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Maximization of the open circuit voltage for hydrogenated amorphous silicon $n-i-p$ solar cells by incorporation of protocrystalline silicon p -type layers

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In studies of hydrogenated amorphous silicon (a -Si:H) $n-i-p$ solar cells fabricated by rf plasma-enhanced chemical vapor deposition (PECVD), we have found that the maximum open circuit voltage (V_{oc}) is obtained by incorporating p -type doped Si:H layers that are protocrystalline in nature. Specifically, these optimum p layers are prepared by PECVD in the a -Si:H growth regime using the maximum hydrogen-to-silane flow ratio possible without crossing the thickness-dependent transition into the mixed-phase (amorphous+microcrystalline) growth regime for the ~ 200 Å p -layer thickness. The strong dependence of the p -layer phase and solar cell V_{oc} on the underlying i -layer phase also confirms the protocrystalline nature of the optimum Si:H p layer. © 2002 American Institute of Physics. [DOI: 10.1063/1.1499735]

High open circuit voltages (V_{oc}) and record high efficiencies for hydrogenated amorphous silicon (a -Si:H) $n-i-p$ solar cells fabricated by rf plasma-enhanced chemical vapor deposition (PECVD) have been achieved by incorporating p -type doped Si:H layers deposited at low temperature ($T \sim 200^\circ\text{C}$) using high hydrogen-to-silane flow ratios (typically $R \equiv [\text{H}_2]/[\text{SiH}_4] \sim 50-200$).¹⁻³ It was proposed that such optimum p layers are, in fact, microcrystalline Si:H (μc -Si:H) and that this material yields improved cell performance through an increase in the built-in potential of the junction and through decreases in series resistance and absorption losses.

In Ref. 1, the high conductivities characteristic of μc -Si:H were measured only on thick p layers (>1000 Å); however, the layers incorporated into the devices were much thinner (~ 100 Å). In subsequent studies, the V_{oc} values obtained with p layers prepared by PECVD at high R were found to increase further as the p -layer deposition temperature (T) was decreased.^{2,3} To explain this behavior, an increase in p -layer crystallinity with decreasing T was hypothesized, yet just the opposite trend for $T < 400^\circ\text{C}$ had been described earlier for four different sets of PECVD films.⁴ Reflection high energy electron diffraction (RHEED) patterns were also presented as evidence that the optimum p layers were μc -Si:H.³ RHEED is a highly surface-sensitive technique, however, and so fails to probe the p -layer material closest to the i/p junction.

In view of these considerations, an explanation of the high V_{oc} values of Refs. 1-3 in terms of a μc -Si:H p layer is not compelling owing to a possible barrier for microcrystalline nucleation on an amorphous i -layer surface.⁵⁻⁷ As a result, 100-200-Å-thick p layers prepared on i layers under certain conditions may be amorphous even at R values as high as 200.⁸ In the present study, the problem of Si:H p -layer opti-

mization has been reconsidered. Light and dark current-voltage characteristics dominated by bulk recombination for state-of-the-art a -Si:H $n-i-p$ solar cells⁹ have been correlated with spectroscopic ellipsometry (SE) results for the corresponding p layers of the $n-i-p$ structures.

Three experimental approaches were applied for p -layer optimization in a -Si:H solar cells.

- (1) Si:H p layers for use in $p-i-n$ solar cells were developed for high nucleation density and single-phase microcrystalline structure in 100-Å-thick films on glass/ZnO and glass/SnO₂/ZnO substrates using a single-chamber rf PECVD system and guidance from real time SE (RTSE). In this approach, p -layer gas mixtures of $[\text{H}_2]/[\text{SiH}_4]/[\text{B}(\text{CH}_3)_3]$ were used, and a deposition phase diagram revealed the preferred conditions of $R = 200$ and $D = [\text{B}(\text{CH}_3)_3]/[\text{SiH}_4] = 0.02$ for immediate high-density μc -Si:H nucleation on ZnO.¹⁰ The $p-i-n$ cell structures incorporated an $R = 0$ i layer to avoid possible p -layer substrate-induced microcrystallinity.⁷
- (2) Si:H p layers for use in $n-i-p$ cells were developed in a similar manner as the p layers for $p-i-n$ cells. In this approach, however, the underlying i -layer surface was subjected to a 2 min H₂-plasma treatment that generates nanocrystalline Si:H nucleation sites for the p -layer deposition. A wide window for single-phase μc -Si:H was found using $[\text{H}_2]/[\text{SiH}_4]/[\text{BF}_3]$ mixtures with $D = [\text{BF}_3]/[\text{SiH}_4] = 0.2$ and $R = 200$.⁸ This preferred p -layer process was then adopted for $n-i-p$ cells on Cr-coated glass using an $R = 10$ i layer.
- (3) After fabrication of $p-i-n$ and $n-i-p$ solar cells with p layers designed for dense, single-phase μc -Si:H structure, a number of state-of-the-art $n-i-p$ devices were fabricated on Cr-coated glass in a multichamber rf PECVD system under a variety of p -layer conditions. For all such cells, the i layer was deposited to 4000 Å with $R = 10$, but the H₂-plasma treatment was eliminated

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to avoid any direct substrate-induced microcrystallinity in the overlying p layers.^{7,8} In this third approach, BF_3 doping gas was used with $D=0.2$, and R was varied from 50 to 200. Solar cells with and without a 200-Å-thick $R=40$ a -Si:H i -layer region⁶ deposited just prior to the p layer were also compared to assess i layer substrate-dependent effects on the p layer.

For all three high R p -layer deposition approaches listed above, the substrate temperature was fixed at 200 °C and the rf plasma power was in the range of 0.3–0.8 W/cm². Where appropriate, the V_{oc} values obtained from solar cells incorporating the high R p layers were compared to the values obtained from cells incorporating a standard $R=0$ a -Si_{1-x}C_x:H p layer with composition $x \sim 0.1$. In the latter p -layer process, a gas mixture of $[\text{SiH}_4]/[\text{CH}_4]/[\text{B}(\text{CH}_3)_3]$ was used with $D=0.01$, $z = [\text{CH}_4]/\{[\text{SiH}_4] + [\text{CH}_4]\} = 0.5$, and an rf plasma power of 0.05 W/cm².

In approaches (1) and (2), RTSE (1.5–4 eV) was performed using a multichannel instrument.¹¹ In approach (3), *ex-situ* SE (1.5–5.5 eV) was performed on identical glass/Cr/ n - i - p structures cofabricated with the solar cells. Phase determinations by SE were corroborated by atomic force microscopy (AFM) and electron microscopies.

First, the final outcome will be summarized for the characterization of a -Si:H p - i - n and n - i - p solar cells incorporating the preferred single-phase μc -Si:H p layers developed with guidance from RTSE according to approaches (1) and (2) above. For a -Si:H p - i - n solar cells deposited on ZnO with an $R=0$ i layer, the μc -Si:H p -layer process gave $V_{oc}=0.64$ V. This value is much lower than the baseline of 0.81 V, which is obtained for p - i - n cells fabricated under identical conditions, but using the standard a -Si_{1-x}C_x:H process designed to ensure a *purely amorphous* p layer. For a -Si:H n - i - p cells with an $R=10$ i layer, the μc -Si:H p layer process gave $V_{oc}=0.76$ V, again much lower than the corresponding baseline of 0.88 V. Such results demonstrate that deposition processes designed to maximize microcrystalline nucleation density and volume fraction for 100 Å p layers do not optimize V_{oc} for a -Si:H p - i - n and n - i - p solar cells, and that record high efficiencies are unlikely for cells incorporating *purely* μc -Si:H p layers.

Thus, it is important to re-address this problem by considering state-of-the art solar cells fabricated by multichamber PECVD and incorporating p layers deposited using a variation in R according to approach (3) above. In this way, the phase of the p layer can be varied from pure amorphous Si:H through mixed-phase amorphous+microcrystalline Si:H [($a+\mu c$)-Si:H]. Figure 1 shows V_{oc} for the series of n - i - p solar cells incorporating p layers prepared with $D = [\text{BF}_3]/[\text{SiH}_4] = 0.20$, but with different R values over the range $50 \leq R \leq 200$.

Also plotted versus R in Fig. 1 is the microcrystalline silicon volume fraction in the p layer as obtained by *ex-situ* SE in the actual n - i - p solar cell configuration. Least-squares regression analyses applying the Bruggeman effective medium theory were performed for the determination of the microcrystalline fractions of the p layers, assuming a three-component mixture of a -Si:H/ μc -Si:H/void.⁵ The component dielectric function for single-phase μc -Si:H in

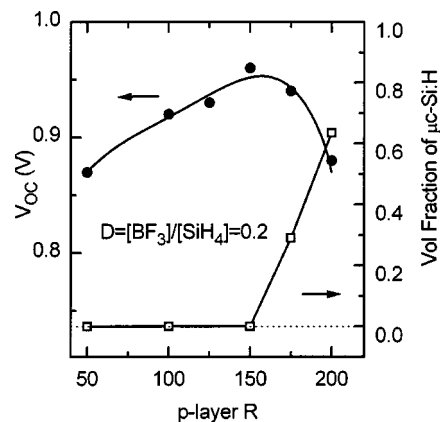


FIG. 1. Open circuit voltage V_{oc} (left scale) plotted vs the p -layer $R = [\text{H}_2]/[\text{SiH}_4]$ value for a series of a -Si:H n - i - p solar cells with one-step $R=10$ i layers (solid points). The p -layer microcrystalline Si:H volume fractions (right scale) are also included, as measured by SE in the actual n - i - p cell configuration (open points).

these analyses was obtained in studies of a 200-Å-thick p layer prepared on H_2 plasma treated a -Si:H at 200 °C using a $[\text{H}_2]/[\text{SiH}_4]/[\text{BF}_3] = 200/1/0.1$ gas mixture. This p layer was measured by RTSE during growth⁸ and then upon cooling to 25 °C. The component dielectric function for single-phase a -Si:H was obtained from an $R=10$ a -Si:H film using *ex-situ* SE. In Fig. 2, the true optical properties (corrected for surface roughness overlayers) are presented for (a) the $R=150$ p layer with no detectable microcrystalline phase (<0.02 in vol. fraction) and (b) the $R=200$ p layer with the highest microcrystalline content (0.63 in vol. fraction), incorporated within the cells with the highest V_{oc} (0.96 V) and reduced V_{oc} (0.88 V) values, respectively. The fact that the p layer in Fig. 2(b) is mixed-phase ($a+\mu c$)-Si:H, rather than single-phase μc -Si:H, may be accounted for by the absence of an i -layer H_2 -plasma pretreatment.⁸

The electrical properties of the p layers reveal overall similar trends. For thin (<1000 Å) $R=100$ p layers deposited on i layers, a thickness-dependent conductivity (σ) and conductivity activation energy (E_σ) are observed with relatively high values of $E_\sigma \sim 0.5$ eV, attributed to transport dominated by the amorphous phase (but with an increasing influence of the microcrystalline phase with thickness). In contrast, thin p layers with $R=200$ exhibit thickness-independent properties with $E_\sigma \sim 0.1$ eV, attributed to transport dominated by the microcrystalline phase.

Thus, from the overall results presented here, it is clear that the maximum V_{oc} is obtained for the cell incorporating the p layer deposited at the maximum possible R , while remaining just below the amorphous-to-(mixed-phase amorphous+microcrystalline) [$a \rightarrow (a+\mu c)$] transition throughout the 200 Å thickness of the p layer. In fact, this is the same optimization criterion as is applied for one-step i layers to maximize not only V_{oc} but also the fill factor stability against light-induced degradation.⁶ Thus, we conclude that V_{oc} is maximized when the p layer is prepared in the *protocrystalline* Si:H state and that the overall highest solar cell performance in annealed and degraded states is attained by using *protocrystalline* Si:H for both p and i layers.

There are two key characteristics that identify the growth regime yielding *protocrystalline* Si:H.⁶ The first characteristic is that the V_{oc} is maximized when the p layer is prepared in the *protocrystalline* Si:H state and that the overall highest solar cell performance in annealed and degraded states is attained by using *protocrystalline* Si:H for both p and i layers.

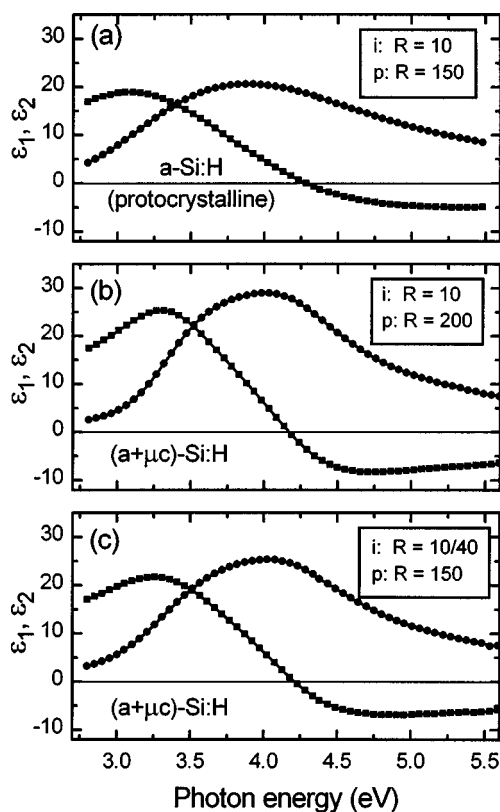


FIG. 2. Real and imaginary parts of the dielectric functions (ϵ_1, ϵ_2) of the p layers of a -Si:H n - i - p solar cells incorporating (a) a one-step $R=10$ a -Si:H i layer and $R=150$ protocrystalline Si:H p layer; (b) a one-step $R=10$ a -Si:H i layer and $R=200$ $(a+\mu c)$ -Si:H p layer; and (c) a two-step $R=10/R=40$ i layer and $R=150$ p layer with substrate-induced $(a+\mu c)$ -Si:H structure.

tic is the accumulated thickness dependence of the phase of the growing material. Although the term “protocrystalline” describes an amorphous Si:H phase, given sufficient thickness protocrystalline Si:H ultimately evolves—as its name implies—first to mixed-phase $(a+\mu c)$ -Si:H and finally to single-phase μc -Si:H. A second characteristic of protocrystalline Si:H is the substrate dependence of the phase evolution. Under protocrystalline growth conditions, microcrystalline nucleation is suppressed on an underlying a -Si:H film; however, under the same deposition conditions local epitaxy is favored on underlying μc -Si:H.

To demonstrate the latter effect, Fig. 2(c) provides the dielectric function for the p layer of a n - i - p solar cell fabricated under conditions identical to those of the optimum cell of Fig. 2(a), with the only difference being the incorporation of a 200 \AA $R=40$ interface i layer⁶ between the $R=10$ bulk i layer and the overlying $R=150$ p layer. Also shown in Fig. 3 is a comparison between the resulting solar cell I - V characteristics in the annealed state for (i) the optimum cell of Fig. 2(a) with the one-step $R=10$ i layer and the $R=150$ p layer, and (ii) the cell of Fig. 2(c) with the two-step $R=10/R=40$ i layer and the identically-prepared $R=150$ p layer. Two important effects are observed in Figs. 2(c) and 3. First, microcrystalline nuclei at the top surface of the $R=40$ interface i layer, as detected by AFM in p - i - n studies, induce microcrystallites in the p layer. In fact, the volume fraction of microcrystalline phase in the p layer in-

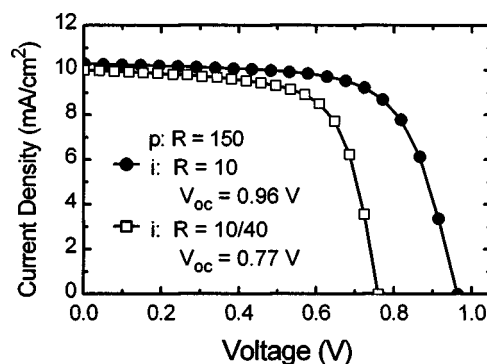


FIG. 3. Annealed state I - V characteristics for the optimum a -Si:H n - i - p solar cell of Fig. 2(a) with the $R=150$ protocrystalline Si:H p layer (solid symbols), and for the n - i - p cell of Fig. 2(c) fabricated under otherwise identical conditions, but incorporating a 200 \AA $R=40$ Si:H i layer at the i/p junction (open symbols).

creases from undetectable levels (<0.02) to 0.31 with the addition of the $R=40$ interface i layer. Second, V_{oc} of the resulting solar cell drops from 0.96 to 0.77 V due to this increase in p layer microcrystalline fraction. These results further demonstrate that protocrystalline Si:H p layers optimize V_{oc} , and that even relatively low substrate-induced microcrystalline fractions in the p layer are detrimental.

In conclusion, we have re-addressed the issue of p -layer optimization for a -Si:H solar cells, finding that the maximum open circuit voltage (V_{oc}) in n - i - p solar cells is obtained using p layers that are protocrystalline in nature, i.e., deposited at the maximum possible $R=[H_2]/[SiH_4]$ without traversing the transition from the a -Si:H growth regime to the mixed-phase $(a+\mu c)$ -Si:H regime for the $\sim 200 \text{ \AA}$ p -layer thickness. The higher V_{oc} values may be due to the wider mobility gaps for the protocrystalline Si:H p layers that are also observed in the case of the i layers.⁷ Owing to the protocrystalline nature of p -layer growth, any microcrystalline silicon nuclei in the underlying i layer, for example, due to excessive H_2 -dilution, induce microcrystallinity in the p layer, which reduces V_{oc} .

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