Fabrication and optimization of single-junction nc-Si:H n–i–p solar cells using Si:H phase diagram concepts developed by real time spectroscopic ellipsometry

Xinmin Cao a,b,*, Jason A. Stoke a, Jian Li a, Nikolas J. Podraza a, Wenhui Du a, Xiesen Yang a, Dinesh Attygalle a, Xianbo Liao a, Robert W. Collins a, Xunming Deng a,b

a Department of Physics and Astronomy, University of Toledo, Toledo, OH 43606, USA
b Xunlight Corporation, 3145 Nebraska Avenue, Toledo, OH 43607, USA

Available online 13 February 2008

Abstract

In this study, we have developed and applied deposition phase diagrams in the plane of the bulk layer thickness d b and the H 2-dilution ratio R = [H 2]/[Si 2H 6] for Si:H materials deposited by 70 MHz VHF PECVD from [H 2] + [Si 2H 6] mixed gases on c-Si/(native-oxide)/n-layer substrates. To establish the phase diagrams, series of Si:H depositions having different R values over the range of 60–150 were measured in real time using a rotating-compensator multichannel ellipsometer. Using phase diagram concepts for guidance, we have fabricated high efficiency single-junction nc-Si:H n–i–p solar cells with ~3 Å/s intrinsic layers using the VHF PECVD process. We have found that the nc-Si:H solar cells with the best performance are obtained by incorporating i-layers deposited in the single-phase nanocrystalline silicon regime near the transition boundary to mixed-phase (a + nc)-Si:H. Applying insights from real time spectroscopic ellipsometry moreover, we have investigated in detail the effects of the phase of the underlying n-layer on the phase evolution of the over-deposited Si:H i-layer and on the overall device performance. With the strategy developed here, a stabilized efficiency of $\eta = 9.46\%$ ($V_{oc} = 0.516$ V, $J_{sc} = 24.65$ mA/cm$^2$, FF = 0.744) has been achieved for nc-Si:H solar cells (0.25 cm$^2$ in active area) fabricated with an i-layer deposition rate of ~2.2 Å/s.

© 2007 Elsevier B.V. All rights reserved.

PACS: 84.60.Jt; 73.63.Bd; 78.20.–Ci; 81.07.Bc

Keywords: Silicon; Solar cells; Photovoltaics; Ellipsometry

1. Introduction

In the field of hydrogenated silicon (Si:H) thin-film photovoltaics, research and development for hydrogenated nano/microcrystalline silicon (nc/μc-Si:H) thin films and solar cells have yielded the most notable progress over the last decade. Saito et al. developed a 10.87% efficient nc-Si:H solar cell (single-junction, n–i–p-type) with an i-layer deposition rate of 4 Å/s [1], whereas Feitknecht et al. achieved an efficiency of 7.8% in a similar cell structure with a higher rate of 7.4 Å/s [2]. Progress has been made more recently at higher rates with Mai et al. developing a 10.3% nc-Si:H cell (single-junction, p–i–n-type) with an i-layer rate of 11 Å/s [3], and Yan et al. achieving an 8.99% nc-Si:H cell (single-junction, n–i–p-type) with a rate in the range of 5–8 Å/s [4]. With the incorporation of a nc-Si:H cell as the bottom junction, a-Si:H/nc-Si:H tandem and a-Si:H/a-SiGe:H/nc-Si:H triple-junction structures with efficiencies exceeding 13% have been successfully fabricated by several groups [5–8].
The deposition phase diagram concept for Si:H growth from \([\text{H}_2] + [\text{SiH}_4]\) gas mixtures has been developed and elaborated by Collins and coworkers using real time spectroscopic ellipsometry (RTSE) [9,10]. This diagram describes the growth regimes of (i) purely amorphous silicon, a-Si:H, (ii) protocrystalline Si:H, (iii) mixed-phase amorphous + micro (or amorphous + nano) crystalline silicon, \((\alpha + \mu)\)-Si:H [or \((\alpha + \text{nc})\)-Si:H], and (iv) single-phase micro- (or nano-) crystalline silicon, \(\mu\text{-Si:H}\) (or nc-Si:H).

The practical challenge for the fabrication of thin-film Si:H-based solar cells by PECVD in this study is to identify expeditiously the optimum conditions for the Si:H deposition process, including the possibility of complicated multistep and graded layer deposition sequences. RTSE has been applied in order to identify the two transition boundaries of the deposition phase diagrams in the plane of the bulk layer thickness and the \(\text{H}_2\) dilution ratio, appropriate for the Si:H i-layer deposition process used in this solar cell study. These boundaries include the amorphous-to-(mixed-phase-microcrystalline) and the (mixed-phase)-to-(single-phase) microcrystalline transitions. The former identifies the conditions under which optimum a-Si:H i-layers are obtained for devices, as we have reported previously [11,12], and the latter identifies the conditions under which optimum nc-Si:H i-layers are obtained, as we report here for Si:H materials deposited by 70 MHz VHF PECVD with \([\text{H}_2] + [\text{Si}_2\text{H}_6]\) mixed gases.

2. Experimental details

The Si:H layers for deposition phase diagram development by RTSE were deposited on c-Si/(native-oxide)/(n-type Si:H) substrate structures using a multi-chamber VHF (70 MHz) PECVD system. In order to apply these phase diagrams for insights into solar cell performance, Si:H n–i–p structures were co-deposited onto stainless steel substrates coated with textured Ag/ZnO back-reflectors in the device configuration simultaneously with the specular c-Si/(native-oxide) substrates. For depositions performed versus the phase diagram variable \(R = [\text{H}_2]/[\text{Si}_2\text{H}_6]\), all other parameters were selected within the range used for the previously-optimized top a-Si:H and bottom nc-Si:H i-layers in a-Si:H/nc-Si:H or a-Si:H/a-SiGe:H/nc-Si:H multi-junction structures [13], including a VHF plasma power of \(\sim 8\) W, a low total gas pressure in the range \(p_{\text{tot}} \sim 0.1–0.5\) Torr, and a nominal substrate temperature in the range of \(T \sim 200–400\) °C.

It should be emphasized that the Si:H i-layer phase diagram is very sensitive to the underlying n-layer. As the standard process, a-Si:H n-layers which serve effectively as memory erasing layers have been used as the underlying film in phase diagram development relevant for the i-layers of a-Si:H solar cells. In contrast, the standard process for nc-Si:H solar cell fabrication by VHF PECVD involves the use of a nc-Si:H n-layer. In order to establish the n-layer phase dependence of the solar cell performance, the phase evolution, as recorded by RTSE with analysis using the virtual interface technique, has been compared for Si:H i-layer depositions on a-Si:H and nc-Si:H n-layers. After fabrication of the n–i–p single-junction structures, the cells were completed, measured, and compared. To complete the cells, indium tin oxide (ITO) transparent conductive layers were deposited by RF magnetron sputtering through a mask to serve as the front contacts. For characterization of the as-deposited cells, each having an active area of \(0.25\) cm\(^2\), dark current–voltage (\(J–V\)) AM1.5G light \(J–V\), and QE measurements were performed, the latter over the wavelength range of 350–1000 nm. Light soaking experiments were undertaken with \(\sim 100\) mW/cm\(^2\) white light at 50 °C.

3. Results and discussion

3.1. Example Si:H deposition phase diagram

Fig. 1 shows an example of a Si:H deposition phase diagram in the plane of the bulk layer thickness \(d_b\) and the \(\text{H}_2\)-dilution ratio \(R = [\text{H}_2]/[\text{Si}_2\text{H}_6]\) for 70 MHz VHF PECVD with \([\text{H}_2] + [\text{Si}_2\text{H}_6]\) mixed gases on c-Si/(native-oxide)/(a-Si:H n-layer) substrates. A series of Si:H depositions having different \(R\) values in the range of 60–150 was measured in real time using a rotating-compensator multichannel ellipsometer. A nominal substrate temperature of \(T = 200\) °C was set for this series of Si:H depositions. This nominal value corresponds to a calibrated value of \(T = 107\) °C, however, as determined by RTSE from the shifts in the \(E_1\) and \(E_2\) critical point energies for an uncoated c-Si substrate under similar gas flow conditions. Fig. 1 displays the bulk layer thickness at which the \(a \rightarrow (a + \mu)\) transition (solid...
line, squares) occurs as determined from a roughening onset, and the thickness at which the \((a + \mu c) \rightarrow \mu c\) transition (dashed line, circles) occurs as determined from a smoothening (coalescence) onset. Up-arrows indicate that the transitions occur at thicknesses above the indicated values. Contour lines in the microcrystallite volume fraction \(f_{\mu c}\) are plotted ranging from 0.05 to 0.60 (dotted lines). An expanded scale in \(f_{\mu c}\) shows that the \(a \rightarrow (a + \mu c)\) transition (solid line, squares) as determined from the roughening onset occurs when \(f_{\mu c} \sim 0.01\). The diagram of Fig. 1 demonstrates that, under the deposition conditions used here, the Si:H films remain amorphous throughout at least 2000 Å of bulk layer growth for \(R \leq 80\). At higher \(H_2\) dilution (100 \(\leq R \leq 150\)), the Si:H films initially nucleate as a-Si:H but undergo the \(a \rightarrow (a + \mu c)\) transition at a thickness that decreases with increasing \(R\). This newly-developed Si:H phase diagram exhibits features similar to those reported previously by Collins and coworkers, for Si:H growth from \([H_2] + [SiH_4]\) mixed gases [9,10], but with a different \(H_2\)-dilution scale due to the use of \(Si_2H_6\) in this case as well as a different plasma power density. In addition, a more recently developed advanced virtual interface analysis enables the plotting of contours in the crystallite volume fraction.

### 3.2. Underlying Si:H n-layer dependence

#### 3.2.1. Evolution of microcrystalline volume fraction and surface roughness for Si:H i-layers

Using such Si:H phase diagrams for guidance, we have fabricated high efficiency single-junction nc-Si:H n-i-p solar cells with intrinsic layers deposited by the VHF PECVD technique at rates of 2–3 Å/s using \(H_2\)-dilution ratio \(R = [H_2]/[Si_2H_6]\) of \(\sim 100\). To demonstrate explicitly the role of the substrate, the phase evolution of Si:H i-layers has been compared for a-Si:H and nc-Si:H n-layers in Figs. 2 and 3. All other deposition conditions were kept at constant for the 120 min, \(\sim 1.5 \mu m\) Si:H i-layer depositions, including a \(H_2\)-dilution ratio of \(R = [H_2]/[Si_2H_6] = 100\), a nominal substrate temperature of \(T = 400^\circ C\), a pressure of \(p = 0.2\) Torr, and a plasma power of \(P = 8\) W. These conditions are the same as those of the phase diagram of Fig. 1, except for the higher nominal substrate temperature of \(400^\circ C\) (which corresponds to a calibrated temperature of \(210^\circ C\)).

Fig. 2 shows the microcrystalline volume fraction in the top 10 Å of the bulk layer plotted versus the bulk i-layer deposition time as determined from virtual interface analysis of RTSE data for the \(R = 100\) Si:H i-layers deposited on a-Si:H and nc-Si:H n-layers (denoted A and B, respectively). Fig. 3 shows the corresponding results for the surface roughness evolution (denoted C and D).

The combined results for the \(R = 100\) i-layer deposited on the a-Si:H n-layer, demonstrate that the Si:H i-layer remains predominantly amorphous for the first \(\sim 5\) min. Microcrystallites then nucleate from the amorphous phase and their preferential growth leads to surface protrusions that account for the rapid increase in roughness. At \(t \sim 44\) min, corresponding to an i-layer thickness of \(\sim 5500\) Å, the microcrystalline volume fraction of the as-grown bulk i-layer reaches \(\sim 100\%\). At the same time, the surface roughness reaches its maximum value of \(\sim 80\) Å, indicating fully contacting crystallites at the surface and thus the (mixed-phase)-to-(single-phase) microcrystalline transition. A smoothening effect occurs with increasing bulk i-layer thickness over the deposition time from 44 to 80 min due to continued coalescence of contacting crystallites, a process that is completed by \(t \sim 80\) min after which...
the surface roughness stabilizes at a thickness of \( \sim 60 \text{ Å} \). Thus, for \( t = 44–120 \text{ min} \), the growth of single-phase microcrystalline structure is maintained; however, a decrease in the microcrystalline fraction near the end of bulk i-layer deposition appears to be attributable, not to the inclusion of an a-Si:H phase, but rather to voids as the microcrystallite grain size increases.

For the phase evolution of the \( R = 100 \) i-layer deposited on the nc-Si:H n-layer, as demonstrated by the results in Figs. 2 and 3, the Si:H i-layer grows initially as an \((a + nc)\)-Si:H mixed-phase material. The initial microcrystalline volume fraction \( f_{\text{ic}} \) is \( \sim 0.3 \), however, \( f_{\text{ic}} \) quickly reaches \( >0.8 \) at \( t \sim 4 \text{ min} \) with a corresponding i-layer thickness of \( \sim 500 \text{ Å} \). In this case, a nearly pure single-phase nc-Si:H material dominates throughout the entire 1.5 \( \mu \text{m} \) bulk i-layer. As the nearly single-phase nc-Si:H film grows, the surface roughness increases gradually with deposition time and reaches a maximum value of \( \sim 48 \text{ Å} \) at the end of i-layer deposition, which is smoother than the nc-Si:H i-layer deposited on the a-Si:H n-layer. This observation is likely to result from the fact that when the underlying n-layer is nc-Si:H, the i-layer is likely to grow by local epitaxy, which continues the structural evolution of the starting n-layer. When the n-layer is amorphous, the i-layer must nucleate from a growing a-Si:H i-layer, which is likely to lead to a more non-uniform morphology and thus greater roughness due to the low nucleation density.

3.2.2. \( J-V \) and QE performance

The corresponding device performances were measured and compared for solar cells fabricated using the a-Si:H and nc-Si:H n-layer processes on SS/Ag/ZnO back-reflectors. Fig. 4 shows the initial dark and light \( J-V \) curves for a nc-Si:H cell made using the a-Si:H n-layer. The dark and light \( J-V \) curves exhibit cross-over associated with a low fill factor of \( FF = 0.520 \) (\( V_{\text{oc}} = 0.522 \text{ V} \), \( J_{\text{sc}} = 23.45 \text{ mA/cm}^2 \), and \( \eta = 6.37\% \)), which is expected to be due to the presence of the high volume fraction amorphous phase in the initial stage of i-layer evolution on the a-Si:H n-layer. Fig. 5 shows corresponding results for a nc-Si:H cell fabricated using the nc-Si:H n-layer process. For this cell, very well-behaved initial dark and light \( J-V \) curves have been obtained, and the FF and \( J_{\text{sc}} \) values have been greatly improved relative to those of Fig. 4. As listed in Table 1, an initial efficiency of \( \eta_{\text{ini}} = 9.22\% \) (\( V_{\text{oc}} = 0.516 \text{ V} \), \( J_{\text{sc}} = 25.17 \text{ mA/cm}^2 \), \( FF = 0.701 \)) and a stabilized efficiency after 1000 h of light soaking of \( \eta_{\text{stab}} = 9.46\% \) (\( V_{\text{oc}} = 0.516 \text{ V} \), \( J_{\text{sc}} = 24.65 \text{ mA/cm}^2 \), \( FF = 0.744 \)) have been obtained for the VHF PECVD nc-Si:H cells with the \( R = 100 \) i-layer deposited on a nc-Si:H n-layer. In contrast, a stabilized efficiency of only 5.99\% (\( V_{\text{oc}} = 0.496 \text{ V} \), \( J_{\text{sc}} = 21.96 \text{ mA/cm}^2 \), \( FF = 0.550 \)) has been obtained for the corresponding cells made with an a-Si:H n-layer. Fig. 6 shows the external quantum efficiency (QE) curves plotted for the cells of Figs. 4 and 5 in the initial state and after 1000 h light soaking. These results show clearly that the nc-Si:H solar cell with the nc-Si:H n-layer has much better long-wavelength spectral response and more stable QE values after 1000 h light soaking than that with the a-Si:H n-layer. The nc-Si:H solar cell with the nc-Si:H n-layer yields AM1.5G initial and stabilized \( J_{\text{sc}} \) values.

![Fig. 4. The initial dark and light \( J-V \) curves for the \( R=100 \) VHF-PECVD nc-Si:H solar cell fabricated on a SS/Ag/ZnO back-reflector over-deposited with an a-Si:H n-layer.](image)

![Fig. 5. The initial dark and light \( J-V \) curves for the \( R=100 \) VHF-PECVD nc-Si:H solar cell fabricated on a SS/Ag/ZnO back-reflector over-deposited with a nc-Si:H n-layer.](image)
of 10.36 and 10.08 mA/cm², respectively, integrated over the QE wavelength range from 650 nm to 1000 nm. In contrast, the solar cell with an a-Si:H n-layer yields initial and stabilized QE $J_{sc}$ values of 9.30 and 8.20 mA/cm², respectively. The thick layer of mixed-phase (a + nc)-Si:H i-layer material resulting from growth on the a-Si:H n-layer is responsible for the poor device performance and stability.

We have also calculated the short circuit current density from the integral of the QE curves (Fig. 6) with AM1.5G spectrum over the range of measurement from 380 nm to 1000 nm. The nc-Si:H solar cell with the nc-Si:H n-layer yields AM1.5G initial and stabilized $J_{sc}$ values of 24.25 and 23.89 mA/cm², respectively, integrated over the QE wavelength range from 380 nm to 1000 nm. In contrast, the solar cell with an a-Si:H n-layer yields initial and stabilized QE $J_{sc}$ values of 22.89 and 20.96 mA/cm², respectively. In comparison with the solar cell with an a-Si:H n-layer, the corresponding integrated QE $J_{sc}$ values from the integral of the QE curves (Fig. 6) with AM1.5G wavelengths (Table 1) are shown for the QE in the initial state as well as after 1000 h light soaking.

Typically, the crystalline volume fraction in nc-Si:H is deduced from Raman spectroscopy, and the i-layers of the best nc-Si:H solar cells exhibit crystalline volume fractions of ~0.50 using this method. In this study, we applied RTSE for estimation of crystalline volume fraction and have found much higher crystalline fractions - in fact, close to unity for the i-layers of high-performance nc-Si:H solar cells. A correlation among RTSE, Raman, and TEM is underway for evaluating the origin of the differing results.

### 4. Conclusions

This study has used as a foundation previous intensive research on thin-film silicon based solar cell fabrication and characterization and built on this foundation with additional recent investigations that apply RTSE in the development of deposition phase diagrams. This foundation has been applied for guidance toward optimum solar cell fabrication. The following list provides the general conclusion of this research. (i) The phase of the underlying Si:H n-layer has a dominant controlling effect on the phase evolution of the overlying nc-Si:H i-layer in the optimum i-layer growth regime and hence greatly affects the corresponding device performance under practical conditions of deposition. (ii) nc-Si:H solar cells with the highest performance are obtained when the entire bulk i-layer is prepared in the single-phase nc-Si:H regime but near the mixed-phase (a + nc)-Si:H to single-phase nc-Si:H transition boundary, whereas high performance a-Si:H single-junction top cells are obtained when the entire i-layer is prepared near the amorphous a-Si:H to mixed-phase (a + nc)-Si:H transition boundary. Finally, one can conclude that (iii) the evolution of a significant portion of the bulk i-layer in the form of (a + nc)-Si:H mixed-phase material should be avoided both for high-efficiency a-Si:H top or nc-Si:H bottom cells in tandem and triple-junction devices.

### Acknowledgements

This research was supported by the National Renewable Energy Laboratory ‘Thin Film Photovoltaics Partnership Program’ under subcontract No. ZXL-5-44205-06. The authors would like to thank Nirupama Adiga for $J-V$ and QE measurements.

### References