

Fab & Facilities

Materials

Cell Processing

Thin Film

PV Modules

Power Generation

Market Watch

Industry–academia partnership helps drive commercialization of new thin-film silicon technology

Subhendu Guha, United Solar Ovonic, Auburn Hills, Michigan; **David Cohen**, University of Oregon, Eugene, Oregon; **Eric Schiff**, Syracuse University, Syracuse, New York; **Paul Stradins**, National Renewable Energy Laboratory (NREL), Golden, Colorado; **P. Craig Taylor**, Colorado School of Mines, Golden, Colorado, & **Jeffrey Yang**, United Solar Ovonic, Auburn Hills, Michigan, USA

ABSTRACT

The low material cost and proven manufacturability of thin-film silicon has made this material very attractive for low-cost photovoltaics (PV). It is widely recognized that increasing the light-to-electricity conversion efficiency will play a critical role in expanding the acceptance of these products. The first commercial thin-film silicon solar cell consisted of a single-junction structure using amorphous silicon; multijunction cells incorporating amorphous silicon and silicon germanium were later used to further improve efficiency. An even later development was the incorporation of nanocrystalline silicon as an active layer. This very interesting material, which consists of nanocrystallites embedded in an amorphous tissue, has already given rise to a significant increase in the performance of these multijunction cells. Most recently, some very innovative light-trapping concepts have been suggested that can improve the efficiency further. Both these topics, however, have required expertise not readily available within one organization. A thin-film silicon team has been established under a US Department of Energy's Solar America Initiative programme to address the material, device and manufacturability issues for this technology. United Solar Ovonic is the team leader, with Colorado School of Mines, University of Oregon, Syracuse University and the National Renewable Energy Laboratory (NREL) as members. The collaborative effort has resulted in a new understanding of the material and devices; innovative light-trapping ideas were developed, and world-record initial efficiencies of 16.3% for small-area cells and 12% for large-area encapsulated cells were reached. Of equal importance is United Solar's decision to introduce this technology into production. This paper presents the important technical results obtained under this programme and will discuss future directions.

Introduction

Hydrogenated amorphous silicon alloys (a-Si:H) have received a great deal of attention as a material for the low-cost manufacture of solar cells and panels. Silicon is non-toxic and abundant in nature. The lack of long-range order in the material allows absorption of sunlight in a very thin film, thereby reducing material costs. a-Si:H alloy is also being extensively used for large-area flat panel displays, proving that the deposition of solar cell material over a large area should not be a limiting issue. Cells can also be deposited on flexible substrates, allowing laminates to be incorporated in building-integrated photovoltaic structures (Fig. 1). The production of solar panels using thin-film silicon technology has grown steadily over the years. It has been reported that production of solar panels using this technology increased from 198MW in 2007 to 1.3GW in 2010 [1].

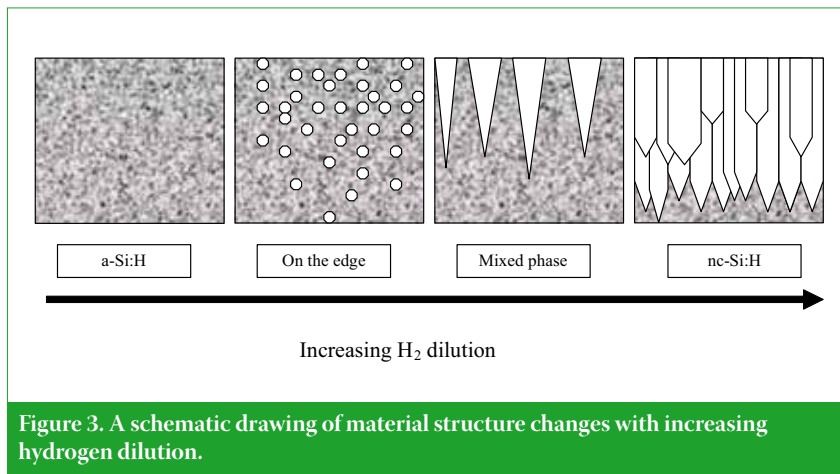
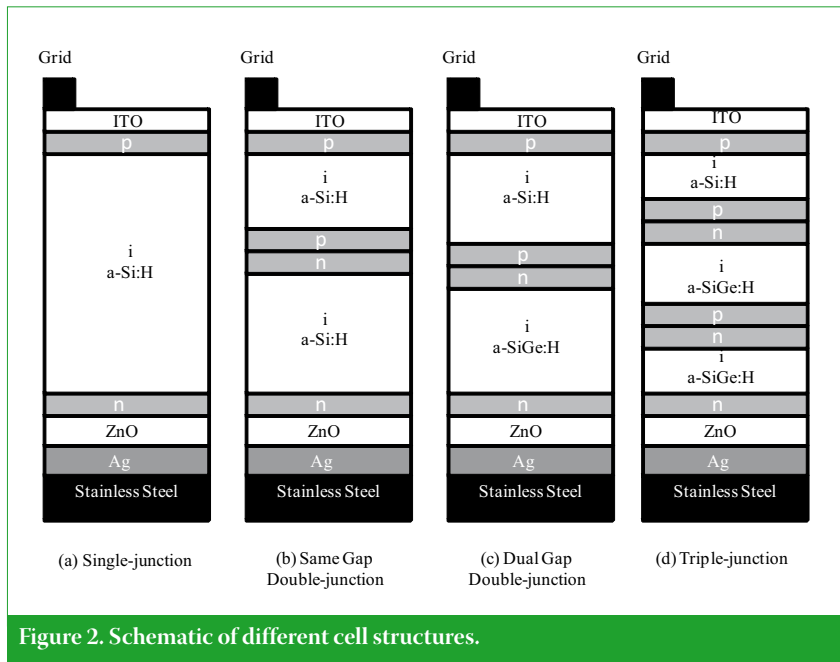
The challenge, however, is to increase the light-to-electricity conversion efficiency. The material a-Si:H is very intriguing: the absence of long-range order facilitates efficient photon absorption and also causes tailing of the conduction and the valence band edges. The material also contains defects such as dangling, strained and weak bonds that act as recombination centres for the electrons and the holes. The efficient

operation of a solar cell depends on a two-step process: 1) photon absorption for the generation of the carriers and 2) subsequent carrier transport and collection. Even though the photon absorption is efficient, the presence of the recombination centres arising from the defects and the band tails impedes the transport of carriers and lowers the efficiency. The other challenge is the phenomenon of light-

induced degradation [2]. Exposure to light increases the defect density in the material, and the cell efficiency decreases. While there has been tremendous progress in the understanding of the problem, it still persists. The degradation, of course, is lower when the cell thickness is small, since the photogenerated carriers do not have to travel a large distance. But that results in less absorption.

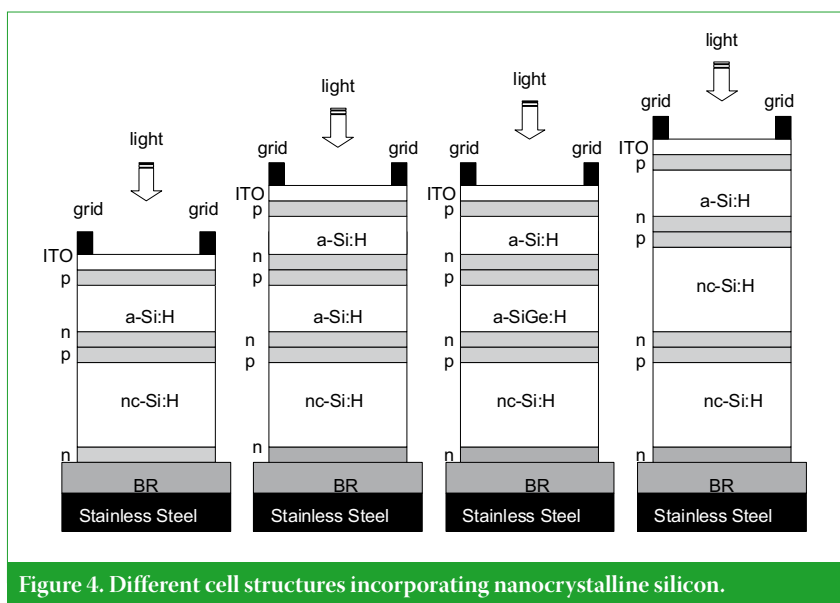


Figure 1. World's largest rooftop system (11.8MW) in Zaragoza, Spain. The system uses flexible thin-film silicon PV laminates.



In the early days, single-junction cells were used to make solar panels; Fig. 2a shows a schematic of a cell on a metal substrate, although many researchers and manufacturers use glass substrates. As the limitation of the single-junction cells

became apparent, double- or tandem-junction cells with or without different bandgap materials (Figs. 2b and 2c) and triple-junction cells with multiple bandgap alloys (Fig. 2d) were developed. These cell structures allowed a wider spectrum



of light to be absorbed in the cell and also reduced light-induced degradation, since the individual component cells were thinner. Until very recently, the highest cell efficiency was achieved with a triple-junction structure, in which the top cell employed a-Si:H of about 1.8eV bandgap to capture the blue photons, the middle cell employed an amorphous silicon-germanium alloy (a-SiGe:H) of about 1.6eV bandgap to capture the green photons, and the bottom cell employed a-SiGe:H of about 1.5eV bandgap to capture the red photons. Any light that has not been absorbed bounces back from the back reflector (BR) to enhance absorption. During the last several decades, many innovations have been made to improve the quality of a-Si:H and a-SiGe:H alloys. Hydrogen dilution of the active gas during deposition was found to improve the quality of the intrinsic layers; bandgap profiling of a-SiGe:H improved the built-in field, thus facilitating superior carrier collection. Another area of development was the use of BR for light trapping. Use of textured BR and incorporation of the improved alloys resulted in world-record initial cell efficiency of 14.6% using a triple-junction structure [3]. The technology is also used for large-volume manufacture of solar panels [4].

“The efficient operation of a solar cell depends on a two-step process: 1) photon absorption for the generation of the carriers and 2) subsequent carrier transport and collection.”

While the use of a-SiGe:H led to significant increases in performance, incorporation of Ge in a-SiGe:H generally reduces the quality of the material; therefore, a new class of materials named nanocrystalline silicon (nc-Si:H) or microcrystalline silicon alloys emerged [5] to replace a-SiGe:H in the bottom cells of a multijunction structure. The best quality a-Si:H uses hydrogen dilution of the active gas (silane) during plasma deposition, which improves the order in the film. As the hydrogen dilution increases, the transition to the nanocrystalline phase takes place. The material is characterized by formation of nanocrystallites embedded in an amorphous matrix; the volume fraction and the size of the nanocrystallites grow with increasing hydrogen dilution. Fig. 3 shows a schematic of nanostructure evolution as hydrogen dilution increases.

The tiny crystallites grow with increasing hydrogen dilution, forming cone-shaped structures as the hydrogen dilution further increases. For a very dilute

mixture, columnar growth starts taking place and cracks develop in the film with adverse effects on material quality. The best material is thus grown just above the edge of hydrogen dilution for the amorphous to nanocrystalline transition.

The alloy nc-Si:H has been found to have superior long-wavelength absorption, which, coupled with the fact that it does not show degradation under long-wavelength light, makes this alloy an attractive candidate to be used in the bottom cells of a multijunction structure, with the promise of increasing the efficiency of multijunction cells further. Different cell structures have been investigated (Fig. 4) to determine the highest efficiency.

Research challenges

It was apparent that, in order to improve small-area cell efficiency beyond 14.6%, a clearer understanding of nc-Si:H was needed. A BR that can result in better light trapping than obtained with the conventional random texture also needs to be developed. The complexity and breadth of the issues demand that a multidisciplinary approach be used. The programme needs expertise in materials research, optics and device physics. Under the DOE's Solar America Initiative programme, United Solar formed a team drawn from industry, a national lab (NREL) and academia (Colorado School of Mines, Syracuse University and University of Oregon) to address the complex issues that will result in further increase in cell efficiency. Some highlights of the collaborative work are given below.

Back reflector for light trapping

One approach to increasing the effective harvesting of long-wavelength photons, thus enhancing current generated in thin-film silicon solar cells, is to use textured and highly reflective substrates or BRs. The conventional light-trapping method uses a randomized texture in which maximum light trapping has been shown to be limited by $4n^2$, where n is the refractive index of the absorber material. Commonly used BRs are Ag/ZnO-coated stainless steel (SS) substrates [6]. The desired texture of the Ag and ZnO layers can be obtained by optimizing deposition conditions. The texture has a wide distribution of features of different sizes.

Using near-infrared quantum efficiency spectra, a collaboration with Syracuse University was undertaken to calculate the enhancement factors for the cells. It was found that the very best enhancement factors are ~ 25 [7]. This is much less than the classical limit of ~ 50 , and as seen in Fig. 5, one can have an additional gain of $\sim 3\text{mA}/\text{cm}^2$ when the classical limit is reached.

To further increase the efficiency, advanced light trapping with a gain in

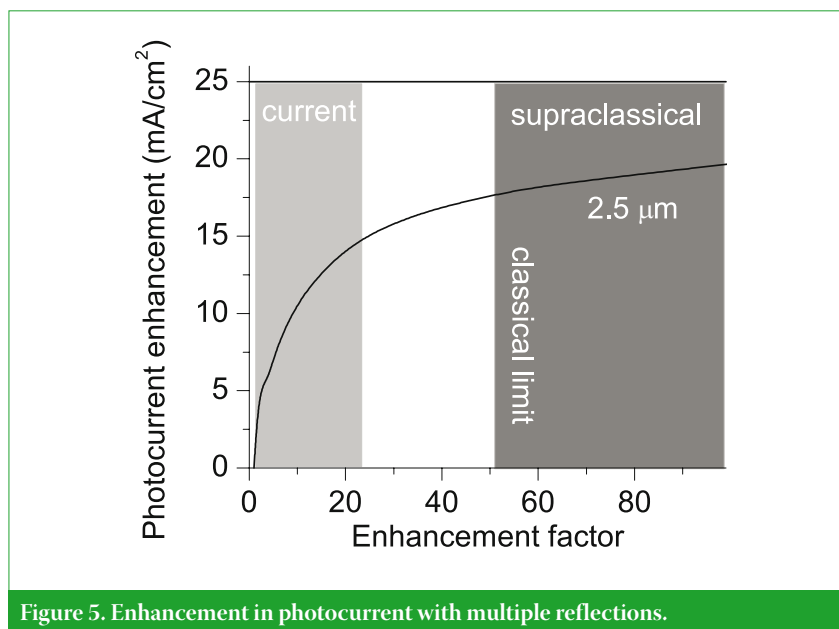


Figure 5. Enhancement in photocurrent with multiple reflections.

photocurrent exceeding the classical $4n^2$ is needed. In recent years, several advanced light-trapping approaches have been investigated, including BRs with periodic gratings, photonic structures, and plasmonic scattering by metal nanoparticles [8]. A theoretical analysis showed that, by using metal nanoparticles embedded in the BRs, the gain from plasmonic light trapping could exceed the classical limit of $4n^2$. Schiff has recently derived a non-resonant limit of light-trapping enhancement (E) with plasmonic scattering for weakly absorbed light in a solar cell of thickness d [9]:

$$E = 4n^2 + \frac{n\lambda}{d} \quad (1)$$

where λ is the wavelength of the light. For a $1\mu\text{m}$ -thick solar cell at the long-wavelength region of 1000nm , the additional gain from the surface plasma polaritons is n , and the increase in short-circuit current density, J_{sc} , is predicted to be about $0.6\text{mA}/\text{cm}^2$. It is clear from Equation 1 shown above that the additional gain is more pronounced in thinner cells. For a $0.25\mu\text{m}$ -thick cell, the additional gain is $4n$, which is equal to about 16 for Si. In principle, even larger gains are possible using resonant enhancement, for which the surface plasmon resonance is matched to the semiconductor bandgap.

With an increase in J_{sc} in the bottom cell as a result of superior light trapping, one has to worry about increasing the current density in the other cells to obtain proper current matching. The cell thicknesses cannot be increased, since that will result in higher light-induced degradation. Reflection from intermediate layers between the cells has been suggested using different materials. A dual-function nc-SiO_x:H layer made

with proper hydrogen dilution and doping with P has been shown to be effective in increasing the top cell and middle cell currents in a-Si:H/nc-Si:H double-junction and a-Si:H/a-SiGe:H/nc-Si:H triple-junction solar cells [10].

Materials research

Structure

The nc-Si:H films show a profound inhomogeneity in the growth direction, as can be seen by transmission electron microscopy (TEM) and atomic force microscopy (AFM) micrographs. We start with an amorphous zone, followed by a layer consisting of a mixture of amorphous and nanocrystalline silicon. Our collaboration with NREL showed that cone-shaped structures containing large numbers of nanometre-sized grains appear as the growth continues [11]. These composite cones result from the nanocrystalline phase growing faster than the amorphous phase, as shown by the 'cone kinetics model' developed at NREL [12].

“By optimizing the profiling parameters, such as the amount of hydrogen and the rate of change in hydrogen dilution ratio, the nc-Si:H solar cell performance was significantly improved.”

To overcome the negative effect of the nanocrystalline evolution on solar cell performance, a hydrogen dilution profiling technique was designed to control the growth of the nanocrystalline phase [13,14]. A very high hydrogen dilution was used to deposit a seed layer to reduce the thickness

of the incubation layer, and then a hydrogen dilution profiling was used, with decreasing hydrogen dilution ratio over time to keep the material close to the transition from the nanocrystalline phase to the amorphous phase. By optimizing the profiling parameters, such as the amount of hydrogen and the rate of change in hydrogen dilution ratio, the nc-Si:H solar cell performance was significantly improved.

In order to understand the nature of hydrogen bonding, hydrogen-effusion mass-spectroscopy measurements on a series of nc-Si:H cells with different degrees of crystallinity and hydrogen content were carried out in collaboration with NREL[15]. Fig. 6 shows corresponding hydrogen-effusion time profiles taken at a fixed temperature–time ramping rate, with the area under the curves representing hydrogen content. Samples A and C were grown under conditions in which the crystalline volume fraction of the nc-Si:H cell absorber layer was only about 30%, while B and D were highly crystalline at about 75%. The latter films have lower overall hydrogen content, since most of the hydrogen resides in the amorphous phase. Importantly, however, low-crystallinity cells show strong low-temperature hydrogen-effusion peaks at 400°C, signifying that the nc-Si grain boundaries are well passivated by hydrogen. Indeed, these cells A and C show significantly better performance: an increase of 80mV in open-circuit voltages, and efficiencies higher by 2.5% absolute. Thus, the low-temperature hydrogen-effusion peak serves as a good metric for cell absorber optimization.

Several techniques were used, in collaboration with the Colorado School of Mines, to probe the nanostructure of nc-Si:H thin films [16]. The x-ray diffraction data (XRD) reveal crystallites of approximately 11 to 24nm in length with a preferred $\langle 220 \rangle$ orientation in the film growth direction. Small-angle x-ray scattering (SAXS) experiments show crystallite sizes four times smaller than those revealed by XRD, demonstrating that crystallites are elongated along the growth direction (Fig. 7). Based on 10 to 14% atomic hydrogen measured in the a-Si:H phase, the SAXS and nuclear magnetic resonance results indicate that the crystallite interfaces are up to 35% hydrogenated.

Defect density

In collaboration with the University of Oregon, detailed measurements have been carried out to examine the defect density of nc-Si:H with varying crystalline volume fraction, using drive-level capacitance profiling (DLCP) as well as transient photocapacitance and transient photocurrent spectroscopy techniques [17,18]. In general, defect density is lower than in a-Si:H; moreover, deep defects lying about 0.4eV below the conduction band

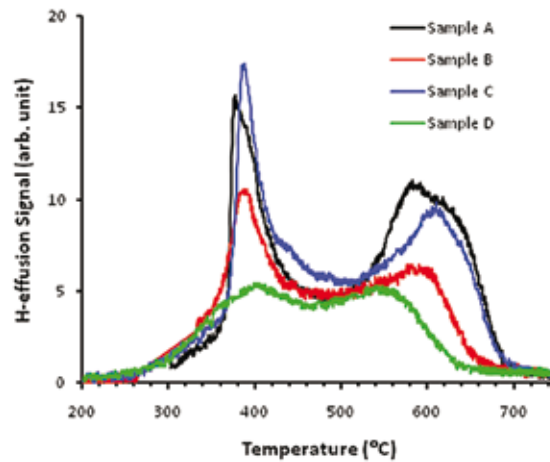


Figure 6. Hydrogen-effusion time profiles for four different nc-Si:H solar cells. Samples A and C have low crystalline volume fraction, while B and D are highly crystalline.

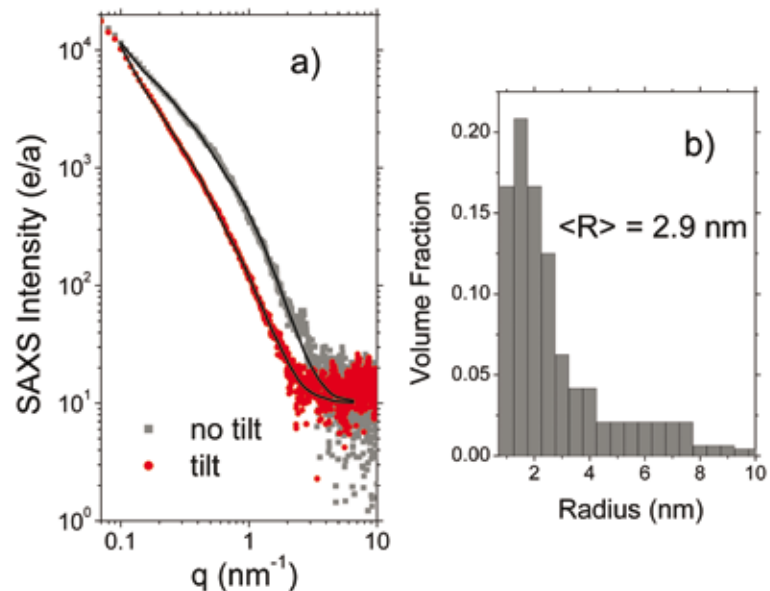


Figure 7. SAXS measurement on nc-Si:H films showing elongated crystallites.

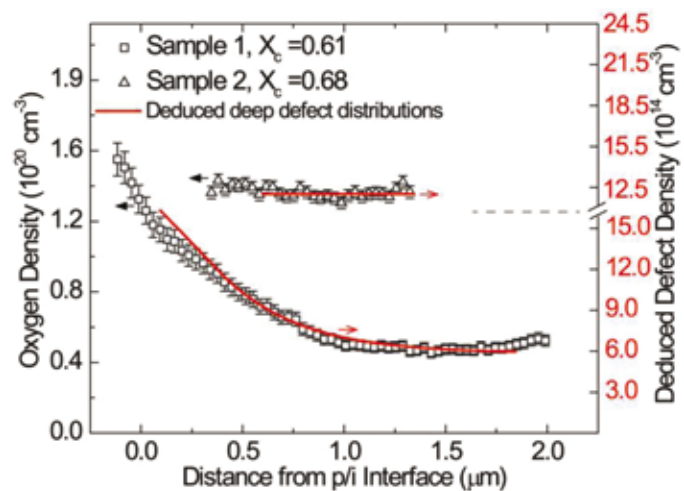


Figure 8. Correlation between oxygen content and deep defect density for two samples with different volume crystalline fraction X_c .

edge (E_c) were correlated with the presence of Si crystallites. The work was later extended to examine the effects of oxygen impurities on the electronic properties [19]. Because the DLCP measurements allow spatial distributions of defects to be mapped, these could be compared with secondary ion mass spectrometry (SIMS) concentration profiles of impurity species within the film. In this manner, a clear correlation was established between the oxygen content and a prominent deep defect band located about 0.7eV from E_c (Fig. 8). These findings are corroborated by photoluminescence measurements performed in collaboration with the Colorado School of Mines.

Device performance

Based on the understanding gathered from the research work as outlined above, United Solar has been steadily increasing the cell efficiency over the past few years [20]. Improvements have been made in hydrogen dilution profiling, design of seed and buffer layers, optimization of pressure and cathode-to-substrate distance, cathode design and gas flow dynamics, random BR, and interlayer. Two world-record efficiencies have been reported: a small-area (0.25cm²) initial cell efficiency of 16.3% (Fig. 9) and a large-area (400cm²) encapsulated initial cell efficiency of 12% (Fig. 10). The large-area efficiency has already been confirmed by NREL, and the small-area cell is being sent to NREL for efficiency confirmation.

Future directions

Significant improvements in the efficiency of multijunction cells have been made in recent years by incorporating nc-Si:H in the cell structure. United Solar has already initiated a programme to modify one of its existing deposition machines to incorporate the new structure into production. Our understanding of nc-Si:H is in its infancy. Further improvements in efficiency can be made; Table 1 shows the highest efficiencies that can be reached using different structures [21], with calculations being based on realistic cell parameters of the component cells. Module efficiencies approaching 20% using low-cost thin-film silicon technology will have a big impact on module and system cost. Innovation has to continue and

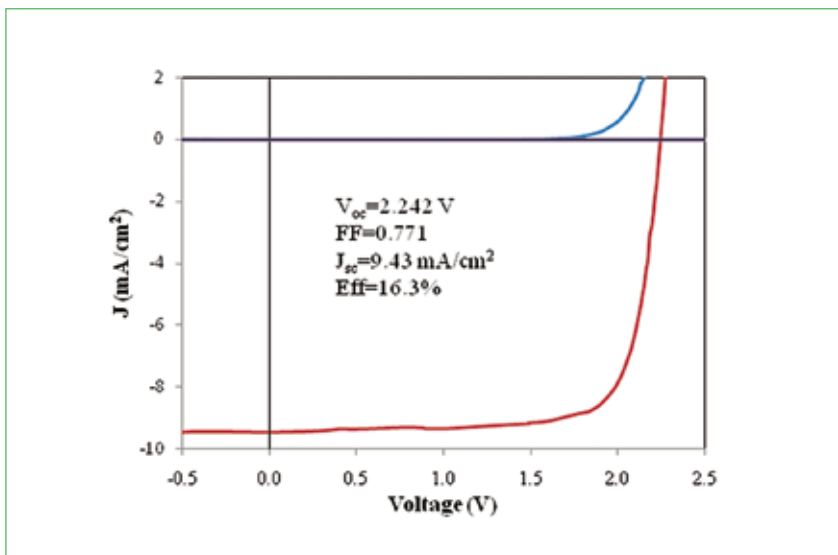


Figure 9. Initial small-area cell efficiency using a triple-junction structure incorporating nc-Si:H.

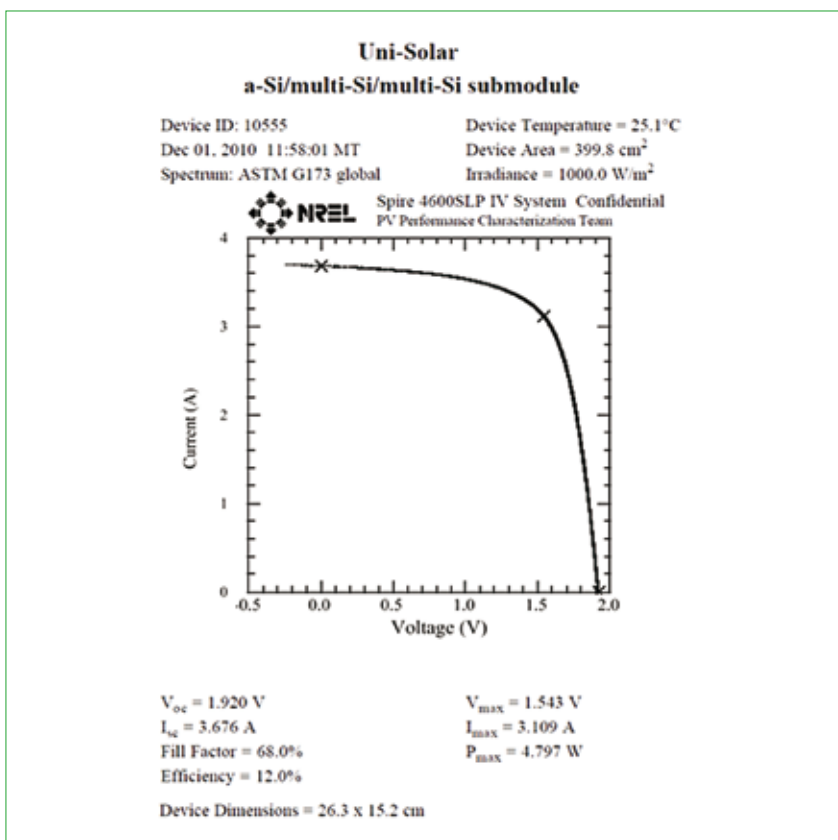


Figure 10. Initial large-area encapsulated cell efficiency using a triple-junction structure incorporating nc-Si:H, as measured by NREL.

Cell structure	Current status a-Si/a-SiGe/nc-Si	Option 1 a-Si/a-Si/nc-Si	Option 2 a-Si/a-SiGe/nc-Si	Option 3 a-Si/nc-Si/nc-Si
V_{oc} (V)	2.24	2.50	2.30	2.15
J_{sc} (mA/cm ²)	9.13	11.8	12.3	12.6
FF	0.75	0.85	0.85	0.85
Efficiency (%)	15.4	25.1	24.0	23.0

Table 1. Highest cell efficiencies obtainable with different structures [21]. Note that since the publication of [21] in 2010, a 16.3% efficiency has now been achieved.

sustained collaboration between industries and academia will facilitate the progress.

Acknowledgements

We would like to thank the many colleagues in our organizations who collaborated with us in this research to advance the technology. This work was supported by the US Department of Energy under the Solar America Initiative Program Contract No. DE-FC36-07 GO 17053.

Thin
Film

References

- [1] Mehta, S. 2011, "27th annual data collection results," *PV News*, Vol. 30, No. 5, p. 3.
- [2] Fritzsche, H. 2001, "Development in understanding and controlling the Staebler-Wronski effect in a-Si:H," *Annu. Rev. Mater. Res.*, Vol. 31, p. 47.
- [3] Yang, J., Banerjee, A. & Guha, S. 1997, "Triple-junction amorphous silicon alloy solar cell with 14.6% initial and 13.0% stable conversion efficiencies," *Appl. Phys. Lett.*, Vol. 22, p. 2975.
- [4] Yang, J., Banerjee, A. & Guha, S. 2003, "Amorphous silicon based photovoltaics – from earth to the 'final frontier'," *Solar Energy Mat. & Solar Cells*, Vol. 78, p. 597.
- [5] Shah, A. (ed.) 2011, *Thin Film Silicon Solar Cells*, EPFL Press, Switzerland.
- [6] Yue, G. et al. 2009, "Optimization of back reflector for high efficiency hydrogenated nanocrystalline silicon solar cells," *Appl. Phys. Lett.*, Vol. 95, p. 263501.
- [7] Zhao, H. et al. 2011, "Classical and supra-classical light trapping in thin film solar cells," *Solar Am. Initiative Rev. Meet.*, April [unpublished].
- [8] Zeman, M. et al. 2010, "Advanced light trapping in thin-film silicon solar cells," *Mat. Res. Soc. Symp. Proc.*, Vol. 1245, p. 65.
- [9] Schiff, E.A. [unpublished].
- [10] Yan, B. et al. 2011, "Effect of dual-function nano-structured silicon oxide thin film on multi-junction solar cells," *Proc. 37th IEEE PVSC*, Seattle, Washington, USA.
- [11] Jiang, C.-S. et al. 2008, "P-induced nanocrystallite dispersion in amorphous-nanocrystalline mixed-phase Si:H thin films," *J. Appl. Phys.*, Vol. 103, p. 063515.
- [12] Stradins, P., Teplin, C.W. & Branz, H.M. 2009, "Phase evolution in nanocrystalline silicon films: Hydrogen dilution and the cone kinetics model," *Phil. Magazine*, Vol. 89, pp. 2461–2468.
- [13] Yan, B. et al. 2004, "Hydrogen dilution profiling for hydrogenated microcrystalline silicon solar cells,"

Appl. Phys. Lett., Vol. 85, p. 1925.

- [14] Guha, S., Yang, C.C. & Yan, B. 2011, "Method for depositing high-quality microcrystalline semiconductor materials," US Patent 7902049 B2.
- [15] Su, T. et al. 2010, "Effects of grain boundaries on performance of hydrogenated nanocrystalline silicon solar cells," *Mat. Res. Soc. Symp. Proc.*, Vol. 1245, p. 113.
- [16] Kiriluk, K.G. et al. 2010, "A SAXS study of hydrogenated nanocrystalline silicon thin film," *Mat. Res. Soc. Symp. Proc.*, Vol. 1245, p. 271.
- [17] Hugger, P.G. et al. 2008, "Properties of light-induced degradation and the electronic properties of nanocrystalline silicon solar cells grown under functionally graded hydrogen dilutions," *J. Non-Cryst. Sol.*, Vol. 354, p. 2460.
- [18] Hugger, P.G. et al. 2009, "Insights and challenges toward understanding the electronic properties of hydrogenated nanocrystalline silicon," *Phil. Magazine*, Vol. 69, p. 2541.
- [19] Hugger, P.G. et al. 2010, "Relationship of deep defects to oxygen and hydrogen content in nanocrystalline silicon photovoltaic materials," *Appl. Phys. Lett.*, Vol. 97, p. 252103.
- [20] Guha, S., Yang, J. & Yan, B. 2011, "Amorphous and nanocrystalline silicon solar cells and modules," in Bhattacharya, P., Fornari, R. & Kamimura, H. (eds), *Comprehensive Semiconductor Science and Technology*, Vol. 6, Amsterdam, Elsevier, pp. 308–352.
- [21] Guha, S. & Yang, J. 2010, "Thin film silicon photovoltaic technology – from innovation to commercialization," *Mat. Res. Soc. Symp. Proc.*, Vol. 1245, p. 3.

About the Authors



Subhendu Guha is chairman emeritus of United Solar Ovonic, the world's largest manufacturer of flexible solar laminates. An international authority in the science and technology of thin-film silicon-alloy solar cells, Dr. Guha has received much recognition for his work, including the World Technology Award in the Energy category in 2005 and the PVSEC Award in 2009 for outstanding contribution to the science and technology of photovoltaics.



David Cohen is a professor at the University of Oregon. He received his Ph.D. degree from Princeton in 1976, and his interest in disordered semiconductors

relevant to photovoltaic technology began 32 years ago while at Bell Labs. Professor Cohen joined the University of Oregon in 1981, where he has been pioneering new experimental methods for characterizing the defect physics of amorphous semiconductors.



Eric A. Schiff is a professor at Syracuse University and has been researching solar cells and thin-film semiconductors for 25 years. He has published more than 100 papers and has been granted several patents. Professor Schiff has a Ph.D. in semiconductor physics from Cornell University.



Paul Stradins is a scientist at the NREL. He has made key contributions in understanding light-induced defect creation and electronic transport in a-Si:H, in particular the Staebler-Wronski effect (SWE) at liquid helium temperatures, as well as the cone kinetics growth model and suppression of SWE in mixed-phase a-Si:H/nc-Si:H.



P. Craig Taylor is a Professor at the Colorado School of Mines and Director of Renewable Energy Materials Research Science and Engineering Center. He received the Ph.D. degree from Brown University in 1969, and was employed at the Naval Research laboratory from 1969 to 1982, after which he joined the Physics Department at the University of Utah. Professor Taylor is a Fellow of the American Physical Society.



Jeffrey Yang is the Senior VP of Technology at United Solar Ovonic. He has worked in the thin-film silicon photovoltaics field for more than 30 years, and published more than 250 papers. Dr. Yang has co-organized IEEE Photovoltaic Specialist Conferences and Materials Research Society symposia and workshops.

Enquiries

Subhendu Guha
United Solar Ovonic LLC
3800 Lapeer Road
Auburn Hills
Michigan 48326
USA
Email: sguha@uni-solar.com
Website: <http://www.uni-solar.com>