Research on Stable, High-Efficiency Amorphous Silicon Multijunction Modules

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Preface

This report describes work done at Advanced Photovoltaic Systems in Phase I of the NREL contract "Research on Stable, High-Efficiency Modules." The goal of the contract is the development of same bandgap, amorphous silicon, tandem-junction modules. The research involved a coordinated effort among three groups in the Research Department of Advanced Photovoltaic Systems: the Device Group, the Non-Semiconductor Materials Group, and the Module Group. The approach taken was to develop improved semiconductor materials properties in the Device Group. The Device Group and the Non-Semiconductor Materials Group worked jointly on improving device structure. The results of their efforts were then transferred to the Module Group. The Module Group is responsible for scale up of the small-area device results and for optimization of module processing techniques. In addition to the various groups in the Research Department, there was also a substantial contribution from APS' Manufacturing Department, which allowed the use of some of their facilities.

Executive Summary

OBJECTIVES

The principal objective of the research described in this report is the development of stable, high-efficiency two-terminal, similar-bandgap, amorphous silicon multijunction photovoltaic modules. Related objectives involve developing cost-effective fabrication processes for these modules and obtaining data on the reliability of the modules. The major goal of the overall research program is the demonstration of a stable, aperture-area efficiency of at least 10% for two-terminal, similar-bandgap, amorphous silicon multijunction modules having an aperture area greater than 900 cm^2. The major goal of the first phase of the contract was demonstration of aperture-area efficiency of 7% for such modules.

APPROACH

The approach taken involved deposition and characterization of individual semiconductor and non-semiconductor films, single and tandem-junction devices, and tandem-junction modules. Deposition techniques used were Plasma Enhanced Chemical Vapor Deposition for the various silicon films and layers and Atmospheric Chemical Vapor Deposition and magnetron sputtering for the non-semiconductor films and layers. Individual layers were characterized by dark and photoconductivity (where appropriate), by thickness uniformity measurements, and by optical characterization (where appropriate). Devices were characterized for initial and light-soaked characteristics using I-V and quantum efficiency measurements. Modules were characterized by I-V measurements.

SUMMARY OF RESULTS

Semiconductor films were deposited with properties equalling or exceeding those called for in the contract. Non-semiconductor films were deposited with properties approaching those in the contract. However, stabilized efficiencies of tandem-junction devices and modules fell about 20% short of the major milestones. This was mainly due to our failure to achieve a good contact between the two p-i-n sections of the tandem structure. An additional problem was that of finding the correct layer thicknesses to obtain good current matching at stabilization.

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Semiconductor Materials Research

Introduction

Semiconductor layers for individual film studies and for device and module studies were deposited in three different deposition systems. The first of these, the "B" system, is a small-area deposition system which uses 5.1 cm x 5.1 cm (2" x 2") substrates. It was used for depositions of semiconductor layers and single-junction and tandem-junction devices. Typically, a number of 1 cm² devices would be prepared from each run. The second system, the "D2" system, can hold four substrates up to 33 cm x 33 cm (13" x 13") in size. This system was used primarily for deposition of individual layers. Also, one of APS' Manufacturing Department silicon deposition systems was used for fabricating tandem-junction modules. These systems hold forty-eight substrates, 78.7 cm x 154.9 cm (31" x 61") in size. Modules with different combinations of semiconductor layer thicknesses were prepared during individual depositions by taking advantage of the multiple rf inputs to the manufacturing deposition systems.

I Layers

Dark and photoconductivity

I-layer depositions were performed in two systems: the B system, which uses 5.1 cm x 5.1 cm (2" x 2") substrates, and the D2 system, which uses 4 substrates up to 33 cm x 33 cm (13" x 13") in size. This phase of the contract set goals of photosensitivity (photoconductivity at 1000 W/m² divided by dark conductivity) $> 10^5$ and hole diffusion length (measured by Steady-State Photocarrier Grating) > 150 nanometer for I-layers with an optical bandgap of 1.7-1.8 eV. These goals were exceeded for several deposition runs in the B system. Results for two deposition runs are given in Table 1.

Table 1. Properties of some I layers made in the B system

Sample Number	B-267	B-545
Property		
E_g (eV)	1.74	1.71
σ_p (Ω^{-1} cm^{-1})	1.7×10^{-6}	7.6×10^{-5}
σ_d (Ω^{-1} cm^{-1})	6.1×10^{-11}	7.2×10^{-12}
σ_p / σ_d	3.6×10^6	1.1×10^7
hole diffusion length (μm)	0.42	not measured

A number of runs were performed in the D2 system to optimize the I layer deposition conditions.

The deposition parameters varied included temperature, pressure, flow rates, and hydrogen-to-silane ratio. The results of some of the runs with different hydrogen-to-silane ratios are shown in Table 2. All other deposition parameters were the same for these runs.

Table 2. Properties of some I layers made in the D2 system

$[H_2] / [SiH_4]$	0.0	0.5	1.0	2.0
Property				
E_g (eV)	1.71	1.70	1.73	1.73
σ_p (Ω^{-1} cm^{-1})	4.6×10^{-5}	7.8×10^{-5}	1.1×10^{-4}	1.3×10^{-4}
σ_d (Ω^{-1} cm^{-1})	3.2×10^{-11}	1.4×10^{-10}	9.3×10^{-11}	2.9×10^{-11}
σ_p / σ_d	1.4×10^6	5.6×10^5	1.2×10^6	4.5×10^6

Uniformity

The contract also contained goals for I-layer uniformity. More specifically, the non-uniformity (defined as twice the standard deviation divided by the average) in thickness was required to be less than 10% for I layers approximately 400 nm thick, deposited over areas of at least 900 cm^2. A detailed study of the I-layer thickness distribution on 8 substrates 30.5 cm x 30.5 cm (12" x 12") was performed. Thickness was measured at 72 points on each substrate. The average I-layer thickness on the 8 substrates ranged from 457 to 501 nm. Three of the I layers had non-uniformities of less than 10%. The average non-uniformity for the 8 substrates was 10.1%.

P Layers

There were two conductivity goals for p layers in this phase of the contract. The first was to achieve a conductivity $\geq 2 \times 10^{-5}$ S/cm for a bandgap ≥ 1.95 eV, for p layers grown with trimethylboron. The second was a conductivity $\geq 5 \times 10^{-6}$ S/cm over an area of 900 cm^2 or more. The first goal was nearly achieved in the B system. The goals and the results achieved are shown in Table 3.

Table 3. P-layer conductivities and bandgaps achieved in the B-system

Sample	B-391	B-394	goal
E_g (eV)	1.91	1.94	≥ 1.95
σ_d (Ω^{-1} cm^{-1})	2.2×10^{-5}	1.1×10^{-5}	$\geq 2 \times 10^{-5}$

The goal for a conductivity $\geq 5 \times 10^{-6}$ S/cm over an area of 900 cm^2 or more was easily achieved in the D2 system. Actually, a conductivity of 6×10^{-5} or higher was achieved over the whole area.

N Layers

Amorphous

There was one goal in the contract applicable to amorphous n layers: achievement of a conductivity $\geq 1 \times 10^{-3}$ S/cm for a 200-nm thick n layer with a bandgap ≥ 1.85 eV. This was achieved in the B system by a sample with a conductivity $= 1.5 \times 10^{-3}$ S/cm, having a bandgap of 1.85 eV.

Microcrystalline

Microcrystalline n layers were deposited both in the small-area B system and the 930 cm^2 (1-ft^2) D2 system, even though the contract goals all specified areas of 900 cm^2 or more. The initial experiments were done in the B system and the process conditions transferred to the D2 system.

The contract goals for microcrystalline n layers were the achievement of a conductivity ≥ 1 S/cm for a 15-50-nm thick layer over an area ≥ 900 cm^2 and demonstration of thickness non-uniformity $\leq 20\%$ for a 100-nm thick layer over an area ≥ 900 cm^2. These two goals were easily achieved in the D2 system. A conductivity of 7-10 S/cm was obtained for a microcrystalline n layer with thickness ranging from 22-30 nm. A layer with an average thickness of 104 nm had a top-to-bottom non-uniformity of 5.5% and a left-to-right non-uniformity of 3.4%.

Microcrystalline n layers were not used in devices or modules in the first phase of the contract. However, they are being used for devices in the current phase and will be used for modules as well.

Non-Semiconductor Materials Research

Tin Oxide

High-haze, high-transmission, low sheet-resistivity transparent-conducting-oxide-coated glass is essential for achieving high efficiency amorphous silicon devices and modules. One goal of this phase of the contract was achievement of $\geq 82\%$ integrated transmittance and ≤ 7 ohms/square sheet resistance for SiO$_2$ / SnO$_2$-coated glass with a resistance non-uniformity $\leq 10\%$ over 900 cm^2 and optimized diffuse transmission. We found that we could closely approach this goal by annealing APS-prepared SiO$_2$ / SnO$_2$-coated glass in an inert atmosphere. Table 4 shows the results of a number of anneals as compared to the goal. APCVD (Atmospheric Pressure Chemical Vapor Deposition) was used to prepared the SiO$_2$ and the fluorine-doped SnO$_2$ films.

Hall-effect measurements on some of the samples indicate carrier concentrations of approximately 3×10^{20} cm^{-3} and mobilities of 30 and 39 cm^2 V^{-1} sec^{-1}, for unannealed and annealed specimens, respectively. This increase in mobility on annealing is probably due to a decrease in carrier scattering from excess oxygen at grain boundaries.

The effect of annealing temperature was studied by performing annealing at two different temperatures. The data in Table 4 gives results from the lower temperature. Annealing at the higher temperature resulted in an increase in sheet resistance and a drop in transmittance for APS tin oxide

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and for tin oxide from one commercial vendor. Tin-oxide-coated glass from a second commercial vendor improved in properties at the higher annealing temperature, but less so than the lower temperature. The poorer results at the higher temperature are believed to be due so sodium diffusion through the silica barrier.

Table 4. Tin-Oxide Properties Before and After Annealing in an Inert Gas

Sample	Sheet Resistance before Annealing (ohms/square)	Sheet Resistance after Annealing (ohms/square)	Transmittance before Annealing (%)	Transmittance after Annealing (%)
7R92-36	11.0	7.3	81.6	80.5
11R92-39A	11.2	8.4	83.0	82.8
13R92-63A	11.9	8.6	82.4	82.2
13R92-88B	10.3	7.5	82.8	81.4
13R92-89A	10.4	8.6	83.0	82.3
15R92-46	9.9	8.4	84.2	84.0
16R92-30A	11.6	7.8	82.8	82.9
16R92-30B	11.7	7.8	82.9	82.1
goal		≤ 7.0		≥ 82.0

Sheet resistance non-uniformity was measured on two samples: 7R92-36 and 13R92-88B. Non-uniformities (twice the standard deviation divided by the average) were found to be 8.1% and 5.0%, respectively, over the 900 cm^2.

Zinc Oxide

Transparent Conducting Oxide

The contract also contained a goal of using zinc oxide deposited by LPCVD (Low Pressure Chemical Vapor Deposition) as a transparent conducting oxide. The zinc-oxide films that were prepared by this technique were too non-uniform to be useful. Consequently, it was decided not to pursue this area of research during future phases of the contract.

Buffer Layer

A series of experiments was performed to see if a zinc-oxide buffer layer between the transparent-conducting oxide and the p layer would be beneficial. The buffer layer was deposited by sputtering, and thicknesses between 40 and 140 nm were tested. Its use was found to result in higher short-circuit current densities for single-junction and tandem-junction devices. Subsequently, it was found that modifying the conditions used in the a-Si deposition eliminated the difference between devices

prepared with and without the zinc-oxide buffer layer. The tandem-junction device with the highest stabilized efficiency was prepared with the zinc-oxide buffer layer.

Back Reflector

Sputtered zinc oxide was also used as a back reflector to increase the red response and short-circuit current density of single-junction and tandem-junction devices. The goal in the contract for this activity was the demonstration of a quantum efficiency ≥ 0.40 at a wavelength of 700 nm for a single-junction device with an I-layer thickness ≤ 450 nm. Many depositions were performed, both on single-junction and tandem-junction devices and modules. Increases in J_{sc} of 1-2 mA/cm^2 for single-junction devices and 1.0-1.3 mA/cm^2 for tandem-junction devices were obtained by the use of the back reflector. However, fill-factor losses as large as 0.20 often resulted also. The problem was finally overcome with the discovery that the n-layer deposition conditions also required optimization. A quantum efficiency of 0.399 was obtained at 700 nm on a device with the structure glass / SiO$_2$ / SnO$_x$:F / p-i-n / ZnO / Ag / Al . The I-layer thickness was 480 nm, somewhat higher than the value specified in the goal.

Device Research

Single-Junction Devices

Although the main thrust of the contract concerns amorphous silicon tandem-junction devices, the contract did contain a single-junction device-stabilized efficiency goal. The contract goal and the results achieved are shown in Table 5.

Table 5 . Single-Junction Device Light-Soaking Results

Parameter	Initial Value	Value after 600 hours light soaking	Goal
V_{oc} (Volts)	0.776	0.812	≥ 0.900
J_{sc} (mA/cm^2)	14.58	13.79	
Fill Factor	0.754	0.653	
Efficiency (%)	8.53	7.31	≥ 7.5
I-Layer thickness (nm)	350	350	≤ 450

The data in the table show that the goal of 7.5% efficiency after 600 hours of light soaking was nearly achieved. However, the V_{oc} of the device was considerably less than the 0.9 volts given as a goal in the contract.

Tandem-Junction Devices

One of the two major milestones of the first phase of the contract was a 1-cm^2 tandem-junction device with a stabilized efficiency of 8.5% or more. As usual, the stabilized efficiency is defined as the

efficiency after 600 hours of exposure to 1000 W/m² of light with an AM1.5 spectrum, with the device being held at a temperature of 50 °C. The best result fell about 20% short of this goal. The initial and light-soaked parameters of the device with the best stabilized efficiency are given in Table 6. The cell structure was MgF$_2$ / Asahi Type-U tin oxide / ZnO / p-i-n-p-i-n / ZnO / Ag / Al.

Table 6. Parameters of Best 1-cm² Tandem-Junction Device

Parameter	V$_{oc}$ (Volts)	J$_{sc}$ (mA/cm²)	Fill Factor	Efficiency (%)
initial	1.632	7.62	0.697	8.66
690 hours	1.561	7.55	0.571	6.73
goal				8.50

We believe that our failure to develop a good contact (recombination layer) between the two stacks of the tandem devices is a major reason for our failure to achieve the goal in the contract. Three types of recombination layers were tried: p$^+$ a-Si, TiO$_x$, and Nb$_2$O$_5$. These layers improved the contact between the two stacks, as evidenced by decreased series resistance. However, the p$^+$ layer absorbed too much light, and the oxide layers, which were thermally evaporated, were not reproducible. Niobium pentoxide recombination layers were also prepared by sputtering but were too resistive. Short-circuit current densities and series resistances for similar devices with some of the recombination layers tested are shown in Table 7.

Table 7. Effect of Different Recombination Layers

Recombination Layer	Series Resistance (ohm-cm²)	J$_{sc}$ (mA/cm²)
none	36.8	6.72
p$^+$ - a-Si	28.3	5.46
TiO$_x$	28.5	6.21

As a result of these problems with recombination layers, the best stabilized efficiency was obtained in a tandem-junction device with no recombination layer. The J-V curve of this device shows a weak inflection near V$_{oc}$ prior to light soaking, indicating a contact problem. This inflection was much more apparent after light soaking. It is expected that the use of microcrystalline n1 layers in the second phase of the contract will greatly reduce this problem.

Module Research

The second major milestone of the first phase of the contract was the demonstration of a tandem module with an aperture-area efficiency ≥ 7.0% after 600 hours of light soaking. The aperture area of the module is required to be greater than 900 cm², and the active-area loss due to laser scribing is required to be less than 5%. Our best result for this goal was an aperture-area efficiency of 5.48%

after 888 hours of light soaking.   An aperture-area loss due to laser scribing of 3.5% was achieved. However, the module with 5.48% stabilized efficiency had an aperture area of 795 cm^2 due to limitations on the size of the sputtering system used for depositing zinc-oxide back reflectors. This problem has since been alleviated.

The contract had other goals for tandem modules, as well as the major milestone described above. The first of these was obtaining thickness non-uniformity of the combined semiconductor layers of less than 20% over 900 cm^2. Thickness non-uniformity over a 900-cm^2 module for the semiconductor layers was found to be approximately 8%. The second requirement was that modules suffer less than 10% loss in efficiency after 200 thermal cycles or 20 humidity-freeze cycles and 50 thermal cycles, as described in the NREL Interim Qualification Tests. This requirement was met by APS standard encapsulation techniques.

Tandem junction modules measuring 0.09 m^2 (1 ft^2) were all fabricated using APS' manufacturing silicon deposition systems, which uses 78.7 cm x 154.9 cm (31" x 61") substrates. Modules measuring 0.09 m^2 (1 ft^2) were cut from these substrates. The use of the manufacturing systems was necessary because cross-contamination problems in the D2 system prevented the fabrication of good single-junction or tandem-junction modules. (These problems have since been solved by rebuilding the system.)

Tandem modules were fabricated using both commercially available tin oxide and APS-produced tin oxide, both with and without a ZnO back reflector. Thicknesses of all six semiconductor layers were also varied. The 0.09 m^2 (1 ft^2) module with the highest light-soaked efficiency had the following structure: APS tin oxide / p-i-n-p-i-n / ZnO / Al. The use of a special recombination layer between the two stacks was not attempted as we had not been able to successfully develop this layer on 1-cm^2 devices. The thicknesses of the n1 and p2 layers were varied to obtain the best possible contact without the use of a separate recombination layer. It was found that making these two layers as thin as possible without serious loss of voltage gave the best contact.

Quantum efficiency measurements using red -and blue-bias light were performed on diagnostic devices to determine the spectral responses of the top and bottom cells of the tandem structures. It was found that the dependences of the integrated currents of the top and bottom cells on layer thicknesses could be fitted quite well using a multilinear regression analysis. Also, quantum efficiency measurements were made on some diagnostic devices over the course of light soaking. The results of one such study are shown in Table 8. This particular device used commercial tin oxide and had a ZnO back reflector.

Table 8. Initial and Light-Soaked Integrated Quantum Efficiency Measurements

Light-soaking time (hours)	J_{sc} top cell (mA/cm^2)	Degradation (%)	J_{sc} bottom cell (mA/cm^2)	Degradation (%)	J_{sc} device (mA/cm^2)
0	6.31	0.0	6.00	0.0	6.09
240	5.91	6.4	5.12	14.7	6.00
888	5.77	8.6	5.13	14.5	5.76

The data in Table 8 show that the degradation in J_{sc} of the top cell is approximately half of that for the bottom cell. This is expected, since the top cell is considerably thinner than the bottom cell. The overall device J_{sc} is close to the bottom cell J_{sc} initially, as the device is bottom-cell limited. After light soaking, the overall device J_{sc} is close to the top-cell J_{sc}, even though the device is still bottom-cell limited. This implies that, after light soaking, the bottom cell is reversed biased when the total device is short circuited, showing the complexity of interpreting tandem device J-V curves.

The tandem module with the best stabilized efficiency was initially top-cell limited, unlike the device described above. Initial and light-soaked parameters of four 0.09 m² (1-ft²) modules are shown in Table 9, along with some pertinent deposition conditions. The short-circuit current densities given for the top and bottom cells are estimates from the regression analysis described earlier.

Table 9. Light-Soaking Results on Selected 0.09 m² (1-ft²) Modules

APS SnO$_x$	p1 time sec	i1 time min	ZnO b.r.	hours light soak	cell V_{oc} Volts	J_{sc} mA/ cm²	fill factor	Eff. %	J_{sc} top cell	J_{sc} bot. cell
No	30	5.0	No	0	1.619	5.40	0.724	6.33	5.64	5.64
				720	1.542	5.18	0.606	4.86		
No	30	6.0	No	0	1.573	5.07	0.740	5.90	6.30	5.60
				720	1.519	4.98	0.651	4.92		
Yes	45	5.5	No	0	1.619	5.99	0.711	6.89	5.96	5.96
				600	1.523	5.56	0.608	5.15		
Yes	30	6.0	Yes	0	1.536	6.29	0.642	6.20	6.51	6.99
				888	1.484	6.16	0.601	5.48		

A number of conclusions can be drawn from the data in Table 9. As mentioned above, the module with the highest stabilized efficiency was initially top-cell limited. The use of the higher-haze APS tin oxide and the use of a ZnO back reflector both increased the bottom-cell current. The low initial V_{oc} and fill factor of the best module are believed to be due to shunting from a too-thin p layer. The higher-haze APS tin oxide requires a thicker p layer than the lower-haze commercial tin oxide. This is to prevent shunting due to poorer coverage of the p layer on the rougher surface. As with the tandem devices described earlier, drops in V_{oc} on light soaking arise from degradation of the contact between the two stacks.

A major effort will be made in the second phase of the contract to improve the contact between the two p-i-n structures of the tandem devices. One approach to be taken will be the use of microcrystalline n1 layers. The use of multiple p2 layers with different bandgaps will also be investigated. Furthermore, the results of the regression analysis of the dependence of top and bottom cell current density will be used to design tandem structures with current matching optimized for the stabilized state, rather than the initial state.

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16. Abstract (Limit: 200 words)

This report describes results from the first phase of a three-phase contract for the development of stable, high-efficiency, same-band-gap, amorphous silicon (a-Si) multijunction photovoltaic (PV) modules. The research program involved improving the properties of individual layers of semiconductor and non-semiconductor materials and small-area single-junction and multijunction devices, as well as the multijunction modules. The semiconductor materials research was performed on a-Si p, i, and n layers, and on microcrystalline silicon n layers. These were deposited using plasma-enhanced chemical vapor deposition. The non-semiconductor materials studied were tin oxide, for use as a transparent-conducting-oxide (TCO), and zinc oxide, for use as a back reflector and as a buffer layer between the TCO and the semiconductor layers. Tin oxide was deposited using atmospheric-pressure chemical vapor deposition. Zinc oxide was deposited using magnetron sputtering. The research indicated that the major challenge in the fabrication of a-Si multijunction PV modules is the contact between the two p-i-n cells. A structure that has low optical absorption but that also facilitates the recombination of electrons from the first p-i-n structure with holes from the second p-i-n structure is required. Non-semiconductor layers and a-Si semiconductor layers were tested without achieving the desired result. Work in the second phase of the contract will concentrate on this issue.

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