Development of High, Stable- Efficiency Triple-Junction a-Si Alloy Solar Cells

**Annual Technical Progress Report
October 1995 - October 1996**

X. Deng, M. Izu, S.J. Jones, R. Kopf,
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Energy Conversion Devices
Troy Michigan

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National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393
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the U.S. Department of Energy
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PREFACE

This Annual Technical Progress Report covers the work performed by Energy Conversion Devices, Inc. (ECD) for the Phase II period: July 18, 1995, to October 17, 1996, under NREL Subcontract ZAN-4-13318-11 entitled "Development of High, Stable-Efficiency Triple-Junction a-Si Alloy Solar Cells". This research was carried out under the general directions of Mr. S. R. Ovshinsky and Dr. Masat Izu. The large area solar cell research using the 5MW a-Si solar cell processor was done in collaboration with the research team at the United Solar System, Corp. (United Solar).

The research was performed by:

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with the help of the entire photovoltaic team at Energy Conversion Devices, Inc. We would like to thank Dr. H. Fritzsche for discussions, and Drs. S. Guha, J. Yang and other PV project team members at United Solar for discussions, experimental helps and collaborations. We also would like to thank Dr. S. S. Hegedus of the Institute of Energy Conversion, Dr. E.A. Schiff of Syracuse University, and Dr. D. Han of the University of North Carolina for collaborations.

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EXECUTIVE SUMMARY

Objectives

The overall objective of this amorphous silicon research program is to develop high efficiency a-Si solar cells and to develop and improve processes for large area deposition of a-Si solar cells and modules. The knowledge obtained and technologies demonstrated in this program will be incorporated into ECD's continuous roll-to-roll deposition process to further enhance its photovoltaic manufacturing technology.

Technology

In ECD's solar cell design, triple-junction a-Si alloy solar cells are deposited onto stainless steel substrates coated with Ag/ZnO back reflector. This type of cell enables us to use a continuous roll-to-roll deposition process to manufacture a-Si PV materials in high volume. Using this design, ECD has previously achieved record high initial solar cell efficiency using the following features: 1) a triple-junction, spectrum-splitting solar cell design; 2) a microcrystalline silicon p-layer; 3) a bandgap profiled a-SiGe alloy as the bottom cell i-layer; 4) a high performance Ag/ZnO back reflector; and 5) a high performance tunnel junction between component cells. The research team at United Solar has recently used the same design to prepare a 14.6% initial efficiency device, a new world record.

Approaches and Accomplishments

In this program, we are further advancing ECD's existing PV technology by performing the following tasks:

- Task 1: Optimization of large-area plasma deposition of a-Si films;
- Task 2: Optimization of large-area plasma deposition of a-SiGe films;
- Task 3: Research on $\mu\text{c-Si p}^+$ deposition using VHF plasma; and
- Task 4: Optimization of a-Si solar cell back-reflector.

In the following, we highlight some areas of our research under the tasks of this program.

Improvement of deposition uniformity and quality over large-area for a-Si and a-SiGe

Through alternations in the deposition conditions and system hardware, we have improved our understanding for the deposition of uniform and high quality a-Si and a-SiGe films over large areas. This improvement has led to the achievement of uniform deposition of a-SiGe films in terms of both film thickness and Ge content over large area. For the large area deposition of a-Si top solar cell, solar cells with fill factor (FF) up to 0.73 and open circuit voltage (V_{oc}) up to 1.00 V have been achieved over large area.

Research on $\mu\text{c-Si p}^+$ deposition using VHF plasma

We have conducted comprehensive research to develop $\mu\text{c-Si p}^+$ layer using Very High Frequency (70 MHz) deposition process with the objectives of 1) establishing a wider process window for the deposition of high quality p-materials, and 2) further enhancing the performance of a-Si solar cells by improving its p-layers. High performance microcrystalline materials with superior properties have been achieved using a modified VHF process. The new process and new p-layer lead to a 6-10% improvement in solar cell efficiency for single junction solar cell mostly due to enhanced blue light transmission.

Optimization of a-Si solar cell back-reflector

We have performed extensive research to optimize the deposition process of the newly constructed 5MW back-reflector deposition machine. With our optimized highly textured and highly reflective Ag/ZnO back-reflector, we have prepared a-SiGe solar cells with a short circuit current J_{sc} of 25.6 mA/cm², indicating the high performance of the back-reflector.

SECTION 1

INTRODUCTION

During the past fifteen years, ECD has pioneered and developed a unique, proprietary a-Si based PV technology embodying several important innovations.¹⁻¹⁴ These include: 1) a record-setting, high efficiency, triple-junction spectrum-splitting thin-film a-Si alloy device structure; and 2) a fully automated roll-to-roll continuous substrate thin-film solar cell manufacturing process.

Record high solar cell efficiencies have been achieved by ECD and its PV joint venture United Solar Systems, Corp. (United Solar) using the following features: 1) a triple-junction solar cell design; 2) a microcrystalline silicon p-layer; 3) a bandgap profiled a-SiGe alloy as the bottom cell intrinsic layer; 4) a high performance Ag/ZnO back-reflector; and 5) a high performance tunnel junction between the component cells.^{3,6,8} United Solar recently achieved a 10.2% stable triple-junction a-Si alloy solar panel with over 1 ft² area⁸, and a 14.6% initial and 13% stable efficiencies for small area a-Si alloy solar cells.¹³ ECD has achieved 4 ft² production modules with 9.5% initial and 8% stable module efficiencies using a 2MW continuous roll-to-roll manufacturing line.⁶ All of these have established world records. Under this Amorphous Silicon Research program, we are further advancing this technology to meet long-term efficiency and cost goals set by the Department of Energy.

The overall objective of this amorphous silicon research program is to develop high efficiency a-Si solar cells and to develop and improve processes for large area deposition of a-Si solar cells and modules. The knowledge obtained and technologies demonstrated in this program will be immediately incorporated into ECD's continuous roll-to-roll deposition process to further enhance its photovoltaic manufacturing technology.

This research consists of studies on small and large area deposition issues critical to the improvement of the existing a-Si PV technologies. The specific tasks are in the following four areas:

- Task 1: Optimization of large-area plasma deposition of a-Si films;
- Task 2: Optimization of large-area plasma deposition of a-SiGe films;
- Task 3: Research on μ c-Si p⁺ deposition using VHF plasma; and
- Task 4: Optimization of a-Si solar cell back-reflector.

In ECD's solar cell design, triple-junction a-Si alloy solar cells are deposited onto a SS substrate coated with Ag/ZnO back-reflector layers (see Figure 1-1). This type of cell design enables us to use a continuous roll-to-roll deposition process to manufacture a-Si PV materials in high volume at low cost.

On the small area solar cell research, we are primarily utilizing three PECVD systems designated as Load Lock 1 (LL1), Load Lock 2 (LL2), and the Box System to perform deposition of materials and devices. The first two systems are multi-chambered, load-locked

Grid	
	ITO
p3	μ c-Si p
i3	a-Si intrinsic
n3	a-Si n
p2	μ c-Si p
i2	a-SiGe intrinsic
n2	a-Si n
p1	μ c-Si p
i1	a-SiGe intrinsic
n1	a-Si n
	ZnO
	Ag
	Stainless Steel

Figure 1-1 Device structure of ECD's triple-junction, triple-bandgap a-Si/a-SiGe/a-SiGe solar cells on Ag/ZnO back-reflector.

systems and the Box System is a single chamber deposition system. On the large area deposition research, we use the 5 Megawatt continuous roll-to-roll solar cell processors that ECD designed and built for United Solar, in collaboration with a team of scientists at United Solar.

This report summarizes the main results of the research effort under phase II of this subcontract. In Section 2, we describe our research on small area solar cells including the use of a VHF plasma for the deposition of high quality microcrystalline p-layer materials, and the research on wide bandgap a-Si solar cells using high hydrogen dilution. In Section 3, we describe our research on large area depositions using the large area 5MW production machines. This part of the work includes the optimization of large area deposition of a-Si and a-SiGe films and solar cells, and the optimization of back-reflectors. All of the work related to the 5 MW production machine was carried out in collaboration with scientists at United Solar.

SECTION 2

SMALL AREA SOLAR CELL RESEARCH

2.1 VHF plasma deposition of high performance microcrystalline p-layer

2.1.1. Introduction

Energy Conversion Devices developed a microcrystalline p material for use in amorphous silicon solar cell fabrication.⁴ Such a p-layer increases solar cell V_{oc} , J_{sc} and FF compared with amorphous p-layers. Microcrystalline Si p-layer materials have then been widely used in a-Si solar cell research and manufacturing to achieve record high solar cell efficiency. However, the process window in parameter space to produce a high performance p-layer is relatively narrow using conventional RF PECVD. Thus high quality p materials can not be easily reproduced at different laboratories or on different manufacturing machines. We have investigated the deposition of μ c-Si p materials using a 70 MHz Very High Frequency (VHF) PECVD process^{15,16} with the objectives of 1) establishing a wider process window for the deposition of high quality p-materials, and 2) further enhancing the performance of a-Si solar cells by improving their p-layers.

We deposited μ c-Si p-materials using a VHF plasma enhanced CVD process in a research scale multi-chamber load-locked solar cell deposition system (LL2). The substrate is SS/n-i in which the doped n-layer and the undoped a-Si intrinsic layer were deposited previously in a roll-to-roll process. Thus, these SS/n-i substrates have high uniformity, which is important for optimizing the p-layer with a wide parameter space.

2.1.2. Process optimization using Design of Experiment

For the p-layer research, a design of experiments (DOE) approach¹⁷ was used for the exploration and optimization of deposition parameter space. Such statistical analysis is widely used in semiconductor industry when each experiment is time-consuming and costly, and there are many interacting process conditions that affect the final device performance. By taking advantage of the symmetry and orthogonality of the designed experiments, we were able to obtain in, only a few experiments, the amount of information that otherwise requires a large number of experiments without using DOE. The benefit of using DOE would be even greater if more process parameters are involved. The DOE approach has led us to obtain a quick optimization of a new deposition process covering a broad parameter space.

Table 2-1 lists the initial deposition parameter space used for the p-layer research. It is a four-factor, five-variable Draper-Lin small composite design with face-centered design characteristic. The limits of the design parameters were carefully selected based on our understanding of the deposition process. These four parameters were chosen because they should most strongly affect the performance of the p-layer. Other parameters that are not explored and are set at constants in this specific set of DOE design include VHF power (75W), Hydrogen flow, and chamber pressure (2 Torr).

Table 2-1 Design parameters and experimental results for the optimization of VHF deposition of microcrystalline p-layer using a 4-factor Draper-Lin small composite design with face-centered design characteristic. Other deposition parameters including VHF power, hydrogen flow and pressure are kept constant for this set of experiments.

Run #	Exp.#	Temp (°C)	BF ₃ (sccm)	SiH ₄ (sccm)	Time (min)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	R _s (Ω•cm ²)	P _{max} (mW/cm ²)
L2372	1	100	4	0.6	4	0.879	10.02	0.67	9.7	5.76
L2373	2	100	4	0.8	4	0.88	8.91	0.651	10.8	5.1
L2374	3	100	4	0.6	6	0.81	9.39	0.61	10	4.64
L2375	4	60	6	0.8	6	0.864	9.07	0.633	11.1	4.96
L2376	5	100	4	0.4	4	0.868	9.73	0.64	13	5.29
L2377	6	60	2	0.8	2	0.873	9.09	0.619	19.7	4.91
L2378	7	140	2	0.4	6	0.876	9.12	0.678	8.5	5.3
L2379	8	100	4	0.6	2	0.89	9.83	0.657	10.4	5.75
L2380	9	100	2	0.6	4	0.884	10.13	0.643	12.4	5.76
L2381	10	140	4	0.6	4	0.843	8.48	0.661	8.7	4.73
L2382	11	140	6	0.8	2	0.856	8.51	0.671	8.8	4.89
L2383	12	60	6	0.4	6	0.831	10.31	0.56	36	4.71
L2384	13	100	6	0.6	4	0.891	9.28	0.67	10.9	5.44
L2385	14	140	2	0.8	6	0.882	8.89	0.658	7.1	5.16
L2386	15	60	4	0.6	4	0.889	9.74	0.649	11.2	5.52
L2387	16	140	6	0.4	2	0.88	8.91	0.663	8.2	5.2
L2388	17	60	2	0.4	2	0.861	9.31	0.621	23.6	4.98
L2389	18	100	4	0.6	4	0.887	9.48	0.664	8.9	5.47

Figure 2-1 is the Pareto chart of J_{sc} of n-i-p solar cells with VHF μ c-Si p-layer as a function of temperature, BF_3 , SiH_4 and deposition time. The Pareto chart shows how each variable of interest depends on various process parameters, and the degree of sensitivity is reflected by the height of the bar chart. We found that within the above described four dimensional block of parameter space, the J_{sc} is most statistically dependent on the SiH_4 flow and deposition temperature. Figure 2-2 is the response surface plot of J_{sc} as a function of SiH_4 flow and temperature while keeping the values of BF_3 and deposition time at the center values (average values). Figures 2-1 and 2-2 suggest that J_{sc} increases with decreasing SiH_4 flow and temperature within the selected parameter ranges. The increase of J_{sc} at low SiH_4 is most likely due to two reasons: 1) the decreased p-layer thickness when less SiH_4 is used in the gas mixture of SiH_4 , BF_3 and H_2 ; and 2) the increased hydrogen dilution (H_2/SiH_4) could increase the microcrystallinity and hence the transmission through the p-layer. The increase in J_{sc} with lower deposition temperature is likely due to the increased microcrystallinity when the process temperature is lowered. As a reminder, the actual substrate temperatures could be much higher than the temperature values read from the thermal couples reported here due to the heating of intense VHF plasma. The surface plot in Figure 2-2 suggests that within the selected parameter space, the optimum J_{sc} value could be achieved at a temperature of 60 C and a SiH_4 flow of 0.5 sccm when the BF_3 and deposition time are set at 4 sccm and 4 min, respectively.

Figure 2-3 is the Pareto chart for V_{oc} in this set of experiments. The V_{oc} is most sensitive to the deposition time and the first order interaction of substrate temperature and BF_3 flow. The surface response plot in Figure 2-4 also illustrates the dependence of V_{oc} on deposition time and temperature. The decrease in V_{oc} at longer deposition time beyond 3 min could be due to the rapid increase of real substrate temperature during the VHF deposition. The Pareto chart in Figure 2-5 is for the total peak power output P_{max} (proportional to efficiency) of the solar cells within the selected parameter space. The dependence of P_{max} on deposition time, temperature and BF_3 flow are mostly due to the strong dependence of V_{oc} on these parameters. Using the design of experiments, we have successfully surveyed the dependence of solar cell performance on these four crucial parameters using 18 experiments.

We have indeed found a wide parameter space that could produce solar cells with V_{oc} near 0.90 V, indicating μ c-Si p-material deposition. Figure 2-6 is the J-V curve for a representative device with VHF p-layer after further improvement, showing a V_{oc} of 0.93 V.

2.1.3. Microcrystalline p-layer using a modified VHF plasma deposition

In order to further improve the performance of p-layers in solar cells, we have investigated the application of a modified VHF plasma for the μ c-Si p-layer growth, with the anticipation that the new process would further improve the solar cell performance and offer an even wider parameter space for the growth of high quality p-layers.

For a comparison with conventionally made p-layers, we explored the deposition of microcrystalline p-layers at VHF (70 MHz) and RF (13.56 MHz) frequencies. The μ c-Si p-

Pareto Chart for J_{sc}

Figures 2-1 Pareto chart for J_{sc} of n-i-p solar cells with VHF μ c-Si p-layer as a function of temperature, BF₃, SiH₄ and deposition time.

Estimated Response Function

Figure 2-2 Response surface plot for J_{sc} as a function of SiH_4 and temperature while keeping the values of BF_3 and deposition time at the center values.

Pareto Chart for Voc

Figure 2-3 Pareto chart for V_{oc} of n-i-p solar cells with VHF μ c-Si p-layer as a function of temperature, BF_3 , SiH_4 and deposition time.

Estimated Response Function

Figure 2-4 Response surface plot for V_{oc} as a function of deposition time and temperature while keeping the values of BF_3 and SiH_4 at the center values.

Pareto Chart for Pmax

Figure 2-5 Pareto chart for $P_{\max}$ of n-i-p solar cells with VHF $\mu\text{c-Si}$ p-layer as a function of temperature, BF_3 , SiH_4 and deposition time.

12399424234 Single NIP 8 Nov 96 VHF M107A P-LAYER

Figure 2-6 J-V curve for a representative device with VHF p-layer, showing a V_{oc} of 0.93 V.

layers were deposited onto the SS/n-i substrates followed by an evaporation of ITO as the top electrode. The deposition of p-layers in the LL2 system is made using plasma CVD at different frequencies from a gas mixture of SiH_4 , BF_3 , and/or H_2 .

J-V and QE measurements were performed for these devices to evaluate the solar cell and compare the effect of different p-layer depositions. Since the cells were made using nominally the same SS/n-i substrates and ITO layers, the change in the device performance reflects the effect of the p-layers.

Table 2-2 shows the results of solar cells whose p-layers were deposited using these different frequencies. Three types of devices are listed in the table, corresponding to the use of different plasma frequencies for the p-layer deposition. Each type of device is individually optimized for optimum performance. Besides the use of the same substrate, the ITO layer for these three devices are made in the same run (ITO4408) to ensure consistency. The data listed in Table 2-2 is the average of data for many small area solar cells on the same sample.

As we can see from these data, the device with p-layer deposited using the modified VHF process (Sample L2523) shows the highest performance. The V_{oc} and FF are the highest among the group. The largest amount of improvement is in J_{sc} , about a 6% increase in J_{sc} compared with the conventional RF sample (L2525). To confirm the improvement in the modified VHF configuration, we repeated a modified VHF sample (L2527), with ITO coated in a separate evaporation (ITO4409). The improvement in the J_{sc} as well as V_{oc} and FF over the conventional RF sample was reproduced.

Figure 2-7 and 2-8 show the J-V curves for samples L2523 and L2525 corresponding to the modified VHF and the conventional RF p-layers. As a reminder, the results listed in Table 2-2 are averages of many cells on the same sample including those shown in Figure 2-7 and 2-8.

Figure 2-9 and 2-10 show the quantum efficiency curves for the modified VHF device (L2523) and the conventional RF device (L2525). The improvement in J_{sc} in the modified VHF device is mainly due to the 11% increase in the blue response. The lower absorption loss in the blue indicate that the modified VHF p-layer is more transparent to the sun light. The increased J_{sc} is indeed due to the improved transparency in this modified VHF p-layer.

We deposited a p-layer using the modified VHF process on a SS/Ag/ZnO/n-i structure prepared at United Solar to form a hybrid test device.¹⁸ Figure 2-11 is the QE curve for such a device with a blue response of 83% at 400nm.

The improved microcrystallinity using VHF deposition process compared with conventional RF process is also supported by the RHEED measurement. Figure 2-12 shows a RHEED pattern of a device with VHF p-layer on the top. The sharp lines in the 220 and 311 rings and the dark background in between these rings indicate that the VHF p-layer is a microcrystalline material with a high degree of microcrystallinity.

Table 2-2 Results of solar cells whose p-layers were deposited using different processes:
conventional RF, conventional VHF and a modified VHF process

p-layer	ITO	p process	Voc	Jsc	FF	Rs	Pmax	Jsc from QE	QE@400nm
Run No.	Run No.		(V)	(mA/cm ²)		(Ohm,cm ²)	(mW/cm ²)	(mA/cm ²)	(%)
L2523	4408	modified VHF	0.959	10.39	0.664	11.5	6.62	10.71	65.5
L2525	4408	conventional RF	0.948	9.82	0.63	14.8	5.86	10.09	59.1
L2526	4408	conventional VHF	0.933	8.78	0.651	12.2	5.33	10.04	56
L2527	4409	modified VHF	0.958	10.4	0.654	13.1	6.52	11.27	72.1

L252342M13A Single MP 9 Jan 97 VHF RF M107J P-LAYER

Figure 2-7 J-V curve for an a-Si n-i-p device (Sample L2523) with p-layer deposited using the modified VHF PECVD.

L2525M1M136 Single MIP 9 Jan 97 RF M107J F-104ER

$J_{sc} = 9.740$ $J_{mp} = 8.147$
 $V_{oc} = .952$ $V_{mp} = .723$
 $FF = .635$
 $\eta = .25 \text{ cm}^2$ $P_{max} = 5.89 \text{ mW/cm}^2$

$R_s = 15.1 \Omega \text{ cm}^2$
 $R_{sh} = 1.663 \Omega \text{ cm}^2$

Figure 2-8 J-V curve for an a-Si n-i-p device (Sample L2525) with p-layer deposited using the conventional RF PECVD.

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Figure 2-9 Quantum efficiency curve for an a-Si n-i-p device (Sample L2523) with p-layer deposited using the modified VHF PECVD, showing high blue response.

Figure 2-10 Quantum efficiency curve for an a-Si n-i-p device (Sample L2525) with p-layer deposited using the conventional RF PECVD.

Figure 2-11 QE curve for an a-Si solar cell with ECD-deposited VHF p-layer and United Solar-deposited n-i layer on a SS/Ag/ZnO substrate, showing QE=83% at 400nm.

Figure 2-12 RHEED pattern of a device with VHF p-layer at the top, showing high volume fraction of microcrystalline phase in the p-layer.

The use of the modified VHF p-layer in an a-Si solar cell increases the solar cell J_{sc} , V_{oc} and FF. The increased J_{sc} and V_{oc} are most likely due to the improved microcrystalline formation in the p-layer. As an additional benefit, the new VHF process can be easily incorporated into a large scale production process such as ECD's continuous roll-to-roll amorphous silicon PV production line.

2.2 High V_{oc} a-Si:H single junction cells

In phase I of the program, we reported the use of low substrate temperatures and large amounts of hydrogen dilution during i-layer deposition to prepare a-Si cells with initial V_{oc} of 1.053 V and stable V_{oc} of 1.014V. J-V curves for the initial and stable cells are shown in Figures 2-13 and 2-14, respectively. In order to understand the fundamental properties of this i-layer, in phase II of the program we have begun an effort to investigate the structure and electronic properties of this material. After gaining a better understanding in the material properties, we anticipate to further improve the V_{oc} and other cell parameters.

We have prepared films for Infrared Absorption (IR), Small-Angle X-ray Scattering (SAXS) and Raman structural studies. The IR and Raman analysis was done in-house while the SAXS measurements were done at the Colorado School of Mines by Don Williamson. Figure 2-15 displays IR data for one of these low T_s , high dilution films. One can see the presence of small peaks between 840 and 890 cm^{-1} associated with scissors and wag modes of $(\text{SiH}_2)_n$ in the figure. The presence of a small amount of polyhydride modes is consistent with a film prepared at rather low substrate temperatures and the recent findings of the group at United Solar for their films prepared under high hydrogen dilution conditions. Because the films used for IR analysis peeled off the substrate during film thickness measurements, we were not able to obtain accurate thickness measurements and, thus, bonded hydrogen contents were not obtained. As a general note, these films peeled off glass and c-Si substrates easily upon exposure to the atmosphere when the film thickness was greater than 0.3 μm . This is consistent with films with very high compressive stresses, which is usually associated with a-Si material with high densities and few voids.

SAXS data for a 1 μm thick film is shown in Figure 2-16. Very little scattering is seen suggesting that there are few voids in the material. As a comparison, the dashed line represents the amount of scattering expected from a film with a void fraction of 0.1%. The amount of scattering from our sample is clearly less implying that the void fraction is even less than 0.1%. As might be expected from a sample with very weak SAXS, no change in the data was observed when the sample was measured in the tilted configuration suggesting that the voids that might be present are not of a columnar nature. Comparing the IR and SAXS data, it seems that the hydrogen bonding which leads to the polyhydride IR signals are not related hydrogen near void surfaces.

L1031A4W14A Single NIP 23 Mar 95 WBI SS 2000A 10HR

$J_{sc} = 7.287$ $J_{mp} = 6.329$

$V_{oc} = 1.053$ $V_{mp} = .887$

$FF = .732$

$A = .25 \text{ cm}^2$ $P_{mx} = 5.612 \text{ mW/cm}^2$

$R_s = 10.9 \Omega \text{ cm}^2$

$R_{sh} = 3.1E3 \Omega \text{ cm}^2$

Figure 2-13 J-V curve of a solar cell with wide bandgap a-Si intrinsic layer, showing 1.053 V initial open circuit voltage.

L1036A1W33C Single NIP 7 Jul 95 LIGHT SOAKED 130 DAY

Figure 2-14 J-V curve of a solar cell with wide bandgap a-Si intrinsic layer, showing 1.014 V stabilized open circuit voltage after 2500 hours of 1 sun light soaking.

Absorbance / Wavenumber (cm-1)

Number of Scans= 32 Apodization= Strong

File # 1 : LL-1204F

3/1/96 10:03 AM Res=4 cm-1

a-Si:H High VOC on c-Si, Baseline Flattened

Figure 2-15 IR spectrum of an a-Si film deposited at low temperature and with high hydrogen dilution.

Figure 2-16 Small Angle X-Ray Scattering spectrum of an a-Si film deposited at low temperature and with high hydrogen dilution.

2.3 Other Related Solar Cell Research

In our solar cell fabrication process, the top conducting electrodes (indium-tin-oxide, ITO) are deposited by evaporating an alloy of In and Sn in oxygen at elevated substrate temperature. To ensure effective a-Si solar cell research, it is extremely important to maintain the deposition of ITO layer in an optimum and consistent condition. The crucial deposition conditions in the ITO evaporation include the substrate temperature, oxygen partial pressure and deposition thickness. For example, when the substrate temperature is too low, the deposited ITO film would include amorphous phase and therefore is not as transparent as higher temperature deposited films. However, when the substrate temperature is too high during evaporation, an out diffusion of hydrogen would occur in the amorphous silicon semiconductor layers, which would cause a solar cell degradation. Since the ITO top electrode also serves as the anti-reflection coating for the device, the thickness of the ITO layer also needs to be carefully adjusted so that the reflection is minimized at the peak of $QE \times I_{1.5}$, where QE is the device quantum efficiency and $I_{1.5}$ is the AM1.5 global solar spectrum.

We have established a standard procedure to maintain the ITO evaporation under optimum conditions. A set of ITO runs are made routinely on a standard, uniform a-SiGe n-i-p solar cell produced in a roll-to-roll machine. Table 2-3 is a typical set of samples made for a routine check of the ITO deposition consistency, reproducibility, and if the standard conditions are still optimum. In the table, each row represent the average of the device performance for all the cells (typical 8-16) in a 2"x2" sample. The two positions represent samples placed at two sides of the substrate, therefore indicating the uniformity within the same ITO run. Int.Q in the table shows the short circuit current as calculated by integrating the QE response over AM1.5 global spectrum. Q_{400} is the QE at 400 nm, indicating the blue response. Q_{max} is the maximum QE value in the spectrum, which reflects the ITO absorption and the effect of anti-reflective coating.

Sample ITO4455 was deposited under the standard condition that we previously established. The purpose of this group of samples is to see whether this deposition condition still remain optimum and how sensitive the solar cell performance depends on the variation of each deposition parameter. Sample ITO4470 was deposited under the identical condition as ITO4455 but at a different time. The very similar performance of these two samples demonstrates the level of reproducibility of the system.

Comparing ITO4478 and ITO4459 with ITO4455, a decrease in the deposition temperature results in a loss in J_{sc} , up to 3.4%. This is because at 205C, there is slightly more amorphous phase of ITO and therefore the absorption is increased.

In terms of the ITO thickness, a 10% variation on both sides does not show a significant change in the P_{max} . Comparing ITO4469 with ITO4468, the thicker ITO caused small loss in J_{sc} and small gain in FF due to the reduced sheet resistance, resulting in no significant changes in P_{max} .

Table 2-3 Performance of reference solar cells coated with different ITO in a routine check of the ITO deposition consistency and reproducibility

ITO run #	position	Ts (C)	Relat. Thick (A)	O2 pressure (0.1 mTorr)	Voc (V)	Jsc (mA/cm2)	FF	Rs	Pmax (mW/cm2)	Int. Q (mA/cm2)	Q400	Qmax
4455	1	220	1400	5.1	0.653	13.88	0.627	7.9	5.68	15.41	0.618	0.869
	2	220	1400	5.1	0.657	14.44	0.63	7.5	5.98			
4477	1	235	1400	5.1	All shorted							
	2	235	1400	5.1	0.661	15.05	0.628	7.7	6.25	15.54	0.595	0.878
4478	1	235	1400	5.1	0.67	14.86	0.624	8.4	6.21	15.38	0.632	0.874
	2	235	1400	5.1	0.671	15.17	0.61	9	6.2			
4459	1	205	1400	5.1	0.65	13.51	0.635	7.8	5.57			
	2	205	1400	5.1	0.653	13.85	0.63	8	5.71	14.92	0.527	0.828
4460	1	220	1600	5.1	0.66	13.37	0.644	7.6	5.69			
	2	220	1600	5.1	0.661	13.61	0.623	8.7	5.6			
4461	1	220	1400	7.4	0.659	14.24	0.609	9.3	5.72			
	2	220	1400	7.4	0.663	14.44	0.614	9.1	5.88	15.43	0.646	0.872
4462	1	220	1400	3.5	0.654	12.66	0.638	8.2	5.29			
	2	220	1400	3.5	0.653	12.36	0.639	8.3	5.16	13.77	0.479	0.766
4468	1	220	1250	5.2	0.662	14.88	0.638	7.1	6.28	15.83	0.687	0.902
	2	220	1250	5.2	0.662	14.25	0.641	7.3	6.04			
4469	1	220	1550	5.1	0.663	14	0.647	6.7	6.01			
	2	220	1550	5.1	0.66	14.14	0.644	6.8	6.01	15	0.535	0.846
4470	1	220	1400	5.1	0.652	13.55	0.635	7.7	5.61			
	2	220	1400	5.1	0.657	14.35	0.628	7.8	5.92			
4471	1	220	1600	7.5	0.658	14.46	0.624	8.4	5.94			
	2	220	1600	7.5	0.66	14.47	0.62	8.6	5.92	15.64	0.617	0.884
4472	1	220	1200	3.5	0.656	13.11	0.625	9	5.37	13.84	0.617	0.784
	2	220	1200	3.5	0.659	13.22	0.624	8.8	5.43			

Comparing samples ITO4461 (with higher oxygen pressure) and ITO4462 (with lower oxygen pressure) with the standard sample ITO4455, higher oxygen pressure increases J_{sc} . This is mainly because that a higher oxygen incorporation in the alloy reduces the oxygen deficiency and hence the free carrier absorption. However, when the amount of free carriers is reduced, the resistivity of the ITO increases, as we see from the increase in series resistance and the decrease in fill factor in Sample ITO4461. Another factor with the change with the oxygen pressure is the possible variation in ITO thickness. When the chamber oxygen pressure is varied during evaporation, the calibration factor for thickness monitor could be slightly different. The overall power output P_{max} of the test cell is reduced for higher oxygen pressure due to the relatively larger loss in FF and smaller gain in J_{sc} compared with the standard sample. When the oxygen pressure is reduced from the standard value during the evaporation, as we see for sample ITO4462, there is a sizable loss in J_{sc} as expected yet no gain was observed in the FF, resulting a net loss in the P_{max} . Figure 2-17 and 2-18 show the QE curves of ITO4461 and ITO4462 with different oxygen pressures during evaporation. Sample ITO4461 shows much higher ITO transmission, suggesting a reduced oxygen deficiency in the oxide.

The loss in P_{max} for different oxygen pressure can be somewhat compensated with a thickness adjustment, as shown in the comparison of Samples ITO4471 and ITO4472 with Samples ITO4461 and ITO4462. For the ITO deposition at higher oxygen pressure, increased thickness compensates the loss in FF (See ITO4471). However, for the sample deposited with low oxygen pressure, reduced thickness does not fully recover the loss in J_{sc} (See ITO4472).

This set of test samples with various ITO evaporation conditions ensures that the ITO is deposited under optimum conditions. The consistent and reproducible ITO deposition is extremely important to the solar cell device research.

Figure 2-17 QE curve of a device with higher oxygen pressure during the ITO

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Figure 2-18 QE curve of a device with lower oxygen pressure during the ITO evaporation (sample ITO 4462).

SECTION 3

LARGE AREA SOLAR CELL RESEARCH

3.1 Introduction

ECD pioneered the development of multi-junction a-Si alloy solar cells, and the company is now aggressively commercializing the technology through United Solar. Recently, ECD has designed and constructed a 5MW production facility, as shown in Figure 3-1, for United Solar to produce a-Si thin film photovoltaic products at higher volume, higher efficiency, and lower cost. The 5MW machines are used for this research program to gain an understanding of large area related deposition processes and consequently improve the efficiency of large-area triple junction solar cells. These areas of research are critical to the success of the ECD's commercialization effort and to the achievement of DOE/NREL mid-term goal for thin film photovoltaics.

Continuous roll-to-roll manufacturing technology utilizing a thin, flexible stainless steel substrate developed by ECD offers a number of advantages in a fully automated, high-throughput PV module production plant. The stainless steel substrate is rugged, and this improves production yield by eliminating substrate breakage - a significant problem in many glass substrate a-Si alloy PV module manufacturing plants. The transport mechanism on a thin, flexible stainless steel substrate is also mechanically simpler and significantly less expensive than the transport mechanism for conventional glass substrates. Heating and cooling of the substrate during solar cell deposition can also be accomplished quickly, compared to glass substrate manufacturing. As a result, the capital equipment cost for a large-volume plant utilizing continuous roll-to-roll technology will be relatively low.

Previously, ECD designed and built a 2MW a-Si PV manufacturing line for its Russian joint venture, Sovlux. This 2MW production line consists of a continuous roll-to-roll substrate washing machine, a continuous roll-to-roll back-reflector deposition machine, a continuous roll-to-roll a-Si alloy deposition machine, a continuous roll-to-roll top clear conductor deposition machine, and a continuous step and repeat cell cutting machine. This production line produces triple-junction two-bandgap a-Si alloy solar cells consisting of a-Si/a-Si/a-SiGe structure on a 5 mil. thick, 14 in. wide, 2500 ft. long stainless steel roll at a speed of 1 ft./min. 4 ft² PV modules with 9.5% initial and 8% stable efficiencies were demonstrated from this production line.⁶

3.2 ECD/United Solar's 5MW a-Si PV Processor

The state-of-the-art 5MW production equipment incorporates major advances in solar cell design and manufacturing processes achieved by United Solar and ECD, with support from DOE/NREL.¹⁴ The advanced continuous roll-to-roll triple-junction a-Si module production technologies will reduce the module production costs, increase the stabilized module efficiency, and expand the commercial production capacity.

Figure 3-1 5MW Continuous roll-to-roll a-Si alloy solar cell processor.

The 5MW continuous roll-to-roll a-Si alloy solar cell processor, shown in Figure 3-1, is designed to produce triple-junction, triple-bandgap a-Si/a-SiGe/a-SiGe solar cells in a single pass through a continuous roll-to-roll process. The solar cell structure was shown in Figure 1-1. Utilizing a similar solar cell structure, United Solar recently produced solar cells with a 14.6% record-high efficiency.

The input to the process is a roll of stainless steel coated with back-reflector in a previous roll-to-roll process. Web rolls are approximately 2,500 feet in length, 14 inches in width, and weighing up to 1,000 pounds. The beginning of the input roll will be welded to the end of the preceding roll in situ. Web transport through the system will be single pass at a rate of 2 ft/min.

The triple-junction cell structure will consist of doped and undoped thin films of a-Si alloy semiconductor deposited sequentially and simultaneously in proper order as the web is transported through each successive chamber section. Deposition is achieved by low-pressure RF plasma chemical vapor deposition.

The multi-section a-Si alloy deposition machine consists of a pay-off chamber, nine process sections for depositing the triple-junction cell, and a take-up chamber. Each chamber is separated by a "gas gate." The gas gates are designed so that the migration of dopants and other process gases between chambers is eliminated. The position, tension and speed of the web through the processing chambers are computer-controlled. Web passage through the process chambers is such that deposition takes place on the underside, and front facing in the web transport system is not allowed.

Pay-off and take-up chambers contain all of the necessary web-drive components, auxiliary rolls, tension sensors and steering mechanisms. Pumping for these chamber sections is done by a Roots blower and mechanical displacement-type vacuum pumps.

In each of the process chambers, transport of reactant and diluent gases to the reaction zone is from mixing manifolds designed to provide the specified mixture to be appropriately distributed in each individual reaction zone. Reaction zone pressures are controlled by a gas-pumping system using variable conductance valves, flow controllers, and pressure transducers used together in a closed-loop computer-controlled feedback system for each process section.

Each of the layers making up the cell structure is deposited sequentially and simultaneously. Heat is provided to maintain the web at the specified temperature by an array of quartz-type lamps which radiate downward onto the web and are controlled by thermocouples in individual closed-loop circuits.

In this advanced solar cell processing machine, several important new features are incorporated:

- The machine is designed to minimize incorporation of contaminants into deposited material. The machine has been fabricated, constructed and assembled under a strict procedure to minimize contaminants.
- The machine operation is computer-controlled. With improved software developed by ECD which enables an operator, monitoring interactive CRT displays, to start, operate, and shut-down the machine using computer keyboards that control all the machine functions including pumping, gas recipes, flow meters, heaters, supplies, valves, and web drive systems. The computerized system incorporates automatic sequence of operations with many safety interlocks, and other special design features that make the production operation safe and reliable. The computer system also provides a historical data acquisition system which monitors and stores all the processing data in computer discs.
- The machine is equipped with a maintenance-free effluent scrubbing exhaust system consisting of a burn-box and scrubber.
- The web transport system is improved, and the web pass line is horizontal and flat, as seen in Figure 3-1. Previously built machines utilized a catenary web pass line.
- The gas-feed and cathode systems for depositing bottom and middle intrinsic layers incorporate diffusion-controlled gas-feed/deposition mechanism which allows adjustment of grading of Ge and Si in the layers.
- The cathode configuration and deposition conditions have been optimized to deposit microcrystalline p-layers.
- Improved mechanical parts designs for internal components of the process chambers have significantly reduced component heat distortion during processing.
- Serviceability and accessibility have been improved with new non-catenary design. Using powered lid lifts for all chambers, all internal chamber components are accessible for servicing at waist-high levels. Further, the use of separate above-the-ground troughs for wiring and piping has improved the appearance as well as the accessibility of the external machine components.

During the past year, this advanced 5MW system was under process optimization. Members of ECD's and United Solar's research staffs have participated in a joint effort to optimize the this 5MW production line. In particular, scientists involved with this NREL high efficiency, triple-junction solar cell program have made extensive contributions to the optimization effort participating in the experimental design, processing of the web, preparation of top contacts and characterization of small area cells. Presently, the 5MW program is in the final stages of the optimization and will soon be in full scale production. Below we describe some of the results from the optimization program.

3.3 Optimization of Large Area Deposition of a-Si Films and Solar Cells

In terms of a-Si:H films and devices, we have focused our efforts on optimizing the component layers of the top cells for the triple-junction devices. As is usually observed for a-Si:H devices, the best cells have been made using high H₂ dilution and moderate substrate temperatures (225-250°C). Tables 3-1 and 3-2 display properties of top component cells

(0.25 cm² size test cell) made on bare stainless steel (without back reflector) with i-layers made under different hydrogen flows and substrate temperatures. The thickness of these devices were measured by the capacitance technique and found to be approximately the same within experimental error. The cell with the i-layer prepared at twice the H₂ flow of 10,000 sccm has a significantly higher FF and a slightly higher V_{oc}, showing the importance of high hydrogen dilution to the quality of the top cell i-layer. From Table 3-2, the FF improves by roughly 0.15 when the i-layer substrate temperature is increased by 50°C. Both of these trends were expected due to the well documented improvements in a-Si:H quality with higher hydrogen dilution and moderate substrate temperatures due to higher adatom surface mobilities or enhanced etching of weakly bonded material on the growing film surface which lead to denser, more homogeneous films.

Table 3-1 Performance of top component cell as a function of hydrogen dilution, showing an improvement in V_{oc} and FF with increasing H₂ flow. The other deposition conditions such as substrate temperature and RF power are kept constant for these devices.

H ₂ Flow (sccm)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	P _{max} (mW/cm ²)	R _s (Ω•cm ²)
standard	6.2	0.954	0.692	4.1	9.6
standard	6.1	0.969	0.694	4.1	8.1
2 x standard	6.0	0.977	0.721	4.2	8.3

Table 3-2 Performance of top component cell as a function of top i-layer web temperature during deposition, showing an improvement in FF and J_{sc} with higher substrate temperature. The other deposition conditions such as hydrogen flow and RF power are kept constant for these devices.

Substrate Temperature (C)	J _{sc} (mA/cm ²)	V _{oc} (V)	FF	P _{max} (mW/cm ²)	R _s (Ω•cm ²)
standard	7.0	0.977	0.707	4.8	7.3
50°C higher	7.4	0.972	0.724	5.2	6.8

In contrast, the behavior of the cell properties with varying applied power was contrary to the commonly observed improvement in a-Si:H quality with lower powers and the accompanying lower deposition rates. As can be seen from Table 3-3, with increasing power up to 200W higher, the FF was found to improve even when the i-layer thickness of the cells increased with the higher powers. Increasing the power further, the thickness changes very little however there is still an improvement in the FF showing that our best material is made at the highest powers, which are presently limited by the machine hardware. Along with the

improvement in FF, the cells prepared at the higher powers also have slightly higher V_{oc} . The improvement in cell properties with increased power is the subject for further studies.

Table 3-3 Performance of top component cell as a function of RF power, showing an improvement in V_{oc} and FF with increasing RF power

Applied RF Power (W)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF	P_{max} (mW/cm ²)	R_s ($\Omega \cdot \text{cm}^2$)
standard	6.1	0.969	0.694	4.1	8.1
200W higher	7.0	0.969	0.705	4.8	6.5
400W higher	6.9	0.975	0.719	4.8	8.1

Incorporating the best conditions to date for n-, i- and p-layer preparation, top cells have the following typical device performance: J_{sc} =7.5-8.0 mA/cm², V_{oc} = 0.97-0.98V, FF=0.72-0.73. Figure 3-2 shows a J-V curve for a typical top cell. Under different conditions, we have obtained cells with V_{oc} as high as 1.00 V, as shown in Figure 3-3.

3.4 Optimization of Large Area Deposition of a-SiGe Films and Solar Cells

Optimization of deposition uniformity

For optimization of the bottom and middle a-SiGe cells, one important issue is to find process conditions which allow for the uniform deposition across the entire width and length of the cathodes. This is obviously important in the roll-to-roll manufacturing process because nearly all of the cathode area is utilized for the large area solar module production. In addition, these uniformity issues have become more important in this generation of ECD's production lines because larger cathodes are used in the 5MW line.

Figure 3-4 depicts one of the uniformity problems encountered for a-SiGe thin film solar cell deposition over large area. The figure displays data for small area (0.25 cm²) single junction a-SiGe n-i-p test devices whose doped layers were prepared with the web in motion and the i-layers made with the web in the static condition (a static burn). These special types of cells are produced to study the deposition uniformity in the roll-to-roll machine for a particular layer which, in this case, is the a-SiGe i-layer. Following this procedure, static burns are made for each of the cathodes associated with i-layer depositions and cells can be made from any section of the burns allowing for characterization of uniformity across the burns and thus across the cathodes. To test the uniformity of cell properties across the length of the cathode (also the length of the web) and the gas flow direction, solar cells were made from different parts of the static i-layer depositions as is shown for one such static deposition in Figure 3-4. The cells for which data is shown in this figure were made under unoptimized conditions and

5MWUSS 127B281 #32 TOP NIP/SS 14 Dec 1996

$J_{sc} = 7.872$ $J_{mp} = 6.83$
 $V_{oc} = .978$ $V_{mp} = .818$
 $FF = .726$
 $A = .25 \text{ cm}^2$ $P_{max} = 5.588 \text{ mW/cm}^2$

$R_s = 6.8 \Omega \cdot \text{cm}^2$
 $R_{sh} = 2.5E3 \Omega \cdot \text{cm}^2$

Figure 2.2 I-V curve for a typical test cell measured in large area in the 5MW a-Si solar

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Jsc = 6.582 Jmp = 5.422

Voc = .997 Vmp = .849

FF = .701

A = .25 cm² Pmx = 4.603 mW/cm²

Rs = 11.1 Ω cm²

Rsh = 2.14 Ω cm²

J (mA/cm²)

V (volts)

Room Voc = .769

Figure 3-3 J-V curve of a top cell produced in 5MW machine, showing a V_{oc} of 1.00 V.

Figure 3-4 Performance of a-SiGe solar cells with i-layer deposited in a static mode near the exhaust side, the center and the gas inlet side of the cathode burn, showing the unoptimized deposition uniformity with a large area cathode.

without the benefit of an Ag/ZnO back reflector and the J-V measurements for cell characterization were made using 530 nm cutoff filtered AM1.5 light. When cells were made from the exhaust side, the center and the gas inlet side of the cathode burn, it was found that the Ge content (as measured with Energy Dispersive Spectroscopy) for the bottom cell increased on average by 8-12% as one scanned from the exhaust to the inlet side of the cathode. As can be seen from the data in the figure, this increase in Ge content led to the expected decreases in V_{oc} and FF and an increase in J_{sc} when the properties were scanned across the cathode length. Along with this increase in Ge concentration an increase in the i-layer thickness was also found as can be seen from the data in Figure 3-4.

This uniformity problem leads to fluctuations in the cell properties across the thickness of the solar cell i-layers prepared with the web moving. The variations in cell properties across all of the 10 cathodes used to make the bottom cell a-SiGe layer are shown in Figure 3-5. In the figure, each cathode is 4 units long on the horizontal scale. The cells used to obtain the data for this figure were again made from different parts of i-layer burns as they were to obtain the data from Figure 3-4. The oscillations in each of the cell properties are clearly apparent. The fluctuations in the Ge content were also observed in SIMS profile for a cell made under standard conditions (all layers made with the web in motion) in the form of a near zigzag profile of the Ge concentration. Such fluctuations in the Ge content lead to variations in the bandgap and mobility edges across the i-layer which could hinder carrier collection.

Figure 3-6 shows that this uniformity problem is strongly related to the film deposition rate. In the figure, the ratio of thickness of films taken from the inlet side of an i-layer burn to the thickness of films taken from the outlet side of the same burn is plotted as a function of deposition rate for several cathodes with the burns prepared under a variety of deposition conditions. As can be seen from the figure, the inlet/outlet ratio used to judge the film uniformity increases from the uniform value of 1 as the deposition rate increases. Since a significant amount of deposition is observed at the exhaust side of the cathode, this effect is likely not related to gas depletion.

In order to minimize this uniformity problem, we have studied the dependence of the film uniformity on a number of deposition conditions and found that by carefully selecting a combination of deposition parameters including, for example, RF power and deposition temperature, we can obtain uniform depositions at relatively high deposition rates. Figure 3-7 displays how the film thickness can be made more uniform across one cathode, as an example, when the power is lowered. At the higher powers, the non-uniformity likely represents the depletion of gas species as the gas moves towards the pumping exhaust port with the higher Ge contents at the inlet side related to an enhanced depletion of GeH_4 . While the use of the lower powers improved the uniformity, they also led to a low deposition rate not compatible with the rated 2 ft/min line speed, i.e., 5MW/yr production throughput.

By lowering the temperatures in certain critical areas of the process chamber during deposition, the uniformity of the a-SiGe films can be significantly improved without a loss of deposition rate. As is shown in Figure 3-8, the inlet/outlet ratio of film thickness approaches unity in the desirable range of deposition rate when the temperatures in the critical areas are

Figure 3-5 Deposition uniformity for a-SiGe solar cell before optimization for all of the 10 cathodes used to make the bottom cell a-SiGe layer.

Figure 3-6 Ratio of thickness of films taken from the inlet side of an i-layer burn to the thickness of films taken from the outlet side of the same burn is plotted as a function of deposition rate for several cathodes with the static burns prepared under a variety of deposition conditions, showing that this uniformity problem is strongly related to film deposition rate.

Figure 3-7 Deposition thickness uniformity over large area cathode with different RF power, showing improved uniformity at lower power.

I/O Uniformity as a Function of Deposition Rate

Figure 3-8 Deposition thickness uniformity over large area cathode with different deposition rate, showing high uniformity (I/O uniformity=1) at desirable deposition rate (Relative deposition rate=1) as required by the machine line speed.

lowered, as indicated with the diamond point in the figure in the lower right side of the curve. This improvement in the uniformity with decreased temperatures is likely not related to a decrease of CVD decomposition of process gases, but is probably related to the decrease of some type of excitement of the gas species by the high temperatures which allows for easier decomposition of the gas species at the moment the gas reaches the RF plasma at the inlet side of the cathode.

With the combination of the lower temperatures and slightly lower powers, we were able to obtain reasonably thick i-layers and uniform depositions across the cathode as is displayed in Figure 3-9. The figure displays data for one of the cathodes, as an example, before the improvements and after the improvements. The cells were again made with static i-layers and dynamic doped layers (the same method as described for the data in Figure 3-4, see above). There is no bandgap profiles for these a-SiGe cells due to the static i-layer deposition. One can see that the uniformity in terms of Ge content and cell properties is dramatically improved under these conditions allowing for the production of uniform i-layers when the web is in motion.

Optimization of middle cell a-SiGe deposition using Design of Experiments

Besides the uniformity issue, another important aspect of a-SiGe deposition is the film quality. We have optimized the deposition to improve the film quality using a Design of Experiments approach.¹⁷ A 5-factor Draper-Lin small composite design with face-centered design characteristic is used with the deposition conditions covering applied RF power (power), disilane flow (Si_2H_6), hydrogen dilution (H_2), germane to silicon ratio (Ge/Si), and bandgap grading (PI). Due to the proprietary nature of the parameters, the detailed value of these conditions are not disclosed in this report. Table 3-4 list the design parameters and the solar cell results for the experiments.

All other deposition conditions not included above were previously optimized. For this study the cells were deposited on bare stainless steel without a back reflector. It was later proved that the conditions that were found optimum for from these studies were also optimum for cells deposited on back reflector material. All cell data to be discussed here were obtained using 530 nm cutoff long-pass filtered light. For the middle cell, a cell on bare stainless steel needs to have a J_{sc} value of at least 7.0 mA/cm^2 with the 530 nm filtered light. Thus, we were looking for conditions which would make the best cell with 7.0 mA/cm^2 and V_{oc} around 0.70 V.

Figure 3-10 and 3-11 display the Pareto charts for the J_{sc} and cell efficiency measured under the 530 nm filtered light (power output under filtered red light, red pwr). In figure 3-10, the expected strong dependence of J_{sc} on the Ge/Si ratio is observed due to the increase in current with increasing Ge content. The strong dependence with power is likely related to the increase in i-layer thickness with increased power leading to more light absorption and higher currents. The influence the cross term between the Si_2H_6 and the H_2 flow has on J_{sc} is again likely related to the i-layer thickness since the thickness usually decreases with increasing H_2 dilution.

Before Improvements

Voc (V)	0.67	0.61	0.57
Jsc (mA/cm ²)	8.6	9.7	10.4
FF	0.63	0.55	0.46
Pmax (mW/cm ²)	3.6	3.3	2.7
Relative Thickness	18% thinner than Std	Std	42% thicker than Std

After Improvements

Voc (V)	0.65	0.65	0.66
Jsc (mA/cm ²)	8.7	8.7	8.8
FF	0.57	0.58	0.57
Pmax (mW/cm ²)	3.3	3.2	3.3
Relative Thickness	3% thinner than Std	Std	4% thicker than Std

Figure 3-9 Performance of a-SiGe solar cells with i-layer deposited in a static mode near the exhaust side, the center and the gas inlet side of the cathode burn, before and after uniformity optimization.

Table 3-4 Five-factor Draper-Lin design for the optimization of middle cell a-SiGe i-layer quality.

RUN	Power (W)	Si ₂ H ₆ (sccm)	H ₂ (sccm)	Ge/Si ratio	Bandgap grading	P _{max} (red) (mW/cm ²)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF	Integ.Q (mA/cm ²)
1	High	High	Low	High	High	3.72	0.728	7.92	0.645	13.9
2	High	Low	High	High	High	2.89	0.716	5.71	0.707	12.4
3	Low	High	High	High	Low	2.84	0.694	6.12	0.667	12.34
4	High	High	High	Low	Low	3.54	0.804	6.67	0.661	12.98
5	High	High	Low	Low	Low	3.51	0.824	6.38	0.668	12.82
6	High	Low	Low	Low	High	2.73	0.846	4.39	0.734	10.37
7	Low	Low	Low	High	Low	2.63	0.751	4.88	0.717	11.41
8	Low	Low	High	Low	High	2.13	0.8	3.65	0.729	9.76
9	Low	High	Low	High	High	2.5	0.68	5.4	0.67	10.51
10	High	Low	High	High	Low	2.92	0.75	5.6	0.695	
11	Low	High	High	Low	High	2.81	0.775	5.17	0.703	11.12
12	Low	Low	Low	Low	Low	2.13	0.8	3.65	0.729	9.76
13	Low	Mid	Mid	Mid	Mid	2.51	0.75	4.81	0.703	10.82
14	High	Mid	Mid	Mid	Mid	3.54	0.789	6.54	0.687	12.76
15	Mid	Low	Mid	Mid	Mid	2.89	0.799	5.1	0.729	11.47
16	Mid	High	Mid	Mid	Mid	3.61	0.731	7.29	0.677	13.52
17	Mid	Mid	Low	Mid	Mid	3.52	0.776	6.5	0.696	13.1
18	Mid	Mid	High	Mid	Mid	3.4	0.744	6.48	0.705	13.11
19	Mid	Mid	Mid	Low	Mid	3.22	0.8	5.63	0.714	11.74
20	Mid	Mid	Mid	High	Mid	3.67	0.711	7.86	0.657	13.88
21	Mid	Mid	Mid	Mid	Low	3.51	0.771	6.52	0.698	12.86
22	Mid	Mid	Mid	Mid	High	3.37	0.748	6.38	0.706	12.88
23	Mid	Mid	Mid	Mid	Mid	3.34	0.758	6.52	0.677	13.11
24	Mid	Mid	Mid	Mid	Mid	3.34	0.758	6.52	0.677	13.11

Pareto Chart for red_jsc

Figure 3-10 Pareto chart for J_{sc} of middle a-SiGe solar cell measured under 530 nm filtered light, for the 5-factor middle cell experimental design.

Pareto Chart for red_pwr

Figure 3-11 Pareto chart for red $P_{\max}$ of middle a-SiGe solar cell in the 5-factor middle cell experimental design.

From Figure 3-11, the cell efficiency is strongly influenced by the applied power. In Figure 3-12, a contour plot of the efficiency is shown with the x and y axes being the applied power and Si_2H_6 flow, respectively. This plot was obtained by fixing the H_2 flow, $\text{GeH}_4/\text{Si}_2\text{H}_6$ ratio and the steepness of the Ge/Si profile across the i-layer at center values. Overlapping parts of the efficiency contour lines are darker contour lines which represent different J_{sc} values. As was mentioned earlier, we are searching for cells with J_{sc} values around 7.0 mA/cm^2 . Following the 7.0 mA/cm^2 contour line, one can see that the highest P_{max} , around 3.64 mW/cm^2 , is obtained at a high power and mid Si_2H_6 flow values as marked by a cross in the figure. We later proved that there was no benefit in using higher powers. Figure 3-13 is a plot similar to the one shown in Figure 3-12 except here the $\text{GeH}_4/\text{Si}_2\text{H}_6$ flow is at a higher value. Here again for $J_{sc}=7.0 \text{ mA/cm}^2$ the optimum power seems to be near high power, however the optimum Si_2H_6 flow is near the low value. Under these high $\text{GeH}_4/\text{Si}_2\text{H}_6$ conditions, the highest P_{max} for $J_{sc}=7.0 \text{ mA/cm}^2$ is between 3.4 and 3.5 mW/cm^2 while under the moderate $\text{GeH}_4/\text{Si}_2\text{H}_6$ ratio the highest P_{max} is between 3.6 - 3.7 mW/cm^2 . Thus, using the lower $\text{GeH}_4/\text{Si}_2\text{H}_6$ conditions will give higher performance cells. The data also showed that there is no benefit in using even lower $\text{GeH}_4/\text{Si}_2\text{H}_6$ ratios.

Other contour plots for the efficiency are shown in Figures 3-14 and 3-15 where this time the x and y axes are the Si_2H_6 flow and $\text{GeH}_4/\text{Si}_2\text{H}_6$ ratio, respectively. In both figures, moderate H_2 flows and Ge/Si profile across the i-layer were assumed with a high power assumed in Figure 3-14 and a moderate power (mid value) assumed in Figure 3-15. One can see from Figure 3-14 that at high power, the highest P_{max} is 3.63 mW/cm^2 , and from Figure 3-15 that at mid power, the highest P_{max} is 3.56 mW/cm^2 . Comparing these two cases, the optimum power is near the high power. After the optimization of the middle cell, high performance a-SiGe middle cell is achieved. Figure 3-16 shows a J-V curve of a typical a-SiGe middle cell for use in a triple junction solar cell.

3.5 Optimization of Large Area Deposition Ag/ZnO and Al/ZnO Back Reflectors

In the ECD/USSC triple-junction solar cell design, a metal/metal-oxide back reflector is used to create multiple passes of photons through the a-Si/a-SiGe/a-SiGe absorbing structure allowing for enhanced absorption of the photons and higher currents. In this report, we limit our discussions to the optimization of Ag/ZnO back-reflector.

A reactive magnetron sputtering process is used to prepare the back reflectors. Targets of Ag and ZnO are sputtered in Ar from different sputtering cathodes in this roll-to-roll back-reflector deposition machine.

The deposition of the Ag/ZnO back reflector was optimized to improve its performance. The optimization covers a parameter space of sputtering current, deposition temperature, Ar pressure and the thickness of Ag and ZnO layers. a-SiGe solar cells were deposited on these back-reflectors to evaluation its performance in a solar cell structure. J-V measurements were done to these cells with AM1.5 light and with AM1.5 after a 630 nm and 645 nm long-pass cutoff filters. Table 3-5 displays cell data taken for cells prepared using different ZnO currents and different ZnO targets manufactured by different vendors. In this table, Q is the

Eff (530nm filter)
H2=mid, GeSi_ratio=mid, steepness=mid

Figure 3-12 Contour plot of the P_{max} as a function of the applied power and Si_2H_6 flow for middle Ge/Si ratio. The dark lines represent the contours with the same J_{sc} value, as marked. The point with the highest P_{max} on the 7.0 mA/cm^2 J_{sc} contour line is marked by a cross, indicating a P_{max} value of 3.64 mW/cm^2 .

Eff (530nm filter)
H2=mid, GeSi_ratio=hi, steepness=mid

Figure 3-13 Contour plot of the $P_{\max}$ as a function of the applied power and Si_2H_6 flow for relatively higher Ge/Si ratio, compared with the plot in Figure 3-12.

Eff (530nm Filter)

H2=mid, Power=hi, steepness=mid

Figure 3-14 Contour plot of the P_{max} as a function of the Si_2H_6 flow and $\text{GeH}_4/\text{Si}_2\text{H}_6$ ratio with high RF power.

Eff (530nm Filter)

H2=mid, Power=mid, steepness=mod

Figure 3-15 Contour plot of the $P_{\max}$ as a function of the Si_2H_6 flow and $\text{GeH}_4/\text{Si}_2\text{H}_6$ ratio with relatively lower RF power.

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Jsc = 13.107 Jmp = 11.251

Voc = .755 Vmp = .611

FF = .694

A = .25 cm² Pmax = 6.869 mW/cm²

Rs = 5.5 $\Omega \cdot \text{cm}^2$

Rsh = 1.3E3 $\Omega \cdot \text{cm}^2$

Figure 3-16 J-V curve of a typical a-SiGe middle cell after preliminary optimization process.

solar cell short circuit current determined from the integrated quantum efficiency curves over AM1.5 spectrum and P630 is the power determined from the data obtained using the 630 nm filtered light. With increasing ZnO sputtering current a decrease in J_{sc} is observed, however the FF improves significantly leading to a relatively constant efficiency with increasing ZnO thickness. The increase in FF suggests that we are improving collection with the thicker ZnO layer, however increased absorption by the ZnO lowers the solar cell current.

In another part of the optimization of the Ag/ZnO back reflector, we tested a number of ZnO targets from a variety of vendors to test if one product may be superior over the others. Table 3-6 lists properties for a-SiGe bottom cells deposited in the same deposition run on Ag/ZnO back reflectors made with the ZnO targets manufactured by different vendors L, T and K. As is displayed in the table, the data for the cells prepared with the different ZnO targets are similar within experimental error and are also similar to the reference back reflector used by United Solar for small scale R&D research. This reference back reflector was made under similar conditions to those used to prepare triple-junction cells with world record 14.6% efficiencies. The similarity is also displayed in Figure 3-17 which displays quantum efficiency plots for one of the cells made in the same deposition run on one of the 5MW back reflectors showing 25.6 mA/cm² integrated current from QE (solid line in the curve) and on the reference back reflector (dashed line in the curve). We therefore conclude that the back reflector made in the 5MW line is of high quality.

Table 3-5 Device performance of a-SiGe test solar cells deposited on Ag/ZnO back-reflectors produced in 5MW back-reflector machine with different ZnO sputtering currents.

BR #	Manufacturer	ZnO target	Area	AM1.5 Results				Q>630nm				Q645	FFb	FFr
				Voc	FF	Q	Rs	Voc	FF	Q	P630			
		Sputter Current												
5mw18-25	L	Std Current	0.25	0.659	0.458	24.71	13.6	0.621	0.539	11.31	3.79	10.36	0.652	0.625
5mw18-26		1.5xStd	0.25	0.655	0.547	24.55	7.5	0.616	0.588	10.84	3.93	9.86	0.649	0.630
5mw18-27		2.0xStd	0.25	0.669	0.563	23.32	7.2	0.627	0.584	10.59	3.88	9.61	0.637	0.611
5mw18-22	T	Std	0.25	0.645	0.515	25.03	10.8	0.608	0.566	11.44	3.94	10.47	0.649	0.621
5mw18-23		1.5xStd	0.25	0.640	0.540	24.41	7.2	0.605	0.592	10.98	3.93	10.02	0.644	0.617
5mw18-24		2.0xStd	0.25	0.648	0.563	24.59	7.2	0.612	0.603	11.09	4.09	10.11	0.652	0.635
5mw18-13	K	Std	0.25	0.644	0.531	25.16	8.0	0.606	0.575	11.86	4.13	10.91	0.639	0.601
5mw18-14		1.5xStd	0.25	0.644	0.537	24.58	7.2	0.605	0.588	11.29	4.02	10.34	0.642	0.617
5mw18-15		2.0xStd	0.25	0.660	0.561	24.30	7.1	0.620	0.595	10.66	3.93	9.69		

Table 3-6 Device performance of a-SiGe test solar cells deposited on Ag/ZnO back-reflectors produced in 5MW back-reflector machine using ZnO targets manufactured by different vendors L, T and K.

BR #	Description	Area	AM1.5 Results				Q>630nm				Q645	FFb	FFr
			Voc	FF	Q	Rs	Voc	FF	Q	P630			
5mw18-30	Manufacture L	0.25	0.655	0.575	24.09	7.2	0.616	0.606	10.83	4.04	9.85	0.664	0.643
5mw18-27	Manufacture L	0.25	0.669	0.563	23.32	7.2	0.627	0.584	10.59	3.88	9.61	0.637	0.611
5mw18-18	Manufacture L	0.25	0.672	0.561	24.10	7.8	0.631	0.592	10.65	3.98	9.71	0.671	0.641
5mw18-24	Manufacture T	0.25	0.648	0.563	24.59	7.2	0.612	0.603	11.09	4.09	10.11	0.652	0.635
5mw18-21	Manufacture T	0.25	0.650	0.552	24.74	7.1	0.610	0.592	11.33	4.09	10.35	0.651	0.632
5mw18-15	Manufacturer K	0.25	0.660	0.561	24.30	7.1	0.620	0.595	10.66	3.93	9.69		
R2679	Reference	0.25	0.657	0.517	25.11	7.9	0.617	0.578	11.39	4.06	10.42	0.636	0.637
R2679	Reference	0.25	0.660	0.541	24.55	5.3	0.625	0.602	11.07	4.17	10.12	0.658	0.645
R2679	Reference	0.25	0.657	0.571	24.08	7.1	0.622	0.609	10.7	4.05	9.71	0.638	0.625

Figure 3-17 QE curves of an a-SiGe solar cell deposited on an optimized Ag/ZnO back-reflector made in the 5MW back-reflector sputtering machine (solid line), showing a J_{sc} of 25.6 mA/cm² from the integrated QE, and a reference back-

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