A Summary of 4-1/2 Years of Research Experience of the U.S. Amorphous Silicon Research Teams

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SUMMARY

The four national amorphous silicon research teams held their 8th guidance team and technical team meetings in conjunction the 25th Anniversary Symposium of the Institute of Energy Conversion at the University of Delaware. The teams were formed in 1992 and represent a success story of teamed photovoltaics research, integrating the efforts of industrial groups, universities, and national laboratories (NIST and NREL). In this paper, we will make an attempt to summarize the accomplishments and the lessons learned during this period.

INTRODUCTION

The national amorphous silicon effort is organized in 4 teams, namely the Wide-Bandgap Team, the Mid-Bandgap and Metastability Team, the Narrow-Bandgap Team, and the Device Design Team. These teams focus on improving the 3 component cells as well as the overall performance of the triple-junction amorphous silicon two-terminal stacked cell, to meet the mid-term U.S. Department of Energy goal for a 15% efficient thin film photovoltaic module. The Midgap team also focuses on the light-induced degradation phenomena in amorphous silicon which are commonly referred to as the Staebler-Wronski effect. The Device Design team focuses on generic device issues such as device modeling, transparent and reflecting contacts, and recombination at the internal n^+/p^+ junctions to minimize losses in the multijunction.

The teams encompass the vast majority of entities working in the U.S. on amorphous silicon based solar cells. Team members receive financial support and guidance from the U.S. Department of Energy (DOE) Thin-Film Partnership Program, administered through the National Renewable Energy Laboratory (NREL), and from the Electric Power Research Institute (EPRI). The program managers at NREL and EPRI were instrumental in the team formation process, which has helped to bring strategic focus and resources to the critical technological issues, and has resulted in a highly effective knowledge transfer between the academic and manufacturing entities.

In a recent publication[1], we summarized the value of teaming and described the high operational efficiency that these teams have reached. We also reported on the recent technical achievements and technical highlights. In the present paper, we review a larger perspective of the teamed research effort since the inception of the teams. From the beginning, the teams addressing the optimization of the three subcells established parameters for each subcell which were deemed necessary to achieve the 15% triple-junction module goal. Table I summarizes the goals and the accomplishments. The numbers for each subcell were only slightly revised as new information was generated. The incremental progress made resulted in the recent achievement of a 13% (active-area) efficient triple junction cell by United Solar Systems Corp. ("Uni-Solar")[2]. Solarex (now a business unit of Amoco/Enron) decided to commercialize a dual-junction PV module, rather than a triple junction,

as their first generation a-Si large-area module. This change in approach did not necessitate a redirection of the team efforts, however.

WIDE-BANDGAP TEAM

The NREL/EPRI Wide-Bandgap Team aims to demonstrate a solar cell generating 6.8 mW/cm^2 (i.e., having 6.8% efficiency) using only the blue/green portion of the solar spectrum. The exact spectral region available to this cell is determined by the detailed engineering of a triple-junction, a-Si-based solar cell; the provisional requirement is $\lambda < 530$ nm ($h\nu > 2.4$ eV), corresponding to a maximum short-circuit current density (J_{SC}) of about 8.2 mA/cm^2. The targets for the stabilized fill-factor (FF) and open-circuit voltage (V_{OC}) are 0.75 and 1.10 V, respectively.

Table I. Stabilized parameters of the component cells necessary to achieve a 15% efficient triple-junction a-Si module, and the best stabilized component cell parameters achieved to date (from Uni-Solar). Experimental data on single-junction component cells are obtained from measurements with filtered light. (* single-junction component cell, $^\#$ light-soaked for 280 hours)

Component cell i-layer bandgap **goal,** *achieved*	V_{OC} (V)	J_{SC} (mA/cm^2)	Fill factor	Stable efficiency (%)
Low-gap cell **goal, E_g≥1.40 eV**	**0.68**	**>8.6**	**0.68**	**4.0**
Low-gap cell *achieved*	*0.612*	*11.55*	*0.609*	*4.30*[*)#)]
Middle-gap cell **goal, E_g~1.65 eV**	**0.89**	**8.4**	**0.70**	**5.2**
Middle gap cell *achieved*	*0.717*	*8.9*	0.59	*3.75*[*)]
High-gap cell **goal, E_g~1.85 eV**	**1.10**	**8.3**	**0.75**	**6.8**
High-gap cell *achieved*	*0.953*	*8.78*	0.71	*5.93*[*)]
Triple-junction cell **goal**	**2.67**	**8.3**	**0.72**	**16.0**
Triple-junction cell *achieved*	*2.294*	*8.27*	*0.684*	*13.0*

Industrial members of the NREL/EPRI Wide-Bandgap Team (United Solar, Energy Conversion Devices, Inc., and Solarex) have demonstrated solar cells that are fairly close to these wide-bandgap targets. An open-circuit voltage of 1.054 V and a power of 5.0 mW/cm^2 have been achieved. The most significant factor in obtaining the higher voltages and powers has been optimization of deposition from hydrogen diluted silane (deposition from H_2/SiH_4 gas mixtures with a ratio >10). The most recent work at Uni-Solar indicates that this approach can *both* increase the optical gap and reduce the susceptibility of a-Si:H to illumination-

induced, metastable degradation (the Staebler-Wronski effect).

At the outset, the team decided to work on wide-bandgap absorber layers, new p^+-type contact layers, and characterization techniques to determine the factors limiting V_{OC}. The first approach was to increase the bandgap of the top cell's intrinsic layer by replacing a-Si:H with a-SiC:H. Work at Solarex showed that as the bandgap was increased, the open-circuit voltages increased until they saturated near 1.04 V. Unfortunately, a-SiC:H alloys were often found to result in poorer fill-factors (at constant thickness) and to exhibit accelerated light-induced degradation compared to a-Si:H i-layers. When it became evident that similarly high open circuit voltages could be achieved with hydrogen diluted intrinsic a-Si:H layers, the team decided to discontinue work on wide-bandgap a-SiC:H intrinsic layers. As will be discussed shortly, fundamental work on effects limiting V_{OC} (such as the saturation just noted) has continued.

The original team plan included exploration of novel p^+ window layers. Syracuse University reported boron-phosphorous alloy layers with promising optical and electrical properties. These proved difficult to reproduce under conventional plasma-enhanced chemical vapor deposition (PECVD) conditions, which generally yielded transparent, but highly resistive films. The work on p^+-layers now focuses on more traditional approaches: optimization of the individual a-SiC:H and microcrystalline Si:H p-type layers, and employment of "buffer" layers, interface "treatments," or grading schemes (e.g., with respect to hydrogen

dilution, C-content, or dopant content) near the p^+/i interface of the cells. Some improvements in cells resulting from work on microcrystalline p-layers have been reported by Energy Conversion Devices. As more and more university researchers focused their device work on stainless steel/n-i-p/TCO ("substrate") cells instead of on glass/TCO/p-i-n ("superstrate") cells, the university groups were able to develop their own processes for microcrystalline p^+ layers. We note that deposition of very thin microcrystalline p^+ layers on SnO_2-coated glass remains problematic; ellipsometric studies indicate that the PECVD conditions needed to rapidly nucleate such films also tend to reduce or degrade the SnO_2 layer.

The academic members of the team have placed great emphasis on understanding and improving the open-circuit voltage for wide-bandgap cells. Several new insights have emerged recently from this work. At Pennsylvania State University, researchers have done extensive studies on the *intensity-dependence* of V_{OC}. For nip cells from United Solar with high V_{OC} (up to 1.02 V) at 1-sun, open-circuit voltages beyond 1.10 V (at nearly 500 mW/cm^2) are limited by the bulk properties of the intrinsic layer. However, test cells with poorer properties tend to exhibit an interface effect which limits the ultimate magnitude of V_{OC} to lower values, perhaps due to lower values of the built-in potential V_{BI} or to photocarrier recombination in interface states.

Estimates of the V_{BI} from Syracuse University using an electroabsorption

technique generally give values for V_{BI} which are lower than expected from bulk optoelectronic properties of the p and n layers. For microcrystalline p-layers deposited onto a-Si:H it was suggested that an *interface dipole* may reduce V_{BI} and limit V_{OC} in some cells. Interesting, more direct Kelvin-probe measurements at University of Illinois (Urbana) during the growth of an amorphous p^+/i junction do *not* reveal dipoles at the a-SiC:H/a-Si:H interface in these cells.

The team is currently also focusing on understanding the light-induced degradation of V_{OC}. The kinetic behavior and magnitude of V_{OC} degradation are found to depend critically on the deposition conditions used to prepare the cells.

These studies of V_{OC} have raised two important modeling issues which require resolution. First, the V_{OC} degradation cannot generally be explained in terms of the same material parameters used to explain degradation of other cell parameters such as the FF. Second, in order to account for the observed magnitudes for V_{OC} using conventional materials parameters, modelers using Penn State's AMPS program have been inserting (*ad hoc*) a very thin, narrow bandgap, "dirty" layer at the p^+/i interface; this procedure reduces the predicted value for V_{OC} enough to agree with measurements. However, careful studies using spectral ellipsometry at Penn State have not found any such narrow-bandgap layer—and thus reveal the significant gap both between predicted and measured values for V_{OC} and in our understanding of this crucial property of wide bandgap cells. Increasing the photocurrent of the top cell is also critical, since work by Uni-Solar indicated that

it is beneficial to limit the currents of the triple-junction devices by their top cells. Thus, the J_{sc} of the top cell is the J_{sc} of the triple cell.

METASTABILITY AND MID-BANDGAP TEAM

The primary goal of the Mid-bandgap Team has been to solve the degradation problem in a Si:H materials and devices. A secondary goal has been to obtain such stable materials with a somewhat lower optical gap than standard a Si:H (i.e., less than 1.7eV compared to about 1.8eV in standard material). The team approach to tackle these problems was initiated 4-1/2 years ago and focused on new materials prepared as follows: (1) hydrogen diluted PECVD a Si:H, (2) hot-wire deposited a-Si:H, (3) a-Si:H deposited via a method utilizing electron cyclotron resonance excitation of a hydrogen diluted silane plasma ("H-ECR"), and (4) Uni-Solar's use of a low Ge-content a-SiGe:H alloy for the middle cell in their triple-junction devices. A truly major breakthrough has been our realization that amorphous silicon exists in several fundamentally different forms, some of which are intrinsically more stable.

The hydrogen diluted material has been investigated in detail by several team members and has now become an industry standard in the fabrication of much more stable devices. We have confirmed that this material exhibits very different kinetics in the manner in which it degrades. A key insight, based on studies carried out by Uni-Solar researchers, is that the increased stability may be due to

an increase in the ordering of the silicon atomic structure. Hot-wire deposited amorphous silicon was developed by team members at NREL and really turned the traditional understanding of a-Si:H on its head. First, it was confirmed to behave as a very stable, low defect density material even when the hydrogen content was reduced to 2 at.%. Since the optical gap of a Si:H varies with hydrogen content, this had the extra advantage of providing a means to reduce the optical gap of the mid-gap material without alloying. While the existence of a low hydrogen form of a Si:H with good electronic properties is surprising enough, NMR studies carried out at the University of North Carolina showed that the hydrogen microstructure was also very different than in the traditional PECVD material. This has led to the critical insight that the hydrogen microstructure can be dramatically altered in amorphous silicon depending on growth method.

The third major area of new materials development, H-ECR a Si:H, was spearheaded at Iowa State University. This material has now been incorporated into p-i-n devices which have exhibited remarkable stability: only 5% degradation in fill factor after 1000 hours of operation. Since the major difference between this material and traditional PECVD a-Si:H has to do with the details of the plasma, this provides the key insight that the hydrogen chemistry is very important for improving the performance of a-Si:H base photovoltaic devices.

In addition to these lessons based on materials development, we also mention a couple of significant new insights of a more general nature. The first regards

characterization techniques that can enhance our ability to understand devices. We noted that, because the a-Si:H materials have improved so dramatically, one must also apply much more sophisticated evaluation methods to distinguish qualities that are important for device performance. These have included several probes of electronic properties that could be applied directly to devices or device-like structures (capacitance profiling, photomixing, electroluminescence, field profiling), and also more sensitive methods to learn about network microstructure (SAXS, grazing angle x-ray diffraction, internal friction, positron annihilation spectroscopy). The utility of some of this information for predicting device performance has been well demonstrated, some is still of uncertain value, and some methods, such as field profiling, really have not yet reached a level of accuracy to be considered very useful.

The second area of general understanding concerns the kinetics of the degradation process itself. Five years ago there was a serious concern that degradation in a Si:H based devices would proceed indefinitely. Now we understand, because of the existence of light-induced annealing or a diminishing degradation process, that amorphous silicon degradation definitely stabilizes. The stabilized performance level is however significantly affected by the details of material preparation. Work at Solarex has recently been clarifying some of the annealing processes in more detail, including a role for electric-field induced recovery. Some new mechanisms involving hydrogen motion are being examined

within the context of improved theoretical calculations being carried out at Iowa State University.

However, in spite of the great progress that has been made, we are well aware that we still don't know exactly why some materials are more stable. We haven't singled out a specific microscopic mechanism that controls the degradation process. Therefore, a great deal of work remains. Areas of investigation that are currently being given high priority include understanding the role of microstructure for stability, the role of hydrogen chemistry, and ways in which the complex nature of the deep defects may affect the relationship between materials and devices.

Some of this points to the need for better theory; i.e., calculations that can predict productive directions for device improvement. Also, we need characterization methods that can give us a more detailed picture of what is going on inside actual devices; for example, the appearance of the electric field profiles under actual operating conditions, and how they evolve with increasing degradation. Finally, we definitely need to continue exploring novel methods of materials growth such as combining some of the methods described above. In particular, there will be a critical need to identify growth methods that increase deposition rates while still maintaining device stability.

NARROW-BANDGAP TEAM

The a-SiGe:H cell designed as the bottom cell of the triple-junction device has apparently surpassed the 4% efficiency target. However, this observation may be misleading, because the current is more than the target (8.4 mA/cm^2), whereas the FF and V_{OC} are below the target values. Therefore, more improvement is needed (especially in terms of FF and V_{OC}) than what would appear from having obtained the present stabilized 4.3% efficiency result for the bottom cell.

Like the Mid-Bandgap and Metastability Team, considerable effort went into preparing the material using alternate deposition techniques or new precursors, specifically: (1) Microwave ECR deposition, (2) hotwire deposition, (3) use of halogenated precursor gases, (4) high hydrogen dilution PECVD, and (5) replacement of the a-SiGe:H bottom cell absorber with microcrystalline thin Si. It appears that it is more difficult to obtain reasonable performance in a-SiGe:H devices using some of the above techniques as compared to unalloyed a-Si:H devices. Most of the progress in advancing the efficiency of the bottom cell came from incremental optimizations using hydrogen dilution and PECVD deposition. The progress also critically depends on optimizing grading strategies (graded Ge content) and optimized p^+, n^+, and buffer layers. The team did not attempt to develop microcrystalline bottom cells due to a lack of resources.

As in the case of the Midgap Team, succinct differences were identified between differently prepared materials even if these materials were similar in terms of material parameters that were generally accepted to determine the

material quality before the teams were formed. Conversely, schemes that had been reported to improve the material parameters such as the mobility-lifetime product, for example ion- or electron bombardment schemes during deposition, were found not to have beneficial effects on device performance. Research at the University of Oregon identified the importance of charged dangling bond defects that were clearly as important as the total number of midgap defects in a-SiGe:H alloys in determining mobility lifetimes.

MULTIJUNCTION DEVICE TEAM

The Multijunction Device Team seeks to improve device performance independent of specific i-layer bandgap or alloy. The research priorities of this team have been to develop new transparent conductive oxide (TCO) layers with reduced absorption losses and good light-scattering properties, more reflective back contacts, and to reduce losses at the n/p recombination "tunnel" junctions. Analytically, the focus has been on obtaining material and device parameters for better modeling, determining optimum device designs for a 15% efficient multijunction device, and developing a realistic light-trapping model.

More efficient photon utilization (less TCO absorption, better light trapping, more reflective back contacts) has an impact far beyond generating higher J_{SC}. Those benefits include improved stability from using thinner absorber layers, and shorter deposition times as thinner layers are used.

Amorphous silicon cells are produced either in superstrate or in substrate configuration (see Wide Bandgap section above for definitions). Each of these structures has different challenges for optical enhancement, good electrical contacts, and TCO materials. Optical enhancement schemes for both types of cells were explored.

Transparent conductive SnO_2 layers are the most commonly used material for the contact layer deposited on the glass for superstrate-type configuration. For many years, it was attempted to replace the SnO_2 transparent conductor in the superstrate cells with ZnO, because ZnO is more transparent and has been found to be more stable and show less deterioration upon exposure to the SiH_4/H_2 plasma used to deposit the amorphous silicon layers. The Institute of Energy Conversion evaluated the suitability of ZnO layers for superstrate solar cells. The sheet resistance of low pressure CVD (LPCVD) ZnO films were found to be unstable upon annealing in air or vacuum at 250°C while atmospheric pressure CVD (APCVD) ZnO films were unchanged by such annealing. Both types of ZnO films were stable under hydrogen plasma while all SnO_2 films suffered reduced transmission. The performance of single-junction cells on different types of TCO showed that increasing the haze (ratio of diffuse to total transmission at 700 nm) beyond ~5% was of limited use to increase the red response. Single junction a-Si solar cells with ZnO generated current densities about 0.6 mA/cm^2 higher than cells on SnO_2. However, V_{OC} and FF were generally higher with SnO_2,

confirming a problematic nature of the ZnO/p^+ contact.

A robust atmospheric pressure chemical vapor deposition (APCVD) process to deposit textured ZnO has been developed at Harvard University with much better uniformity and reproducibility than previous processes. This was achieved by developing a new metal-organic Zn precursor. Aside from allowing better process control, the new precursor is not pyrophoric (unlike diethyl zinc), making the handling less critical. The new ZnO layers were evaluated at Solarex and at IEC in tandem and single-junction devices. Improved values of J_{SC} and V_{OC} were obtained, but the FF was still low compared to cells prepared on SnO_2 substrates. Laser-scribing and shunting studies were conducted at Solarex and showed that the patterning steps are more critical and require reoptimization if SnO_2 were to be replaced by ZnO in superstrate modules.

In order to protect the SnO_2 from the H_2 plasma, a thin layer of Nb-doped TiO_2 was deposited on the SnO_2. Devices on TiO/SnO_2 superstrates had similar V_{OC} and FF as those prepared directly on SnO_2, but ~10% lower J_{SC}, indicating sufficient electrical conductivity but excessively high absorption. Similarly, it was thought that a TiO_2 layer deposited by APCVD on a textured Ag/stainless-steel back reflector substrate could act as a diffusion barrier and minimize reactions that might reduce back reflector reflectivity. When Uni-Solar back-reflectors were coated with TiO_2 at Harvard, it was found that the TiO_2 had no effect on the red response or other cell parameters. Light trapping also requires very highly

reflective back contacts which typically consist of TCO/metal layers. Analyses of both substrate and superstrate devices indicate considerable losses in J_{SC} (~4 mA/cm^2) which were attributed to parasitic absorption in the back reflector. The NREL optical model now explains why the TCO/metal back reflector is optically better than pure metal. Absorption in the metal is a significant loss, and the placement of a dielectric layer with n~2 between Si and metal reduces transmission into the metal by increasing reflection into the Si. This work should help to refocus work on optical solar cell enhancement, by working on eliminating the absorption losses in the metal layers rather than attempting to increase the texture or randomness of the TCO layers.

New structures were developed at IEC to characterize the back reflector (BR) in conjunction with substrate texture. An optically coupled, external BR allows separation of substrate texture and reflection properties on the same device. It was found that substrate texture is more important than BR reflectivity to enhance the red response. Texture also has positive impact on reducing front reflection losses.

Modeling with Penn State's computer model AMPS provided insight into optimizing the design of single- and triple junction cells to achieve the 15% efficiency goal. However, further discrepancies between the model and experimental results also became evident. For example, a simple attempt at Penn State to model the photoconductivity of a-Si:H when the generation intensities

were varied by several orders of magnitude suggested that the model could only fit the photoconductivity results when a defect spectrum was used that was much more complex than defect distributions used hitherto. In August of 1996, the effectiveness of using a computer model for cell optimization was reviewed by the teams. Most researchers appreciated the availability of a numerical model and appreciated the insight provided from the modeling work, but a majority of the team members agreed that the model is presently not advanced enough to predict absolute cell efficiencies from the commonly measured material parameters.

Tunnel or n/p recombination junction losses were reduced at ECD, Uni-Solar and APS by depositing a thin highly doped µc-Si n or p layer. Higher doping of the surface at the junction increases recombination and lowers the contact resistance, thus increasing V_{oc} and FF of the multijunction device. Lower absorption of the µc-Si layers increases the current available in the middle and bottom cells.

CONCLUSIONS

An important aspect of doing research in teams is to accept unexpected results. For example, the teams now agree that hydrogen dilution appears to be a suitable technique to improve the stability of all three component cells of the triple-junction device. This result had not been predicted or expected as the teams first developed their lists of activities. On the other hand, the teams accept the reality

that materials with improved properties (such as lower midgap defect density, or higher ambipolar diffusion length or hole mobility lifetime products) do not necessarily result in component cells with greater stabilized performance. The groups carrying out specialized material characterizations have established succinct differences for differently prepared materials. The teams acknowledge that such succinct differences, which may be small on the scale established at the beginning of the teamed research effort to measure the electronic material quality, may yet lead to substantial differences in cell performance, light-induced cell degradation, and the kinetic behavior of the degradation. Thus, the teams have accepted as a *modus operandi* that any claims of improved electronic materials properties have to be verified by showing a corresponding improved device performance.

The team effort also allowed the nondevice-making researchers to recognize that device–making is an interactive exercise. For example, when the transparent conductive oxide layer in a cell is changed, the amorphous silicon n^+ and p^+ layers and buffer layers may have to be reoptimized. Cell optimization is thus no longer an exercise to optimize individual layers used in a cell by themselves. It is now appreciated by the non device-makers that successful integration of a new material into a device structure may be very complex and frustrating experience.

At the meeting, the team members agreed upon issues critical for making significant progress in amorphous silicon. Table II lists the issues grouped under

the following categories: materials growth and processing, experimental techniques, and understanding. The last category, "understanding," reflects areas where more knowledge of atomic and electronic processes and mechanism is needed. Much of this understanding can be synthesized from the results of activities in the first two categories. The next step for the teams will be to prioritize these issues, and to develop strategies how to tackle them.

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Table II: Summary of Critical Issues from the 4/30/97 a-Si Guidance Team Meeting

Materials and Processing Issues	**Techniques**	**"Understanding"**
Deposition rate effects, material utilization, yields, etc.	Cell level measurements (e.g., field profile measurements)	Device physics
Network microstructure	Probes to measure order and microstructure	Kinetics of degradation
H microstructure	Electrical measurements	H motion
Processing of novel materials	Modeling a) electrical b) optical c) process ("reactor/reaction")	Defects and potential fluctuations
Plasma chemistry	*In situ* diagnostics	Network order
Interfaces		Junctions and contacts
Heterogeneities		Nucleation and growth
Microcrystalline Si		Understanding of transport and recombination
Impurities		