

# THE EFFECT OF HYDROGEN-PLASMA AND PECVD-NITRIDE DEPOSITION ON BULK AND SURFACE PASSIVATION IN STRING-RIBBON SILICON SOLAR CELLS

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**ABSTRACT:** We have investigated whether an in-situ hydrogen or ammonia rf-plasma treatment prior to a PECVD-nitride deposition would promote bulk defect passivation independently of surface effects. We also studied whether the predeposition of a thin silicon-nitride protective layer before performing the plasma treatment would serve to minimize surface damage. We used five different deposition strategies and compared the resulting cell performance with that of cells processed using the industry-standard TiO<sub>2</sub> ARC. We found that for the limited set of deposition conditions investigated so far, the direct deposition of PECVD-nitride produces the best cells on String Ribbon silicon wafers to date, with efficiencies up to 14.5%. Hydrogen and ammonia plasma pretreatments without a protective nitride layer resulted in better bulk passivation, but damaged surfaces. Pretreatments after deposition of the protective layer produced the best surface passivation, but were not effective in passivating the bulk.

## 1. INTRODUCTION

Evergreen Solar, Inc. is pursuing a unique solar cell design based on the advanced wafer technology called String Ribbon, formerly known as Edge Stabilized Ribbon. This continuous silicon sheet method produces long ribbons of multicrystalline silicon using a simple, robust and inexpensive process [1]. The growth technique has a wide process latitude in temperature and requires control only to within  $\pm 10^\circ\text{C}$ . The resulting ribbon-Si has a density of dislocations  $\leq 10^5 / \text{cm}^2$ . The defects in the central region of the ribbon consist almost entirely of coherent twin boundaries. As in other multicrystalline Si materials, the dislocations and grain boundaries in ribbon-Si require bulk passivation for best cell performance.

A low-cost method of cell processing which simultaneously improves material quality and provides an antireflection coating (ARC) is highly desirable. The use of Plasma-Enhanced Chemical Vapor Deposition (PECVD) as a low-temperature passivation process for silicon solar cells is a topic of current interest for this purpose. Other work has shown that different multicrystalline materials respond differently to hydrogen plasma passivation [2]. This work was conducted to study how to best use PECVD techniques to improve the performance of cells made using String Ribbon silicon.

Our process can include an in-situ hydrogen or ammonia rf-plasma treatment prior to a PECVD-nitride deposition to promote bulk defect passivation independently of surface effects. We also studied whether the predeposition of a thin silicon-nitride protective layer before performing the plasma treatment would serve to minimize surface damage. Our goal is to define a process to optimize cell performance by minimizing both surface and bulk recombination while also providing an effective antireflection coating.

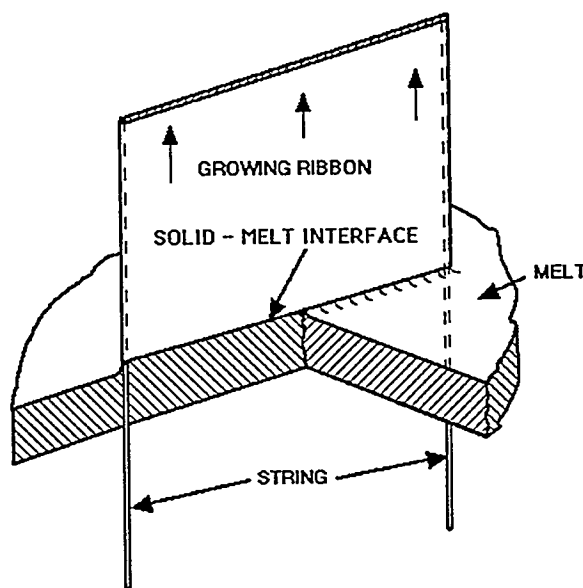
## 2. EXPERIMENTAL PROCEDURE

### 2.1 String Ribbon Crystal Growth

Silicon sheet material used for this study was grown using a method developed by Prof. Emanuel Sachs of M.I.T., formerly known as Edge Stabilized Ribbon and now called String Ribbon [1]. Evergreen Solar, a new photovoltaic company, is in the

process of commercializing photovoltaic modules based on String Ribbon.

The String Ribbon growth method is illustrated in Figure 1. Two strings of a high temperature material are brought up through a graphite crucible containing a shallow melt of silicon. The strings serve to stabilize the edges of the silicon ribbon as it grows above the melt surface. The process is meniscus rather than temperature controlled. Therefore, temperature variations of  $\pm 10^\circ\text{C}$  can be tolerated, resulting in a very robust crystal growth method. The material grown for this study was 5-cm-wide ribbon, p-type with a bulk resistivity of 1 - 2  $\Omega \text{ cm}$  and 300- $\mu\text{m}$  thick.



STRING RIBBON GROWTH PROCESS

Figure 1: String Ribbon Growth Process

### 2.2 PECVD Deposition Conditions

The depositions were performed using a modified Pacific Western Coyote PECVD reactor. This is a commercial, radio-frequency (rf), parallel-plate reactor operating at 13.56 MHz with large batch-size and high-throughput potential. Reaction gases for

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nitride deposition were a 3% mixture of silane in nitrogen and pure ammonia. The deposition parameters were similar to those that were previously determined to result in the lowest surface recombination on other multicrystalline material [3]. The rf power was 70W, the deposition temperature was 350°C, and the pressure was 1.4 torr. Wafer pretreatments were done *in-situ* using either H<sub>2</sub> or NH<sub>3</sub> plasmas for 15 minutes at 350°C using an rf-power of 60W. The depositions were followed by evaporated metallizations and an anneal in forming gas at 300°C. All wafers received an etch in dilute HF to remove any surface oxide before the deposition of a PECVD-nitride or an evaporated TiO<sub>2</sub> ARC.

We used five different deposition strategies and compared the resulting cell performance with that of cells processed using the industry-standard TiO<sub>2</sub> ARC.

1. 70-nm nitride layer with no pretreatments.
2. H<sub>2</sub>-plasma pretreatment followed by a 70-nm nitride layer.
3. 20-nm nitride protective layer, followed by H<sub>2</sub>-plasma, followed by 50 nm of nitride.
4. NH<sub>3</sub>-plasma pretreatment followed by a 70-nm nitride layer.
5. 20-nm nitride protective layer, followed by NH<sub>3</sub>-plasma, followed by 50 nm of nitride.

The 4-cm<sup>2</sup> cells were fabricated using a single-step phosphorus diffusion at 875°C resulting in a sheet resistance of 100  $\Omega / \square$ . This was followed by an aluminum alloy of the back surface at 875°C. The nitride depositions were performed next, followed by photolithography to define open areas through the nitride for metal contacts. TiPdAg gridlines were evaporated on the front and Al was evaporated on the back.

### 3. RESULTS

Internal Quantum Efficiency (IQE) curves for cells processed using each of the five PECVD sequences are compared with that of a cell having an evaporated-TiO<sub>2</sub> ARC in Figure 2.

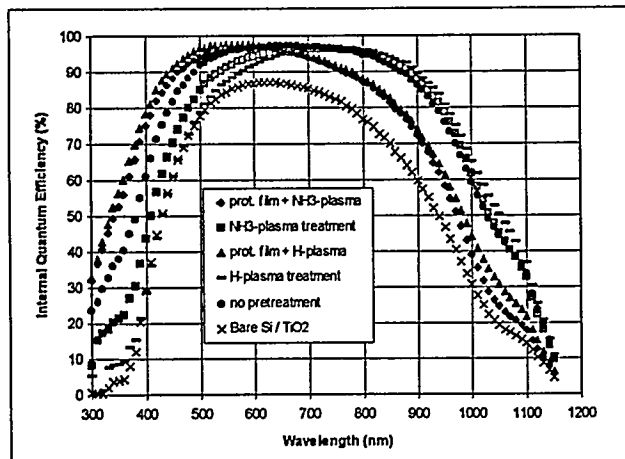


Figure 2: Internal Quantum Efficiency for each of the five PECVD sequences and the evaporated-TiO<sub>2</sub> ARC.

#### 3.1 Short-Wavelength Response

The short-wavelength region of the IQE curves are sensitive to the degree of emitter-surface passivation and the amount of recombination within the emitter region. All the cells used in this study had identical, low-recombination emitters, so that most of the emitter-recombination occurs at the emitter surface. Well-passivated emitters have higher blue response. Figure 3 shows the IQE at 400 nm more clearly.

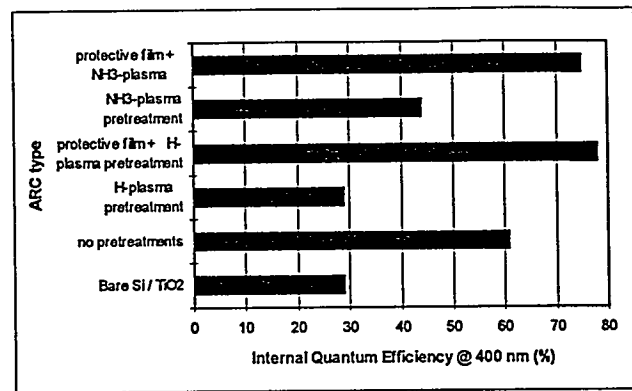


Figure 3: Internal Quantum Efficiency at 400 nm for each of the ARC types.

The direct deposition of the PECVD-nitride without pretreatments resulted in a substantial improvement in short-wavelength response over that of the TiO<sub>2</sub>-covered emitter, consistent with our previous work [3]. Also consistent with that work is the indication that a hydrogen plasma pretreatment prior to the nitride deposition results in poorly passivated surfaces, presumably due to surface damage, which are no better than an unpassivated, TiO<sub>2</sub>-covered surface. The ammonia-plasma pretreatment prior to the nitride deposition does result in some improvement of the surface, but not as much as the direct deposition. This suggests that the amount of surface damage caused by the ammonia plasma may be less than that caused by the hydrogen plasma.

When the hydrogen or ammonia plasma treatments are performed after a 20-nm protective nitride layer has been deposited, significant additional surface passivation is achieved. In fact, the 78% IQE value obtained for the H<sub>2</sub>-plasma with the protective film is equal to the highest value that we have been able to obtain using PECVD coatings [3]. This is certainly an indication that the protective nitride film does an excellent job of protecting the silicon surface from the damaging effects of the plasma pretreatments. This may also indicate that the presence of a thin, protective nitride film before the plasma pretreatment causes the passivating hydrogen ions to accumulate in the nitride near the silicon interface, where they are most beneficial in tying up dangling bonds and passivating interface states.

#### 3.2 Long-Wavelength Response

The long wavelength portion of the IQE curves is sensitive to the bulk diffusion length and the amount of back surface recombination. Since all the cells fabricated in this study used the same Al-alloyed back surface structure, differences in the long wavelength IQE curves are due to differences in bulk defect passivation. The bulk diffusion lengths were calculated using the method in reference 4, and are plotted together in Figure 4.

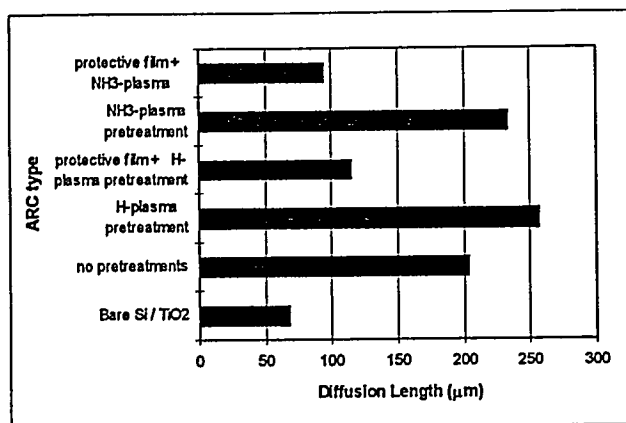


Figure 4: Bulk minority carrier diffusion length vs. ARC type.

Here again we see that the direct deposition of the nitride without pretreatments results in a significant improvement, this time in diffusion length, over that of the TiO<sub>2</sub>-coated control cells. However, it is evident that additional improvements are obtained by first pretreating the wafers with either an ammonia or hydrogen plasma before the nitride deposition. The diffusion length of over 250 μm obtained with the hydrogen-plasma pretreatment is as high a value as has ever been obtained on this material.

Interestingly, there is only a marginal improvement in the diffusion length over that of the control cells when the protective nitride film is deposited on the cells before a pretreatment in either the ammonia or the hydrogen plasmas. This suggests that either the film was too thick or the duration of the pretreatments too short to allow the passivating agents, presumably hydrogen ions, to diffuse in sufficient numbers through the films to penetrate the bulk of the wafers.

### 3.3 Measured Cell Efficiencies

The measured one-sun, global-spectrum efficiencies of cells fabricated using the five PECVD sequences are compared with that of the control cells in Figure 5.

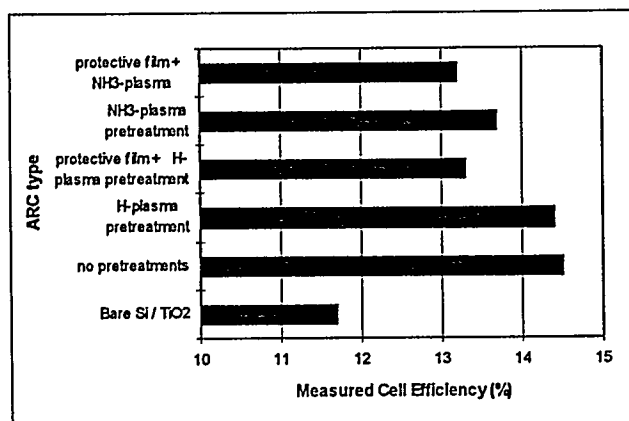


Figure 5. Measured cell efficiency vs. ARC type.

The overall cell performance is dependent on both surface and bulk recombination. For this reason, even though the cells fabricated with no pretreatments had only intermediate levels of surface and bulk passivation, their performance overall was superior to those which used more complex treatments and were considerably inferior in one area or the other. This is significant for the commercialization of String Ribbon and other multicrystalline Si cells and modules, where the simplest and most cost-effective method to improve the product performance is preferred. The

parameters for the best cell at 25°C were  $V_{oc} = 600$  mV,  $J_{sc} = 31.1$  mA/cm<sup>2</sup>, FF = 0.78, and efficiency = 14.5%.

## 4. CONCLUSIONS

The use of PECVD-nitride on String Ribbon Si as an antireflection coating produces far better surface and bulk passivation than does the industry-standard TiO<sub>2</sub> ARC, resulting in an efficiency increase from 11.7 to 14.5%, equivalent to a 24% increase in output power. The direct deposition of the nitride, without the use of any plasma pretreatments or protective films resulted in the best cell performance on this material to date, with an efficiency of 14.5%.

The H<sub>2</sub>-plasma and NH<sub>3</sub>-plasma pretreatments done without a protective nitride layer resulted in better bulk passivation than the direct deposition, but severely damaged surfaces. Because of the surface damage, these cells were slightly less efficient.

The H<sub>2</sub>-plasma and NH<sub>3</sub>-plasma pretreatments done after a 20-nm nitride protective layer produced the best surface passivation, but were not effective in passivating the bulk. Further work is needed to optimize film thicknesses, pretreatment durations, and plasma pretreatment and deposition parameters to simultaneously obtain both the best surface and bulk passivation for optimum cell performance.

## 5. ACKNOWLEDGEMENTS

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