

Status of Amorphous and Crystalline Thin Film Silicon Solar Cell Activities

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*Presented at the National Center for Photovoltaics and Solar Program Review Meeting
Denver, Colorado
March 24-26, 2003*



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Contract No. DE-AC36-99-GO10337

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Status of Amorphous and Crystalline Thin-Film Silicon Solar Cell Activities

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ABSTRACT

This paper reviews the recent activities and accomplishments of the national Amorphous Silicon Team and a (crystalline) thin-film-Si subteam that was implemented in 2002 to research solar cell devices based on thin-crystalline-Si-based layers. This paper reports the evolution of team organization, technical highlights from recent team meetings, and an outlook on commercialization potential.

1. Background

In 1992, the NREL/Electric Power Research Institute (EPRI) Amorphous Silicon Research Team was established as the first of its kind under the guidance of NREL and EPRI project managers. Around 1999, EPRI's Renewable Energy Program lost the ability to fund the development of thin-film photovoltaics (PV), leaving this program solely supported by the NREL-Thin Film Partnership Project. In earlier years, regular updates on team activities were presented [1]. Originally, three subteams were focussing on each component cell for the triple-junction stacked cell. The midgap team also addressed the Staebler-Wronski (light-induced) degradation of hydrogenated amorphous silicon (a-Si:H). A fourth subteam addressed the issues pertaining to the entire triple-junction device.

In 2000, the team decided that a new organization of the subteam structure could be beneficial. It was felt that cooperative research between different groups was proceeding well. Hence, it was agreed to have research highlights reported and summarized by reporters under the following "umbrella" topics:

- (a) Higher deposition rates
- (b) Improved narrow-bandgap materials, including microcrystalline Si
- (c) Fundamental aspects of metastability
- (d) High-performance and device-integration issues.

Besides receiving and discussing the reports, the team began holding one-day workshops to explore a specific topic in depth during the team meetings. The most recent workshop topics were: (a) metastability, (b) amorphous silicon film growth, (c) voltage limitation in a-Si:H-based solar cells, and (d) requirements for achieving high-performance crystalline Si thin-film cells.

As the NREL Thin-Film Partnership Project recompeted its subcontracts in 2001, R&D on thin film crystalline Si was specifically encouraged, and several of the selected subcontractors proposed projects or tasks addressing thin-film crystalline Si solar cells. In 2002, a new subteam to the a-Si team was established to work on crystalline thin film Si, an area of research that has received significant attention in Europe and Japan. Although the U.S. program was late in establishing

comprehensive research activity in this area, near-state-of-the-art solar cell prototypes have been fabricated. The approach is two-pronged, including both nanocrystalline films (nc-Si) deposited at low temperatures, as well as much larger-grain films grown at higher temperatures on suitable insulating substrates.

2. Status of the Industry

In 2002, there were four U.S.-based manufacturers of commercial a-Si PV products. BP Solar operated a plant in Toano, VA, at a significant fraction of its rated capacity (10 MW_p). The "Millennia" module produced there was an 0.8-m² superstrate module with a-Si/a-SiGe tandem cell structure. When manufacturing started several years ago, the (stabilized!) power rating of this module was 43 – 48 W. Refinements in the manufacturing process increased this power recently to between 50 and 60 W. BP Solar and NREL received a joint R&D100 award in 2002 for the PowerView™ module, which is a Millennia module where, by laser ablation, a portion (usually <10%) of the solar cell material is removed, allowing some light to pass through, for daylighting in building-integrated applications. BP used these modules for the canopies of PV-powered gas stations. In November 2002, BP Solar made the business decision to terminate all commercialization of thin-film PV technology. The plant in Toano was shut down and put up for sale.

United Solar Systems manufactures modules on stainless steel using an a-Si/a-SiGe/a-SiGe triple-junction cell structure. Until now, a line with 5 MW_p annual capacity was used [2]. The largest standard module produced is conservatively rated at 64 W (0.93-m² aperture area corresponding to 6.8% efficiency). NREL tested a number of selected such commercial modules and determined stabilized power levels greater than 70 W, corresponding to efficiencies >7.5%. In 2002, United Solar celebrated the opening of a new plant in Auburn Hills, MI. A new roll-to-roll machine simultaneously processes six stainless-steel webs at annual manufacturing capacity of 25 – 30 MW_p. The new machine is not only enhancing throughput capacity, but also has increased the power of each cell by 5% – 10% [3]. The most suitable application for United Solar's product may be in PV-shingle or metal-roofing integrated applications [4]. The new factory in Auburn Hills is not only set up to produce solar cells, but also for the robotic assembly of large roofing laminates. United Solar's near-term challenge appears to be to operate its new manufacturing facility as planned and find markets, especially in roofing applications, for the substantial amounts of product produced.

Energy Photovoltaics (EPV) operates a prototype manufacturing line in New Jersey. There are several manufacturing subsidiaries, and the one with the highest actual output is Duna Solar in Hungary. The product is a same-bandgap a-Si:H/a-Si:H double-junction module with

an aperture area of 0.75 m² and a power rating of 40 W_p. This module may be the lowest-cost commercially available today, being offered at \$2.25/W_p. EPV's strategy is to supply business partners with manufacturing equipment and technology, at present for a-Si double-junction modules. EPV anticipates only a limited potential for significant performance enhancements of a-Si:H/a-Si:H double-junction modules. Under the Thin-Film Partnership, EPV is developing technology to manufacture a-Si:H/nc-Si:H ("micromorph") cells and later modules to enhance the performance of the a-Si product.

Iowa Thin Film (ITF) is manufacturing a-Si cells using roll-to-roll deposition on polymer foils. It established itself as a successful niche player making lightweight flexible PV generators for a variety of consumer applications.

AstroPower is a successful crystalline Si PV manufacturer, using either reclaimed Si wafers from the electronic Si industry or in-house deposited APEX™ multicrystalline Si wafers. As next-generation PV technology, the development of high-temperature processed Si films on ceramic substrates is undertaken.

3. Amorphous Silicon Status

In recent years, the wish list of the a-Si PV manufacturers has been:

- (a) reduce light-induced degradation
- (b) increase the deposition rate by a factor of 2 – 10
- (c) find processes to fabricate a better narrow-bandgap bottom cell for a double- or triple-junction device.

The ubiquitous way of achieving greater a-Si:H device stability and greater cell voltages has been to deposit the layers using high hydrogen dilution. The industry uses dc or rf plasma-enhanced chemical vapor deposition (PECVD), at low substrate temperatures (~200°C). However, hydrogen dilution reduces the deposition rates. The a-Si national team has reached agreement that adjusting the operating parameters (typically, temperature, power, pressure, and gas flow) on the present dc and rf PECVD deposition systems is not likely to result in acceptable stabilized device performance at higher deposition rates. In particular, the narrow-bandgap a-SiGe:H bottom cell, already the limiting component cell in a multijunction stack, has stubbornly resisted all attempts to increase its deposition rate without significant loss in stabilized performance. Therefore, alternative deposition methods were investigated to overcome this limitation, with limited success to-date. The most promising method appears to be very high frequency (VHF) PECVD deposition [5].

With respect to Staebler-Wronski degradation, it has finally become clear that the degradation of the electronic properties, such as solar cell fill factor (FF) or the photoconductivity (pc) of the intrinsic layer (i-layer), is not controlled by a simple, single, straightforward mechanism. In the past, the generation of neutral dangling-bond defects (D₀) was assumed to be a dominating mechanism. It is now confirmed that the kinetics with which observables such as D₀, pc, or cell

FF change upon light-soaking or annealing show differences, and there is a lack of quantitative correlation between the D₀ generation and pc and FF losses, but better correlation between pc and FF instead [6]. Such findings suggest that perhaps too much effort went into developing materials with lower stabilized (D₀) defect densities. Materials with lower stabilized D₀ densities were synthesized, but they have not led to improved stabilized solar cell performance.

It is also found that degradation and annealing behavior in most instances can typically be separated into two mechanisms: a "fast" (low-temperature annealable) and slow (below 100°C non-annealable) mechanism. Any comprehensive Staebler-Wronski model must account for both mechanisms, which appear linked. The effects of the two mechanisms on degradation and annealing are large enough to affect the power output of a-Si:H-based modules by ±10% [7]. Although previous work focussed on understanding the creation/annealing of localized metastable D₀ defects by breaking weak bonds, work on a-SiGe:H alloys suggests both a localized and global mechanism dominating the degradation and annealing behavior [8]. Interest in mitigating Staebler-Wronski degradation remains high, because if it were possible to maintain today's solar cell performance in the annealed state, 16%-efficient multijunction cells and 10% commercial modules would likely be a reality. However, to date, no stable a-Si:H or related alloys have been produced that result in desirable stabilized solar cell performance. It is now widely accepted that the degradation is "intrinsic" to a-Si:H and related alloys. The instability appears not to depend systematically on hydrogen content or on how tightly bonded the hydrogen is. In fact, some of the more stable ("deuterated and high-hydrogen-dilution, lower substrate temperature") cell recipes were achieved with materials that contain larger amounts of loosely bonded hydrogen [9]. It appears that a lack of scientific understanding and guidance from inadequate models relating material properties and solar cell performance remains an obstacle toward progress.

The prospects for significant increases in a-Si:H-based stabilized PV module efficiencies (to reach 10% commercial modules) appear somewhat diminished, unless some unexpected breakthrough occurs. This situation has the a-Si PV industry focusing on market applications where lower efficiencies are less critical. Elimination of the a-SiGe:H alloy from the cells has also been considered (because of Ge cost and Ge-alloying being an impediment for higher deposition rates), but are not implemented by entities using them because even the modest efficiency loss associated with such change is deemed unacceptable. Outside the United States, we are not aware of significant new a-Si module manufacturing capacity under development. Entities in Japan and Europe are rather focussing on developing commercial micromorph devices with presumed higher efficiency, holding off on adding manufacturing capacity until such developments reach greater maturity.

4. Thin-Crystalline Si Film Solar Cells

Early in 2002, the Thin-Film Partnership assembled a subteam to the present a-Si team, addressing various issues

of crystalline thin-film solar cells. About a year into the program, the following results were obtained:

- (a) Several entities in the United States achieved “near-state-of-the-art” nanocrystalline (nc-Si) cells (about 7% efficient) using low-temperature deposition approaches (the term “microcrystalline” has also been used for such films; however, grain sizes are always $\ll 1 \mu\text{m}$).
- (b) Similar to findings by the group in Jülich [10], the best cell efficiencies are found for small-grain mixed-phase films, not larger-grain films.
- (c) United Solar, using a reproducible but inhomogeneous deposition method, produced solar cells gradually varying from amorphous to nc-Si i-layers.
- (d) Because many researchers believe that larger grain sizes should lead to greater device performance, approaches are pursued to achieve crystalline Si thin films with larger grain sizes, involving high-temperature deposition or recrystallization.

First, we will discuss the low-temperature approaches. Companies involved are United Solar, EPV, and MV Systems, as well as several universities and the group at NREL. Most work is geared toward replacing the bottom cell in current a-Si cells. The efficiencies achieved to date appear too low to justify development of single-junction nanocrystalline PV technology. To function as a bottom cell, the nc-Si cell has to generate $>24 \text{ mA/cm}^2$ and have a sufficiently high red response to generate $>8 \text{ mA/cm}^2$ in a triple-junction stack cell or $>12 \text{ mA/cm}^2$ for a double-junction device. Using a state-of-the-art backreflector, Yang et al. at United Solar were able to demonstrate such performance with nc-Si absorbers that are $\leq 2 \mu\text{m}$ thick, using a bottom cell deposited (at low deposition rates) by modified VHF PECVD [11].

It appears from the optimization of such nc-Si cells that experimentally a regime is encountered where higher short-circuit current densities (J_{SC}) are obtained by “sacrificing” open-circuit voltage (V_{OC}) or vice versa. Such a trade-off between voltage and current is not uncommon both for thin-film and wafer-based crystalline silicon [12]. It remains to be seen what the highest voltages for the nc-Si cell – in conjunction with the required high J_{SC} values – will be. Better optimization and better understanding of the mechanism leading to such a trade-off are both required.

Researchers at United Solar have prepared cells spanning the amorphous to nanocrystalline transition. It is found that cells with a large fraction of amorphous phase in their i-layer show large voltages, but also light-induced degradation. Light-soaking actually enhances V_{OC} , but decreases FF. With such unstable i-layers, the high J_{SC} values required for multijunctions could not be demonstrated. It is important to point out that even the stable cell recipe with the largest grain size and best-ordered i-layers did not result in the highest efficiency, similar to the findings of Luysberg et al. [10].

Two additional universal findings about nc-Si cells should be mentioned. As in a-Si alloys, to date, the best

cell results are obtained when the i-layer deposition rate is slow ($<0.5 \text{ nm/s}$). However, some deposition methods (such as “hot-wire” CVD) have shown that different film structures and modest cell efficiencies (about 5%) can be obtained at higher deposition rates ($1 - 2 \text{ nm/s}$). The second observation is that some nanocrystalline Si films are “porous” and therefore subject to post-deposition oxidation. After oxidation, solar cell performance degrades severely. Such films have to be avoided, because it has been reported that oxidation occurs even when such devices are “capped,” e.g., by a p-layer in a solar cell.

An area of concern for nc-Si is that in recent years cell efficiency records have been somewhat stagnant. Given the current performance, it appears that there is opportunity for incrementally improving a-Si:H-based multijunctions by using the nc-Si cell as a bottom cell. Given the large variety of nc-Si films that can be produced, it may well be possible that cell recipes, at greater deposition rates, can be found that result in even higher cell efficiency.

Next, we will briefly discuss the higher-temperature, large-grain crystalline Si films. Several entities are working on growing larger-grain-size thin Si films on glass, e.g., CalTech and the University of Delaware (IEC), relying on “induced” crystallization schemes. It is presently not clear what the grain-size requirements may be for high-efficiency solar cells. Two approaches to date have resulted in larger grain sizes. AstroPower uses an approach to thin-film solar cells that relies on melt-recrystallizing a CVD-deposited ($\sim 100\text{-}\mu\text{m}$ -thick “growth” layer) on a ceramic substrate. Then, active solar cell layers are deposited epitaxially by chemical vapor deposition. The active Si layers used are a $5\text{-}\mu\text{m}$ -thick back-surface field and contact layer (boron-doped $\sim 0.1 \Omega\text{cm}$) and a very lightly boron-doped $30 - 35\text{-}\mu\text{m}$ -thick absorber layer. The cell emitter is formed by a P-diffusion process. For years, AstroPower worked on the development of a ceramic substrate that would allow deposition or recrystallization of Si near its melting temperature. The parameters for the best cell obtained are as follows: $\eta = 9.2\%$, $V_{\text{OC}} = 0.543 \text{ V}$, $\text{FF} = 0.732$, $J_{\text{SC}} = 23.11 \text{ mA/cm}^2$. Because the substrate is insulating, monolithic interconnection of the cells can be accomplished and has been demonstrated. Interestingly enough, the current generated and collected in these $30 - 35\text{-}\mu\text{m}$ -thick absorbers is rather similar to those current densities measured in the only $1.5 - 2\text{-}\mu\text{m}$ -thick nc-Si absorbers. There are indications that, contrary to popular belief, current generation in thin, “optically enhanced” Si films is quite efficient; however, the collection of carriers, especially those generated in thicker films some distance away from the junction, remains a challenge.

Wang et al. at NREL developed a process for growing large-grain films in the $750 - 950 \text{ }^\circ\text{C}$ substrate temperature range using an iodine vapor transport reaction [13]. Heterojunction cells using the so-called “HIT” structure developed by Sanyo [14] were fabricated at NREL.

It appears quite beneficial to have team collaboration among researchers pursuing both nanocrystalline low-temperature and large-grain high-temperature Si film approaches. Previously, thin crystalline Si solar cells have been attempted by groups having either a bulk (wafer or

ribbon) crystalline Si background or an a-Si background. For wafers, combining such expertise at Sanyo [14] has resulted in a fast-growing commercial product with a top efficiency rating in the entire PV industry. Our experienced a-Si cell makers have quickly adapted their know-how to make reasonable nc-Si cells.

5. Summary

It is argued that the efficiency potential for a-Si solar cells evident today may be somewhat limiting their competitiveness for applications where PV product is sold “by the watt,” as crystalline Si technologies appear to maintain an almost ~2:1 efficiency lead. Lower efficiencies may be less of a factor in building-integrated (BIPV) applications. Dedicated BIPV products may currently be considered a “niche” application, but will ultimately have huge market volumes by themselves. In these applications, other a-Si performance advantages could play a role, e.g., better temperature coefficients.

“Micromorph” a-Si/nc-Si multijunctions offer the potential to incrementally improve a-Si:H multijunction technology. Based on the limited present knowledge, no dramatic increase in the performance over a-Si/a-SiGe multijunctions is to be expected. The ultimate potential of the nanocrystalline cell is yet unknown. Although conventional wisdom equates larger grain size with higher cell performance, near the a-Si to nc-Si transition, a regime has been found where increased grain sizes and better grain order lead to lower cell performance. Significant further improvement for the efficiencies of large-grain high-temperature deposited/recrystallized cells is also required to make them suitable candidates for single-junction modules. As in the case of nc-Si, the potential of such technology is presently unknown, requiring further consistent research to determine success.

6. Acknowledgement

This paper was made possible by the insight that the author, a program manager, gained with those doing the original research. Sharing of results and continued debate over the mechanisms controlling and limiting cell performance are much acknowledged.

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REPORT DOCUMENTATION PAGE

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OMB NO. 0704-0188

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE May 2003	3. REPORT TYPE AND DATES COVERED Conference Paper	
4. TITLE AND SUBTITLE Status of Amorphous and Crystalline Thin Film Silicon Solar Cell Activities			5. FUNDING NUMBERS PVP3.5001	
6. AUTHOR(S) B. von Roedern				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393			8. PERFORMING ORGANIZATION REPORT NUMBER NREL/CP-520-33568	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) This paper reviews the recent activities and accomplishments of the national Amorphous Silicon Team and a (crystalline) thin-film-Si subteam that was implemented in 2002 to research solar cell devices based on thin crystalline Si based layers. This paper reports the evolution of team organization, the technical highlights from the recent team meetings, and an outlook on commercialization potential.				
14. SUBJECT TERMS amorphous silicon; crystalline silicon; Thin Film Partnership; national team; potential			15. NUMBER OF PAGES	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	