Final Technical Report

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Name of recipient: PLANT PV, Inc.

Project title: Novel wide band gap materials for highly efficient thin film tandem solar cells

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Executive Summary

Tandem solar cells (TSCs), which use two or more materials to absorb sunlight, have achieved power conversion efficiencies of >25% versus 11-20% for commercialized single junction solar cell modules. The key to widespread commercialization of TSCs is to develop the wide-band, top solar cell that is both cheap to fabricate and has a high open-circuit voltage (i.e. >1V). Previous work in TSCs has generally focused on using expensive processing techniques with slow growth rates resulting in costs that are two orders of magnitude too expensive to be used in conventional solar cell modules.

The objective of the PLANT PV proposal was to investigate the feasibility of using Ag(In,Ga)Se$_2$ (AIGS) as the wide-bandgap absorber in the top cell of a thin film tandem solar cell (TSC). Despite being studied by very few in the solar community, AIGS solar cells have achieved one of the highest open-circuit voltages within the chalcogenide material family with a Voc of 949mV when grown with an expensive processing technique (i.e. Molecular Beam Epitaxy). PLANT PV’s goal in Phase I of the DOE SBIR was to 1) develop the chemistry to grow AIGS thin films via solution processing techniques to reduce costs and 2) fabricate new device architectures with high open-circuit voltage to produce full tandem solar cells in Phase II. PLANT PV attempted to translate solution processing chemistries that were successful in producing >12% efficient Cu(In,Ga)Se$_2$ solar cells by replacing copper compounds with silver. The main thrust of the research was to determine if it was possible to make high quality AIGS thin films using solution processing and to fully characterize the materials properties.

PLANT PV developed several different types of silver compounds in an attempt to fabricate high quality thin films from solution. We found that silver compounds that were similar to the copper based system did not result in high quality thin films. PLANT PV was able to deposit AIGS thin films using a mixture of solution and physical vapor deposition processing, but these films lacked the p-type doping levels that are required to make decent solar cells. Over the course of the project PLANT PV was able to fabricate efficient CIGS solar cells (8.7%) but could not achieve equivalent performance using AIGS.

During the nine-month grant PLANT PV set up a variety of thin film characterization tools (e.g. drive-level capacitance profiling) at the Molecular Foundry, a Department of Energy User Facility, that are now available to both industrial and academic researchers via the grant process. PLANT PV was also able to develop the back end processing of thin film solar cells at Lawrence Berkeley National Labs to achieve 8.7% efficient CIGS solar cells. This processing development will be applied to other types of thin film PV cells at the Lawrence Berkeley National Labs. While PLANT PV was able to study AIGS film growth and optoelectronic properties we concluded that AIGS produced using these methods would have a limited efficiency and would not be commercially feasible. PLANT PV did not apply for the Phase II of this grant.
Comparison of Phase I objectives and actual accomplishments

In Phase I, PLANT PV’s primary goals were to determine the feasibility of fabricating AIGS thin films using hydrazine solution processing routes with sufficient materials properties to produce high open-circuit voltage solar cells. PLANT PV developed a work plan with the tasks listed below followed by a brief description of the results and status. Greater scientific details are provided in the Summary of Project Activities section.

**TASK 1 OBJECTIVES: DEVELOP MOLECULAR PRECURSORS IN HYDRAZINE**

The objective of this task was to synthesize precursor solutions (“precursor”), known as chalcogenide nanoclusters, which can be mixed in solution and processed to form solid films. Molecular nanoclusters are formed by dissolving solid compounds (e.g. In$_2$Se$_3$) in hydrazine forming precursors. The precursors containing the separate molecular nanoclusters are then mixed together to form a composite solution, which can be deposited onto substrates via spin casting, spray deposition or printing. The stoichiometry of the films is controlled by adjusting the mixing ratio of the separate precursors. Solution processing AgIn$_{1-x}$Ga$_x$Se$_2$ films will require the synthesis of three hydrazinium precursors: In$_2$Se$_3$, Ga$_2$Se$_3$, and Ag based precursors. Indium and Gallium precursors have previously been synthesized so the main thrust of PLANT PV is the development Ag based complexes that could be used in hydrazine.

**TASK 1 FINAL STATUS - Complete**

PLANT PV was successfully able to form In$_2$Se$_3$ and Ga$_2$Se$_3$ nanoclusters that resulted in smooth, crack free thin films. To demonstrate that we could control the stoichiometry, we also synthesized and mixed Cu$_2$S nanoclusters with In$_2$Se$_3$ and Ga$_2$Se$_3$ nanoclusters to achieve slightly copper poor CIGS thin films with an In/(In+Ga) ratio of 0.7.

PLANT PV attempted to develop several different solution chemistries including Ag, AgSe and AgCl nanoclusters as well as Ag and AgSe nanoparticles, which are described in more detail in the subsequent section. We discovered that Ag complexes were not compatible with hydrazine; AgSe complexes are insoluble in hydrazine and attempts to use nanoparticles in the nanocluster host matrix (e.g. In$_2$Se$_3$) resulted in significant agglomeration and inhomogenous thin films.

In order to continue the study we used a hybrid route to form AIGS thin films; we deposited layers of In, Ga, and excess Se using the hydrazine route and thermally evaporated Ag to form a layered structure. The In$_x$Ga$_y$Se$_z$/Ag film stack was subsequently annealed in an inert atmosphere, and uniform AIGS was produced. Furthermore, this method avoided carbon inclusion and allowed fine-tuning of film stoichiometry.

**TASK 2 OBJECTIVES: CRYSTAL PHASE AND MORPHOLOGY CHARACTERIZATION OF SOLUTION PROCESSED AIGS FILMS**

The objective of this task is to determine the crystal structure, crystallite size, and general film morphology of AIGS films produced via solution processing. PLANT PV staff will determine these properties as a function of processing conditions and coarse stoichiometric control. PLANT PV will vary these parameters in order to fabricate high quality films. In TASK 2 we specifically looked to use SEM, EDX, XPS, and XRD to study film morphology and crystal structure.

**TASK 2 FINAL STATUS - Complete**

Using the solution processing/evaporation method we were able to produce silver indium diselenide (AIS) thin films with the expected stoichiometry of AgInSe$_2$ and AIGS films with moderate Ag deficiency. X-ray
diffraction was used to identify the phase and EDX showed that despite using a stacking method the Ag, In, and Se distributions were homogenous. SEM showed that thin AIGS films were void free with relatively small grain sizes (e.g. 100-200 nm), but thicker films often resulted in cracked thin films, which often caused shunting. More details on film characterization are provided in the next section.

**TASK 3 OBJECTIVES: OPTICAL AND ELECTRICAL CHARACTERIZATION OF AIGS FILMS TO DETERMINE CHARGE TRANSPORT AND RECOMBINATION RATES**

The objective of this task is to identify which precursor mixtures and processing steps produce AIGS films with the lowest charge recombination rates, highest charge carrier mobilities, and also determine the doping type and density. In this list we plan to study:

1) Charge Transport, Doping density and type using the Hall measurement technique.  
2) Bulk recombination rates using time resolved photoluminescence decay measurements.  
3) Defect Chemistry using drive-level capacitance profiling.  
4) Absorption Coefficient, Valence and Conduction Band Energies using UV-VIS and photoelectron spectroscopy in air (PESA).

**TASK 3 FINAL STATUS - Complete**

The most important metrics for analyzing thin film PV is doping density and the minority carrier lifetime. We found that our AIGS thin films were extremely insulating in the SEM and that it was challenging to make ohmic contact to AIGS thin films. Measuring AIGS doping was challenging due to low doping density and film growth sensitivity to the substrate. Film growth studies using Mo covered glass were too conductive to be used for Hall measurements. We made several attempts to grow AIGS thin films on insulating substrates such as glass, silicon, and alumina in order to perform Hall measurements. However, AIGS did not spin well onto these substrates, often resulting in cracked films that would delaminate upon subsequent depositions required to make thicker films. We estimate that the doping density of AIGS films produced using the hybrid process was well below $10^{15}$ cm$^{-3}$. In CIGS literature it is well documented that Cu poor stoichiometry is required to achieved p-type doping. We attempted to vary the stoichiometry in order to increase doping but could not detect a noticeable difference. We also studied inclusion of dopants (e.g. Antimony) in order to increase the doping density, which will be discussed in the next section.

Time resolved photoluminescence decay measurements resulted in very low lifetimes (e.g. <0.5 ns) that would not result in a high open-circuit voltage. The photoluminescence signal was extremely low, but is not clear if the bulk recombination or surface recombination resulted in this fast recombination process. It should be noted that minority carrier lifetimes between 5-50 ns would likely be required to achieve an open-circuit voltage greater than 1V.

We built the drive-level capacitance profiling tool at the Molecular Foundry and attempted to test AIGS thin films. In DLCP the applied voltage is varied to change the depletion width at the p-n junction to study the doping profile. It is also possible to vary the temperature and measure the change in capacitance to study defect energy levels. We deposited n-type CdS to form an n-p junction with AIGS thin films on molybdenum/glass and subsequently evaporated gold contacts on CdS to perform DLCP. While DLCP is a powerful tool to study films that are moderately doped (i.e. >$10^{15}$ cm$^{-3}$), given the low doping density of AIGS it was not effective. The calculated depletion width (e.g. W = 3-4 μm) even for low bias and modulating voltages using DLCP was greater than the actual film thickness (1-1.5 μm). This prevented us from measuring any bulk properties and we did not attempt to study defects by changing the temperature.
PLANT PV was able to determine that the band gap of AIGS was 1.8 eV by measuring the photoluminescence spectrum at room temperature. PLANT PV did not perform UV-Vis on AIGS thin films, which were generally deposited on Mo covered glass substrates. Attempts to place them on bare glass and alumina substrates that were transparent in the visible portion of the spectrum usually resulted in delamination or in highly cracked thin films. PLANT PV did not perform PESA in order to spend more time fabricating thin films and study alternative methods to measure the doping density.

**TASK 4 OBJECTIVES: FABRICATE AIGS PV DEVICES ON MOLYBDENUM SUBSTRATES**

Once AIGS films have been characterized we will fabricate devices on the traditional Mo coated soda lime glass substrates with the goal of producing solar cells with an efficiency >9%. Initially PLANT PV will leverage the same cell architecture used by CIGS manufacturers since this has been shown to be capable of producing moderately efficient AIGS devices. In this architecture, 2um of photoactive chalcogenide (e.g. CIGS, AIGS) is deposited on molybdenum coated soda lime glass. CdS is subsequently deposited on the active layer via chemical bath deposition, which forms the p-n junction. This step is followed by the sputter deposition of i-ZnO/Al-ZnO with a final step of thermal evaporation of an Al/Ni grid.

**TASK 4 RESULTS - Complete**

Prior to making AIGS solar cells, PLANT PV made CIGS solar cells using the above architecture to ensure that the back end processing (e.g. CdS, ZnO/Al-ZnO, and Al/Ni grid) were sufficient. PLANT PV fabricated 8.7% CIGS solar cells at Lawrence Berkeley National Lab, which are described in the next section. The results of the CIGS study confirmed that the processing conditions for the various layers of the solar cell were adequate to study AIGS solar cell fabrication.

We fabricated AIGS solar cells using the previously described architecture that were able to rectify in the dark but were sub-0.5% efficient when illuminated. These lower power conversion efficiencies were related to low p-type doping, which resulted in poor ohmic contact, and to shunting from cracked films.

**TASK 5 OBJECTIVES: OPTIMIZE AIGS DEVICE ARCHITECTURE TO PRODUCE HIGHEST Voc**

Task five objectives were to optimize the device architecture and more carefully study defects and interfaces related to AIGS. In order to more accurately determine film property targets and to predict achievable power conversion efficiencies, PLANT Solar will model the entire AIGS solar cell architecture using SCAPS-1D software to determine which architectures will be more amenable to high Voc. Key input parameters such the doping density, charge carrier mobility, minority carrier lifetime, bulk absorption coefficient and optical bandgap will be measured.

**TASK 5 FINAL STATUS - Incomplete**

Toward the end of the project PLANT PV focused on growing higher quality films to reduce cracking (and thus shunting) and attempted to more heavily dope AIGS using the hybrid processing scheme. Given the poor results of AIGS solar cells PLANT PV did not attempt to model the device.

**TASK 6 OBJECTIVES: OPTICAL AND ELECTRICAL MODELING OF AIGS/LOW BAND GAP TANDEM SOLAR CELLS TO DETERMINE EXPECTED DEVICE PERFORMANCE**

In the final stage, PLANT PV will do modeling to determine the maximum possible efficiency that can be obtained using AIGS top cells in conjunction conventional low band gap solar materials (e.g. CIGS, CZTS(Se), etc.).
TASK 6 FINAL STATUS - Not attempted

Rather than model tandem AIGS based solar cells, which did not achieve our initial goals, we chose to look at alternative doping methods in the final month. We found that antimony mixed in the nanocluster precursor solutions may result in higher doping levels than intrinsic AIGS thin films.

Project activities

TASK 1 WORK AND RESULTS: DEVELOP MOLECULAR PRECURSORS IN HYDRAZONE

Several different types of Ag complexes were studied in the first three months of the project. It is preferable to directly dissolve selenide compounds in hydrazine to synthesize nanoclusters. We found that In$_2$Se$_3$ and Ga$_2$Se$_3$ could be dissolved into pure hydrazine in 0.6M and 0.3M, respectively, using methods described by Mitzi et al. After 24 hours of stirring, the In compound turned into a clear, viscous yellow solution and the Ga compound turned into a clear green solution.

We tested whether the silver chalcogenides could be dissolved into hydrazine in the presence of excess chalcogenide as well. Since the final Ag hydrazinium structures are unknown, high ratios of chalcogen to silver chalcogenide were attempted initially, and dissolution was monitored over the course of two weeks by filtering and coating of the hydrazine solution by spin coating. Upon heating, the absence of any film on the substrate implied no dissolution of the silver chalcogenide. Solutions were attempted by dissolving Ag$_2$S, Ag$_2$Se, and Ag$_2$Te, with the corresponding chalcogen and none showed any dissolution under any conditions.

The next attempt at incorporating Ag into hydrazine ink was to parallel the process by which Zn can be added into Cu-Sn-S inks by the dissolution of ZnCl into Sn nanocluster solutions. AgCl, while virtually insoluble in aqueous solutions, seems to have moderate solubility in neat hydrazine. However, upon mixing with either In nanocluster, Se-hydrazine, or Cu nanocluster solutions, immediate precipitation of a grey solid occurs. While it is abstractly interesting whether there is a chalcogenide-assisted reduction of AgCl to Ag or if the chalcogenide simply reacts with AgCl to form the insoluble Ag chalcogenide, this approach appeared unpromising.

We then began to synthesize Ag and Ag$_2$Se nanoparticles to be mixed with In and Ga nanoclusters. Ag nanoparticles were synthesized by both a standard borohydride reduction in aqueous solution and the polyol method in ethylene glycol. The borohydride reduction synthesis created ~20nm nanoparticles with a weakly bound citrate ligand shell. By contrast, the polyol method makes similarly sized nanoparticles with a tightly bound, chemically robust poly(vinylpyrrolidinone) ligand shell. Ag$_2$Se particles were also synthesized by the solvothermal reaction of Ag(NO$_3$)$_2$ in a pyridine solution saturated with elemental selenium.

In order to reduce carbon contamination and include the nanoparticles in the hydrazine process, we attempted a ligand exchange in hydrazine. Nanoparticles of Ag$_2$Se and Ag were dried and transferred into solutions of hydrazine with and without excess chalcogen. However, nanoparticles of Ag and Ag$_2$Se could not be stabilized as colloids in hydrazine-based solutions. The stripping of the native citrate, polymer, and pyridine ligands induced irreversible agglomeration in each case, which prohibited the solutions from coating evenly. A spun cast sample of Ag NPs made by the polyol process is shown on the left of Figure 1. A representative AIS film made on Mo via the hybrid AgNP/nanocluster processing route can be seen in the middle and an EDS map of another area of the film is shown on the right of Figure 1. The film is clearly discontinuous with a nanocrystalline morphology and the elemental distribution Ag, In and Se all overlap, as expected, while the Mo signal is stronger away from the AIS region.
Figure 1. (Left) SEM of Ag nanoparticles on Si substrate. (Middle) SEM image of representative area of AIS thin film. (Right) Energy dispersive spectroscopy map of discontinuous AIS made from hybrid AgNP/nanocluster ink.

**TASK 2 WORK AND RESULTS: CRYSTAL PHASE AND MORPHOLOGY CHARACTERIZATION OF SOLUTION PROCESSED AIGS FILMS**

After a great deal of effort trying to develop Ag based complexes for hydrazine, PLANT PV decided to fabricate thin films using a multilayer method. The initial thin film was deposited by mixing In and Ga nanoclusters in solution and spin casting onto the substrate at 900 RPM for 90 seconds. The film was subsequently heated to 300ºC for 5 minutes to remove hydrazine and form a 100-150nm thick In$_x$Ga$_y$Se thin film. This deposition was repeated until three quarters of the desired film thickness was deposited, after which the film was annealed at 500ºC. A thin silver layer was then deposited on top of the In$_x$Ga$_y$Se using evaporative deposition (10$^{-6}$ Torr, 99.999% pure Ag). Another set of layers of Se-rich In$_x$Ga$_y$Se was deposited by the aforementioned method to provide sufficient Se for the final AIGS film. A final anneal, which was between 550-575ºC, was critical for elemental homogeneity, since the Ag layer needed to diffuse as far as 1µm into the film.

Film morphology was generally small grained with little texture, though higher temperature annealing induced grain growth. In addition, higher temperatures were also critical for interdiffusion of Ag throughout the film. Figure 2 shows a comparison of two films deposited by identical methods but annealed at different temperatures. The film shown in figure 2(a) is annealed at 525ºC, and thus retains the original small-grained In$_x$Ga$_y$Se/Ag/In$_x$Ga$_y$Se structure. However, the film in figure 2(b) is heated at 575ºC and is elementally homogeneous throughout the thickness of the film and larger grained. Elemental homogeneity was confirmed by cross-sectional EDS mapping of a sample heated at 550ºC (figure 3), wherein the Ag, In and Se signals have strong overlap in the bottom panels.

Figure 2. Thick (1µm) films of AIGS with stoichiometry of Ag$_{1}$In$_{0.52}$Ga$_{0.44}$Se$_{2}$, annealed at (a) 525ºC and (b) 575ºC for 20 minutes.
In addition to testing the effect of annealing temperature, the Ga content was also varied to create AgIn$_{0.8}$Ga$_{0.2}$Se$_2$ and AgIn$_{0.6}$Ga$_{0.4}$Se$_2$ thin films, with the latter having the higher band gap required for a high $V_{OC}$. XRD patterns shown in figure 4 confirmed that films of both Ga contents were almost entirely a single phase, though trace components of Ga$_2$Se$_3$ were sometimes seen in films with high Ga concentrations, as indicated by the green markers. In the cases of insufficient Se in the film or low temperature annealing, secondary phases, such as elemental Ag and In$_2$Se$_3$, were observable.

Importantly, morphological issues arose for thicker films that limited their use in electrical devices. The interdiffusion of Ag into the In$_2$Se$_3$ during the final anneal led to varying degrees of detrimental void formation as seen in figure 5 (left). In addition, the phase transformation involved a large volumetric contraction, which commonly caused film cracking and delamination. Cracking and delamination, as seen in the right micrograph of figure 5, produced conductive pathways between the top and bottom of the film, which limited the performance of thicker films of AIGS.
**Figure 5.** SEM images of (left) void formation and (right) film cracking and delamination in AIGS films.

**TASK 3 WORK AND RESULTS:** OPTICAL AND ELECTRICAL CHARACTERIZATION OF AIGS FILMS TO DETERMINE CHARGE TRANSPORT AND RECOMBINATION RATES

While AIS/AIGS films could be deposited readily onto Mo-coated glass, continuous AIS/AIGS could not be deposited on bare glass. Therefore, we could not perform UV-Vis measurements to determine the absorption coefficient of our films. However, we were able to determine the band gap of AIGS by measuring the photoluminescence spectrum. Over the course of the grant we built a time-resolved photoluminescence decay measurement system at the Molecular Foundry as shown in figure 6. In this set-up a Coherent Mira 900 Ti:Sapphire laser produces a near-IR pulse at 830 nm which is converted to 560 nm by an optical parametric oscillator (Mira OPO), which is then optically coupled to a confocal microscope (60x objective) with a dichroic beam splitter and an objective lens that focuses the light onto the sample, as shown in figure 6. In this scheme, green light excites carriers in the semiconductor at the focal point that then radiatively decay, emitting photons through the objective lens (green lines) and into the photodetector (or spectrometer which is not shown in the diagram).

**Figure 6.** Time-resolved photoluminescence decay measurement system built at the Molecular Foundry.
Photoluminescence was performed on AIGS films deposited onto Mo using the set-up in figure 6 but modified with a spectrometer and CCD camera. The photoluminescence spectrum in figure 7 has a peak at 677nm (1.8eV), which is inferred to be the optical band gap of the AIGS thin film. The emission spectrum is close to the ideal band gap (1.7 eV) for two junction tandem solar cells.

Figure 7. Emission spectrum of an AIGS thin film when excited with 500nm light. The background was not subtracted and the rising edge at 780 nm is background noise and was observed when the shutter was closed.

Time-resolved photoluminescence (TRPL) measurements were used to study the minority carrier lifetime of AIGS. Initial attempts to illuminate the sample with moderate light intensity (20µW average power, Δn ~10^16 cm^-3) could not produce a high enough PL signal to measure the decay. A much larger power intensity >10mW average power was used to generate enough signal to produce the PL decay shown in figure 8 and the PL spectra shown in the figure above. The TRPL results show sub-0.5 ns lifetime of AIGS, which could be due to 1) high bulk recombination, 2) high surface recombination, and/or 3) non-linear processes (e.g. Auger because of the excitation intensity). Regardless, the low PL signal and fast decay time indicate that the minority carrier is significantly less than the 5-50 ns required to make PV devices with a Voc greater than 1V. It should be noted that we measured >3 ns lifetimes for CIGS thin films and we verified a 4ns mono-exponential decay using a PL standard, Rhodamine 6G laser dye, for our home-built TRPL system.
Figure 8. Time resolved photoluminescence decay of 675nm emission from an AIGS thin film after a 1ps pulse of 500nm light.

**TASK 4 WORK AND RESULTS: FABRICATE AIGS PV DEVICES ON MOLYBDENUM SUBSTRATES**

Prior to fabricating AIGS solar cells PLANT PV fabricated CIGS PV devices to ensure that the back end processing was of sufficient quality for an efficient solar cell. Cu$_2$Se, In$_2$Se$_3$, and Ga$_2$Se$_3$ were mixed to provide a copper poor solution with an In/In+Ga ratio of 0.7. The solutions were spin cast at 900 RPM for 90 seconds and then annealed to 350°C for 2 minutes on a Mo covered soda lime glass substrate. Between 7-11 coats were applied to achieve a film thickness greater than 1µm; a final anneal at 550°C induced grain growth and removed Se residues. CdS was subsequently deposited via chemical bath deposition using recipe out of NREL. Al doped ZnO (AZO) was coated onto devices by means of pulsed cathodic arc deposition in a high-vacuum system. Specifically, a 4% Al:Zn alloy rod was pulsed 1,000 times (~100nm) with a high voltage, which induced arcing onto the grounded device. It was found that depositing a 30nm layer of intrinsic ZnO (i-ZnO) improved electrical properties considerably. All arcing was performed in 3mTorr of oxygen with light heating of the device, which successfully formed a highly conductive film stack of i-ZnO/AZO.

After deposition of the conducting top contact, individual cells were scribed down to the metallic back contact. Indium contact pads were fixed onto the AZO top contact, and cells were mounted onto a miniature probe station for analysis. Current-voltage measurements were performed in the dark and under AM1.5 illumination using a Newport 300W Thermo-Oriel Xenon lamp whose power was set with an NREL calibrated photodiode. Figure 9 shows an I-V from a CIGS film that was fabricated to test the efficacy of the backend processing.
AIGS solar cells were also fabricated using the same architecture used for CIGS above. However, due to the high resistivity of all films of AIGS and AIS diode behavior was not initially observed (i.e. the J-V curves looked like the device was open).

We attempted to improve the doping levels by incorporating Sb into the In$_x$Ga$_{1-x}$Se$_y$ films by first dissolving Sb$_2$Se$_3$ solids in hydrazine and including one atomic percent in the In/Ga mixture. These films were more conductive and were able to rectify in the dark as shown in figure 10 (red line). While this I-V was taken in the dark, no change in short circuit current was observed upon illumination. The light I-V curve (black line) indicates that the device has a low shunt resistance that is likely due to voids and cracking and a moderate photoconductivity. Overall, no device with respectable power conversion efficiency could be fabricated using AIGS during this project.
Conclusions

Solution processing with hydrazine:
It is useful to highlight the advantages and disadvantages of solution processing with hydrazine as an R&D tool during the course of the project. We originally decided to use solution processing routes to AIGS because we thought that the development of hydrazine chemistry would be relatively quick, leaving significant amounts of time to spend tweaking the recipe to make good solar cells. The main advantage of solution processing is a low barrier to entry given the simplicity of the fabrication equipment (i.e., glove box, hot plate and oven). The ability to modify the stoichiometry and morphology of thin films is also trivial. However, while elements that comprise CIGS all readily dissolve hydrazine it should be noted that most selenides (e.g. Cd, Zn, and Ag) do not. Therefore it was possible to quickly develop CIGS thin films using hydrazine chemistry but it was not straightforward to make Ag based thin films. A great deal of our research efforts went toward developing Ag inks and this limited the time that we could eventually spend developing solar cells.

While solution processing is easy to get started, depositing thin films is often a time consuming task that can have lower yields than physical vapor deposition techniques. The primary problem with hydrazine inks is that they cannot be highly concentrated (i.e. <1M) and typically result in 100-150nm thick films, which require 7-10 coats to achieve 1µm. Using nanoparticles to create a suspension can change the viscosity and enable thicker films to be deposited but this route was ineffective for Ag nanoparticle approaches we used. Therefore, depositing a series of four cells would often require over seven hours given the required heating and cooling steps during deposition and the final anneal. Furthermore, any debris on the surface (or poor surface wetting by the solution) could ruin the thin film, which reduced the yield to ~75%. Finally, when using solution processing techniques, the surface adhesion properties are extremely important and it was not possible to switch to insulating substrates to perform many of the crucial measurements. We believe that molybdenum is likely required for this system because MoSe$_2$ readily forms during annealing, which promotes adhesion during subsequent annealing steps. Even continuous thin films that could be deposited on UV-ozone treated glass could not survive a second coat because of adhesion issues. In the end the hydrazine-based solution processing technique turned out to be a labor intensive process that had less variable control than might have been achieved with other techniques.

Prospects of AIGS as a wide-band gap solar cell material:
Given the lack of success in fabricating working solar cells in this project, we do not feel that hydrazine routes for AIGS will be worth pursuing in the future. However, we still believe that AIGS PV devices should continue to be researched and developed. Our initial goal of studying defects in AIGS using DLCP is still very valid and would be worthwhile for future researchers that are able to deposit higher quality films with adequate doping. Developing a similar system like AIGS would allow researchers to better understand the role that copper plays in pinning the defect levels in CGS/CIGS, which may be a limiting factor for high Voc devices.

PLANT PV and Phase II:
PLANT PV is committed to performing high quality R&D work on novel materials for solar cells. We greatly appreciate the support provided by the DOE through the SBIR phase I grant, which allowed us to begin working full time on PV research at the Molecular Foundry. During the last nine months were able to set up many key pieces of characterization equipment and establish back-end processing to make efficient solar cells. This grant was vital to our business, allowing us to explore one potential PV innovation that we ultimately felt would not be commercially viable in the future. Given the results of the SBIR Phase I we decided not pursue Phase II funding.
Products developed under the award and technology transfer activities

Publications (list journal name, volume, issue), conference papers, or other public releases of results:
PLANT PV has not published any results related to the AIGS project.

Web site or other Internet sites that reflect the results of this project:
PLANT PV has not put any results on the Internet.

Networks or collaborations fostered:
Due to the SBIR Phase I grant, PLANT PV began collaborating with Andre Anders, a sputtering expert at Lawrence Berkeley National Lab to use his pulsed cathodic arc system to deposit AZO. We also began collaborating with Jim Schuck at the Molecular Foundry to work on optoelectronic characterization of AIGS. This collaboration led to a joint proposal to the Next Generation PV II program.

Technologies/Techniques:
PLANT PV developed a drive-level capacitance profiling measurement system at the Molecular Foundry as well as back-end processing (e.g. CdS bath deposition) and evaporative deposition of metal grids. We also built PV testing boxes for thin film devices and software to analyze I-V curves.

Inventions/Patent Applications, licensing agreements:
PLANT PV filed a provisional patent application related to AIGS based tandem devices.

Other products, such as data or databases, physical collections, audio or video, software or netware, models, educational aid or curricula, instruments or equipment:
PLANT PV did not create other products during the Phase I SBIR grant.