylformamide exposure for glass/perovskite/C_{60}/125 cyc ALD SnO_x with increasing duration of ozone exposure applied after the initial 40 cycles of SnO_x capping layer growth. (D and E) Glass/perovskite/C_{60}/125 cycle ALD SnO_x films after aging for 1,000 h at 150°C in an ambient oven using (D) a control SnO_x and (E) ozone-nucleated (15 s) SnO_x ALD process.

Finally, the UVO process can be accomplished in-line with the ALD tool used to process the SnO2 which reduces the overall number of processing steps. The recombination layer work was published in Joule, doi: 10.1016/j.joule.2023.10.009

Failures

Although several items needed to commercialize these two technologies were accomplished under the initial scope of work, there were several others that were not successful. Most notably was the inability to use the vapor deposition equipment available at NREL to successfully deposit the wide gap material. Tasks 3 and 4 in the initial scope of work were dependent on vapor deposition. The failure here was not the use of vapor processes but the specific deposition chambers available. During the course of this work several other groups brought vapor deposition capabilities online, most groups reporting vapor deposition with both high performance and high yield did so using thermally isolated sources with large numbers of cooling shields to avoid cross contamination of the sources. The more important effect was to limit the background vapor pressure of the organic components of the HHP layers. NREL's chamber did not have sufficient thermal isolation or internal cooling to accomplish this, although this was not known at the start of the performance period.

Given the inability to migrate the wide gap material to vapor deposition, as well as the interruption caused by the pandemic, the program was paused until viable alternatives could be found. The changes made under the next section only affected the wide gap material, the recombination layer work was unaffected.

Scope Change 1

During the pause noted above, we stood up a new vapor deposition chamber with an alternative approach to depositing HHPs. This was a flash evaporation chamber which was funded from other sources and so we will not report those details here. However, once that chamber was brought online we hypothesized that it could be used for inorganic wide gap materials. A major scope change was made and new tasks, detailed below, were included.

In addition to the technical roadblocks, Swift made several changes to their business model and shifted their initial focus from all perovskite tandems to silicon/perovskite tandems. Swift's change to their initial focus on silicon/perovskite tandems also informed the scope change.

It was decided that NREL could focus on all inorganic, wide gap absorbers and still add a similar efficiency improvement to a tandem device in spite of the all inorganic absorbers not having the theoretically optimal band gap.

Tasks

The tasks listed under the initial scope were re-written to include the following major tasks:

1. Understanding the voltage limitations of inorganic perovskites. Although the inorganic perovskites show better stability, a key issue for commercialization, they suffer from a much larger Voc deficit than the HHP counterparts. The goal of this task was to understand the nature of the Voc deficit and eliminate as much of it as possible.
2. Improve the overall performance of vapor deposited inorganic perovskites. This task sought to leverage the understanding from task 1 to produce viable wide gap materials for use in a silicon/perovskite tandem processed by vapor deposition.
3. Translate the recombination layer materials to spatial ALD equipment. The principal work on the recombination layer was demonstrated during the initial scope. The purpose of this task was to show that the process could be translated to spatial ALD, a commercially viable process with much higher throughput than lab scale ALD systems.
4. Demonstrate a silicon/perovskite tandem using the inorganic perovskites and recombination layers made by spatial ALD.

Successes

Inorganic perovskites. We were successful in vapor deposition of the all inorganic perovskite materials across the entire I/Br range.

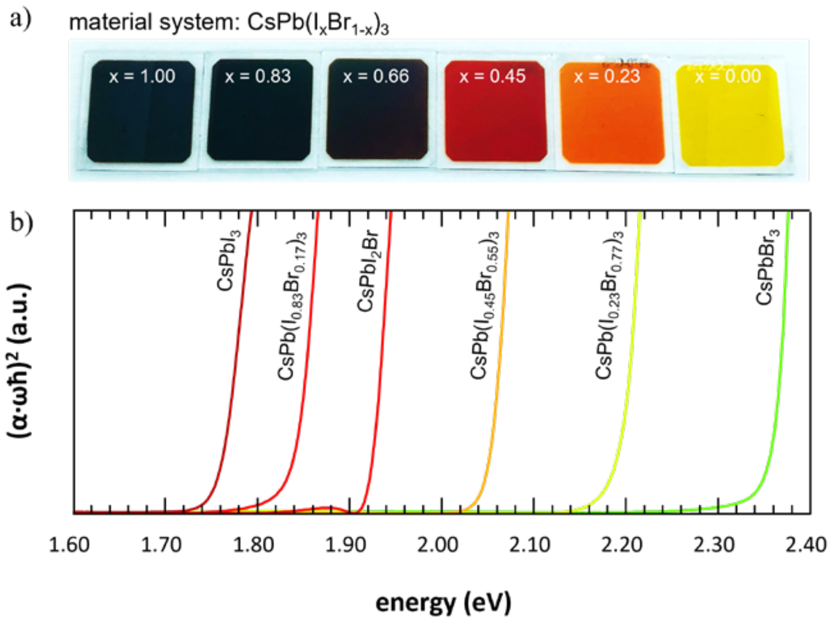


Figure 4: All inorganic perovskite thin films (a) and the corresponding absorption spectra (b).

The films are made by a continuous flash sublimation process which maintains the stoichiometry of the as-prepared powders and is dramatically faster than previously demonstrated techniques. Figure 4 shows the raw materials as deposited while figure 5 shows the comparison between vapor and solution deposited devices. It should be noted that almost all reports of the inorganic absorbers are processed from solution with the vapor deposited reports typically showing much lower performance.

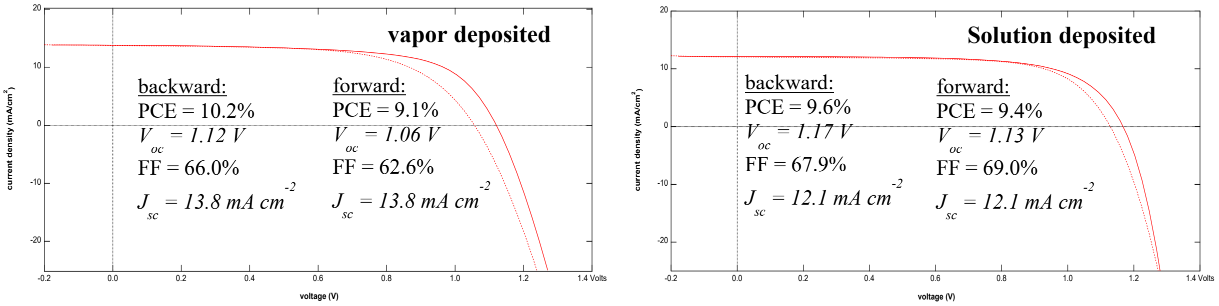
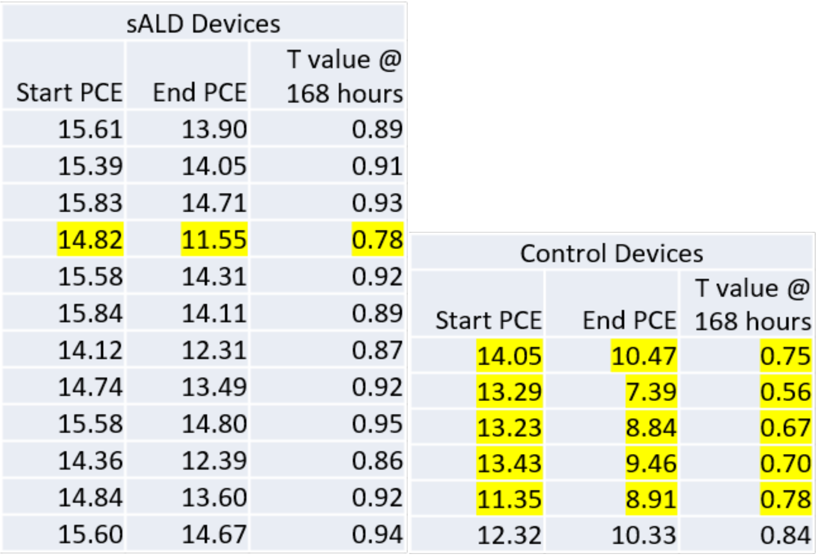


Figure 5: Initial runs of vapor deposited, inorganic perovskites. Composition is $CsPbI_2Br$.

The champion devices we produced were mixed I/Br, similar to those shown in Figure 5, and achieved the highest reported efficiencies for all vapor processed inorganic perovskites of their composition at 14.9%. This work was reported in the Journal of Materials Chemistry A, doi: 10.1039/D3TA05881F

Recombination Layer. Swift secured a spatial ALD tool for use in their facilities. The material and process developed under the initial scope of work was successfully translated to their spatial ALD tool. Table 1 details the final results for 12 separate device runs; 6 of those runs were compared to lab scale ALD processes on devices made during the same run to show the differences between batch, and spatial ALD processes.

Table 1: Comparison of device aging for devices with recombination layers processed by spatial ALD (sALD) and batch ALD (Control).The PCE shown is the average for all devices in the run.



sALD Devices		
Start PCE	End PCE	T value @ 168 hours
15.61	13.90	0.89
15.39	14.05	0.91
15.83	14.71	0.93
14.82	11.55	0.78
15.58	14.31	0.92
15.84	14.11	0.89
14.12	12.31	0.87
14.74	13.49	0.92
15.58	14.80	0.95
14.36	12.39	0.86
14.84	13.60	0.92
15.60	14.67	0.94

Control Devices		
Start PCE	End PCE	T value @ 168 hours
14.05	10.47	0.75
13.29	7.39	0.56
13.23	8.84	0.67
13.43	9.46	0.70
11.35	8.91	0.78
12.32	10.33	0.84

The performance metric for this milestone was to maintain >80% of the initial PCE after 168 hours of testing under continuous load, max power point tracking, 75C, no encapsulation, and 1-sun intensity. The yellow highlighted items did not meet the performance metric.

Failures

The failure under scope change 1 was the inability to adequately address the Voc deficit metrics. In spite of producing the highest performing, mixed-halide, all inorganic perovskite devices via vapor deposition, the champion devices still only achieved ~ 1.17V at open circuit which represents a 36% Voc deficit. This deficit should be contrasted with the deficit of the HHP devices of only 12-15%. Unfortunately, the low open circuit voltage limits the efficiency added by the wide gap device to only 2-3%, far short of the targets required by Swift for a viable commercial product.

At the point in time when the results in this section were presented, it was decided to re-assess the final goals for the project as there were only two quarters, and little money left. Again, Swift was included in these conversations and the final scope change was derived based on what work could be done that would have the strongest impact on Swift's commercialization plans.

Scope Change 2

At the end of the scope change 1 period several the project had been running for just over four years. During that time the perovskite research community, the perovskite commercial industry, and Swift Solar had made many discoveries and changes. The following are a summary of the notable changes:

1. The durability of perovskite devices was the principal roadblock to commercialization
2. Silicon/perovskite devices were the best candidate for widespread adoption
3. Swift moved silicon/perovskite devices to the top of their development list
4. Post treatment of perovskite materials with ‘capping’ layers was a promising technique for stabilizing the absorber material.

Given the state of the industry, it was decided to focus the remaining time and money available on vapor deposition of various capping materials as a way to stabilize the perovskite layer. Many different capping layers had been demonstrated and reported in the literature, including several by Swift. However, there were no substantial reports of deposition of these materials in the vapor phase which was critical to Swift’s production which is focused on vapor deposition. Most of the capping materials of interest are small organic molecules and the challenge with vapor deposition is a controlled deposition that is conformal at very thin thicknesses and at temperatures that do not decompose the organic molecules.

Tasks

The summary of the tasks under the final scope change were:

1. Determine the viability of vapor depositing 4 target molecules.
2. Check the process viability of the deposited molecules; specifically, can the target molecules be evaporated continuously (no change in source composition) and without contamination to the chamber.

Successes

The viability of vapor depositing molecules consisted of several metrics:

1. Does the molecule survive the temperatures required for a deposition rate >1 Ȧ/s. Measurement of this is done be comparing the NMR spectra of the molecule as received and comparing that to the evaporated film.
2. Does the evaporated molecular film perform in working devices at a similar, or better, level than solution cast films. Measurement of this is done by device performance metrics in working devices.
3. Does the molecule, when evaporated, form a continuous and conformal layer. Measurement of this is done by scanning electron microscopy (SEM).

Three of the four target molecules pass the first test with the films and as-received powders having matching NMR spectra. Only two of those pass the test of conformality by SEM, EDIA and MTEACl. Figure 6 shows the comparison of JV curves for the controls (no EDAI), solution cast, and vapor deposited EDAI films in working devices. The vapor cast EDAI devices show excellent reproducibility and the highest average Voc although they tend to have lower currents. Overall efficiency is statistically no different for all three. We hypothesize that the current difference is due to parasitic absorption by the EDAI due to its thickness which was ~20 nm thicker than our target.

Similar results were found for the MTEACl molecule with positive results on device performance, particularly the increase in Voc.

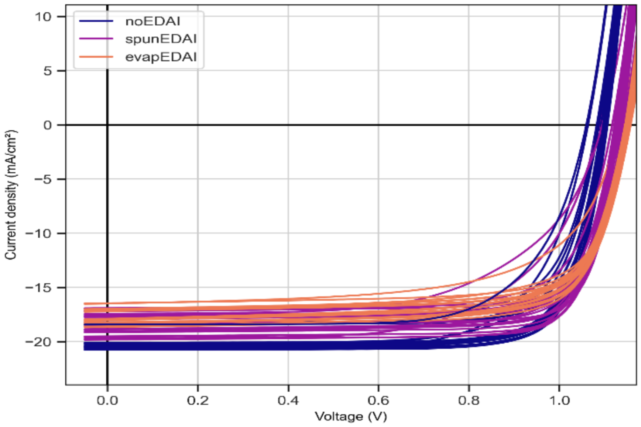


Figure 6: Comparison of no EDAI (blue), solution cast EDAI (magenta), and vapor deposited EDAI (orange).

The challenge to this work was the inability to get a good model done by ellipsometry that allowed good tuning of the overall layer thickness which we wanted to be on the order of 1-3nm. It should be noted that after the program was completed we did a complete PM of the chamber and discovered that the water cooling lines for the quartz crystal monitor were clogged. This leads to inconsistent readings which likely explains our inability to get thinner layers. In spite of the thickness control problems, Swift has recommissioned a chamber at their facilities to continue this work there.

The process viability task is focused on determining the viability of depositing the target molecules in a functioning pilot line. In the present case there are two issue that were targeted:

1. Can the molecule be loaded into a source in large quantities and used over and over without cleaning or reloading. This is in contrast to lab scale depositions in which the source material is usually replenished after each deposition. The measure of this is to do multiple depositions without changing the source material, followed by NMR comparison between the as-received material and any remnant material left in the source.
2. Can the molecule be evaporated without contaminating the chamber. Chamber contamination is a potential issue if the organic molecules will 'build up' a continuous, and changing, background vapor pressure. Several measurements were used to determine this metric including NMR, XRD and ICP-MS taken on silver film evaporated after use of the target molecule, as well as device performance metrics taken on devices made in the same chamber both before and after use of the organic molecule.

Only two of the initial four target molecules were test for process viability as only EDAI and MTEACl passed the initial viability tests. The use of silver was chosen as an indicator as it evaporates at low temperatures and is well behaved; silver also forms halide binaries so residual iodine or chlorine would form the corresponding AgI or AgCl material which is readily detectable. For both molecules tested, no indication of either organic or halide contamination was found in any of the measurements noted above. Finally, the device performance for devices made before and after use of the organic molecules were equivalent.

Conclusions

Although this project had many stops and starts, as well as several specific milestones that were not met, it still served a crucial role in aiding the commercialization efforts of Swift Solar. At the highest level we can consider that a success. Swift has continued to move their R&D efforts forward, has successfully secured additional funding from DOE, has successfully completed several funding rounds from private sources, and continues on their track towards commercialization. Swift's current roadmap, to the best of our knowledge, still contains both the recombination layer and wide gap alloy, on which this program was based.

From the perspective of lessons learned, this program has taught us to limit the lower TRL technologies to a singular entity in order to provide better focus to the work scope. Additionally, a major issue here was the use of experimental and/or processing techniques that were not fully proven out. In future work we will limit the tool set to robust techniques and capabilities to ensure that the 'unknowns' in a project are limited to the focal point of the research.