

# **Porous Polycrystalline Silicon Thin Film Solar Cells**

**Final Report**  
**24 May 1999–24 May 2002**

P. Fauchet  
*University of Rochester*  
*Rochester, New York*



**NREL**

**National Renewable Energy Laboratory**

1617 Cole Boulevard  
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory  
Operated by Midwest Research Institute • Battelle • Bechtel

Contract No. DE-AC36-99-GO10337

# **Porous Polycrystalline Silicon Thin Film Solar Cells**

**Final Report**  
**24 May 1999–24 May 2002**

**P. Fauchet**  
*University of Rochester*  
*Rochester, New York*

NREL Technical Monitor: R. Matson

Prepared under Subcontract No. AAD-9-18668-06



**NREL**

**National Renewable Energy Laboratory**

1617 Cole Boulevard  
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory  
Operated by Midwest Research Institute • Battelle • Bechtel

Contract No. DE-AC36-99-GO10337

This publication was reproduced from the best available copy  
Submitted by the subcontractor and received no editorial review at NREL

### NOTICE

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at <http://www.osti.gov/bridge>

Available for a processing fee to U.S. Department of Energy  
and its contractors, in paper, from:

U.S. Department of Energy  
Office of Scientific and Technical Information  
P.O. Box 62  
Oak Ridge, TN 37831-0062  
phone: 865.576.8401  
fax: 865.576.5728  
email: [reports@adonis.osti.gov](mailto:reports@adonis.osti.gov)

Available for sale to the public, in paper, from:

U.S. Department of Commerce  
National Technical Information Service  
5285 Port Royal Road  
Springfield, VA 22161  
phone: 800.553.6847  
fax: 703.605.6900  
email: [orders@ntis.fedworld.gov](mailto:orders@ntis.fedworld.gov)  
online ordering: <http://www.ntis.gov/ordering.htm>



Printed on paper containing at least 50% wastepaper, including 20% postconsumer waste

## Table of Contents

Statement of Purpose .....	1
Evolution of the Project Goals .....	1
Core Concept – Electrochemical Etching of Silicon .....	2
Graded Refractive Index Coatings .....	3
Major Accomplishments of This Project .....	5
1) Simulation .....	5
2) Graded Index Etching Technique on P-Type Silicon Wafers .....	7
3) Evergreen Solar Collaboration .....	9
4) EBARA Solar Collaboration .....	11
5) Characterization Assistance from NREL .....	12
Conclusions and Future Prospects for PSi Technology .....	12
References .....	13
Appendix: List of Publications .....	15
Journal Publications .....	15
Conference Presentations and Papers .....	15

## List of Figures

Figure 1. The electrochemical etching mechanism in silicon .....	3
Figure 2. Four basic spatial refractive index profiles of thickness $d$ .....	4
Figure 3. Simulated reflectivity of 0% -100% porosity gradients with various thicknesses .....	6
Figure 4. Simulated reflectivity spectra of a complete and a partially graded PSi film of 100 nm thickness .....	6
Figure 5. Total transmission through the first 110 nm of silicon in solar cells with a PSi and a silicon nitride ARC .....	7
Figure 6. Reflectivity comparison of a 100 nm gradient index PSi film and an 80 nm homogeneous 75% porosity film formed on a polished $p^+$ Si wafer .....	9
Figure 7. Substantial reflectivity reduction was achieved on a multicrystalline solar cell substrate after a dynamic PSi etching procedure .....	9
Figure 8. Light IV curves for a string ribbon solar cell with and without a graded index PSi ARC .....	10
Figure 9. A refractive index profile determined using spectroscopic ellipsometry (500 nm excitation) is plotted next to a cross-sectional SEM image of the corresponding PSi film .....	11

# Porous Polycrystalline Silicon Thin Film Solar Cells

## **Statement of Purpose**

Crystalline (including multicrystalline) silicon based devices dominate the present solar cell industry due to their durability, their relatively low cost, and the vast silicon knowledge base developed by the microelectronics industry. However, the high refractive index of crystalline silicon at solar wavelengths (approximately 3.5) creates large reflection losses that must be compensated for by applying antireflective (AR) coatings. Although highly efficient double and triple layer AR coatings are available, most manufactured crystalline silicon photovoltaics employ simple and inexpensive single layer AR coatings, with relatively poor AR properties. This project has focused on the development of a simple and low cost alternative to these deposited AR coatings, using an electrochemical etching technique to form AR layers of porous silicon (PSi).

## **Evolution of the project goals**

The initial focus of this project was to build on previous work performed in our group and investigate the use of PSi as an active material in a solar cell to take advantage of potential bandgap tuning, light trapping, and blue-harvesting photoluminescence effects. However, through our work on various substrate materials we have found that the electrical characteristics of thick (several microns) PSi layers needed for active devices are extremely sensitive to the substrate doping profiles and crystalline morphology. This sensitivity makes reproducibility difficult even in a well-controlled research environment, and therefore prospects for commercial thick-film PSi devices are limited.

We have now focused our investigation on the use of thin PSi layers for AR coating applications. By isolating these layers in the heavily doped surface region of a solar cell, the electrical properties of the p-n junction are relatively unaffected. Provided that good electrical contacts can be made to the material under the porous layer, the electrical properties of the PSi film are not critical, and only the optical properties need to be optimized.

## **Core concept – electrochemical etching of silicon**

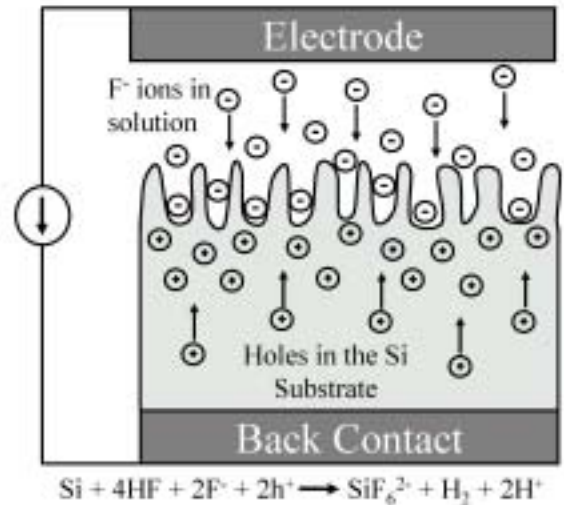
PSi has been widely studied since the early 1990's, due primarily to interest in its development as an efficient light emitting material for optoelectronic applications [1], but had been applied to solar cell research as early as 1982 [2]. The light trapping and anti-reflection properties of PSi, in addition to its simplicity of formation and broadly tunable morphology, make it particularly well suited for photovoltaic applications. It has been used as single or multilayer antireflective coatings (ARCs) by exploiting the tunability of the film's effective index of refraction [3,4]. Demonstrated reflectivities tend to average between 10%-15% over the spectral range 350 nm - 1000 nm, but average reflectivities as low as 2% have been shown with graded index layers [5]. Improvements of 50% in  $I_{SC}$  have also been demonstrated while maintaining fill factor and  $V_{OC}$  [6].

PSi results from the electrochemical dissolution of a silicon substrate in the presence of a hydrofluoric acid (HF) electrolyte and positive charge carriers (holes). Randomly formed pits in the surface form pores that propagate into the substrate when the dissolution reaction is favored at the pore tips. As illustrated in figure 1, this condition exists when current is passed through the electrochemical cell, where holes propagating toward the substrate surface first encounter fluorine ions at the pore tips. If all holes are consumed at the pore tips, the upper porous matrix is protected from dissolution, and a stable PSi layer can be formed [7]. The porosity (percentage of empty space) of the PSi formed at the pore tips is proportional to the current density through the cell at that time. Since the porosity at a given depth is controlled by the electrochemical current density, dynamic control of the current during the etch can produce porosity gradients or alternating layers of varying porosity within the film [8]. Porosity changes correspond to changes in the effective refractive index through the Looyenga effective medium approximation [9], and therefore the engineering of porous layers with desirable optical properties can be achieved.

The morphology of the PSi matrix that remains after electrochemical etching is not only dependent on current density and substrate doping, but is also affected by the HF electrolyte concentration, the duration of the etch, temperature, and ambient lighting conditions. Within this large parameter space, the resulting structure can have feature sizes that vary over a wide range, from nanometers to microns, depending on the nature of the etch. From the physical optics viewpoint, structures with sizes larger than the wavelength of incoming light enhance light trapping by reflecting incoming radiation in random directions [10]. Structures much smaller than the incoming wavelength alter the effective refractive index of the film and allow it to be tuned between that of crystalline silicon (c-Si) and air [9]. Direct control of the effective refractive index depth profile using the etching current density provides an excellent opportunity to form graded index ARCs with properties superior to discrete layer coatings [11]. Graded-index ARCs can eliminate or limit the large discontinuity in index of refraction at solar cell surfaces that is responsible for reflection losses. As mentioned earlier, wide bandwidth graded-index PSi ARCs with extremely low reflectivity have been demonstrated [5].

### Graded refractive index coatings

Refractive index gradients in the direction of light propagation have been theoretically studied for more than 100 years [12]. Physical implementation of this concept for AR applications has also been investigated based on the evaporation of very thin ( $\ll \lambda$ ) alternating high/low index films that create an effective index gradient by varying the thickness ratios in these stacks [11,13]. Chemical dissolution of glass optical elements to produce a porous surface layer with

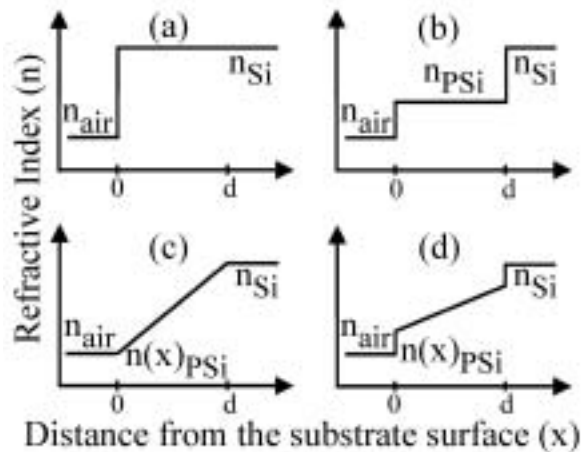


**Figure 1.** The electrochemical etching mechanism in silicon. Holes drifting toward the substrate surface drive the electrochemical process that forms porous silicon. These holes are most likely to react with fluorine ions at the bottoms of pores or pits, deepening these features and creating a porous surface film.

broadband AR properties has also been demonstrated and simulated based on gradient index properties [14] and exhibit the durability necessary for commercial applications [15].

In past PSi studies, porosity gradients are mentioned primarily as artifacts in standard constant current etching [16], as a characterization tool for spectroscopic ellipsometry studies [17], and for rugate filter applications [18]. For silicon solar cells, one group has formed gradient index of refraction ARCs by gradually changing the porosity of discrete layers in a 20-layer stack. Although excellent broadband reflectivity <3% in the visible spectrum has been achieved, the overall thickness of these stacks (>1 micron) would considerably degrade the electrical characteristics of a solar cell [5].

As stated previously, the relatively high reflectivity of a silicon solar cell in the 350 nm – 1000 nm spectral range is due to the large refractive index discontinuity that exists at the air-silicon interface (figure 2a). By placing a single layer ARC of intermediate refractive index on the silicon surface, this large index discontinuity is broken into two smaller steps (figure 2b), resulting in a lower broadband reflectivity. Very low narrowband reflectivity can also be achieved by exploiting the interference of light reflected from the two interfaces. Further



**Figure 2.** Four basic spatial refractive index profiles of thickness  $d$ .  
 (a) No AR film  
 (b) Standard single layer AR film (or constant current PSi etching)  
 (c) Theoretical 100% linear graded film ( $n(x)$  is arbitrary)  
 (d) PSi film with a partial gradient

reduction in broadband reflectivity can be achieved by adding additional intermediate index layers, thus breaking the air-silicon index discontinuity into smaller and smaller steps. Therefore, a gradient index ARC is the limit of this progression, where a single index discontinuity is replaced by a continuous transition from a low to a high index material (figure 2c). If this continuous index transition occurs over several wavelengths of optical path length, broadband reflectivity approaching zero can be achieved [12]. However, such films would be far too thick for practical solar cell applications.

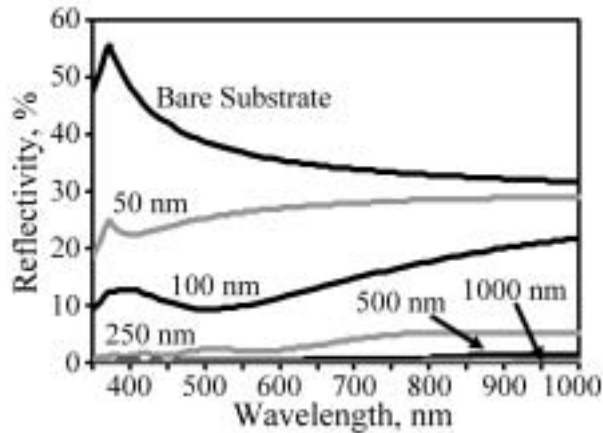


This present work has focused on PSi layers of  $\sim 100$  nm thickness that would minimally affect the electrical characteristics of a typical industrial solar cell with a 300 nm junction depth. From our simulation, we have determined that for PSi layers of this thickness, the optimal solution combines a refractive index gradient with small discontinuities at both interfaces as shown in figure 2(d). This design incorporates a smaller magnitude index gradient that can be effective over shorter length scales and small discontinuities that can be optimized to create a region of destructive interference in the center of the broadband solar spectrum. In our dynamic etching procedure, this type of index profile is formed by initially applying a high current density (high porosity) to the cell and decreasing the current density (lowering porosity) to zero over the duration of the etch. These films are thin enough to be formed on silicon solar cells after emitter diffusion with minimal electrical degradation and offer superior AR characteristics relative to current commercially deposited ARCs.

## **Major accomplishments of this project:**

### **1) Simulation**

Although exact solutions to the problem of light propagation in a stratified medium (gradient index in the direction of propagation) exist, they are only available for a small number of specifically engineered gradient profiles [12]. Therefore, in our simulation, we slice arbitrary continuous profiles into many discrete homogenous layers, to approximate the index profile of interest. If the individual layer thicknesses are  $\ll \lambda$ , the simulated film stack converges to the solution of the original continuous index profile. The reflectivity of thin film stacks can be easily calculated by multiplying the characteristic matrix of each layer with that of each adjacent layer until the resulting matrix, representing the characteristics of the entire stack, is obtained [19]. The reflectivity is then directly calculated from the elements of this resultant characteristic matrix. Our simulation calculates film reflectivity based on a specified spatial porosity profile and accounts for the dispersion of the silicon refractive index in the visible spectrum [20]. Absorption of light (at each wavelength) in the PSi film is also factored into the calculation. Using this technique, the characteristics of films with various thicknesses, porosity profiles, and interface discontinuities were investigated.

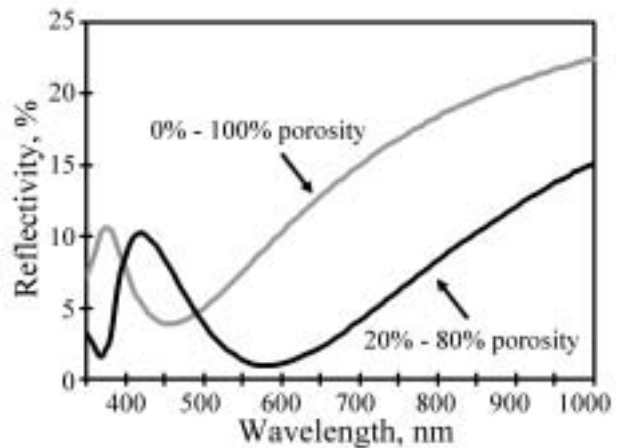


**Figure 3.** Simulated reflectivity of 0% -100% porosity gradients with various thicknesses. The more gradually the porosity changes, the lower the broadband reflectivity.

Using this simulation, the general behavior of graded refractive index films was demonstrated and an optimal thin film index profile (critical for P*Si* photovoltaic applications) was developed. Figure 3 illustrates the simulated reflectivity of P*Si* films with a linear porosity gradient from 100% at the air interface to 0% at the substrate. This complete porosity gradient corresponds to a refractive index profile that makes a continuous transition from 1.0 (air) to ~3.5 (silicon). The graphed data clearly demonstrates a continuous improvement in AR properties as film thickness increases. Thus, as film thickness becomes  $\gg \lambda$ , broadband reflectivity can be almost completely suppressed as predicted by theory [12].

However, P*Si* films approaching 1 micron in thickness would consume the junction of most commercial solar cells during the etch, greatly degrading performance. For practical application in silicon solar cell manufacturing, a much thinner solution had to be found. This thickness constraint led to the discovery that small refractive index discontinuities at each interface will result in lower reflectivity for 100 nm films. A plot of this effect is shown in figure 4, where an 80% - 20% gradient outperforms a 100% - 0% gradient. Although several concepts contribute to this observation, the introduction of two-interface interference effects is the primary factor in this lowered

However, P*Si* films approaching 1 micron in thickness would consume the junction of most commercial solar cells during the etch, greatly degrading performance. For practical application in silicon solar cell manufacturing, a much thinner solution had to be found. This thickness constraint led to the discovery that small refractive index discontinuities at each interface will result in lower reflectivity for 100 nm films. A plot of this effect is shown in figure 4, where an 80% - 20% gradient outperforms a 100% - 0% gradient. Although several concepts contribute to this observation, the introduction of two-interface interference effects is the primary factor in this lowered

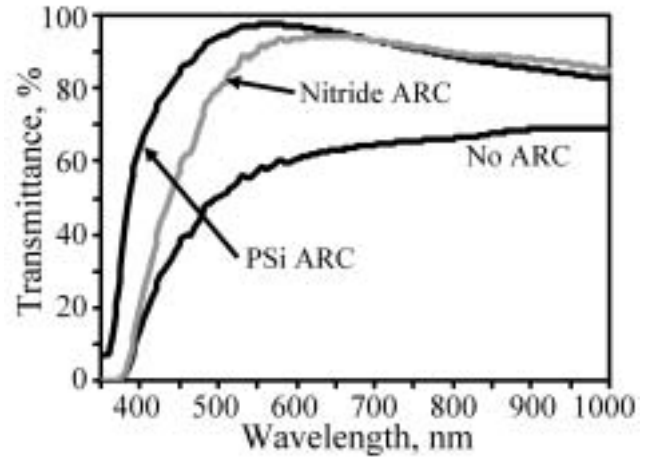


**Figure 4.** Simulated reflectivity spectra of a complete and a partially graded P*Si* film of 100 nm thickness. The broadband reflectivity of the partially graded film is substantially lower across the solar spectrum. At this film thickness, a graded index alone is less effective than a combined graded index-interference coating design.

reflectivity. Therefore this structure combines the features of gradient index and interference coatings to produce a high performance AR coating. This discovery has led to the development of efficient thin film PSi graded index AR films during this project.

Another issue explored using this simulation is the surface absorption loss in cells with silicon nitride and PSi ARCs. This loss is considerable lower in devices with PSi films due to the nature of the etching process. Unlike deposited films, PSi AR technology consumes a portion of the surface material, converting it to a less absorbing material.

Most commercial silicon solar cells have a diffused top junction and as a result of the diffusion process have a thin surface region with extremely high dopant (and defect) concentration. This surface region is not part of the space charge (active) region of the cell, and therefore any light absorbed near the surface is not converted into electrical energy, lowering the efficiency. However, by converting the surface region into a PSi ARC, this absorption loss is greatly reduced and AR benefits are also achieved. Figure 5 illustrates this point by simulating the transmission of light through the first 110 nm of a cell. The reduced surface absorption and enhanced AR properties greatly improve the transmission in the PSi covered cell. The transmission of a bare silicon substrate is also shown. This reduced surface absorption may prove to be the greatest benefit of PSi AR technology as the maximum efficiency limits for nitride coated cells is approached.



**Figure 5.** Total transmission through the first 110 nm of silicon in solar cells with a PSi and a silicon nitride ARC. The substantial improvement in blue response for the PSi coated sample is due to the conversion of the upper layer of silicon to PSi during the etch. PSi exhibits substantially lower absorption than silicon in this spectral range and therefore allows more light to pass through to the underlying junction. The transmittance of a bare substrate is also shown.

## 2) Graded index etching technique on p-type silicon wafers

Based on past experience within our group, heavily doped (0.01 ohm-cm) p-type silicon wafer substrates were used for the first proof of principle experiments with graded porosity etching.

Such substrates have been previously etched to form PSi with a broad porosity range [8,10] and offer consistent material properties from sample to sample. The extremely planar surface of silicon wafers also enables the formation of optical quality PSi films that can be directly compared to simulation results.

A computer controlled etching system was first designed that would be capable of applying a continuously changing current to the electrochemical etching cell. The input parameters consisted of the initial current density, the duration of the etch, and the mathematical function followed by the current density throughout the etch. The current functions were kept fairly simple, starting at the specified initial current value and continuously decreasing to zero following cosine or power law dependencies. Such functions would therefore form PSi films with high porosity (high current) near the surface and lower porosity near the substrate interface. This type of PSi etching has been termed “dynamic etching” by our group.

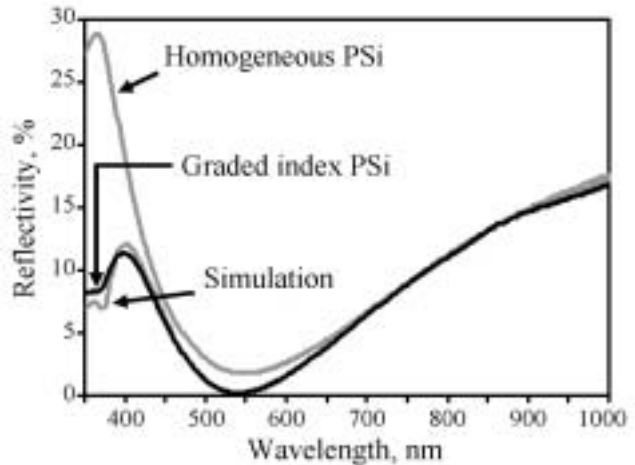
After completion of the dynamic etching setup, a large set of experiments was designed to gain an understanding of how the current function parameters influence the characteristics of PSi films. Because many variables affect the PSi properties, we first decided to etch all samples in the dark to eliminate ambient lighting as a potential variable. After testing several different solution concentrations, it was determined that a 1:2 (HF:ethanol) mixture yielded the most uniform and repeatable films over a wide range of current densities.

The remaining parameters involve the dynamics of the etch itself and were optimized by preparing a matrix of samples in which the initial current density, the etching time, and the current function were variables. The reflectivity of all samples was measured, and SEM images were taken of a critical subset of samples. This optimization focused on minimizing film reflectivity over the spectral range 350 nm to 1000 nm while maintaining thicknesses of ~100 nm. The lowest average reflectivity in this experiment was 8.1% compared to 41.2% for a bare wafer. This result was for a PSi film etched for 5 seconds with an initial current density of 100 mA/cm<sup>2</sup> with a parabolic ( $I(t) \sim (t-t_0)^2$ ) time dependence, where  $t_0$  is the duration of the etch. The measured and simulated reflectivity spectra of this film is plotted in figure 6. Also plotted is the measured reflectivity of a homogeneous (constant refractive index) PSi film. The simulation

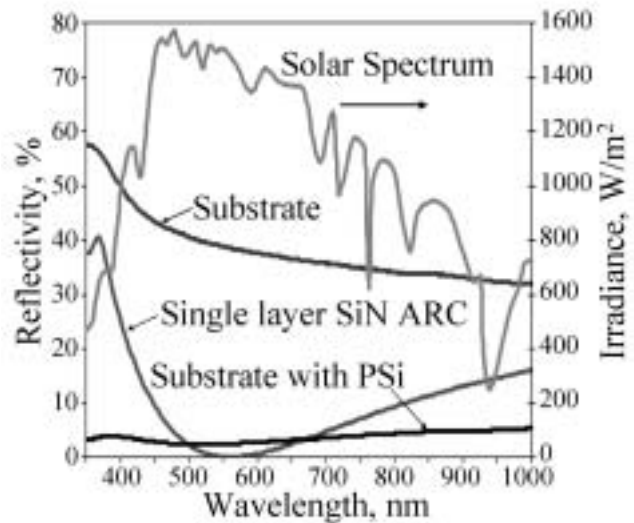
closely matches the experimental spectra and indicates that the porosity varies from 94% to 33%. A film thickness of 100 nm was determined from the simulation and was confirmed by SEM images. In comparison to a homogeneous PSi film, the graded index sample exhibits substantially lower reflectivity in the blue portion of the spectrum.

### 3) Evergreen Solar collaboration

Through a collaboration with Evergreen Solar (initiated through a discussion at an NCPV program review meeting), our group was provided with non-metallized string ribbon multicrystalline silicon solar cell substrates. The goal of this collaboration was to apply our PSi AR technology to commercial cells. Our experiments using silicon wafer substrates demonstrated the potential advantages of graded index films, however because this process is substrate dependent, a study of film properties on working cells was necessary. String ribbon is an inexpensive, thin (~200 microns) multicrystalline silicon substrate material formed directly from a silicon melt [21]. The surface of these substrates have some intrinsic roughening due to crystalline defects and grain boundaries, and are doped with a phosphosilicate glass diffusion process. As a low-cost process, PSi ARC etching is particularly well suited for this type of low cost multicrystalline silicon substrate.



**Figure 6.** Reflectivity comparison of a 100 nm gradient index PSi film and an 80 nm homogeneous 75% porosity film formed on a polished p+ Si wafer. A simulated layer with a porosity gradient from 94% to 33% shows excellent agreement with the measured reflectivity.

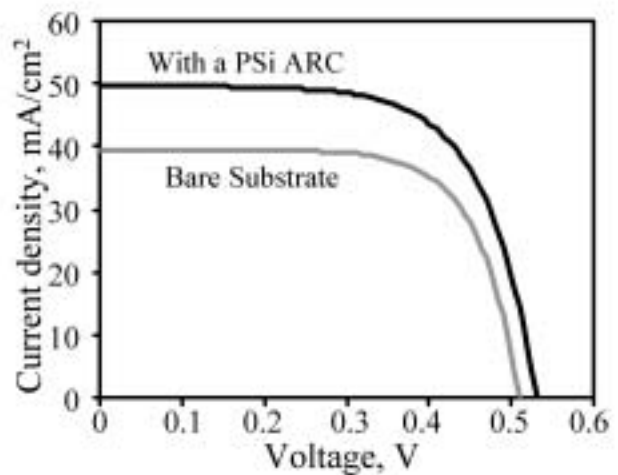


**Figure 7.** Substantial reflectivity reduction was achieved on a multicrystalline solar cell substrate after a dynamic PSi etching procedure. The PSi film thickness was 107 nm determined through SEM cross-sectional analysis. The reflectivity of a standard silicon nitride ARC and the terrestrial solar power spectrum are plotted for reference.

Several test etches determined that uniform PSi films can be formed on these substrates using the same process used on the wafer substrates. A similar optimization process determined that the same etching conditions could be used, but a longer (7 seconds) etch duration achieved the lowest reflectivity. Figure 7 shows the reflectivity of an optimized graded index PSi film relative to a bare string ribbon substrate and an evaporated silicon nitride. The terrestrial AM1.5 solar spectrum is also plotted for reference. The PSi film had an average reflectivity of 3.7% across this spectral range, compared to 10.1% for the silicon nitride ARC and 38.1% for the bare string ribbon substrate.

The reflectivity of graded index PSi films on string ribbon substrates is considerably lower than that obtained on the initial experiments on silicon wafer substrates. This result was expected because the reflectivity of the bare string ribbon substrates is lower than that of a silicon wafer due to its intrinsic surface structure. The surface structure and the dopant profile will also affect the resulting PSi films because the etch is sensitive to these material properties.

After demonstrating the low reflectivity of these films, the electrical properties were examined to determine whether any degradation in the p-n junction characteristics resulted from the etching process. As illustrated by the light IV data in figure 8, both the short circuit current and the open circuit voltage of our test cell improved while maintaining the fill factor. This indicates that that etching of a thin (~100 nm) PSi films minimally affects the properties of the underlying junction material. Thicker films did exhibit degradation in the light I-V curves, stressing the need for a thin film solution.

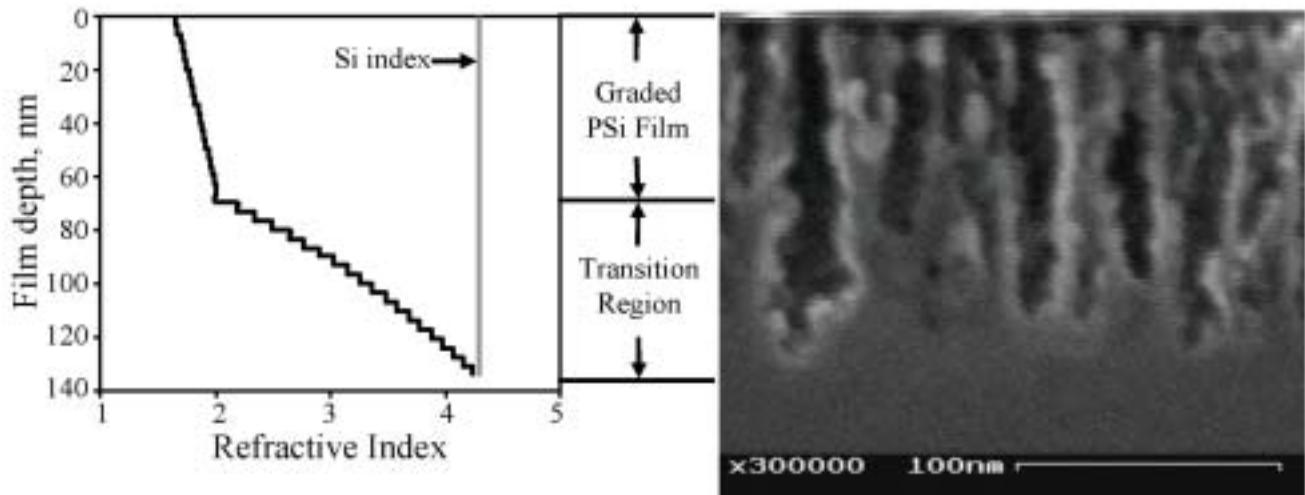


**Figure 8.** Light IV curves for a string ribbon solar cell with and without a graded index PSi ARC. Improvements in both the short circuit current density and the open circuit voltage were achieved by incorporating a PSi ARC.

#### 4) EBARA Solar collaboration

Dendritic web multicrystalline silicon from EBARA Solar was also investigated for compatibility with the dynamic PSi etching treatment. This is another type of inexpensive thin (~ 100 microns) multicrystalline substrate formed directly from a silicon melt [22]. However, the appearance and material properties of these substrates are substantially different than string ribbon silicon. Dendritic web silicon has a very smooth surface with little roughening and all crystal grains exhibit a preferential (111) orientation. The EBARA cells also have a rear junction and the bulk of the cell material is n-type. EBARA Solar provided us with non-metallized sample cells to determine the effectiveness of the dynamic etching procedure on their substrates.

These substrates were easily etched, but finding optimal etching conditions proved difficult because a 1:2 (HF:ethanol) solution did not produce low reflectivity films. Several other solutions were tried and a 1:1 (HF:ethanol) mixture yielded the best results. Unfortunately, we ran out of substrates before the current conditions could be completely optimized. The best films had an average reflectivity of 12%-15%, however we are confident that additional experiments could greatly improve upon these results.



**Figure 9.** A refractive index profile determined using spectroscopic ellipsometry (500 nm excitation) is plotted next to a cross-sectional SEM image of the corresponding PSi film. The two distinct regions of this profile may indicate that a transition region exists, where individual pores terminate at different depths, creating a large index gradient at the PSi-Si interface. The general morphology of a graded porosity film can also be observed in the SEM image.

## **5) Characterization assistance from NREL**

Several samples were tested at the NREL characterization laboratory to gain additional information about the material properties of the PSi films and substrates. Secondary Ion Mass Spectrometry (SIMS) analysis was used to determine the dopant profile in several solar cell substrates and to gain information about the residual elements that remain in the PSi film after etching. Spectroscopic ellipsometry was also employed to obtain the approximate shape of the refractive index gradient that exists in the PSi films. Figure 9 shows an index profile and an SEM cross-sectional image of a typical graded index PSi film. Two distinct regions are visible in the index profile that may correspond to a graded porosity region and a transition region where the porous material mixes with the solid substrate. This transition region also appears more dense relative to the surface region in the SEM image.

## **Conclusions and future prospects for PSi technology**

This project has successfully demonstrated the potential AR performance improvements that could be achieved through the application of graded index PSi technology to commercial multicrystalline silicon solar cells. The advantages of this process include:

- 1) Lower reflectivity than single layer deposited AR films
- 2) Reduced surface absorption relative to cells with deposited AR films
- 3) No vacuum processes or hazardous gasses are necessary
- 4) Film formation in >10 seconds with good repeatability
- 5) PSi etching is relatively independent of crystalline orientation, unlike alkaline texturization that requires (100)-orientated substrates.
- 6) Simultaneous removal of phosphosilicate glass remaining after dopant diffusion
- 7) Potential usage as a substrate cleaning process
- 8) Could be implemented after front side metallization, preventing any disruption of existing manufacturing processes

Future work on PSi AR technology must be conducted in direct partnership with a solar cell manufacturer. Large volume availability of substrates and detailed knowledge of company-specific manufacturing processes are needed for further progress toward the adaptation of this



technology for commercial use. In addition, the ability to customize manufacturing processes like dopant diffusion and screen print metallization would be helpful. A final recommendation would be to experiment with forming PSi after the front surface metal grids are deposited. During this project, all front contacts were formed photolithographically after PSi formation. We believe the PSi layer added series resistance to these contacts, and therefore improved electrical characteristics would be expected if etching followed metallization. Although the photovoltaic community does not consider wet electrochemistry a “standard” process, we believe that substantial efficiency improvements, particularly blue response, can be achieved with minimal investment, if this technology is implemented.

## References

- [1] P.M. Fauchet, *IEEE J. Select. Topics in Quantum Electron.*, **4**, 1020 (1998).
- [2] A. Prasad et al., *J. Electrochem. Soc.*, **129**, 596 (1982).
- [3] S. Strehlke et al., *Mat. Sci. and Eng.*, **B69-70**, 81 (2000).
- [4] A. Krotkus et al., *Solar Energy Materials and Solar Cells*, **45**, 267 (1997).
- [5] S. Uehara, K. Kurose, and T. Matsubara, *Phys. Stat. Sol.*, **182**, 461 (2000).
- [6] P. Vitanov et al., *Thin Solid Films*, **297**, 299 (1997).
- [7] R.L. Smith and S.D. Collins, *J. Appl. Phys.*, **71**, R1 (1992).
- [8] S. Chan and P.M. Fauchet, *Appl. Phys. Lett.*, **75**, 274 (1999).
- [9] W. Theiss, *Surface Science Reports*, **29**, 91 (1997).
- [10] L. Stalmans et al., *Prog. Photovolt. Res. Appl.*, **6**, 233 (1998).
- [11] W.H. Southwell, *Optics Letters*, **8**, 584 (1983).
- [12] R. Jacobsson, in: *Progress in Optics*, vol. 5, Ed. E. Wolf, John Wiley & Sons, New York 1997 (p. 249).
- [13] P.H. Berning, *J. Opt. Soc. Am.* **52**, 231 (1962).
- [14] M.J. Minot, *J. Opt. Soc. Am.* **66**, 515 (1976).
- [15] F.L. Jones and H.J. Homer, *J. Opt. Soc. Am.* **31**, 34 (1941).
- [16] M. Thonissen, M.G. Berber, S. Billat, R. Arens-Fischer, M. Kruger, H. Luth, W. Theiss, S. Hillbrich, P. Grosse, G. Lerondel, U. Frotscher, *Thin Solid Films* **297**, 92 (1997).
- [17] S. Zangoie, R. Jansson, and H. Arwin, *Mat. Res. Soc. Proc.* **557**, 195 (1999).

- [18] M.G. Berger, R. Arens-Fischer, M. Thonisson, M. Kruger, S. Billat, H. Luth, S. Hilbrich, W. Theiss, P. Grosse, *Thin Solid Films* **297**, 237 (1997).
- [19] E. Hecht and A. Zajac, *Optics*, Addison-Wesley, London 1974 (p. 311).
- [20] *Handbook of Optical Constants of Solids*, E.D. Palik, Editor, Harcourt Brace Jovanovich, New York 1985 (p. 561).
- [21] J.I. Hanoka, *Sol. Energy Mat. Sol. Cells* **65**, 231 (2001).
- [22] D.L. Meier, H.P. Davis, R.A. Garcia, J. Salami, A. Rohatgi, A. Ebong, and P. Doshi, *Solar Energy Materials and Solar Cells*, **65**, 621 (2001).

## Appendix: List of Publications

### **Journal Publications:**

C.C. Striemer and P.M. Fauchet, "Dynamic Etching of Silicon for Broadband Antireflection Applications," *Appl. Phys. Lett.*, to be published (October 2002).

C.C. Striemer and P.M. Fauchet, "Dynamic Etching of Silicon for Solar Cell Applications," *Phys. Stat. Sol. A*, to be published (September 2002).

### **Conference Presentations and Papers:**

*Porous Semiconductors Science and Technology Conference – March 2002*

C.C. Striemer and P.M. Fauchet, "Dynamic Etching of Silicon for Solar Cell Applications," *Phys. Stat. Sol. A*, to be published (September 2002).

*National Center for Photovoltaics Program Review Meeting – October 2001*

C.C. Striemer, F. Shi, and P.M. Fauchet, "Electrochemical Etching of Silicon for Inexpensive and Effective ARCs," National Center for Photovoltaics Program Review Meeting, October 2001, Lakewood, CO, pp. 305 (2001).

*11<sup>th</sup> Workshop on Crystalline Silicon Solar Cell Materials and Processes – August 2001*

C.C. Striemer, F. Shi, and P.M. Fauchet, "Rapid ARC Formation Using a Simple and Versatile Etching Process," 11<sup>th</sup> Workshop on Crystalline Silicon Solar Cell Materials and Processes, pp. 194 (2001).

*199<sup>th</sup> Meeting of the Electrochemical Society – March 2001*

C.C. Striemer, F. Shi, and P.M. Fauchet, "Electrochemical Etching of Silicon Substrates for Photovoltaic Applications", *Photovoltaics for the 21st Century II*, edited by R.D. McConnell and V.K. Kapur, Vol. 2001-10, pp. 370 (2001).

*28<sup>th</sup> IEEE Photovoltaic Specialists Conference – September 2000*

C.C. Striemer, F. Shi, P.M. Fauchet, S.P. Duttagupta, "Porous Silicon Texturing of Polysilicon Substrates," 28th IEEE Photovoltaic Specialists Conference, Anchorage, AK, September 2000, pp. 932 (2000).

*National Center for Photovoltaics Program Review Meeting – April 2000*

C.C. Striemer, F. Shi, P.M. Fauchet, "Porous Silicon Texturing of Polysilicon Substrates," National Center for Photovoltaics Program Review Meeting, April 2000, Denver, CO, pg. 169 (2000).

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE October 2003	3. REPORT TYPE AND DATES COVERED Subcontract Report 24 May 1999–24 May 2002		
4. TITLE AND SUBTITLE Porous Polycrystalline Silicon Thin Film Solar Cells: Final Report, 24 May 1999–24 May 2002			5. FUNDING NUMBERS PVP32601 AAD-9-18668-06	
6. AUTHOR(S) P. Fauchet				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Rochester Rochester, New York 14627			8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393			10. SPONSORING/MONITORING AGENCY REPORT NUMBER  NREL/SR-520-34824	
11. SUPPLEMENTARY NOTES NREL Technical Monitor: Richard Matson				
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 ( <i>Maximum 200 words</i> ): The initial focus of this project was to build on previous work performed in our group and investigate the use of porous polycrystalline silicon (Psi) as an active material in a solar cell to take advantage of potential bandgap tuning, light trapping, and blue-harvesting photoluminescence effects. However, through our work on various substrate materials, we have found that the electrical characteristics of thick (several microns) PSi layers needed for active devices are extremely sensitive to the substrate doping profiles and crystalline morphology. This sensitivity makes reproducibility difficult even in a well-controlled research environment, and therefore, prospects for commercial thick-film PSi devices are limited. We have now focused our investigation on the use of thin PSi layers for antireflective coating applications. By isolating these layers in the heavily doped surface region of a solar cell, the electrical properties of the p-n junction are relatively unaffected. Provided that good electrical contacts can be made to the material under the porous layer, the electrical properties of the PSi film are not critical, and only the optical properties need to be optimized.				
14. SUBJECT TERMS: PV; silicon thin films; devices; solar cells; antireflective (AR) coating; electrochemical etching; porous silicon (PSi); photoluminescence; short-circuit current; open-circuit voltage			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	