Low Cost Thin Film Building-Integrated PV Systems

Cooperative Research and Development Final Report

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NREL Technical Contact: Pauls Stradins

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Cooperative Research and Development Final Report

In accordance with Requirements set forth in Article XI.A(3) of the CRADA document, this document is the final CRADA report, including a list of Subject Inventions, to be forwarded to the Office of Science and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

CRADA number: **CRD-07-239**

CRADA Title: **Low Cost Thin Film Building-Integrated PV Systems**

Parties to the Agreement: **United Solar Ovonic, LLC**

Joint Work Statement Funding Table showing DOE commitment:

Estimated Costs	**NREL** Shared Resources
Year 1	$150,000
Year 2	$150,000
Year 3	$150,000
TOTALS	$450,000

Abstract of CRADA work:

NREL's UniSolar SAI CRADA team concentrated on studying and controlling hydrogen bonding environments and network micro- and nanostructure as key for improved performance and stability both in nanocrystalline and amorphous hydrogenated silicon cell absorber materials. Precision hydrogen effusion mass- spectroscopy, vibrational spectroscopy, electron spin and proton nuclear magnetic resonance experiments were carried out to characterize H bonding environments and their change with controlled thermal treatments. Specific H bonding structures clearly correlate with device performance for nc-Si:H, and with absorber layer stability against light-induced degradation by Staebler-Wronski effect.

In this CRADA, NREL's Silicon group members performed the following research activities: 1) investigation of the role of hydrogen in growth of a mixed-phase nc-Si:H/a-Si:H material; 2) role of hydrogen in light-induced degradation of a-Si:H and development of Staebler-Wronski effect resistive a-Si:H; and 3) performing characterizations of UniSolar's a-Si:H and nc-Si materials, with goal to help optimizing large-area uniformity and quality of the UniSolar's nanocrystalline Si:H.

Summary of Research Results:

Our research activities resulted in the following achievements:

1. **Nanocrystalline and mixed-phase Si:H growth morphology and grain passivation.** We developed the "cone kinetics" model that explains the crystalline-amorphous mixed phase growth kinetics and morphology. Previous work have shown that nanocrystalline phase incorporates into a-Si:H as cones (each composed of smaller subgrains) with vortices at the initial growth interface . These composite cones result from the nanocrystalline phase growing faster than amorphous phase, as shown by the "cone kinetics model" developed at NREL as part of this CRADA [1]. The excess growth rate of the nanocrystalline phase relative to amorphous and therefore, the cone formation and growth, decreases with hydrogen dilution and ceases at the amorphous-nanocrystalline transition. Increasing hydrogen dilution up from the amorphous-nanocrystalline transition results in different grain morphologies, see Fig. 1.

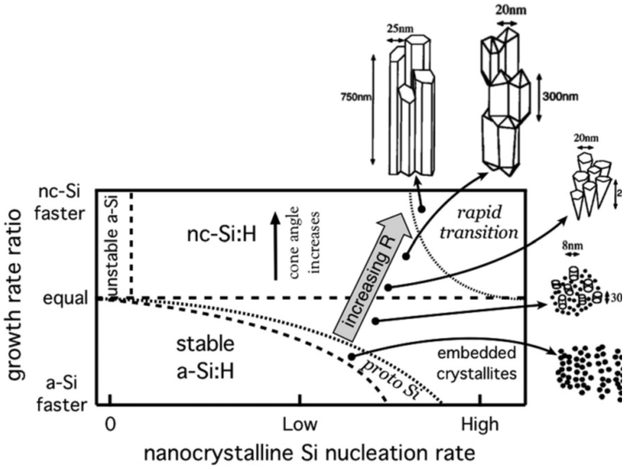

Figure 1. Schematic phase diagram for two-phase growth of silicon films on amorphous substrates. Thin arrows point from approximate locations (solid dots) of various morphologies to sketches of crystallite morphologies observed by Vallat-Sauvain et al. Increased H-dilution (R) during deposition increases both the nc-Si:H nucleation rate and the relative nc-Si:H growth rate, as indicated by the arrow labeled 'increasing R'. From Ref. [1].

To understand the role of hydrogen bonding in nc-Si grain passivation in mixed phase material, we made hydrogen effusion mass-spectroscopy measurements on a series of UniSolar's nanocrystalline Si:H cells with different degree of crystallinity and H-content [2]. Fig. 1 shows corresponding H-effusion time profile taken at a fixed temperature-time ramping rate, the area under the curves representing H content. Samples A and C were grown under conditions where the crystallinity 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 H content, since most of the H resides in the amorphous phase. Importantly, however, low-crystallinity cells show strong low-T H effusion peaks at 400C signifying that the nc-Si grain boundaries are well passivated by hydrogen. Indeed, these cells A and C show significantly better performance: higher open-circuit voltages by 80 mV, and higher efficiencies by absolute 2.5%. Thus, the low-T H effusion peak serves as good metric for cell absorber optimization.

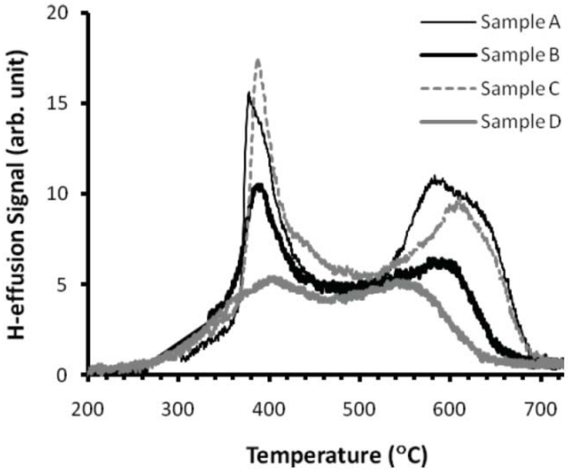

Fig.2. Hydrogen effusion time profiles for four different nc-Si:H solar cells. Samples A and C have low crystalline volume fraction while B and C are highly crystalline (Ref. [2]).

2. Reducing Staebler-Wronski effect in a-Si:H. Hydrogen is considered to be strongly related to the cause of the Staebler-Wronski effect in a-Si:H, however it's detailed role has not been revealed [3]. In our recent experiments, we intentionally manipulated the H bonding environments by controlled, post-deposition thermal treatments [3] in device-quality a-Si:H. Just at the onset of H effusion between 350 °C and 400 °C, those treatments result in remarkable suppression of SWE: the total Si dangling bond defect concentration is 2x lower in treated sample after prolonged degradation by laser pulses, while the light-induced defects alone were suppressed by factor of five [3,4] (see Fig.2).

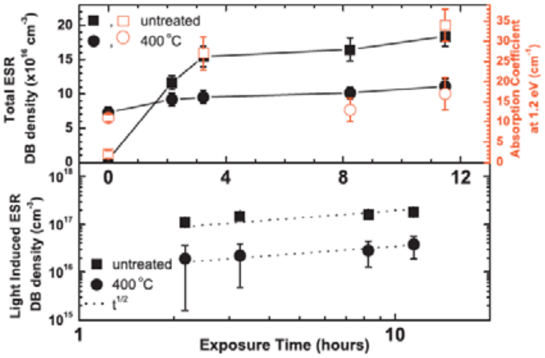

Fig. 2. Top panel: Total Si dangling bond defect spin density (solid symbols) and defect absorption (open symbols) in as-deposited (squares) and 400C treated a-Si:H (circles) as function of laser light exposure time. Bottom: the accumulation of light-induced only defect spins (Ref. [3]).

Proton NMR line narrows as a result of the thermal post-deposition treatments [4], indicating that hydrogen becomes less clustered in the nanovoids. This, together with small-angle X-ray scattering (SAXS) literature data [S. Acco et al., *Phys. Rev. B* 58, 12853 - 12864 (1998)], suggests that changes in H bonding and in Si network nanostructure are responsible for the reduced SWE. In particular, atomic-size void coalescence, accompanied by restructuring of the inner surfaces of resulting larger nanovoids might be responsible. Eliminating the atomic-size hydrogenated voids seems to strongly reduce SWE. The post-deposition annealing treatments, while still challenging to implement into devices, show a clear proof of concept for a SWE-free a-Si:H and reveal a critical metric (hydrogenated void nanostructure) to eliminate the SWE.

3. In addition, NREL team performed numerous **characterizations** of UniSolar's samples that helped them to optimize the deposition techniques and material quality: optically mapping the thickness of their large-area VHF thin-film Si and demonstrating that the thickness variations conform to the tight stage-gate specifications; cross-sectional TEM of H-dilution profile samples from UniSolar; Raman spectroscopy; and optical and defect spectroscopies by photothermal deflection and ESR in mixed-phase and a-Si:H as described above. The H-effusion experiments (above) were particularly useful in correlating the strong low-T H effusion peak with enhanced cell performance and higher resistance to oxidation.

REFERENCES – journal publications resulting from this CRADA

1. P. Stradins, C.W. Teplin, H.M. Branz, "Phase evolution in nanocrystalline silicon films: Hydrogen dilution and the cone kinetics model", Philosophical Magazine,99999:1 (2009)].
2. T. Su, D.C. Bobela, X. Xu, S. Ehlert, D. Beglau, G. Yue, B. Yan, A. Banerjee, J. Yang, S. Guha, "Effects of grain boundaries on performance of hydrogenated nanocrystalline silicon solar cells", *Mat. Res. Soc. Symp. Proc*. 1245 1245-A07-01, pp. 113 - 118 (2011)
3. D.C. Bobela, H.M. Branz, P. Stradins, "Anneal treatment to reduce the creation rate of light-induced metastable defects in device-quality hydrogenated amorphous silicon", *Appl. Phys. Lett*. 98, 201908 doi:10.1063/1.3592264 (2011), and references therein.
4. P. Stradins, D.C. Bobela, H.M. Branz, "Reduced light-induced degradation in a-Si:H: the role of network nanostructure", IEEE PVSC Meeting 2011, to be published in IEEE Journal of Photovoltaics.

Subject Inventions listing:

No inventions resulted from this CRADA.

Report Date: 9/22/2011

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