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## Preprint

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# WIDE-GAP THIN FILM SI *n-i-p* SOLAR CELLS DEPOSITED BY HOT-WIRE CVD

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## ABSTRACT

High-voltage wide bandgap thin-film Si *n-i-p* solar cells have been made using the hot-wire chemical vapor deposition (HWCVD) technique. The best open-circuit voltage ($V_{oc}$) has exceeded 0.94 V in solar cells using HWCVD in the entire *n-i-p* structure. A $V_{oc}$ of 0.97V has been achieved using HWCVD in the *n* and *i* layers and plasma-enhanced (PE) CVD for the *p* layer. The high voltages are attributed to the wide-gap *i* layer and an improved *p/i* interface. The wide-gap *i* layer is obtained by using low substrate temperatures and sufficient hydrogen dilution during the growth of the *i* layer to arrive at the amorphous-to-microcrystalline phase transition region. The optical band gap ($E_{04}$) of the *i* layer is found to be 1.90 eV. These high-voltage cells also exhibit good fill factors exceeding 0.7 with short-circuit-current densities of 8 to 10 mA/cm$^2$ on bare stainless steel substrates. We have also carried out photoluminescence (PL) spectroscopy studies and found a correlation between $V_{oc}$ and the PL peak energy position.

## INTRODUCTION

Open-circuit voltage ($V_{oc}$) is the voltage measured between two terminals of a solar cell under illumination at zero current. It roughly measures or relates to the quasi-Fermi energy between electrons and holes of an absorber layer under illumination. Improvements in $V_{oc}$ can certainly benefit the performance of a solar cell if other characteristics are not compromised. Despite major efforts [1-3], fundamental understanding on how to further improve $V_{oc}$ remains a major issue. Experimentally, many research groups have achieved high $V_{oc}$'s ~1 V by inserting a thin buffer layer between the *p* and *i* layer, such as a wide-gap a-SiC:H or a-SiO:H layer, hydrogen-diluted a-Si:H *i* layer near the amorphous-to-microcrystalline transition, or a wide-gap conductive H-diluted *p* layer, or using a microcrystalline *p* layer [4-7]. In general, the limitation of $V_{oc}$ can be attributed to the bulk *i* layer, doped layers, and interfaces. However, in high $V_{oc}$ cells, it is difficult to separate out effect from each factor, thus making further improvements even more challenging.

For solar cells fabricated by the hot-wire (HW) CVD technique, the reported best initial $V_{oc}$ is 0.92 V in a hybrid devices [8] where the *n* and *i* layers were deposited by HWCVD, and 0.88 V for all-HW solar cells [9] that the *n*, *i*, and *p* layers were entirely made using HWCVD. Many groups have achieved $V_{oc}$'s just below 0.90 V for their best HW solar cells [10-12]. The large difference when compared to the PECVD solar cells of 1.05 V motivates us to search for high $V_{oc}$ HW solar cells. When successful, the high deposition rate, which is one of the advantages of HWCVD, can be finally utilized.

In this paper, we present experimental data for high $V_{oc}$ a-Si:H solar cells where at least the *i* layer was deposited using the HWCVD technique. We focus on optimizing the wide-gap *i* layer using H-dilution such that the material is near the phase transition from amorphous-to-microcrystalline silicon at a high deposition rate of 10 Å/s.

## EXPERIMENTAL DETAILS

High $V_{oc}$ solar cells were developed in the NREL load-locked two-chamber HWCVD T-system. The details of this system were reported elsewhere [13]. We use a SS/*n-i-p*/ITO configuration in all solar cells, where substrates were bare stainless steel (SS). For all-HW solar cells, a 300-Å n-layer was first deposited at 300°C in the dopant chamber. Then an 1800-Å (except for the thickness- dependent study) i-layer was deposited under various conditions to search for high $V_{oc}$. The sample then was transferred back to the dopant chamber for a brief atomic H treatment before depositing an 60-Å buffer layer. Finally, a 140-Å p-layer was deposited at 150°C. The solar cell was completed by evaporating 600-Å indium tin oxide (ITO) top contacts, with dot areas of 0.05 cm$^2$. For hybrid solar cells, the *n* and *i* layers are deposited at the optimized conditions by HWCVD at NREL, then the unfinished solar cell–sealed in $N_2$ filled bag–was sent to United Solar for depositing the *p* layer and the top ITO contact. The cell has a total area of 0.26 cm$^2$ defined by circular ITO top contact. The evaluation of solar cells was done at NREL and United Solar using standard AM 1.5 condition at 25 °C.

The *i*-layer optimization was performed using the above device configuration. The growth conditions, such as substrate temperature, hydrogen dilution, chamber pressure, and thickness, were varied to search for high $V_{oc}$ solar cells. These conditions were near the threshold of the transition from amorphous-to-microcrystalline silicon. The deposition rate for H-diluted *i* layers is about 10 Å/s. The H-dilution ratio (*R*) of $H_2$ to $SiH_4$ is one of the critical parameters that control the phase of the thin film Si.

Photoluminescence was measured on all-HWCVD solar cells using the 514.5-nm, and 632.8-nm light beams from $Ar^+$ and HeNe lasers respectively with power density of 30-100 mW/cm$^2$ for the PL excitation. Samples were mounted on a cold stage which provides a temperature range from 80 to 300K. The PL spectra were analyzed using a grating monochromator and detected by a $LN_2$-cooled Ge detector.

## RESULTS AND DISCUSSIONS

Figure 1 shows the effect of hydrogen dilution of *i*-layers on $V_{oc}$ (solid symbols) and FF (open symbols) for all HW solar cells fabricated at NREL. First, we observed that hydrogen dilution increases $V_{oc}$. For example, $V_{oc}$ has reached over 0.90 V for $R$ =1.8, which is greater than the best $V_{oc}$ of 0.88 V for the solar cell without H-dilution [8]. Symbol ✳ represents the early data for comparison. We also observe that $V_{oc}$ improved by as much as 20 mV with a slight increase of $R$ by 0.45 at $R$=2.25. Further increases of $R$ cause $V_{oc}$ to decline. We chose $R$=2.25 as the optimized H-dilution. With increasing $R$, the i-layer has a tendency to become μc-Si. It is worth noting that the typical $V_{oc}$ of μc-Si solar cells is less than 0.60 V. All solar cells have good FFs that are greater than 0.70.

Despite having only a few samples, the very sensitive behavior of $V_{oc}$ to $R$ agrees well with the general trend that thin-film Si changes the phase transition from amorphous to microcrystalline silicon with increasing $R$, which was concluded from the film study [14]. We believe that the wider-gap *i*-layer that is near or on the edge of the phase transition one of the factors leading to the high $V_{oc}$. The optical bandgap ($E_{04}$) of the film grown on the glass under the same condition of high $V_{oc}$ solar cells shows a higher value (1.90 eV) than the one (1.88 eV) without H-dilution. The 20-meV increase in $E_{04}$ cannot explain more than 20-mV increases in $V_{oc}$ assuming that the $V_{oc}$ has a linear relationship with bandgap. Other factors must be taken into account such as the effect of the H-diluted *i* layer on the *p* and *i* interface and the *p* layer growth afterward.

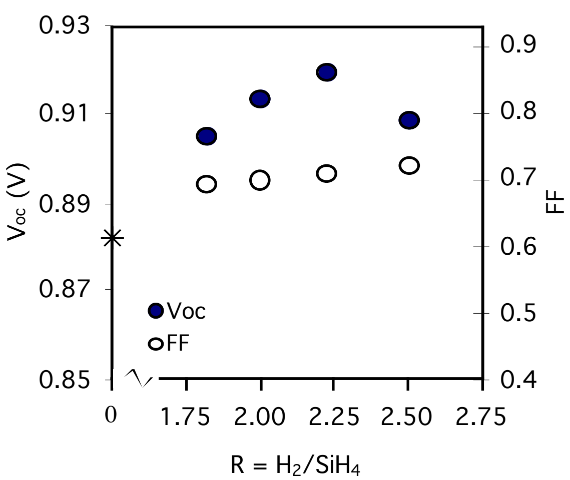


**Fig. 1**. $V_{oc}$ and FF dependence on the hydrogen dilution of the i-layer. The scale of y-axis is magnified.

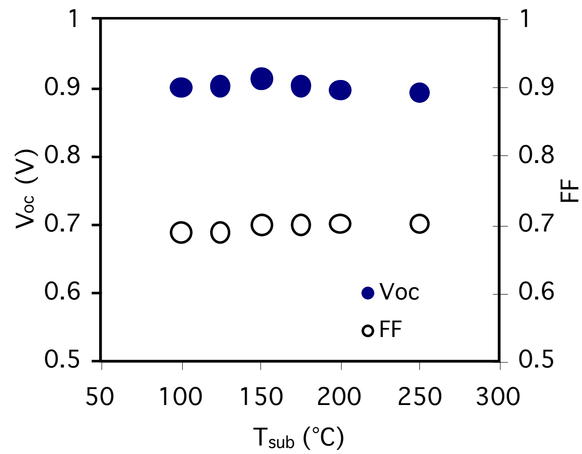


**Fig. 2**. $V_{oc}$ and FF dependence on the substrate temperature for the solar cells with i-layer with H-dilution.

Finally, we concluded that the outcome of increasing $V_{oc}$ using "finite-tuned" H-dilution, which is near the phase transition, is similar for solar cells fabricated by the HWCVD technique or the PECVD method, despite the different growth method and deposition rate.

Figure 2 shows the dependence of solar cell performance on substrate temperature. All HW solar cells have an H-diluted *i* layer with $R$ = 2.25, and the temperature changes from 100°C to 250°C. The temperatures used in the figure are the starting temperature and are monitored using two thermocouples (TC) placed inside the chamber. During the deposition, the radiation from the hot-wire heats up the film and substrate. Therefore, the final temperatures, which depend on the deposition time and other factors, are higher than the starting one. Fortunately, most *i* layer depositions are done within 2-3 minutes and the TC reading changes about 20°-30°C. However, the real temperature at the surface of the film is difficult to determine because of the complicated absorption, heat dissipation, type of substrate, and deposition conditions.

We initially grow the H-diluted solar cells at 250°C. The solar cell has a reasonable high $V_{oc}$ of 0.89 V and FF of 0.70. To search for other solar cells with high $V_{oc}$, we decreased the substrate temperature from 250°C to 100°C. In general, the results suggest that the substrate temperature does not dramatically impact solar cell performance. However, it does cause about 20-mV increase of $V_{oc}$ at 150°C compared to the solar cell at 250°C. Also, at 100°C, we can make a solar cell with $V_{oc}$ slightly higher than 0.90 V. We chose 150°C as the optimized temperature.

To closely examine the effect of *i* layer to the solar cell performance, we selected PL spectra measurements on the same set of solar cells in Figure 2. Most PL signal is believed to come from the *i*-layer, and much less from ITO and thin *p*-layer. Figure 3 shows the correlation between PL peak energy position at 80K and $V_{oc}$ on the same solar cells. In a range of $V_{oc}$ from 0.893 to 0.914 V,

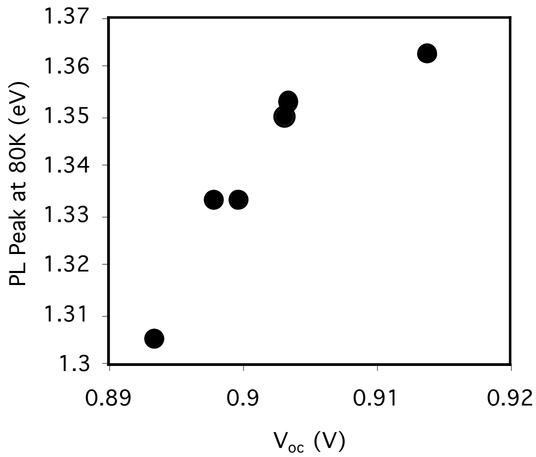


**Fig. 3**. The PL peak energy position measured at 80K correlated to the $V_{oc}$ for the samples in Figure 2. The higher the $V_{oc}$, the higher the peak-energy position.

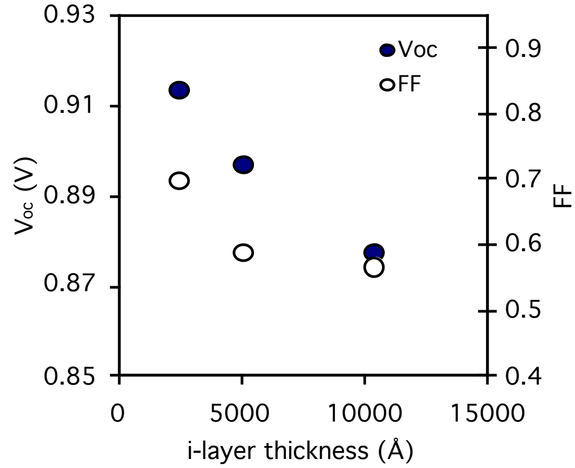


**Fig. 4**. $V_{oc}$ and FF dependence on the thickness of i-layer at the optimized condition of H-dilution.

the PL peak energy position increases with $V_{oc}$ and is independent of the substrate temperature (see Fig. 2).At low temperatures such as 80K, PL measured the radiative recombination energy of excited electron-hole pairs. In a-Si:H materials, the peak energy position relates to the optical gap and the width of band tails. Deconvoluting the PL data to the bandgap and/or band-tail width is not the subject of this paper. The correlation of PL peak energy position with $V_{oc}$ suggests that $V_{oc}$ increases qualitatively with increase of the bandgap of the *i* layer. However, the non-linear relationship between PL peak energy and $V_{oc}$ at higher $V_{oc}$ weakens the argument.

Figure 4 shows the effect of the i-layer thickness on solar cell performance. The *i*-layer was grown at the condition that was optimized for hydrogen dilution with *R* =2.25 at 150°C. The three solar cells were completed at NREL. This experiment is to test the thickness dependence of µc-Si growth that was reported by United Solar [15] in the solar cell. We found that $V_{oc}$ and FF decrease with increasing thickness. Interestingly, the $V_{oc}$ for a solar cell just over 1 µm thick is still quite good (0.88 V), although the FF decreased dramatically. These HW results agree with the previous report PECVD solar cells by United Solar.

In all-HW *n-i-p* solar cell fabricated at NREL, a 60-Å higher H-diluted amorphous silicon layer was inserted between the *i* and *p* layers and was found to help the solar cell performance [8]. We also used the same buffer layer and the same *p* layer that were reported previously [9] for all the high $V_{oc}$ solar cells at NREL.

Table I summarizes the optimized high-$V_{oc}$ solar cells growth condition and performance. The first data show the *i*-layer deposition parameters. For the all-HW *n-i-p* solar cells, the best initial high-voltage solar cell has a $V_{oc}$ of 0.941 V, with FF of 0.749, $J_{sc}$ of 8.2 mA/cm$^2$, and efficiency (Eff.) of 5.8%. High $V_{oc}$ solar cells, in general, are designed for the wide-gap top cell in the multijunction structure. Therefore, the i-layer is thin (1800 Å) and the short-circuit current density is low. To achieve high efficiency for this type of cell, we increase the i-layer thickness such that the efficiency is optimized. The best initial-efficiency solar cell has a $V_{oc}$ of 0.931 V, FF of 0.708, $J_{sc}$ of 10.9 mA/cm$^2$, and Eff. of 7.2% optimized at 2500 Å. The stability test of those solar cells is under way. However, we do have light-soaking data on a solar cell with the *i*-layer grown close to the best high-$V_{oc}$ solar cell. This cell shows a degradation of $V_{oc}$ from 0.898 to 0.861 V.

**Table 1**. Summary of High-$V_{oc}$ Solar Cells.

High-$V_{oc}$ solar cell optimized *i*-layer process parameters

| | $SiH_4$ (sccm) | $H_2$ (sccm) | P (mTorr) | $T_{sub}$ (°C) |
|---|---|---|---|---|
| *i*-layer | 45 | 100 | 18 | 150 |

High-$V_{oc}$ all-HW solar cell performance

| | $V_{oc}$ (V) | FF | $J_{sc}$ (mA/cm$^2$) | Eff. (%) |
|---|---|---|---|---|
| Best Initial $V_{oc}$ | 0.941 | 0.749 | 8.2 | 5.8 |
| Best Initial Eff. | 0.931 | 0.708 | 10.9 | 7.2 |

Light-soaking results from similar *i*-layer to high-$V_{oc}$ cell

| | | | | |
|---|---|---|---|---|
| Initial | 0.898 | 0.661 | 10.31 | 6.1 |
| After 1000 hour | 0.861 | 0.591 | 9.65 | 4.9 |

High-$V_{oc}$ NREL-USSC hybrid solar cell performance

| | $V_{oc}$ (V) | FF | $J_{sc}$ (mA/cm$^2$) | Eff. (%) |
|---|---|---|---|---|
| Best Initial $V_{oc}$ | 0.971 | 0.717 | 9.63 | 6.70 |
| Best Initial Eff. | 0.962 | 0.716 | 10.12 | 6.97 |

The last data show the performance on the collaborated solar cells between NREL and United Solar. Using the same *i*-layer that was optimized for HW high-Voc solar cells, the best initial high voltage solar cell has $V_{oc}$ of 0.971 V, with FF of 0.717, $J_{sc}$ of 9.63 mA/cm$^2$, and Eff. of 6.70%. And the best initial efficiency solar cell has a $V_{oc}$ of 0.962 V, FF of 0.716, $J_{sc}$ of 10.12 mA/cm$^2$, and Eff. of 6.97%.

## CONCLUSIONS

In summary, high-performance, high $V_{oc}$ (0.941 V in all-HW and 0.971 V in hybrid) a-Si:H solar cells have been fabricated. These values are the best results to date of $V_{oc}$ using the HWCVD technique. The $V_{oc}$ improvement was achieved by incorporating materials grown with H-dilution close to the phase transition from amorphous to microcrystalline silicon in the *i*-layer. The $V_{oc}$ is sensitive to the hydrogen dilution near the optimized condition. We also found that a low substrate temperature of 150°C for the *i*-layer was also essential. We believe that the wide-gap *i*-layer is the key for improving of $V_{oc}$. Increasing *i*-layer thickness from 1800 to 10,000 Å at the optimized $R$ = 2.25 causes $V_{oc}$ to decrease.


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