

Use of Very-High-Frequency Plasmas to Prepare a-Si:H-Based Triple-Junction Solar Cells at High Deposition Rates

**Annual Technical Status Report
11 March 1998—11 March 1999**

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Energy Conversion Devices, Inc.
Troy, Michigan



NREL

National Renewable Energy Laboratory

1617 Cole Boulevard
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Preface

This Annual Subcontract Report covers the work performed by Energy Conversion Devices, Inc. for the period March 11, 1998 to March 11, 1999 under DOE/NREL Subcontract No. ZAK-8-17619-18. The following personnel participated in the research program.

M. Izu, S.J. Jones, T. Liu, A. Myatt , S.R. Ovshinsky, D.V. Tsu, B. Viers.

Collaborations with the Colorado School of Mines, University of Toledo, and United Solar Systems Corp. are gratefully acknowledged. We would like to specially thank Professor Xunming Deng for the many discussions and input he has made in advancing this program he previously led.

Executive Summary

Objectives

The main objective of this program is to develop a high rate thin film deposition method in order to increase the throughput of ECD's roll-to-roll solar module production design and in doing so reduce the cost of the solar modules. In particular, a very high frequency (70 MHz) plasma enhanced chemical vapor deposition (PECVD) process is being developed for the fabrication of intrinsic layers for high efficiency amorphous silicon-based triple-junction solar cells at high deposition rates. Intrinsic layers consisting of either amorphous silicon or amorphous silicon germanium alloy materials are being developed. The program goal is to prepare these materials at rates of 10 Å/s or higher while maintaining the cell efficiencies at the high values presently obtained for devices made using the standard 13.56 MHz frequency and low deposition rates (near 1 Å/s). Upon completion of a successful program, this high rate process will be added to ECD's roll-to-roll solar cell production design to reduce solar module cost.

Approach

In order to test the feasibility of using the VHF method for high rate intrinsic layer preparation, the deposition conditions used to prepare small area (0.25 cm²) single-junction amorphous silicon (a-Si:H) and silicon germanium alloy (a-SiGe:H) cells by the very high frequency (VHF) technique are being optimized to obtain the highest cell efficiencies. These component cells will then be combined to create high efficiency a-Si:H/a-SiGe:H/a-SiGe:H triple-junction cells. The deposition conditions for these multi-junction cells will also be optimized to further increase the device performance. In particular for the triple-junction cells, the conditions used to prepare p/n tunnel junctions will be optimized to minimize absorption and series resistance and maximize carrier collection and cell performance. Besides achieving high small area cell performance, large area cathode hardware designs which will allow for the uniform deposition of i-layers over a large area using the VHF technique and high deposition rates will be tested using a single chamber vacuum system. This large area hardware will be required for the future incorporation of the technique into an ECD built roll-to-roll solar cell production line.

Results/Status

The following has thus far been achieved during this year:

1) 8.0% stable efficiencies have been achieved for a-Si:H single-junction cells whose i-layers are prepared at rates near 10 Å/s using the VHF technique. This performance compares with 8.2% stabilized efficiencies for a-Si:H cells made using the same deposition equipment, the standard 13.56 MHz technique and deposition rates near 1 Å/s. While we have yet to achieve the 8.4% program goal for the a-Si:H cells, we hope that our recent improvement of the n-layer conditions as well as further optimization of other deposition conditions will lead to the achievement of the goal in the coming months. This achievement may also come from the general improvement of system baseline efficiencies for all cells by optimization of chamber heating and pre-deposition treatments.

2) In terms of the a-SiGe:H cells, a number of studies of devices with properties appropriate for middle junction cells have been made. The stabilized properties for these cells prepared at i-layer rates near 10 Å/s are again similar to a-SiGe:H cells made using the same deposition hardware and the low rate 13.56 MHz method. We are looking to improve these efficiencies further again through optimization of doped layer conditions and the general improvement of the baseline efficiencies for the semiconductor deposition system.

3) Deposition conditions have been identified for which uniform i-layer deposits can be obtained over our 4" x 4" substrate area at the high 10 Å/s rate. As the deposition rate is increased, the ability to obtain uniform deposits over a significant area becomes more difficult. It was found that by using moderately low chamber pressures, one can maintain uniform thin film deposits at the 10 Å/s rate while other deposition parameters are varied in order to optimize the cell performance.

4) 10.5% efficiencies have been obtained for a triple-junction cells whose i-layers are prepared at the 10 Å/s rate. These efficiencies degrade by 10-13% with long term light exposure. This amount of degradation is similar to that obtained for triple-junction cells prepared at the standard low i-layer deposition rates (1 Å/s). The achievement of higher efficiencies in the coming year is likely with further optimization of the triple-junction structure. In terms of improving the efficiencies for the triple-junction cells, focus has thus far been on optimizing the top and middle component cells. We plan to put a major effort on the optimization of both the bottom cell and tunnel junction performance in the coming months.

Publications

Listed below are some articles in which this work, or portions of this work, were published.

“Preparation of a-Si:H and a-SiGe:H i-layers for nip solar cells at high deposition rates using a very high frequency technique.” S.J. Jones, X. Deng, T. Liu, and M. Izu, *Amorphous and Microcrystalline Silicon Technology – 1998*, edited by R. Scropp, H. Branz, M. Hack, I. Shimizu and S. Wagner, Vol 507, 113.

“Preparation of a-Si:H and a-SiGe:H nip cells at high rates using a 70 MHz VHF PECVD technique.”, S.J. Jones, T. Liu and M. Izu, *NCPV Photovoltaics Program Review; Proceedings of the 15th Conference, Denver, CO, 1998; AIP Conference Proceedings, Vol 462, 303.*

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Introduction

Throughout the past 20 years, Energy Conversion Devices, Inc (ECD) and its commercialization subsidiaries and joint ventures have developed amorphous silicon (a-Si:H) materials for thin film photovoltaic (PV) devices. In particular, ECD has used the 13.56 MHz rf Plasma Enhanced Chemical Vapor Deposition (PECVD) process to deposit the amorphous and microcrystalline layers that comprise its proprietary triple-cell, spectrum splitting thin-film solar cell (Guha et al. 1994). Several energy conversion efficiency world records have been established for small-area devices (Yang et al. 1997) and for 4 sq. ft. modules (Izu et al. 1993) using this technology. To achieve these high stable efficiencies, the 13.56 MHz PECVD processes have been optimized at rather low deposition rates of 1-3 Å/s. Operating this process at higher deposition rates leads to unacceptably low stable solar cell efficiencies due to higher electronic defect densities in the a-Si:H alloys, and to a greater susceptibility to light-induced material quality degradation that results from changes in the film growth kinetics and microstructure at the higher deposition rates.

Increasing the deposition rate at which high performance solar cells can be manufactured would have a significant impact on manufacturing cost, since both the capital depreciation and labor costs would be reduced by higher product throughput. ECD has experimented with a number of novel a-Si:H alloy deposition technologies over the past 10 years, and the company has had considerable success in developing and commercializing a high deposition rate, low pressure microwave PECVD process to make a-Si:H photoreceptors. The process has also been used to prepare a-Si:H alloys for solar cells at rates up to 100 Å/s (Doehler et al. 1988). Although initial device performance was good, the light stability of these devices was poor, with efficiencies degrading by more than 20% after 1000 hrs of light soaking under air mass 1.5 (AM1.5) illumination (where as state-of-the-art PECVD devices degrade by 10-15%).

Prior to the beginning of this program, we have tested the feasibility of using a 70 MHz, Very High Frequency (VHF) PECVD process to prepare semiconductor layers for high efficiency cells at high deposition rates. Earlier studies (Chatham et al. 1989, Shah et al. 1992) have shown that by using the VHF process, the deposition rate of a-Si:H films could be increased to 10-15 Å/s without an observable deterioration in the film and cell properties. We have used this VHF PECVD process to deposit highly conductive, low optical absorbing microcrystalline p-layers which have led to improved solar cell efficiencies (Deng et al 1997). Expanding this work, we prepared i-layers for a-Si:H single-junction cells by the VHF PECVD technique (Deng et al 1997). In these initial studies, a-Si:H based nip cells whose i-layers were prepared at 6-10 Å/s have shown 10% initial active area efficiencies and degrade by only 15% when subjected to the extended 1000 hrs of light soaking .

In this program, we are expanding on these initial encouraging results by conducting extensive optimization studies of the stable efficiencies of single-junction a-Si:H and a-SiGe:H nip cells as well as a-Si:H/a-SiGe:H/a-SiGe:H triple-junction cells prepared by the VHF PECVD technique at high deposition rates. The principal goal of this program is to demonstrate the feasibility of using the alternative VHF PECVD deposition technique to manufacture high stable efficiency, triple-junction solar cells at deposition rates of 10 Å/s. Accomplishing the program's principal goal will permit this new technology to be incorporated into ECD's future solar module roll-to-roll production lines, and the existing 5MW line at United Solar, ECD's joint venture company in Troy, MI. Applying this high deposition rate technique on a large scale to prepare high stable efficiency triple-junction cells and modules will lead to significant cost savings due to:

1) *Reduced material costs -*

The gas utilization for the VHF PECVD process has already been shown to be much higher than for the 13.56 MHz PECVD technique. Thus the amount of process gas used to make a module will be less.

2) *Higher throughput and reduced hardware costs -*

The increased deposition rates will reduce the time required to fabricate each module in the existing manufacturing lines. In the designs for new lines, the amount of a-Si:H deposition hardware, which is the most costly hardware in the lines, can be reduced. Thus incorporation of this new deposition technique will lead to a reduction in the labor and capital depreciation costs per module.

3) *Improved module efficiencies-*

Because of the potential for making improved a-SiGe:H material and cells, implementation of the technique may potentially lead to higher module efficiencies. Any such improvement in the efficiencies will significantly effect the cost of the a-Si:H PV generated energy since the cost is inversely proportional to the efficiency.

This program will provide the basis for incorporation of this high deposition rate technique in ECD's present and future large area, roll-to-roll solar module manufacturing lines (Izu et al. 1984) to increase throughput and reduce module cost. These cost reductions will contribute to DOE's and NREL's long-term goal of fabricating inexpensive thin film modules with 15% stable efficiencies. With ECD's experience in a-Si:H PV technology in both R&D and manufacturing phases as well as the great potential for the VHF PECVD technique, the probability of a successful program is high.

In the first stage of this program, the deposition conditions used to prepare a-Si:H and a-SiGe:H single-junction cells are being systematically varied to optimize the cell properties. The focus of these studies is on optimizing the cell properties while maintaining i-layer deposition rates around 10 Å/s. The information obtained from these studies is being used to prepare high efficiency triple-junction cells with the high i-layer growth rates. In the later stages of the program, large-scale hardware designs will be developed which will allow for the incorporation of this high rate technique into a production line environment.

The exact program goals are:

- 1) Prepare a-Si:H single-junction nip small area devices with stable 8.4% AM1.5 efficiencies using i-layer deposition rates near 10 Å/s,
- 2) Prepare a-SiGe:H single-junction nip small area devices with stable 2.8% efficiencies when measured using 630 cutoff filtered AM1.5 light using i-layer deposition rates near 10 Å/s,
- 3) Prepare a-Si:H/a-SiGe:H/a-SiGe:H triple-junction small area devices with stable 9.4% AM1.5 efficiencies using i-layer deposition rates near 10 Å/s,
- 4) Develop cathode hardware for large area thin film depositions using the VHF technique for future implementation in production.

The following sections outline the progress made in the first year of the program and our future plans.

Experimental

The solar cells used in these studies were composed of nip structures with stainless steel substrates. These nip structures were fabricated using a research scale, multi-chamber load locked deposition system. Figure 1 depicts the structures typically used in optimizing the a-Si:H and a-SiGe:H component cells. To fabricate the a-Si:H and a-SiGe:H i-layers, a fixed VHF frequency of 70 MHz was used while maintaining a deposition rate near 10 Å/s. At the time being, our focus is to prepare only the i-layers at the high rates since they are the thickest layers in the nip structure. Thus, both the doped layers and the a-Si:H buffer layers, grown between the VHF deposited a-SiGe:H i-layers and the doped layers, were prepared using the conventional PECVD process in which a 13.56 MHz frequency is used. To improve the cell properties, several buffer layer and i-layer deposition conditions were altered including the substrate temperature, the hydrogen dilution and active gas flows, and the applied power.

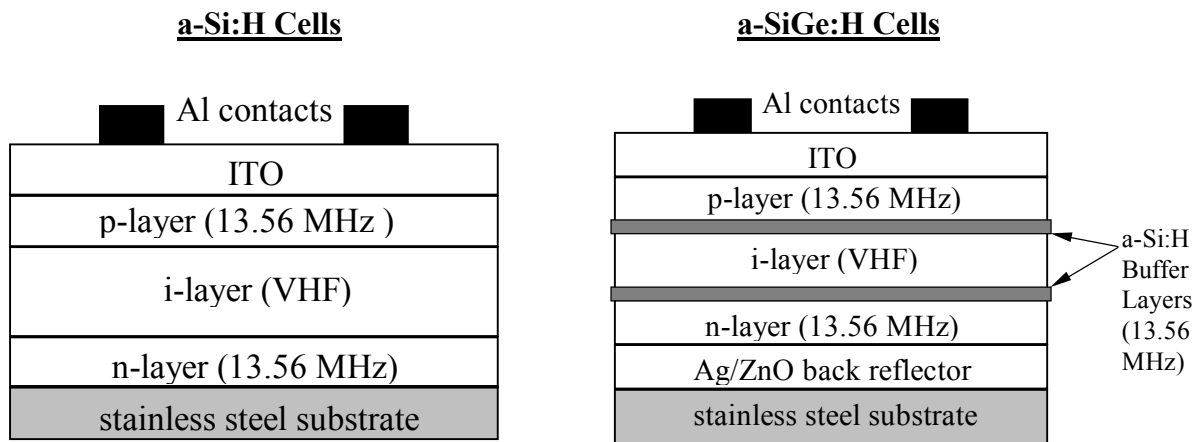


Figure 1. Structures used for optimizing component cells.

After fabrication of the nip structure, the devices were completed by depositing Indium Tin Oxide (ITO) conductive layers and then Al collection grids. Both the ITO and Al layers were prepared using standard evaporation techniques. In some cases, Ag/ZnO back reflectors were deposited on the stainless steel substrates prior to nip fabrication in order to enhance the collected current and improve the overall efficiency. The Ag/ZnO back reflectors were prepared in a roll-to-roll manufacturing machine using a DC sputtering technique.

To characterize the cells, standard IV and spectral response (quantum efficiency) measurements were made. For the a-Si:H and the triple-junction cells, standard white AM1.5 light was used to obtain the IV data. Since our goal is to use the a-SiGe:H cells as middle and bottom cells for triple-junction cells, the AM1.5 light for the IV measurements of the a-SiGe:H cells was filtered to simulate the absorption due to a top a-Si:H cell. For a-SiGe:H cells made without Ag/ZnO back reflectors, a 530 nm cutoff filter was used while 610 or 630 nm filters were used for cells with back reflectors. To complete light soaking studies, the cells were subjected to 600-1000 hrs. of one sun light with the cell temperature fixed at 50°C. The i-layer thicknesses were determined using standard capacitance techniques.

First Year Results

Component Cells

a-Si:H Cells

We have earlier reported results for *a*-Si:H cells whose *i*-layers were prepared using the VHF technique at 10 Å/s (Deng et al 1997). The general conclusion from these studies was that by using the VHF technique and careful selection of deposition conditions, the initial and stable cell efficiencies could be made to remain relatively constant with varying *i*-layer deposition rate up to 10 Å/s. Figure 2 demonstrates this result where the initial and stable efficiencies for a number of cells prepared under a variety of conditions are plotted as a function of deposition rate. All of these cells had J_{sc} near 10 mA/cm², *i*-layers which were roughly 2300 Å thick and had no current-enhancing Ag/ZnO back reflectors. The stable efficiencies were obtained by light soaking the cells for 1000 hrs. Below a deposition rate of 10 Å/s, the initial and stable cell efficiencies are relatively insensitive to the deposition rate with average values of 6.6 and 5.5%, respectively. The small amount of scatter ($\pm 5\%$) is related to experimental measurement procedures and variations in a few deposition parameters. Beyond 15 Å/s, the efficiencies are lower.

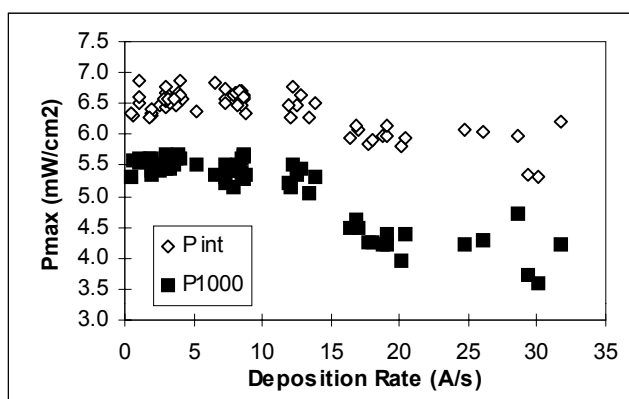


Figure 2. Cell efficiencies for VHF *a*-Si:H devices with $J_{sc} = 10 \pm 0.5$ mA/cm².

To truly demonstrate the advantage of using the VHF technique to prepare *a*-Si:H *i*-layers at high rates, we compare in Table I data for cells whose *i*-layers were prepared using the same deposition hardware by either the standard 13.56 MHz frequency or the VHF 70 MHz frequency at different deposition rates. At low deposition rates of ≤ 1 Å/s, the cells prepared using the 13.56 MHz frequency had efficiencies between 6.5 and 6.6 % which degraded by about 15% after 1000 hrs. of light soaking. These efficiencies and the amounts of degradation are similar to what were found for the cells prepared at 10 Å/s by the VHF method. Thus, we can indeed use the VHF technique to prepare cells at a high rate of 10 Å/s with similar quality to those prepared at 13.56 MHz. Comparing cells made at even higher rates, the cells prepared with the 13.56 MHz frequency have significantly lower efficiencies than the cells produced at the low rates while the efficiencies for the cells made by the VHF method are not as low and are more stable. It is clear that for high deposition rates, the VHF is superior to the standard 13.56 MHz method for *a*-Si:H preparation.

Table 1. Data for a-Si:H nip cells whose i-layers were made using 13.56 or 70MHz frequencies.

Plasma Frequency (MHz)	Deposition Rate (Å/s)	Initial P_{max} (mW/cm ²)	Light Degradation (%)
13.56	0.61	6.65	14.3
70	9.9	6.51	11.8
13.56	16.0	5.30	36.2
70	24.8	6.04	21.9

For a-Si:H cells with Ag/ZnO back reflectors, average initial cell efficiencies of 10.3% have been achieved for cells with i-layer thicknesses of 3000 Å. An IV curve for such a cell is shown in Figure 3. After 1000 hrs. of light soaking in white light, these cell efficiencies degrade by 20%, typical degradation percentages for cells of a similar i-layer thickness prepared by the standard rf PECVD technique at i-layer deposition rates of 1 Å/s. Presently, our best single-junction a-Si:H cell whose i-layer was prepared using the VHF process at 10 Å/s has a stable efficiency of 8.0% (V_{oc} =0.936 V, J_{sc} =14.3 mA/cm², FF=0.599).

In order to improve the a-Si:H cell performance to achieve our 8.4% goal, we have altered our deposition parameters in order to improve the stabilized efficiencies. We have recently completed an optimization study of the conditions used to make the n-layers. Table 2 compares a-Si:H cells made with similar i-layer and p-layer conditions but different n-layer preparation conditions. These cells were made without the benefit of a current enhancing Ag/ZnO back reflector. Using the new n-layer conditions, we have increased the short circuit current significantly due to a less absorbing n-layer. a-Si:H cells with Ag/ZnO back reflectors will be made using the new n-layer recipe in the coming months. Also, these new n-layers will be incorporated into the recipe used for making the triple-junction cells in the second year of the program.

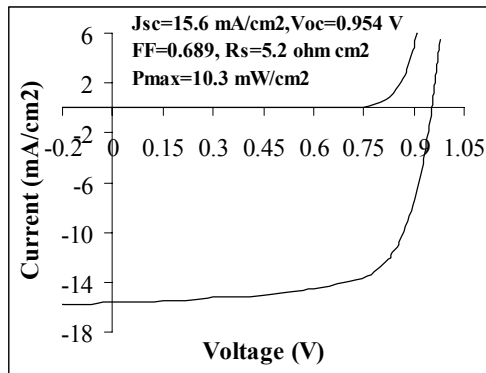


Figure 3. IV plot for a-Si:H cell whose i-layer was prepared at 10 Å/s using VHF technique.

Table 2. Data for a-Si:H cells made using old and new n-layer deposition conditions.

n-layer Conditions	i-layer dep.rate	V_{oc} (V)	J_{sc} (mA/cm ²)	FF	R_s (Ohmcm ²)	P_{max} (mW/cm ²)
Old Standard Conditions	9.0	0.951	10.62	0.689	6.1	6.96
New Optimized Conditions	10.3	0.953	11.29	0.685	6.1	7.35

a-SiGe:H Cells

Variation in cell properties with different deposition conditions

To optimize the efficiencies for the a-SiGe:H cells, a number of common PECVD parameters were varied including the substrate temperature, the gas flows, the amount of hydrogen dilution, and the chamber pressure. As is commonly found for a-SiGe:H materials and cells (Mackenzie et al 1985, Guha et al. 1981), particularly for those made at high rates, use of high substrate temperatures and large amounts of hydrogen dilution are important to obtain good film quality and high cell efficiencies.

A variable that significantly effects the a-SiGe:H cell properties is the Ge grading across the i-layer thickness. Table 3 compares IV data taken using AM1.5 white light for cells made with and without grading of the Ge content through the i-layer. These a-SiGe:H cells were made without a back reflector using deposition rates of 10 Å/s. As has been previously observed by a number of researchers using low rate techniques (Guha et al. 1989), we were able to obtain significantly higher currents as well as improved FF by grading the amount of Ge across the i-layer thickness.

Table 3. Data for a-SiGe:H cells made with and without Ge grading of the i-layer.

Grad. Profile	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	R_s (Ωcm ²)	P_{max} (mW/cm ²)
No	16.5	0.759	0.573	7.2	7.15
Yes	18.1	0.739	0.595	6.3	7.96

Specifically for high growth rate process, improvements in the quality of a-SiGe:H materials with increased ion bombardment have previously been reported. Also several studies of the plasma kinetics have shown that as the frequency of the plasma increases, the average energy of the ions which bombard the growing surface decreases while their number increases (Howling et al. 1992, Heintze et al. 1993, Oda et al. 1991).

Since a moderate amount of bombardment has previously been found to be beneficial in increasing the surface mobilities of adatoms during the growth of a variety of thin film materials (Yehoda et al. 1988), our group has studied the effect of bombardment conditions on the growth of our high rate i-layers. We have varied the bombardment conditions at the growing surface by systematically applying a d.c. bias to the substrate and adding He dilution to the plasma. Table 4 summarizes data for a-SiGe:H cells prepared with various substrate biases. These cells were made without the benefit of the back reflectors and the IV measurements were made using 530 nm filtered AM1.5 light to simulate absorption due to a top a-Si:H cell. With increasing positive electrical bias, the deposition rate of the a-SiGe:H i-layer was found to drop significantly from nearly 10 Å/s at a bias of 0V to less than 5.8 Å/s at 50V. With this drop in deposition rate, there was also a significant decrease in V_{oc} from 0.75V to 0.64V. Increasing the positive bias further to 100V led to a much smaller change in deposition rate and no change in V_{oc} .

With increasing negative bias, there is also a decrease in the deposition rate for the a-SiGe:H i-layers, however the decrease is not as great as in the case of positive bias. Between 0 and -100V bias, there is only a small (less than 7%) decrease in deposition rate and very little change in the cell properties. Beyond -100V, the deposition rate decreases more rapidly and a significant drop in V_{oc} is apparent.

For the a-Si:H cells, many similar trends are noted with varying bias (see Table 5). With increasing positive bias, there is a significant decrease in the i-layer deposition rate as was observed for the a-SiGe:H cells. Also, there is the same decrease in V_{oc} observed for the a-SiGe:H cells with increasing positive bias. Thus, the decrease in V_{oc} for the a-SiGe:H alloys is not, for at least the most part, due to a decrease in Ge content. The changes in V_{oc} for both types of cells are likely due to decreases in the hydrogen content and/or changes in the film microstructure. With increasing negative bias, virtually no change in the V_{oc} is observed however a smaller decrease in deposition rate is seen.

Table 4. Effect of substrate bias on the properties of single-junction VHF a-SiGe:H cells.

Substrate Bias (V)	Deposition Rate ($\text{\AA}/\text{s}$)	i-layer thickness (\AA)	J_{sc} (mA/cm^2)	V_{oc} (V)	FF	R_s (Ωcm^2)	P_{max} (mW/cm^2)
0	9.5	2000	8.15	0.750	0.571	12.1	3.49
50	5.8	1220	7.62	0.638	0.561	15.9	2.73
100	4.4	920	6.74	0.641	0.632	11.9	2.73
-30	10.5	2210	8.15	0.742	0.562	10.3	3.40
-50	9.3	1950	8.18	0.749	0.559	11.1	3.43
-100	8.9	1860	7.74	0.745	0.580	11.1	3.46
-150	8.5	1780	7.33	0.736	0.531	14.5	2.87
-200	6.8	1430	7.40	0.730	0.555	15.4	3.00

Table 5. Effect of substrate bias on the properties of single-junction VHF a-Si:H cells.

Substrate Bias (V)	Deposition Rate ($\text{\AA}/\text{s}$)	i-layer thickness (\AA)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	R_s (Ωcm^2)	P_{max} (mW/cm^2)
0	9.9	3840	0.963	15.68	0.659	6	9.95
100	4.5	3830	0.882	15.66	0.557	6.3	7.69
100	4.8	2960	0.882	15.24	0.613	5.7	8.24
-100	9.8	3750	0.954	15.45	0.675	4.9	9.95
-200	7.6	3200	0.966	15.17	0.664	5.3	9.73
-300	7.0	3380	0.956	15.05	0.658	5.3	9.47

Since the focus of this program is on maintaining a high deposition rate, we found no benefit to using an applied negative or positive substrate bias. This method of altering the ion bombardment, in particular the ion energy, of the film surface does not lead to higher efficiencies.

Table 6 displays the cell data for the devices made with different ratios of He/H₂ dilution. The cells were made using Al/ZnO back reflectors and the IV data was obtained using 630nm filtered AM1.5 light. Also these cells were made without grading of the buffer layer and thus have lower efficiencies than what is typically obtained (see last column in table for cell results for graded cell made at the time when this He dilution study was made). One can see from the data that increasing the He flow lead to lower FF, lower J_{sc} and poorer cell efficiencies. The deteriorations in these properties are unlikely to be a result of the small increase in deposition rate with increased He flow. Thus, at least in the case of the 70MHz rf plasma, use of He dilution leads to lower cell efficiencies and poorer a-SiGe:H i-layer quality. None of the attempts to improve the quality of the a-SiGe:H materials through increased ion bombardment has led to improved cell properties.

Table 6. a-SiGe:H cells made with different amounts of helium and hydrogen dilution.

He (sccm)	H ₂ (sccm)	i-layer thickness (Å)	Deposition Rate (Å/s)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	R _s (Ωcm ²)	P _{max} (mW/cm ²)
0	42	1790	11.9	6.41	0.640	0.523	15.3	2.15
5	42	1820	12.1	5.78	0.646	0.501	19	1.87
10	42	1910	12.7	5.40	0.641	0.491	19.6	1.70
20	42	1870	12.5	5.15	0.646	0.482	23.7	1.61
10	32	1900	12.7	5.52	0.652	0.505	18.1	1.81
20	22	1940	13.0	5.57	0.640	0.490	19.4	1.75
0	graded	1700	11.0	6.93	0.645	0.594	13.7	2.66

Present status of a-SiGe:H cells

In Table 7, we compare data for a-SiGe:H cells prepared using the VHF technique and the 10 Å/s rate with those made using the standard 13.56 MHz and a 1 Å/s rate. These cells were prepared using the same deposition hardware and during the same time period. To judge the potential use of the VHF technique as a method to prepare middle and/or bottom cells for triple-junction structures, we compare in the table IV data obtained using 530 nm filtered AM1.5 light. Again, the 530 nm filter eliminates light typically absorbed by the a-Si:H top cell. Comparing cells with similar J_{sc} values and i-layer thickness, a-SiGe:H cells made by the VHF technique have similar initial efficiencies to those prepared in the same deposition system using the 13.56 MHz frequency.

The high rate VHF produced a-SiGe:H cells and low rate 13.56MHz produced cells also have similar efficiencies after light soaking as can be seen from the data in Table 8. Cells with similar J_{sc} values have similar stable efficiencies. Some interesting results are the properties for the cell made by the VHF method at a rate of 2 Å/s. The stable efficiencies and FF are actually higher for devices made under these conditions than those made by the 13.56 MHz method at low rates. We have recently improved the efficiencies for the VHF prepared cells and are now achieving higher efficiencies for the a-SiGe:H devices. IV plots for these improved cells prior to light soaking are shown in Figures 4 and 5. Again these data were obtained using AM1.5 light filtered with the 530nm low-bandpass filter. These cells are presently being light soaked.

Table 7. Data for VHF a-SiGe:H cells prior to light soaking.

Freq. (MHz)	Dep. Rate (Å/s)	i-layer thickness (Å)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	R _s (Ωcm ²)	Initial P _{max} (mW/cm ²)
13.56	0.95	2400	8.50	0.751	0.552	12.3	3.51
13.56	0.92	2100	7.93	0.752	0.575	11.8	3.42
13.56	6.1	2260	7.43	0.711	0.550	14.4	2.91
70	9.5	2000	8.07	0.760	0.579	10.7	3.55
70	10.2	2150	8.15	0.750	0.571	12.1	3.49

Table 8. Data for a-SiGe:H cells after light soaking for 600 hrs. under white light conditions.

Freq. (MHz)	Dep. Rate (Å/s)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	P_{max} (mW/cm ²)
13.56	0.5	6.93	0.703	0.517	2.52
13.56	0.5	7.02	0.704	0.510	2.52
13.56	0.79	6.97	0.703	0.518	2.54
70	2.0	7.06	0.699	0.543	2.68
70	10.0	7.08	0.675	0.527	2.52
70	9.3	6.92	0.686	0.521	2.47

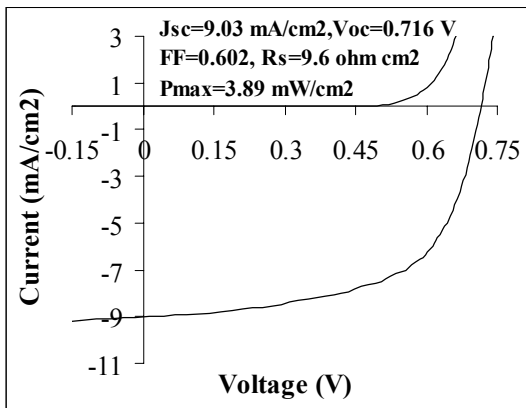


Figure 4. IV curve for a-SiGe:H cell made using the VHF technique.

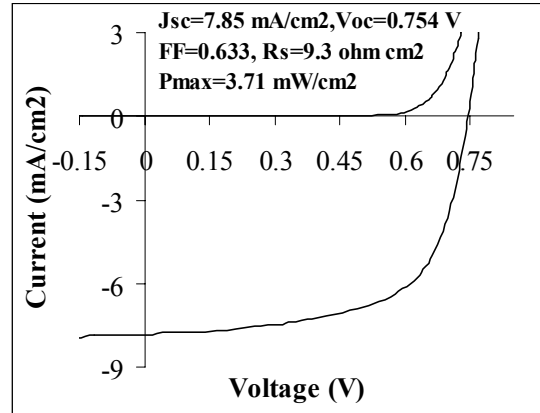


Figure 5. IV curve for a-SiGe:H cell made using the VHF technique.

Triple-Junction Cells

Our initial attempts to prepare high efficiency triple-junction cells using i-layer deposition rates near 10 Å/s and the VHF technique were hindered by non-uniform depositions across the substrate platform. Below we discuss this problem and later discuss the properties for the cells we have prepared after this uniformity problem was solved.

Deposition uniformity across substrate platform

Our early attempts to improve the efficiencies through systematic variations in the deposition parameters led to difficulties in correctly current matching the cells due to non-uniform deposits. Figures 6 displays the severity of this uniformity problem. In the figure, the i-layer deposition rate across the substrate platform area is plotted for two single-junction component cells, the top a-Si:H and the bottom a-SiGe:H cells. The i-layer thicknesses were determined using standard capacitance techniques. In both cases, thicker i-layers are observed near the gas inlet side of the substrate platform and the thinnest layers near the pump port side. A smaller decrease in thickness is seen from the center to the other sides of the platform. Later experiments have shown that these variations in thickness are not entirely due to gas depletion effects.

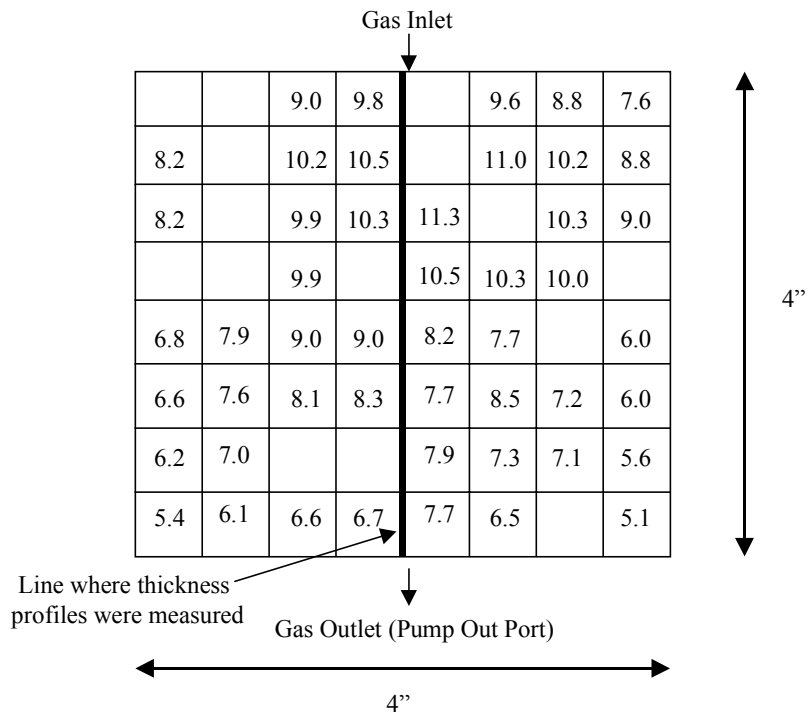
These variations in deposition rate obviously lead to variations in the J_{sc} and FF, which depend strongly on the i-layer thickness, and thus variations in the cell efficiencies. Figure 7 displays a typical variation in J_{sc} values for an a-SiGe:H cell with the currents obtained using AM1.5 light filtered with a 630 nm low pass filter. These large changes in current lead to similar variations in the J_{sc} for the triple-junction cells (See Figure 7) and the production of low efficiency triple-junction cells across a large region of the substrate platform due to improper component cell current matching.

Figure 8 displays the trends in V_{oc} across the platform for the top and bottom cells. The figure shows that while V_{oc} is relatively uniform for the top a-Si:H cell, the V_{oc} varies significantly for the a-SiGe:H cells due to variations in the Ge content in the i-layers. This variation in V_{oc} is also seen for the triple-junction structures.

Using the same deposition system that was used to obtain the profiles shown in Figures 6-8, one can obtain uniform deposits (within $\pm 5\%$) using either the 13.56 MHz or the 70 MHz frequency by lowering the deposition rate to 1-3 Å/s. Thus, the poor uniformity is almost exclusively dictated by the high deposition rates, not the very high frequencies. To further increase the efficiencies of the triple-junction devices, we felt it was necessary to determine a region of deposition parameter space in which fairly uniform deposits could be obtained when high rates were used. Thus during this reporting period, we studied the effect that a number of deposition parameters had on this deposition uniformity profile. This study will prove useful to determine the conditions, if any, at which uniform deposits and high rates might be obtainable with the existing large area cathode design which is a scaled-up version of our R&D reactor.

We have found that the changes in deposition uniformity for the a-SiGe:H i-layers follow similar trends to the changes for the a-Si:H i-layer deposits when disilane gas is used as the source gas. Thus for simplicity, we will discuss in the following sections only changes in the top cell i-layer deposits made with disilane and varying deposition parameters, with the implication that similar trends were noted for the a-SiGe:H i-layers. In later discussions, we will also mention differences between top cells made using silane and disilane.

**Deposition Rate Across Substrate Platform
a-SiGe:H Bottom Cell**



**Deposition Rate Across Substrate Platform
a-Si:H Top Cell**

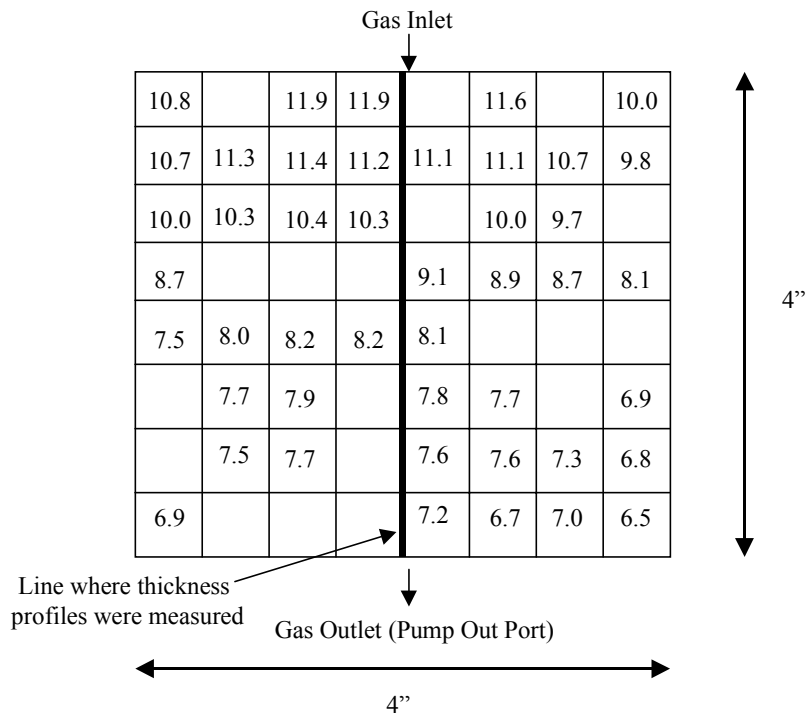
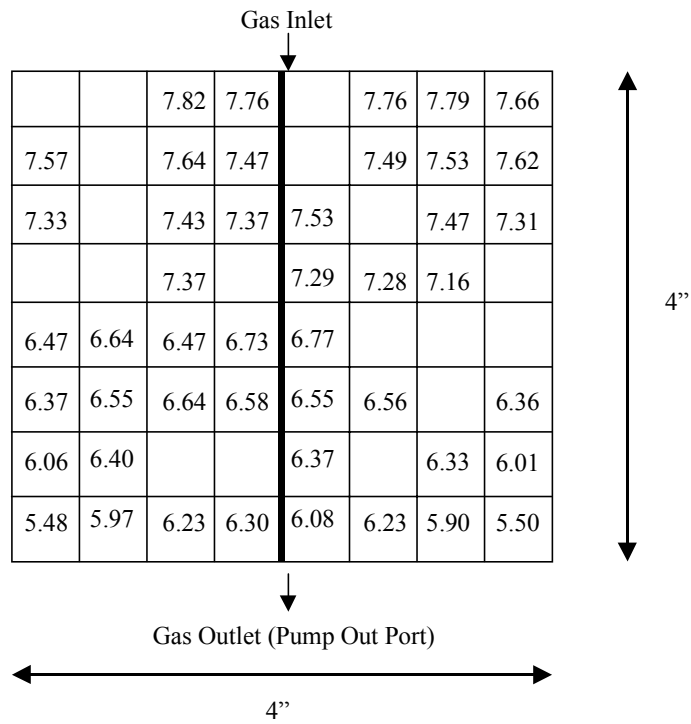


Figure 6. Non-uniform deposition Rate distributions across the substrate platform.

**J_{sc} Across Substrate Platform
a-SiGe:H Bottom Cell**



**J_{sc} Across Substrate Platform
Triple Cell**

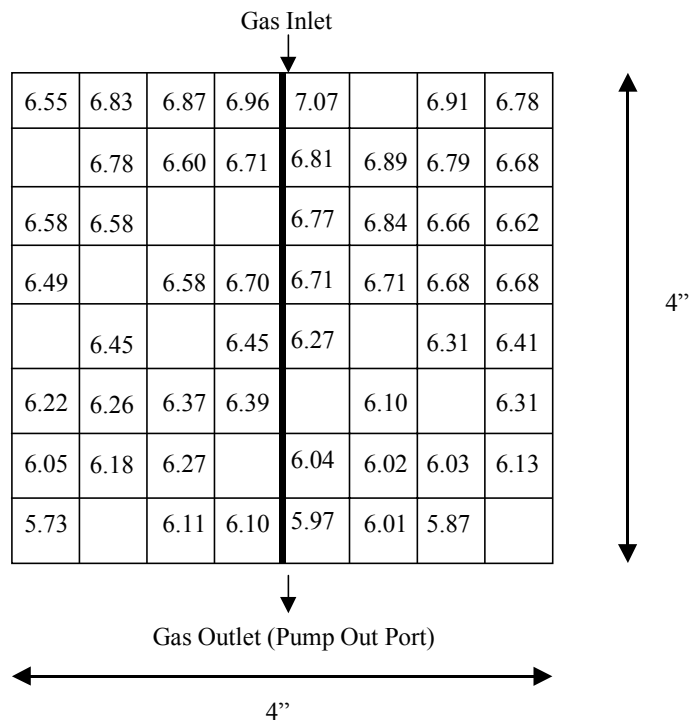
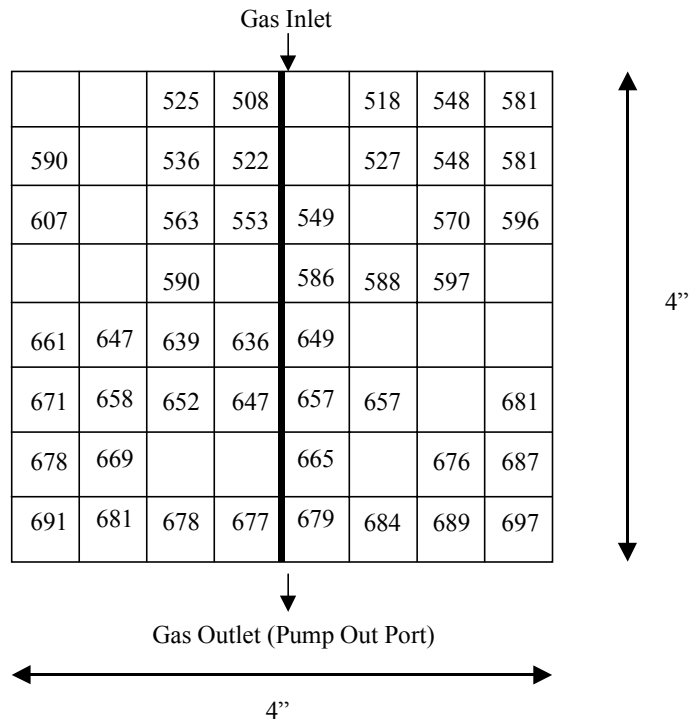


Figure 7. Non-uniform J_{sc} distributions across the substrate platform.

**V_{oc} (mV) Across Substrate Platform
a-SiGe:H Bottom Cell**



**V_{oc} (mV) Across Substrate Platform
a-Si:H Top Cell**

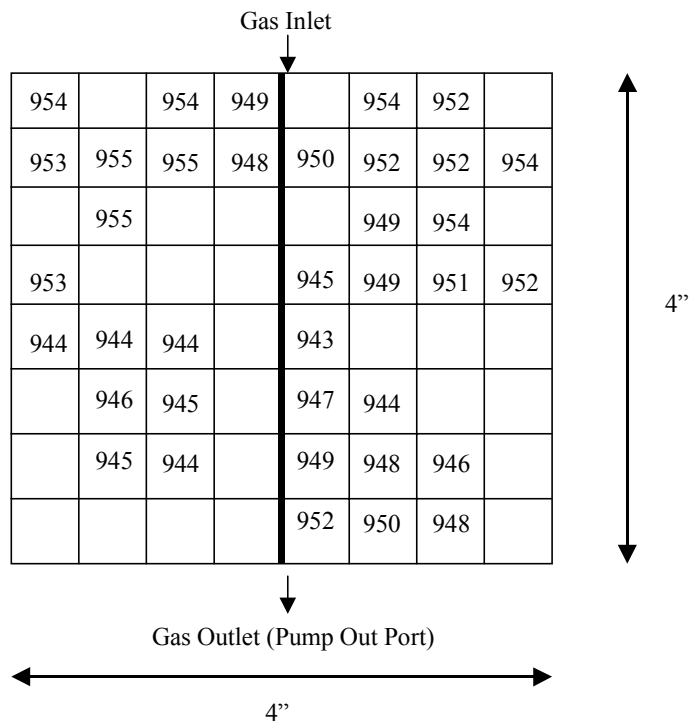
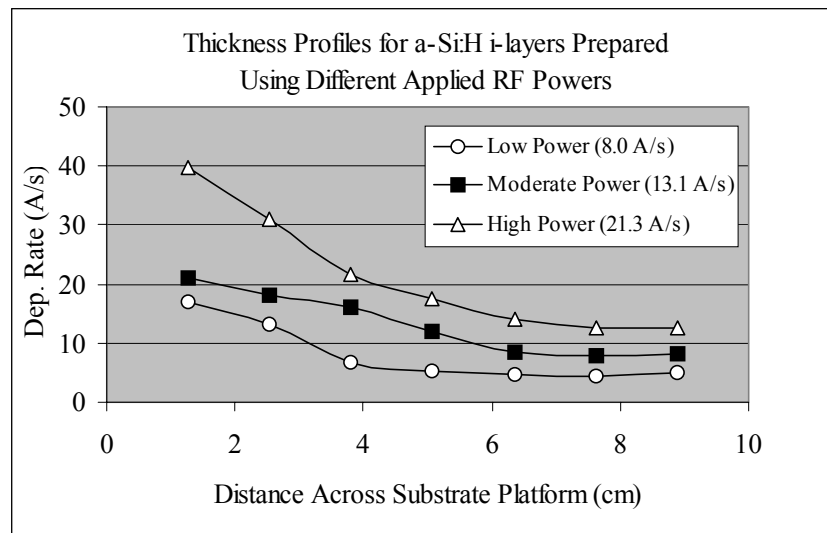


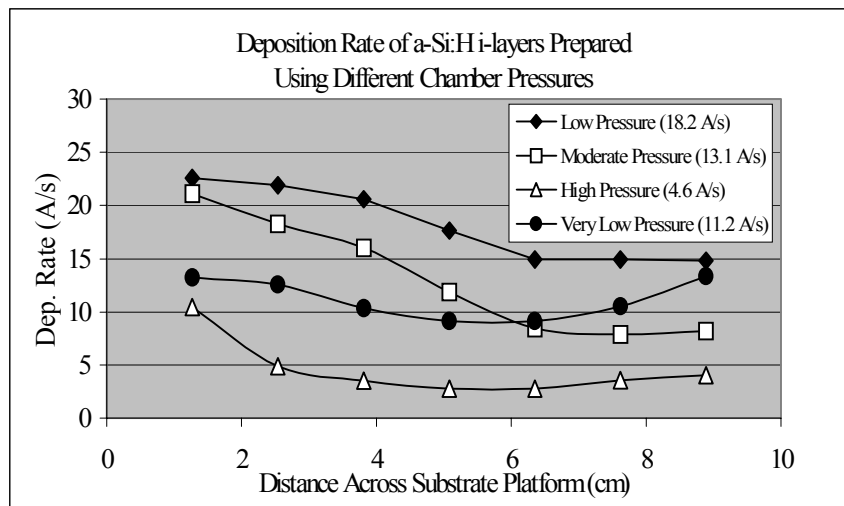
Figure 8. Variation of V_{oc} across the substrate platform.

In Figure 9, the deposition rate across the center of the substrate platform (see note in Figure 6) is plotted as a function of the distance from the gas inlet side of the platform for a number of a-Si:H i-layers prepared with disilane. These i-layers were prepared using different applied powers and chamber pressures with all other deposition conditions nominally fixed. In each figure, the average deposition rate for each deposit is listed in the legend. Figure 9a displays profiles for cells made using moderate chamber pressures and various powers. As the applied power is decreased under moderate chamber pressure conditions, the uniformity across the platform improves slightly. But even at low power levels where the average deposition rate dips below our targeted 10 Å/s, there is still over a factor of two difference in the thinnest and thickest deposits in the 4" x 4" area.

Figure 9b displays the variation of the profile with alterations to the chamber pressure while the applied power is fixed at the moderate value. Increasing the pressure from low to high values leads to a drop in the deposition rate and some improvement in the deposition uniformity. However even at the highest



a)



b)

Figure 9. Variations in the deposition rate profiles as power and chamber pressure are varied.

pressure, a significant drop in the deposition rate is observed near the gas inlet side of the platform remains (also the deposition rate is too low under these conditions). This decrease in the deposition rate with increasing pressure is of interest since in the same pressure regime using the same deposition reactor, the deposition rate increases with increasing pressure, as one might expect, when a 13.56 MHz signal and lower deposition rates are used. Decreasing the pressure from low to very low conditions leads to a drop in the deposition rate. Also at the very low pressure regime, the uniformity is significantly better while high deposition rates are maintained. Thus, in raising the pressure from very low to low values, the uniformity becomes poor as the deposition rate increases, as one might expect. Near this low pressure regime, the plasma chemistry must drastically change causing the sudden downward trend in deposition rate. It is not clear whether this change is related directly to the VHF technique or to the Si radical rich plasmas required for the high deposition rates.

Shown in Figure 10 are profiles for a-Si:H i-layers made in the very low pressure regime using different power levels. At each of the power levels, the deposit is fairly uniform demonstrating that the use of very low pressures is a key to make uniform, high rate a-Si:H deposits when disilane is used as the Si source gas. In the moderate-low pressure regime, we have also attempted to improve the deposition uniformity through systematic variation of the active gas flows, the diluent gas flow, and the total gas flow. While some improvement in the deposition uniformity were observed when these parameters were varied (See Figure 11, for example), the improvements were either small or led to deposition rates below the desired 10 Å/s. To obtain the desired uniformity and deposition rate, very low pressures are required.

Figure 12 displays the uniform deposition rate over the entire substrate area when the new optimized conditions are used. As was mentioned previously, the a-SiGe:H deposits behave similarly to the a-Si:H deposits made with disilane in that very low pressures were required to obtain uniform deposits. Figure 13 demonstrates that the V_{oc} , and thus the Ge content, is also uniform across the substrate area when these new deposition conditions are used.

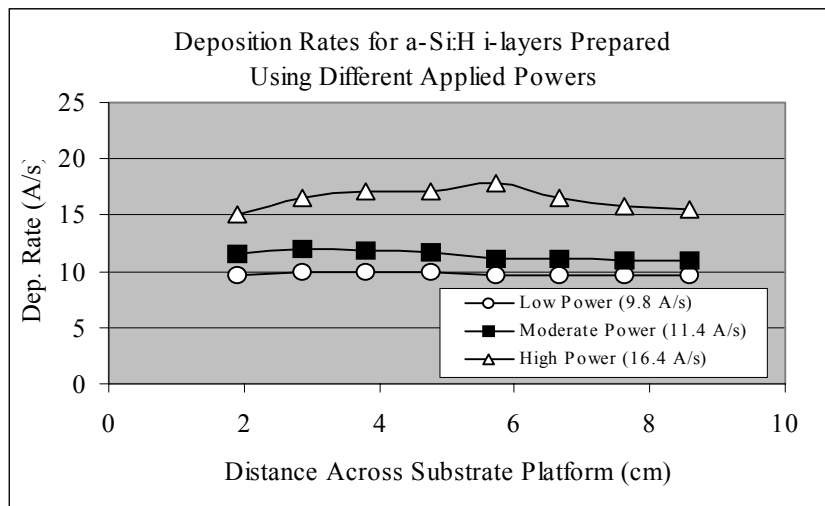


Figure 10. Changes in the deposition rate profiles as power is varied at very low pressure conditions.

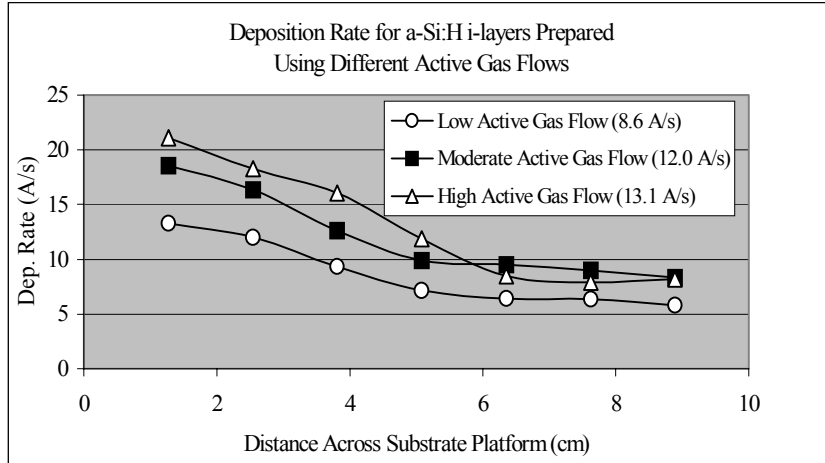


Figure 11. Changes in the deposition rate profiles as active gas flow is varied at moderately low pressure conditions.

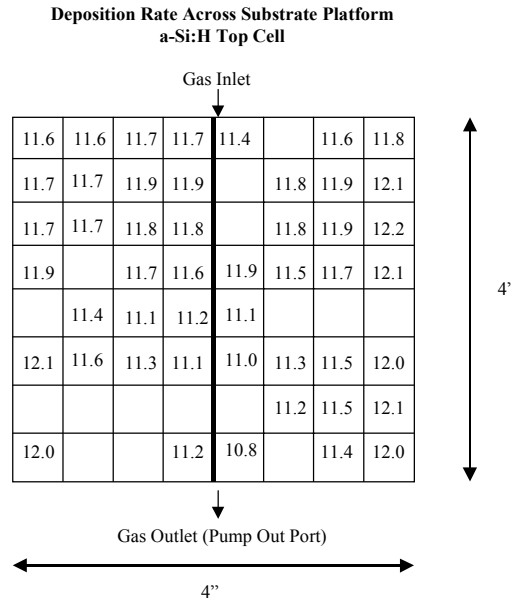


Figure 12. Deposition rate distribution across the substrate platform at low pressure conditions.

When SiH₄ was used to make the a-Si:H i-layers, the 10 Å/s deposition rate could not be obtained using the very low pressures due to the lower decomposition rate. Through systematic variation of the silane flow, the applied power and the chamber pressure, we are presently optimizing the conditions to obtain the desired uniformity. However with the work completed thus far, it is clear that the region of parameter space in which this uniformity is obtained is much smaller than the area in which uniform a-Si:H deposits made with disilane are obtained. Thus there is a benefit to using disilane for this high rate deposition technique in terms of a wider range of parameter space to optimize the thin film growth parameters while maintaining uniform substrate coverage.

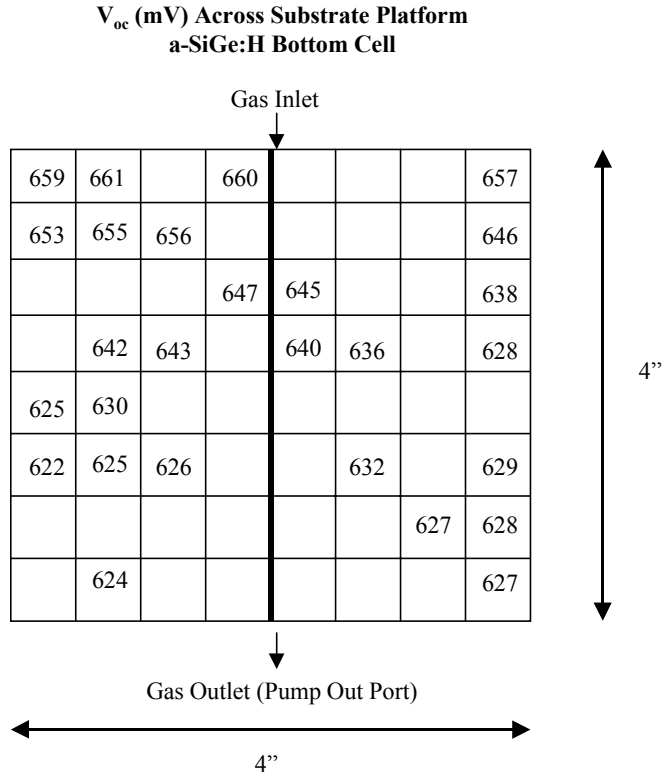


Figure 13. V_{oc} distribution across the substrate platform at low pressure conditions.

As an additional comment to these studies of the deposition uniformity, we specifically focused on varying the deposition parameters without making any geometry changes to the deposition hardware. It is quite possible that several changes in the hardware configuration could lead to a widening of the deposition parameter space in which uniform deposits are obtained. In particular, adjustment of the cathode separation and/or the gas flow geometry could be beneficial.

Present status of a-Si:H/a-SiGe:H/ a-SiGe:H triple-junction cells

Incorporating the new deposition conditions that gave more uniform film deposits led to the achievement of initial triple-cell active area efficiencies of 10.4 -10.5%. Representative IV curves for such devices are shown in Figures 14 and 15 while a representative quantum efficiency curve for a VHF produced cell is shown in Figure 16. The current matching for the cells have yet to be fully optimized, thus further improvement in the efficiencies should come with proper matching. While these cells have yet to be sufficiently light soaked, earlier VHF cells with 9.5-10% initial efficiencies were light soaked for 600 hrs. under white light conditions and the efficiencies were found to degrade by 10-13%. Considering the similarity of the i-layer thicknesses for these cells and those of the 9.5-10% cells, it is likely that 10.4-10.5% cells will also degrade by 10-13% after extended light soaking periods. Further optimization of the deposition conditions for these triple-junction devices should lead to higher stable efficiencies.

In terms of obtaining higher efficiencies, we need to obtain higher currents, in particular for the bottom cell. In this first year of the program, focus for the a-SiGe:H cells has been on the middle cells. In the second year of the program, focus will be on improving the bottom cell properties as well as the quality of the doped layers.

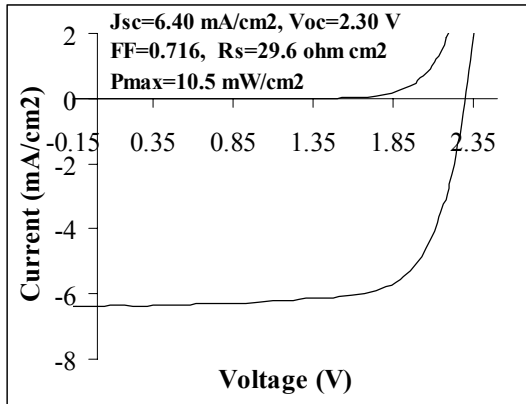


Figure 14. IV curve for triple-junction cell.

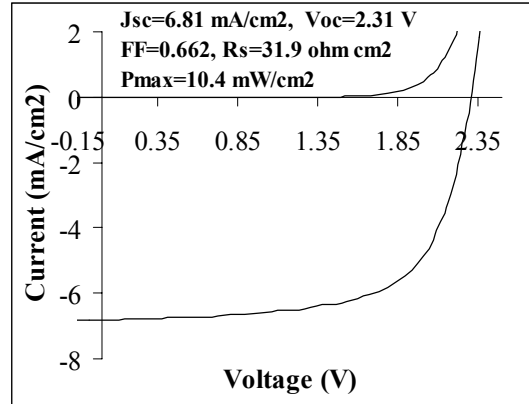


Figure 15. IV curve for triple-junction cell.

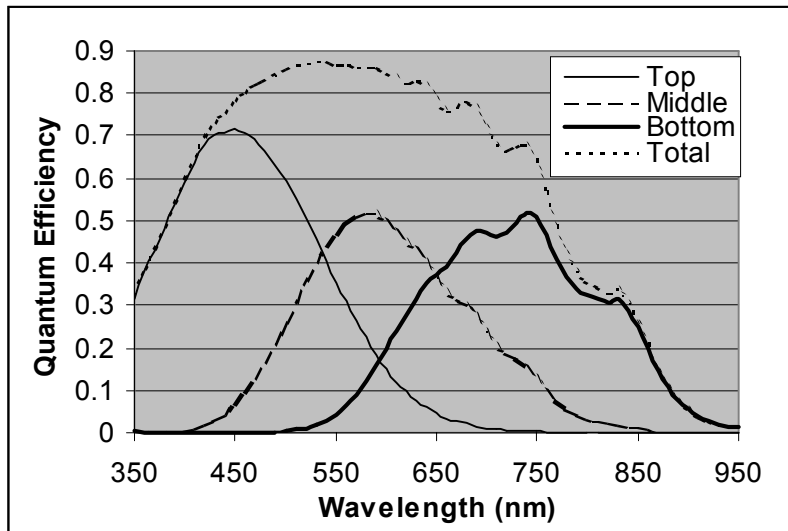


Figure 16. Quantum efficiency plot for triple-junction cell made using VHF technique. Top Cell Current = 6.9 mA/cm^2 , Middle Cell Current = 7.1 mA/cm^2 , Bottom Cell Current = 7.8 mA/cm^2 .

Other Studies

Small –Angle X-ray Scattering Measurements of a-Si:H/a-SiGe:H multi-layered structures

The work completed at the Colorado School of Mines has shown that with the addition of Ge to the a-Si:H lattice, a strong signal in the Small-Angle X-ray Scattering (SAXS) data appears which is associated with the presence of highly oriented, elongated voids which are likely related to a “columnar like” microstructure (Jones et al. 1993). To obtain this information, films that are at least 1 micron thick are required to obtain sufficient SAXS signals for accurate data. As we know, these thicknesses are at least 5 times greater than those typically used for i-layers in high efficiency cell structures. Because of thickness dependent effects such as the degree of coarsening of the film microstructure, there has always been a question as to whether the microstructure described by the SAXS data for the thick films truly reflects the microstructure of 1000-2000 Å thick films used in the devices.

In order to address this issue, we have completed an experiment with Don Williamson at the School of Mines involving the use of a-Si:H/a-SiGe:H multi-layered structures. Specifically, we fabricated three thin film structures depicted in Figure 17 for SAXS measurements. In each of the structures, the a-Si:H films were made under similar conditions which lead to high quality i-layer fabrication: deposition rates near 1 Å/s, low powers, moderate substrate temperatures, significant hydrogen dilution, 13.56 MHz frequency. The a-SiGe:H layers were made under similar conditions except for the substitution of some of the SiH₄ source gas with GeH₄. These conditions led to Ge contents near 35 at. %. In using these conditions, we expected the a-Si:H materials to have few voids and none of the highly oriented voids while the a-SiGe:H films should have a significant amount of the elongated voids. For the multi-layered film shown in Figure 17C, because the a-Si:H layers are homogenous and should have a less coarse, smoother structure, insertion of the 500 Å thick a-Si:H layers between the 2000 Å a-SiGe:H layers should inhibit any large scale coarsening affect for the a-SiGe:H material that is usually observed for the thicker films and thus the bulk of the SAXS from this sample should represent the scattering and microstructure of 2000 Å thick a-SiGe:H layers.

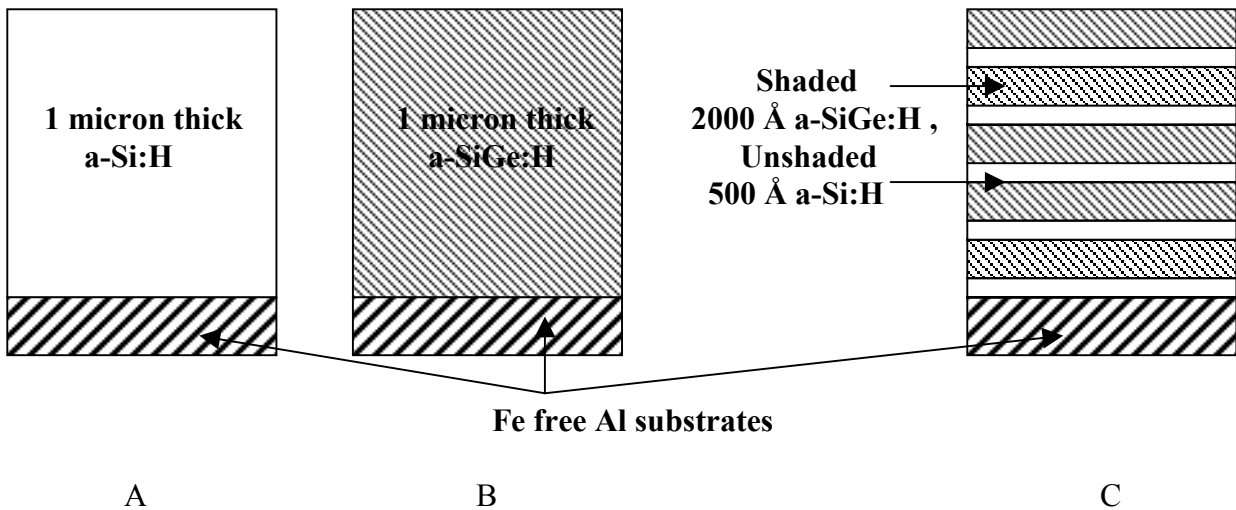


Figure 17. Samples structures analyzed using small angle x-ray scattering.

Figure 18 displays the SAXS from the three samples shown above. As expected, the SAXS from the a-Si:H films is small relative to the large scattering from the a-SiGe:H sample. The scattering from the multi-layered sample depicted in Figure 17C is very similar to the scattering for the a-SiGe:H single-layer. The extra scattering for the multi-layered film at the low q values is probably associated with the thin 500 Å thick a-Si:H layers (see the scattering for the a-Si:H single-layer film in this region of q in Figure 18). The similarity of the SAXS for the a-SiGe:H single-layered film and the multi-layered film suggests that the SAXS data obtained from the measurements of the micron thick films does represent the microstructure of 1000-2000 Å thick films that are used in the solar cells. Other information concerning the SAXS measurements will be reported by Don Williamson.

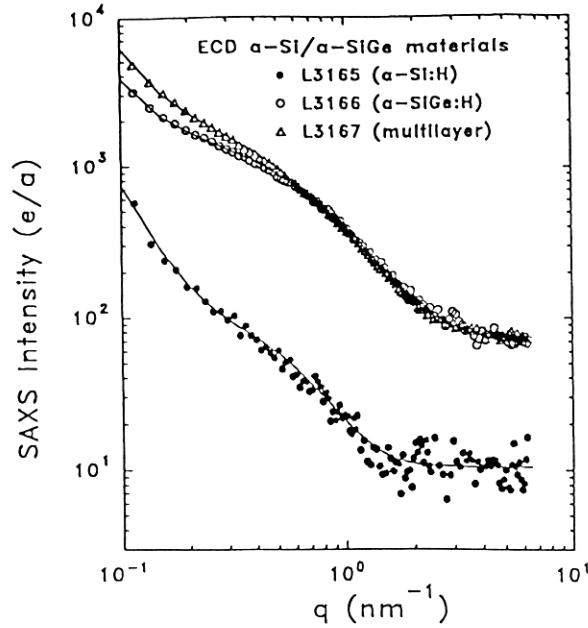


Figure 18. Small angle x-ray scattering results for a-Si:H, a-SiGe:H and multi-layered structures.

Conclusions and Future Plans

In the first year of the program, we have made significant progress in advancing the VHF, high rate technology. We have demonstrated that 8.0% stable efficiencies can be achieved for a-Si:H cells whose i-layers are prepared at rates near 10 Å/s using the VHF technique. While we have yet to achieve to 8.4% program goal for the a-Si:H cells, we hope that our recent improvement of the n-layer conditions as well as further optimization of other deposition conditions will lead to the achievement of the goal in the coming months. This achievement may also come from the general improvement of system baseline efficiencies for all cells by optimization of chamber heating and pre-deposition treatments. Presently, there is not a great difference in the performance of a-Si:H cells made using the VHF technique and i-layer deposition rates near 10 Å/s and that for cells made using the standard 13.56 MHz technique and rates near 1 Å/s in the same deposition system.

In terms of the a-SiGe:H cells, we have completed a number of studies of devices with properties appropriate for middle junction cells. That is, cells without Ag/ZnO back reflectors having V_{oc} values near 0.75V and J_{sc} values near 8.0 mA/cm² when measured using AM1.5 light filtered using a 530 nm low band pass filter. The stabilized properties for these cells prepared at i-layer rates near 10 Å/s are again similar to a-SiGe:H cells made using the same deposition hardware and the low rate 13.56 MHz method. We are looking to improve these efficiencies further again through optimization of doped layer conditions and the general improvement of the baseline efficiencies for the semiconductor deposition system. Optimization of the bottom cell conditions will be an issue we will focus much of our attention in the coming year.

Establishing an initial 10.5% for a triple-junction cell whose i-layers are prepared at the high rates sets the baseline for our future studies. Further optimization of the triple-junction structure should lead to the achievement of higher efficiencies in the coming year. The result that the triple-junction cell degradation (10-13%) with prolonged light soaking is similar to that regularly obtained for cells prepared at low i-layer deposition rates (1 Å/s) is important in light of the fact that the use of high rate methods to prepare i-layers typically lead to less stable materials and cells (Doehler et al 1988). In terms of improving the efficiencies for the triple-junction cells, focus has thus far been on optimizing the top and middle component cells. The conditions used to make the bottom cells for the triple-junction cells with the 10.5% efficiencies were similar to those used for the middle cell except for the use of higher GeH₄ flows for i-layer preparation while the doped layers were made using conditions optimal for cells made using low i-layer growth rates. In the coming months, work will be done on optimizing the bottom cell or the p/n tunnel junctions. Improvement of the bottom cell performance is of particular importance. In order to achieve the high stable efficiencies, obtaining high red-light currents for the bottom cell is critical in order to get the proper current matching between the component cells. We believe that improvement of the bottom cell will come through use of increased hydrogen dilution of the plasma gases, known to be beneficial for a-SiGe:H cell performance. Since increased hydrogen dilution typically leads to lower deposition rates, there will be need to alter other conditions while the dilution is increased in order to maintain the 10 Å/s i-layer growth rates. A great deal of time during the next year will be spent on improving both the bottom cell and tunnel junction performance.

In order to fully understand the benefit of the high rate i-layer growth, the times required to fabricate triple-junction cells with our R&D system using different layer growth rates are compared in Table 9. Each time is the sum of times required to complete each layer deposition and do not include other processing times (baking times, cooling times, chamber pump down time, etc.). By increasing the i-layer deposition rates to 10 Å/s, we are able to decrease the total deposition time by nearly 70%, a significant improvement. The payoff from increasing the rates of the other layers is not nearly as great, but of course is beneficial. For the data in the table, we have taken a conservative approach of increasing the deposition rates for the buffer and doped layers to a high rate of 6 Å/s. Since we have no experience in depositing these layers at rate above 5 Å/s, we thought this conservative approach was appropriate. Increasing the buffer layer deposition rate to 6 Å/s leads to nearly a 15 min decrease in the total deposition time while the increase in the n-layer and p-layer deposition rates both decrease the total time by 5 and 5.8 min, respectively. Thus besides the i-layer growth rates, increasing the buffer layer growth rate has the strongest effect on the deposition time of the triple-junction semiconductor structures. Because of this, we plan on exploring the use of VHF to increase not only the i-layer growth rate but also the buffer layer deposition rate in the coming months. Considering the high quality of the a-Si:H cells made with i-layer growth rates of 10 Å/s, one should be able to increase the rate of the buffer layer without much of a change in the material quality.

Table 9. Deposition times for triple-junction cell fabrication using different layer deposition rates.

i-layer deposition rates (Å/s)	buffer layer deposition rates (Å/s)	n-layer deposition rates (Å/s)	p-layer deposition rates (Å/s)	Total deposition time (min.)
1	1	1	1	123.5
10	1	1	1	38.5
10	6	1	1	23.9
10	6	6	1	18.9
10	6	6	6	13.1

In terms of application the VHF, high rate deposition technique in the production of large area panels, our studies demonstrate that obtaining uniform deposits will be a key issue. Proper selection of the large-area deposition hardware and the hardware geometry will be critical for obtaining the required deposition uniformity in manufacturing. Without good thin film uniformity, obtaining the current matching needed for high performance modules will not be possible. This does not seem to be an insurmountable problem since some research on cathode hardware for the application of the VHF technology has already been done with some reasonable solutions (Sansonnens et al. 1998). One fact that should be pointed is that we have obtained uniform deposits using the VHF technique and low deposition rates (2 \AA/s). Thus for substrate sizes we are using, the non-uniformities we have outlined are primarily due to the high deposition rates we are using, not specific to the use of high frequencies. In the coming months, we plan to test new large area hardware designs in a single chamber for the application of high rate methods, such as the VHF technique, into ECD's module production line.

In summary, we plan to focus on the following issues in the next year,

- 1) Optimization of the bottom cell performance with focus on using increased hydrogen dilution while maintaining the 10 \AA/s i-layer deposition rates to obtain higher currents,
- 2) Optimization of the doped layers in the triple-junction structure to obtain higher efficiencies,
- 3) Improvement of our system baseline efficiencies through careful assessment of the procedures used in preparing the devices,
- 4) Develop a recipe for high rate buffer layer depositions to decrease the processing time for the triple-junction cells,
- 5) Development of large area cathode hardware for the high rate VHF process.

We believe these are the next important issues that need to be addressed to access the feasibility of using the VHF technique for high rate deposition of high efficiency a-Si:H based triple-junction cells.

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13. ABSTRACT (Maximum 200 words) This report describes work performed by Energy Conversion Devices, Inc. (ECD) during this phase of this subcontract. ECD researchers have made significant progress in advancing the very high frequency (VHF), high-rate technology. They demonstrated that 8.0% stable efficiencies can be achieved for a-Si:H cells whose i-layers are prepared at rates near 10 Å/s using the VHF technique. Presently, there is not a great difference in the performance of a-Si:H cells made using the VHF technique and i-layer deposition rates near 10 Å/s and that for cells made using the standard 13.56 MHz technique and rates near 1 Å/s in the same deposition system. In terms of the a-SiGe:H cells, researchers have completed a number of studies of devices with properties appropriate for middle-junction cells—that is, cells without Ag/ZnO back-reflectors having V_{oc} values near 0.75V and J_{sc} values near 8.0 mA/cm ² when measured using AM1.5 light filtered using a 530-nm, low-band-pass filter. The stabilized properties for these cells prepared at i-layer rates near 10 Å/s are again similar to a-SiGe:H cells made using the same deposition hardware and the low-rate 13.56 MHz method. Establishing an initial 10.5% for a triple-junction cell whose i-layers are prepared at the high rates sets the baseline for ECD's future studies. The triple-junction cell degradation (10%-13%) with prolonged light soaking is similar to that regularly obtained for cells prepared at low i-layer deposition rates (1 Å/s). This is important because the use of high-rate methods to prepare i-layers typically leads to less-stable materials and cells. Increasing the buffer-layer deposition rate to 6 Å/s leads to nearly a 15-min decrease in the total deposition time, whereas the increase in the n-layer and p-layer deposition rates both decrease the total time by 5 and 5.8 min, respectively. Thus, besides the i-layer growth rates, increasing the buffer layer growth rate has the strongest effect on the deposition time of the triple-junction semiconductor structures.				
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