

Impacts of nano-structures in p- and i-layer on the performances of amorphous silicon solar cells

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Fine-grained nano-structures were introduced in p- and i-layers of n-i-p type hydrogenated amorphous silicon (a-Si:H) based solar cells deposited on stainless steel substrate, and their impacts on the cell performances were characterized. It is found that the hydrogenated nanocrystalline silicon (nc-Si:H) p-layer with a certain nanocrystalline volume fraction leads to a higher V_{oc} of 1.042 V. For the intrinsic layer, intro-

ducing a middle-range ordered-like structure and a small amount of nanosized silicon crystallites may decrease the light-induced degradation and increase the stabilized efficiency of n-i-p a-Si:H based solar cells up to 10% for single junction nano-structured a-Si:H solar cells with an area of 0.25 cm², AM1.5, 100 mW/cm².

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1 Introduction Light induced degradation in a-Si:H materials is a major obstacle for the application of a-Si:H in photovoltaic solar cells. Hydrogen dilution has been widely used to obtain high quality a-Si:H materials [1]. Recent years there is a strong trend in producing materials at the phase transition region from amorphous to nanocrystalline silicon. Collins et al. reported that the optimum a-Si:H p-layer and i-layer, described as protocrystalline silicon, could be achieved using the maximum possible hydrogen dilution without crossing the transition boundary into a mixed-phase (amorphous + microcrystalline), in another word, just below the onset of crystallinity [2].

However, for the optimum structure of p-layer, there are several conflicting suggestions. For instance, Guha et al. incorporated a wide bandgap microcrystalline silicon (μ -Si:H) p-layer in a-Si:H n-i-p cells, increasing the V_{oc} to 0.96–0.99 V [3], while Rath et al. reported that using a truly μ -Si:H p-layer in a-Si:H p-i-n cells could induce a disastrous effect on the V_{oc} and fill factor (FF), when no buffer layer at the p/i interface was used [4].

For the optimum structure of i-layers, Fontcuberta i Morral et al. reported that using a nanostructured material

as the i-layer in p-i-n solar cells could result in higher stable efficiencies [5]. T. Kamei et al. showed that inclusion of a small volume fraction of crystallites into the amorphous matrix significantly suppresses defect creation against moderate light illumination [6].

Therefore it is important to understand the exact nature of the materials in the transition region and the correlation with the performance of the constructed solar cells. In this paper, we have incorporated nanostructured Si:H into p- and i-layers of n-i-p type a-Si:H solar cells, and compared the initial and stabilized efficiency after 150 hours AM1.5 light soaking. The solar cell V_{oc} is used as the indicator for the i-layer phase transition. Simultaneously the film microstructure was characterized by high resolution transmission electron microscopy (HRTEM). It is found that the solar cells incorporated a nanostructured p-layer exhibit a higher V_{oc} , while solar cells made from nanostructured i-layers have a better stability against light soaking.

2 Experimental For growing the nc-Si:H p-layers, we used a high hydrogen dilution ($H_2/SiH_4 = 166$) and a high gas pressure of 2 Torr, as well as a high RF power density

of 0.7 W/cm^2 at a low substrate temperature of $70 \text{ }^\circ\text{C}$ (Sample A). To enhance the formation of nanocrystalline nucleation sites for the p-layer deposition of the n-i-p type a-Si:H solar cells, we performed a H_2 -plasma treatment for the underlying i-layer surface (Sample B). In contrast, for suppressing the formation of nanostructures in the p-layer, we increased the ion-bombardments on the growing surface by using a larger RF power density of 1.1 W/cm^2 , while keeping the hydrogen dilution unchanged (Sample C). To further increase the microcrystallinity in the p-layers, the deposition parameters were changed to a higher hydrogen dilution ($\text{H}_2/\text{SiH}_4 = 200$), a lower gas pressure of 0.6 Torr , a higher deposition temperature of $200 \text{ }^\circ\text{C}$, and a series of lower RF power densities of 275 mW/cm^2 (Sample D), 240 mW/cm^2 (Sample E) and 24 mW/cm^2 (Sample F).

The i-layer samples were made in the phase transition region, from just below to just above the onset of crystallinity by varying the RF power and gas pressure. The substrate temperature T_s and hydrogen dilution R were fixed at $200 \text{ }^\circ\text{C}$ and $100 (\text{H}_2/\text{Si}_2\text{H}_6)$. Two series of samples were made at 2 Torr and 0.6 Torr . At the pressure of 2 Torr , samples were made with different power between 8 W and 150 W ; another series of samples made at 0.6 Torr , power is between 4 W and 30 W .

The solar cells were completed by sputtering ITO on the top of p-layers after PECVD process. Current-voltage (I-V) parameters were measured before and after 150 hours light soaking. Light soaking was conducted under 100 mW/cm^2 , AM1.5G spectrum and sample temperature around $40 \text{ }^\circ\text{C}$.

HRTEM was used to characterize the structure of the p- and i- layer samples. The p-layer samples were 15 nm -thick boron-doped layer deposited on a 15 nm -thick intrinsic a-Si:H layer. These p-layer samples, with a combined thickness of 30 nm , were first deposited on a glass substrate and peeled off from the substrates in diluted hydrofluoric acid, and then supported by copper TEM grids. The i-layer samples were n-i structure whose deposition conditions were the same as solar cells. The i-layer samples were peeling off from the bare stainless steel substrate and collected by Cu grids in alcohol.

3 Results and discussion

3.1 Nano-structure in p-layers The nanostructures of p-layer sample A and B can be seen clearly from the high-angle annular dark-field (HAADF) image. HAADF image of Sample A exhibits a few separated bright dots which are characteristics of nc-Si:H, as given in Fig. 1a. Most of these bright dots, the nc-Si:H grains, have a size of around 3 to 5 nm . HAADF image of Sample B exhibits much larger volume fraction XC of nc-Si:H grains (not shown). In order to show that these white dots on Samples A and B are indeed nc-Si:H grains, nano-electron diffraction (NED) was measured for one of the bright dots in Fig. 1a (a grain in Sample A) and the result is shown in

Fig. 1b. The interference fringes near the center indicate the white dot corresponds to a single crystalline structure.

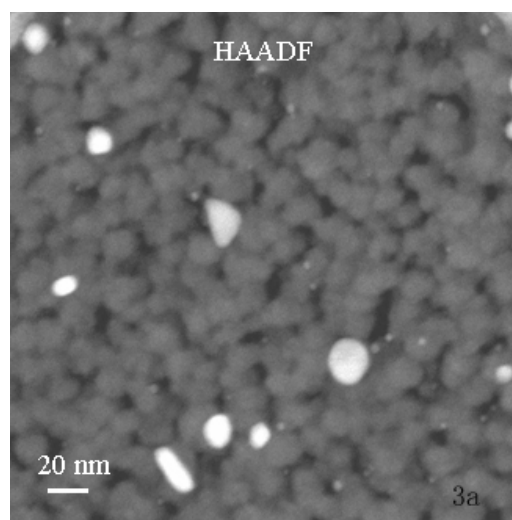


Figure 1 a) The HAADF image of Sample A.

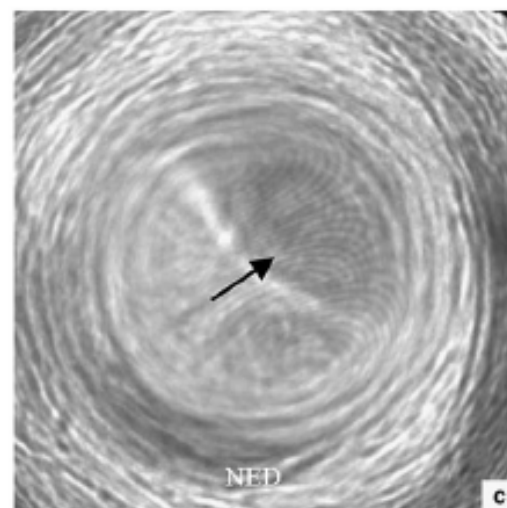


Figure 1 b) The NED image of Sample A.

We prepared a series of n-i-p a-Si:H solar cells on stainless steel substrates (SS) coated with a Ag/ZnO back reflector (BR) at the identical i- and n-layer conditions, but using different p-layers. The deposition conditions for the p-layers used in the solar cells are the same as described for Sample A, B, C, D, E and F, except for the new one, Sample G, the deposition condition of which is the same as used for Sample F, but with a double thickness, in order to avoid the possible influence owing to being partially shunted.

The resultant photovoltaic parameters of the solar cells are summarized in Table 1. It is seen that the V_{oc} value of

the a-Si:H solar cells is varied in a wide range from 1.018–1.042 V for the nc-Si:H p-layers (Sample A and B, Sample B with a larger X_C), 0.973 V for the protocrystalline/amorphous p-layer (Sample C), 0.745–0.676V for the partly microcrystalline p-layers (Sample D and E), to 0.526–0.369 V for the truly μ c-Si:H p-layers (Sample F and G).

Truly μ c-Si:H p-layer has a mean grain size comparable to the thickness of the p-layer (10–15 nm), and a narrow E_g close to that of Bulk c-Si. Considering the trend of columnar growth of grains, they are most likely to form narrow bandgap percolation channels going through the p-layer, even with a small crystalline fraction. That is why even a small crystalline fraction is detrimental for V_{oc} .

Table 1 V_{oc} of a-Si:H solar cells controlled by p-layer

p-layer	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	EFF (%)	p-layer nature
A	1.020	12.1	72.3	8.92	nc-Si on BR
B	1.042	11.5	73.4	8.87	nc-Si on BR
C	0.973	7.3	70.2	5.01	proto-Si on SS
D	0.745	12.2	65.8	5.98	μ c-Si on BR
E	0.676	12.9	64.8	5.65	μ c-Si on BR
F	0.526	12.6	64.4	4.26	μ c-Si on BR
G	0.369	12.6	63.2	2.94	μ c-Si on BR

However, For nc-Si:H p-layers consisting of fine-grained silicon nanocrystallites embedded in a-Si:H matrix, the fine-grains of 3–5 nm are very important, because they are comparable to the De Broglie wavelength of electrons in the material, leading to a larger bandgap, due to a significant quantum confinement effect. Moreover, the fine-grain size is much less than the thickness of the p-layer, therefore, it is not easy to form a percolation channels in the p-layer. The measured T_{auc} optical bandgap for nc-Si:H p-layers deposited under the above conditions is approximately ~ 1.9 eV, and the activation energy is ~ 0.11 eV, which is much less than that of a-Si:H. Therefore nc-Si:H p-layer can provide a larger built-in potential for the solar cells.

3.2 Nano-structure in i-layers

RF-power and gas pressure can be used, together with hydrogen dilution, to change the microstructure of i-layers from amorphous to nanocrystalline states. Table 2 lists the initial and final I-V parameters for three solar cell samples fabricated with different RF-powers of 4 W, 12 W and 16 W at a fixed gas pressure of 0.6 Torr. Sample (a) (4 W) has the highest initial efficiency of 11.5%, and after light soaking of 150 hours the stabilized efficiency is 9.6%. Sample (c) (16 W) has the initial efficiency of 10.3%, and after light soaking of 150 hours the stabilized efficiency is also 9.6%, the same value as that of Sample (a). We observed that the V_{oc}

for sample (c) is increased from 0.986 V to 0.997 V after light soaking. It implies that sample (c) has more nanostructures, because the increase of V_{oc} could be attributed to the reduction of nano-particle sizes in the i-layer [7].

In order to understand the structure of the intrinsic layers of the three samples, HRTEM analyses were also carried out. Figures 2 and 3 gave a comparison of HRTEM images of Samples (a) and (c). Amorphous structure is seen in sample (a), in some area it is well ordered. In sample (c), most structure is identical to sample (a), but a few nanostructures are distinct as the dark area in Fig. 3. The 3rd and 4th diffraction circles are very dim but observable in the selected-area electron diffraction (SAED) pattern for both samples (a) and (c) (not shown). It reflects the existence of very few ordered structures or nanostructures in the film deposited at the high H dilution regime.

Table 2 I-V parameters before and after 150 hours light soaking, on solar cells made at 0.6 Torr with different RF-power.

Power (W)	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	Eff. (%)	State
4	1.027	15.6	71.9	11.5	initial
	1.009	13.8	68.7	9.6	L-soak
12	1.025	14.8	69.1	10.5	initial
	0.999	14.6	65.2	9.5	L-soak
16	0.986	15.1	69.1	10.3	initial
	0.999	15	64.3	9.6	L-soak

High efficiency a-Si:H solar cells can also be fabricated under high pressure 2 Torr with an optimization of RF-power density and a higher deposition rate of ~ 2.5 Å/s. HRTEM image of the sample deposited at 2 Torr shows the existence of very good ordered structure in some area. Figure 4 shows the initial and stabilized I-V curves of a solar cell whose i-layer is prepared at 2 Torr. The stabilized efficiency of 10.4% after 150 hours light soaking is higher than the best value obtained at low pressure 0.6 Torr, under which the i-layer deposition rate is 0.6 Å/s.

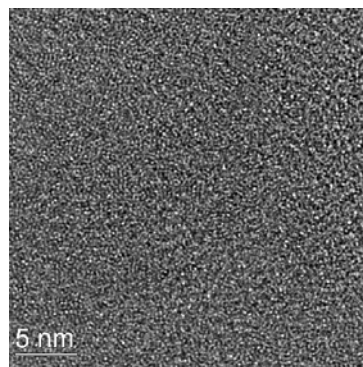


Figure 2 The HRTEM image of Sample a.

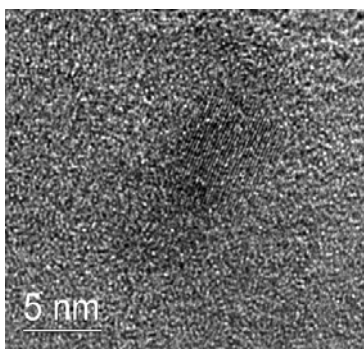


Figure 3 The HRTEM image of Sample c.

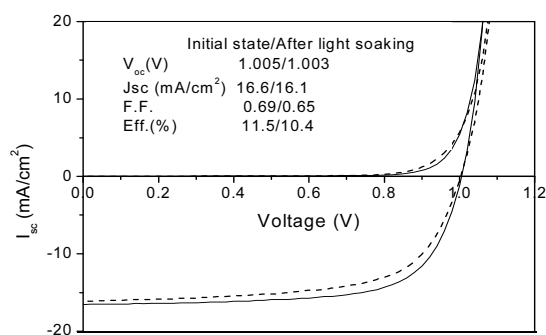


Figure 4 Initial and stabilized I-V curves of a high efficiency a-Si:H solar cell, whose intrinsic layer was made at 2 Torr. Light soaking is under AM 1.5 100 mW/cm^2 for 150 hours.

4 Summary High efficiency single junction n-i-p type a-Si:H solar cells were fabricated, using the p- and i-layers were deposited at the edge of crystallinity. Nano-structures in p-layer could improve the V_{oc} . Solar cells with an i-layer deposited just below the onset of crystallinity show a higher initial efficiency, while solar cells with an i-layer deposited just above the onset of crystallinity show a better stability against light soaking.

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