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Effects of seeding methods on the fabrication of microcrystalline silicon solar cells using radio frequency plasma enhanced chemical vapor deposition

Yuan-Min Li[a], Liwei Li[b], J.A. Anna Selvan[a], Alan E. Delahoy[a], Roland A. Levy[b,*]

[a]*Energy Photovoltaics, Inc., 276 Bakers Basin Road, Lawrenceville, NJ 08648, USA*
[b]*Department of Physics, New Jersey Institute of Technology, 323 King Boulevard, Newark, NJ 07102, USA*

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Abstract

Single junction *p-i-n* μc-Si:H solar cells were prepared in a low-cost, large-area single chamber radio frequency plasma enhanced chemical vapor deposition system. The effects of seeding processes on the growth of μc-Si:H *i*-layers and performance of μc-Si:H solar cells were investigated. Seeding processes, usually featured by highly hydrogen rich plasma, are effective in inducing the growth of μc-Si:H *i*-layers. It has been demonstrated that *p*-layer seeding methods are preferable to *i*-layer seeding. While performance of μc-Si:H solar cells produced by *i*-layer seeding methods was usually limited by very low fill factors, μc-Si:H solar cells with good initial and stabilized conversion efficiencies were obtained by *p*-layer seeding.

Keywords: Solar cells; Silicon; Chemical vapor deposition; Nucleation

1. Introduction

Over the past decade, advances have been made in the fabrication of solar cells with hydrogenated microcrystalline silicon (μc-Si:H) intrinsic (*i*-) layers. High quality μc-Si:H is usually deposited by plasma enhanced chemical vapor deposition (PECVD). Early success in fabricating μc-Si:H solar cells was achieved by *very high frequency PECVD* [1]. Recently, studies on the fabrication of μc-Si:H solar cells using conventional radio frequency (RF-) PECVD have attracted extensive attention due to its compatibility with the existing large-scale manufacturing technology of amorphous silicon (α-Si:H) photovoltaic (PV) modules. In most laboratory scale research, sophisticated, multi-chamber, load-locked deposition systems, expensive laboratory substrates, as well as highly effective back reflector or transparent interlayer were routinely used to obtain high efficiency μc-Si:H solar cells [2–4]. However, the true potential of μc-Si:H solar cells can only be evaluated under conditions of cost-competitive manufacturing of large-area PV modules. Industrial production of 8 Ft^2 α-Si:H PV modules by a massively-parallel batch process in single chamber RF-PECVD systems has been successfully developed [5]. A realistic approach based on this proven technology has been taken to study the manufacturing of μc-Si:H solar cells on a low-cost, large-area basis [6]. Generally, glow discharge of highly hydrogen diluted silane is used as the standard PECVD approach for μc-Si:H deposition. Although the microscopic mechanism of μc-Si:H growth has yet to be better understood, it is generally believed that the initial nucleation of μc-Si:H crystallites on α-Si:H, α-SiC:H or other under-layers is critical to obtaining high quality μc-Si:H films. In this study, therefore, a wide variety of seeding processes were systematically explored and the effects of seeding schemes on the growth of μc-Si:H and device performance of μc-Si:H solar cells were investigated.

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* Corresponding author. Tel.: +1 973 596 3561; fax: +1 973 596 8369.
E-mail address: levyr@njit.edu (R.A. Levy).

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2. Experimental details

Single junction *p-i-n* solar cells with μc-Si:H *i*-layers (absorbers) were fabricated on commercial grade SnO_2 superstrates by RF-PECVD method (13.56 MHz), using silane highly diluted by hydrogen as feed gas mixtures. Substrate temperature was usually kept near 200 °C. This single chamber deposition system, without load-lock, was routinely exposed to air for unloading and loading the substrates. The advantages of this low-cost PECVD system include a large electrode utilization ratio (a single 12 in.×15 in. powered electrode was used to simultaneously coat four substrates equal to its size), high gas utilization, a controllable contamination profile, ease of operation, and low maintenance. The doped *p*-layers and *n*-layers, as well as *i*-layers, were deposited in the same reactor without any movement of the substrates and/or the reactor. A thin α-SiC:H *p*-layer was first deposited on the SnO_2 superstrate. Then, a seeding step was applied to induce crystallization for the Si:H *i*-layer followed by the deposition of bulk *i*-layer. Finally, an α-Si:H *n*-layer was grown. Sputtered Al, without any rear reflection enhancement schemes, was used as the standard back contact.

Device fabrication and performance testing, including current–voltage curve (*I–V*), spectral response (QE), and light soaking, were routinely conducted at Energy Photovoltaics, Inc. (EPV). Parameters obtained from performance testing, such as conversion efficiency, open circuit voltage (Voc), short circuit current density (Jsc), fill factor (FF), and red-light spectral response (QE at 800 nm or longer), were also used to deduce the microstructural properties of μc-Si:H solar cells. In particular, low Voc and high red-light response were used as the signatures of μc-Si:H *i*-layers. Raman Spectroscopy of actual solar cells, performed at New Jersey Institute of Technology (NJIT), was used to study the micro-crystallinity of μc-Si:H solar cells. Due to the contribution from substrates and vary optical properties of Si:H *i*-layers, the micro-crystallinity was presented in terms of the ratio of peak intensities (Ic/Ia) of Raman shift corresponding to μc-Si:H (Ic) and α-Si:H (Ia), respectively.

3. Results and discussion

3.1. Seeding methods for μc-Si:H i-layer deposition

The performance of μc-Si:H solar cells depends on many processing details, chief among which are the seeding steps and the growth conditions for the bulk *i*-layers. Throughout this study, it has been established that, for a fixed set of *i*-layer plasma conditions capable of sustaining μc-Si:H growth, the seeding or incubation procedure (which may comprise several individual steps) largely determines the properties of Si:H absorber, and strongly influences the device performance. Under the same *i*-layer growth conditions, amorphous, mixed-phase, or micro-crystalline (nano-crystalline) Si:H absorbers can be obtained, respectively, depending on the seeding method.

The seeding methods we have explored can be classified into two categories: (i) *p*-layer seeding, which refers to all seeding methods involving boron doped *p*-layer, and (ii) *i*-layer seeding referring to the nucleation methods inside the 'intrinsic' Si:H layer. To grow μc-Si:H on an α-Si:H or α-SiC:H under-layer, a defective transition layer may exist at or near the *p*/*i* interface which may severely affect device performance. Thus, its thickness should be limited. Highly hydrogen rich plasma conditions are usually applied during seeding steps to induce initial μc-Si:H nucleation followed by growth of bulk μc-Si:H *i*-layer under relatively softer plasma conditions. However, the hydrogen rich plasma used in seeding processes could do severe damages to the microstructure and performance of μc-Si:H solar cells. Thus, the *p*-layer seeding approaches take the advantage of limiting the damages associated with energetic seeding plasma within the PV non-active *p*-layer and consequently lead to better overall carrier collection. Conceptually, *i*-layer seeding methods take the advantages of minimized optical loss associated with the thicker, defective *p*-layers resulting from *p*-layer seeding approaches and higher Voc due to the wider band gap of the non-microcrystalline *i*-layer near the *p*/*i* interface. Presumably, the disadvantage of this type seeding methods is the unavoidable defects near the *p*/*i* interface (*i*-layer side) created by the hydrogen rich plasma used to create nucleation sites, which might lead to poor carrier collection.

The *i*-layer seeding processes usually consist of the deposition of a thin α-Si:H buffer layer, an incubation layer deposited by pure hydrogen etching on the buffer layer or seeding using very high hydrogen dilution ratio, and a silane grading step leading to the growth of bulk μc-Si:H *i*-layer. The *p*-layer seeding processes consist of similar approaches with μc-Si:H nucleation occurs within doped *p*-layer.

3.2. Effects of seeding methods on the growth of μc-Si:H

High hydrogen to silane dilution ratio has been widely recognized as the most important factor to induce and sustain the growth of μc-Si:H. Therefore, hydrogen to silane dilution ratio, $R=[H_2]/[SiH_4]$, was used as the major parameter in analyzing the seeding processes. In the relatively large area RF-PECVD system, it has been demonstrated that the seeding schemes so far explored, such as pure hydrogen etching on α-SiC:H or α-Si:H buffer layer and seeding by very high hydrogen dilution ratio, are effective in inducing the formation of μc-Si:H. Without special seeding methods, high hydrogen dilution ratio is necessary for the growth of bulk μc-Si:H *i*-layers.

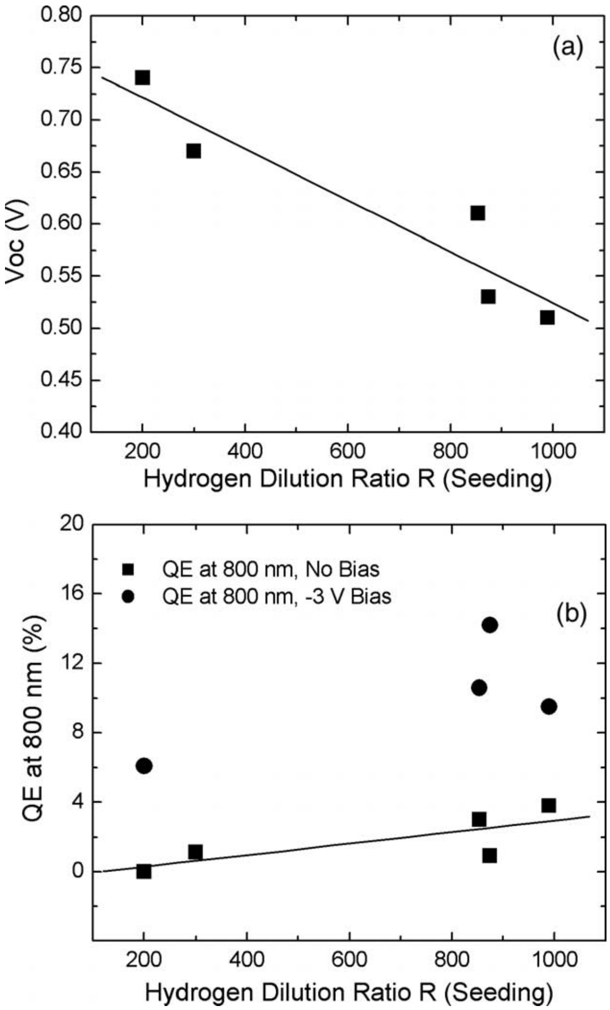

Fig. 1. Open circuit voltage and red-light response of μc-Si:H solar cells as functions of hydrogen dilution ratio used during *i*-layer seeding. (a) Voc vs. *R* (Seeding) and (b) Red-light response vs. *R* (Seeding).

Using *i*-layer seeding as an example, the critical importance of seeding methods in growing μc-Si:H has been demonstrated. In Fig. 1, Voc and red-light response of several solar cells deposited using *i*-layer seeding methods (with bulk *i*-layers deposited under similar plasma conditions) are plotted against *R* (Seeding), i.e., the hydrogen dilution ratios used in seeding steps. Generally, Voc decreases and red-light response increases along with increasing *R* (Seeding), implying that increasing micro-crystallinity was obtained along with enhanced nucleation steps.

It is evident from Fig. 1(b) that, under −3 V bias, collection of μc-Si:H related photo-generated carriers is enhanced as indicated by increasing red-light response. Unlike the red-light response which increases with increasing *R* (Seeding), the difference between red-light response with and without negative bias is relatively constant. Some of the devices deposited with low hydrogen dilution ratios during seeding steps showed Voc comparable with that of α-Si:H solar cells and very low or zero red-light response without negative bias. However, their spectral response, especially in red light range, can be significantly improved, implying the existence of α-Si:H near *p*/*i* interface and μc-Si:H near *n*-layer side.

3.3. Effects of seeding methods on the performance of μc-Si:H solar cells

Device performance of μc-Si:H solar cells is significantly affected by seeding types and plasma conditions used in respective seeding methods. The aforementioned conceptual advantages and disadvantages of *i*-layer and *p*-layer seeding types, i.e., higher Voc but poor carrier collection for *i*-layer seeding methods and lower Voc but better carrier collection for *p*-layer seeding methods were observed throughout this study.

3.3.1. Conversion efficiency

While the highest conversion efficiency obtained so far from *i*-layer seeding methods is about 4%, most devices have efficiencies much lower than 3% featured by extremely low fill factor and short circuit current density. However, these bad solar cells clearly contain μc-Si:H in their *i*-layers as confirmed by *I*–*V* characteristics and QE spectra. Usually, such solar cells exhibit very poor spectral response but that can be significantly improved when measured under negative bias, suggesting that collection of photo-generated carriers is highly suppressed, possibly by the defects within μc-Si:H *i*-layer created by the harsh, hydrogen rich plasma used in *i*-layer seeding.

When using *p*-layer seeding methods, the highly etching plasma was applied only during the deposition of the PV non-active, heavily boron doped *p*-layer and thus of little concern. Since the amorphous-to-crystalline transition mainly occurs inside *p*-layer, the integrity of the critical *p*/*i* interface and uniformity in the growth direction of bulk μc-Si:H *i*-layer can be much improved, leading to higher fill factor and better overall carrier collection. Device performance parameters and seeding methods used for some μc-Si:H solar cells are listed in Table 1. It can be seen that μc-Si:H solar cells deposited using *i*-layer seeding methods exhibit low conversion

Table 1
Performance parameters of selected μc-Si:H solar cells

Voc (V)	Jsc (mA/cm^2)	FF (%)	Efficiency (%)	Seeding methods
0.51	13.3	57	3.8	*i*-layer seeding and grading
0.60	13.5	52	4.2	*i*-layer seeding and grading
0.60	14.8	46	4.0	*i*-layer seeding and grading
0.53	15.0	45	3.6	*i*-layer seeding and grading
0.48	14.1	54	3.9	*p*-layer seeding by etching α-SiC:H
0.50	15.3	66	5.0	*p*-layer seeding by μc-Si:H *p*-layer
0.48	14.4	67	4.6	*p*-layer seeding by μc-Si:H *p*-layer
0.48	13.6	62	4.0	*p*-layer seeding by μc-Si:H *p*-layer
0.49	12.3	68	4.1	*p*-layer seeding by μc-SiC:H *p*-layer
0.48	16.2	64	5.0	*p*-layer seeding by μc-SiC:H *p*-layer

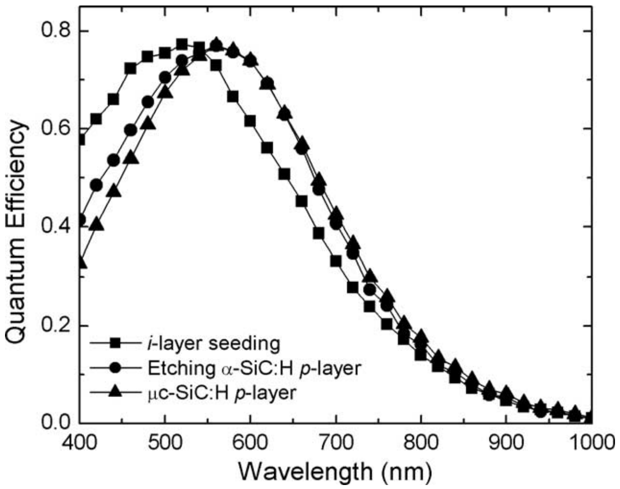

Fig. 2. Effect of seeding methods on the spectral response of μc-Si:H solar cells.

efficiency featuring high Voc but low fill factor (always lower than 60%). Using *p*-layer seeding methods, higher conversion efficiencies were obtained due to very good fill factors.

3.3.2. Spectral response

Compared to *p*-layer seeding, *i*-layer seeding methods result in lower efficiency, but high blue-light response, i.e., higher QE at short wavelength owing to the undisturbed *p*-layer which is more transparent and less defective. The three samples shown in Fig. 2 have comparable Jsc. However, it is evident that *p*-layer seeding results in more optical loss in short wavelength range due to increased *p*-layer thickness, and perhaps damages resulting from *p*-layer seeding as well. Even among *p*-layer seeding category, increased *p*-layer thickness (i.e., μc-SiC:H or μc-Si:H *p*-layer versus *p*-layer seeding by etching α-SiC:H *p*-layer alone), also causes more optical loss in short wavelength range. The red-light response of these μc-Si:H solar cells has been limited by the simple device structure, i.e., no rear light trapping enhancement. Higher conversion efficiency and spectral response, especially in the red-light range, are expected providing rear light trapping schemes, e.g., good rear reflector such as ZnO/Ag back contact and special substrate, e.g., Asahi type U SnO_2, are employed.

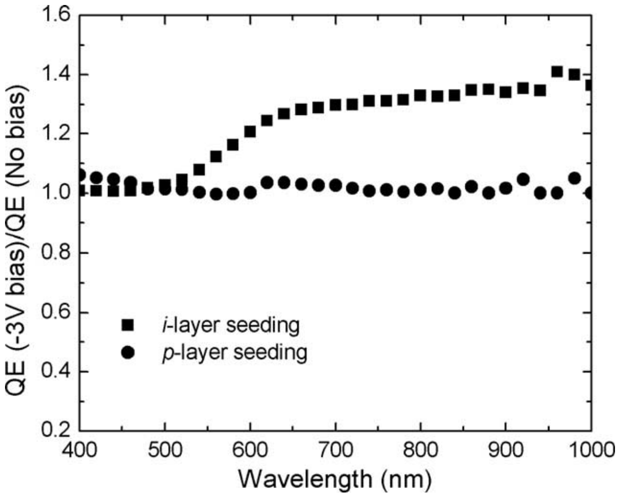

Fig. 3. QE dependence of μc-Si:H solar cells deposited using different seeding methods.

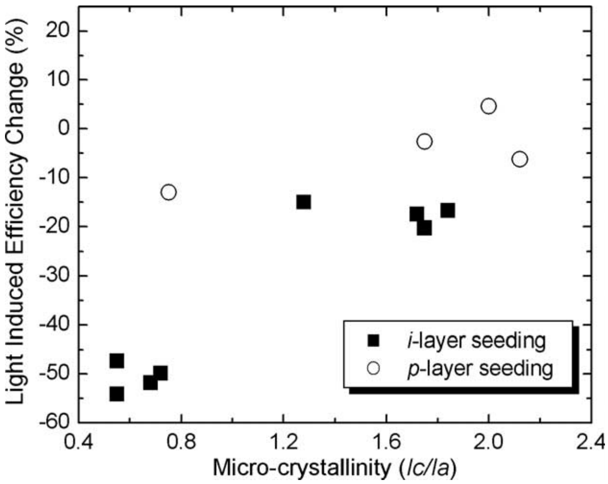

Fig. 4. Light-induced efficiency change under conventional light soaking as a function of micro-crystallinity.

As illustrated in Fig. 3, μc-Si:H solar cells deposited using different seeding methods exhibit different QE dependence which is presented as the ratio of QE measured under −3 V bias to that measured under zero bias. Even though μc-Si:H solar cells deposited by *i*-layer seeding could show red-light response under −3 V bias comparable to that of μc-Si:H solar cells produced by *p*-layer seeding, their red-light response is suppressed without negative bias.

3.3.3. Stability against light soaking

Results of light soaking of various Si:H solar cells under light intensity simulating 1 sun for over 1000 h are shown in Fig. 4. Solar cells with μc-Si:H *i*-layers exhibit very good stability against light-induced degradation. However, it is demonstrated in Fig. 4 that, for solar cells with either mixed-phase Si:H or μc-Si:H *i*-layers as revealed by micro-crystallinity obtained from Raman scattering, *p*-layer seeding always results in much better stability against light-induced degradation than *i*-layer seeding.

4. Conclusions

The critical importance of seeding processes in determining the microstructure of μc-Si:H *i*-layers and performance of μc-Si:H solar cells has been demonstrated. Seeding processes, usually featured by highly hydrogen rich plasma, are effective in inducing the growth of μc-Si:H *i*-layers. The *p*-layer seeding methods are preferable to *i*-layer seeding. While performance of μc-Si:H solar cells produced by *i*-layer seeding methods was usually limited by very low fill factors, μc-Si:H solar cells with good initial and stabilized conversion efficiencies were obtained by *p*-layer seeding in the low-cost, large-area RF-PECVD system.

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