# FINE-GRAINED NANOCRYSTALLINE SILICON P-LAYER FOR HIGH OPEN CIRCUIT VOLTAGE A-SI:H SOLAR CELLS

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### ABSTRACT

thick, deposited on a-Si:H substrates.

#### **EXPERIMENTAL**

Hydrogenated amorphous silicon (a-Si:H) singlejunction solar cells with high open circuit voltage (V<sub>oc</sub>) are fabricated using a wide bandgap boron doped Si:H player deposited at high hydrogen dilution, low substrate temperature and with H<sub>2</sub>-plasma treatment that promotes nanocrystalline silicon (nc-Si:H) formation. This paper presents the structure of this p-type material characterized by Raman scattering spectroscopy and High Resolution Transmission Electron Microscope (HRTEM). It is found that the p-layer that leads to high V<sub>oc</sub> a-Si:H solar cells is a mixed-phase material that contains fine-grained nc-Si:H embedded in a-Si:H matrix.

## INTRODUCTION

A-Si:H single-junction solar cells with high Voc, up to 1.04 V, are fabricated at the University of Toledo (UT) using a wide bandgap boron doped Si:H p-layer deposited at high hydrogen dilution and low substrate temperature [1]. There are several reports in the literature that provide different suggestions about the structure of ptype materials deposited under similar conditions [2, 3] to reach high  $V_{oc}$ . It is important to understand the exact nanostructure of the p-type material used at UT and other laboratories to produce high-Voc solar cells. Unfortunately. it is challenging to obtain results that lead to a definite conclusion since on one hand, the p-layer Si:H material, ~15nm thick, is deposited on an a-Si:H substrate in an a-Si:H n-i-p type solar cell and the commonly used methods to determine the nanostructure of these materials require the films to be at least 100nm in thickness and are deposited on glass or crystalline Si substrates, while on the other hand, the nanostructure of the thin film Si:H based material depends sensitively on the substrates and the thickness in addition to the deposition conditions such as hydrogen dilution and substrate temperature. In an earlier paper, we reported our preliminary finding that these p-type materials used in UT's high-Voc solar cells are fine-grained nc-Si:H, based on a modeling study using AMPS [4]. In this paper, we report our further investigation of the nanostructure of this p-type material using Raman spectroscopy and HRTEM, which allows us to directly measure the nanostructure of the films, ~15nm

A-Si:H solar cells were deposited using rf-PECVD on stainless steel covered with an Al/ZnO back reflector. The n- and i-layers were deposited under the conditions reported earlier [1] and these are the same conditions used in the fabrication of high-efficiency triple-junction solar cells at UT [5]. These p-layers were deposited using a high hydrogen dilution, high rf power, and a low substrate temperature to promote nc-Si:H formation for ni-p type solar cells. H<sub>2</sub>-plasma treatment on i layer, which is reported in Ref.3, was also investigated in n-i-p type a-Si:H solar cells.

Raman scattering was performed to characterize the structure of films. The 488nm laser line from a watercooled  $Ar^+$  laser was used for the excitation. The samples used for Raman study are approximately 300 nm thick and were deposited on glass substrates. Optical transmission was also measured for these samples. Raman spectra were measured from both the front side of the films as well as the backside of films through the glass substrates.

For HRTEM, a Jeol 2010 STEM microscope was used. The samples for the HRTEM study are 15nm-thick boron-doped p-layer deposited on a 15nm-thick intrinsic a-Si:H layer that was grown under the same conditions as the intrinsic layer in a high- $V_{oc}$  a-Si:H solar cell. The Si:H layers, with a combined thickness of 30nm, were first deposited on a glass substrate and then peeled off from the substrates using diluted hydrofluoride acid.

# **RESULTS AND DISCUSSIONS**

# **Raman Scattering Spectroscopy**

Figure 1 shows the Raman spectrum of a 350 nm thick p-layer deposited on a glass substrate. Fig. 1a is spectrum measured from the front surface and it is deconvoluted into three major peaks, located at 480cm<sup>-1</sup>, 514.5 cm<sup>-1</sup> and around 500cm<sup>-1</sup>, corresponding to the amorphous phase, the nc-Si:H phase and the grain boundary interfaces, respectively. According a bond polarizability model [6], a 514.5cm<sup>-1</sup> Raman peak corresponds to a nc-Si:H with mean grain size of approximately 2.0 nm. We believe that the actual grain

size may be larger than this value since the phonon confinement effect may be overestimated in using this model without considering the existence of tensile stress in the film [7].

Since the 300nm sample is thicker than the 15nm layer used in an actual solar cell, the nanostructure of the sublayer probed by Raman may have higher volume fraction of nc-Si:H phase than the initial 15nm deposited on the substrate. To effectively measure the nanostructure of the film initially deposited on the substrate, we measured Raman spectra also from the backside of the sample, through the glass substrate. Raman spectrum taken from backside (Fig1b) shows a smaller crystalline volume fraction, which is 11%, than from front surface, which is 48%. The crystalline volume fraction  $X_c$  was estimated from  $X_c = (I_c + I_{gb})/(I_c + I_{gb} + I_a)$ , where I<sub>c</sub>, I<sub>ab</sub>, I<sub>a</sub> are integrated intensities of the nc-Si:H phase, the grain boundary interface and the amorphous phase. The deconvoluted peaks in Fig. 1b shows a 513cm<sup>-1</sup> Raman scattering peak, indicating the existence of fine-grained nc-Si:H during the initial growth of the film when it is deposited on glass. The nc-Si:H size is about 1.8nm according to the Si spheres formation in Ref.6. One can conclude that the nc-Si:H size is increased with the increased thickness.



Figure 1 The Raman spectrum taken from the front side surface (top, Fig.1a) and the backside through the glass substrate (bottom, Fig.1b). The scattered dots are measured data and the lines are deconvoluted fitting curves.

One may still question the results from Raman spectrum obtained through the glass substrate because 1) at 488nm laser line, the Raman scattering may be from the sublayer of the film that is up to 100 nm thick which corresponds to the absorption depth for this laser line; and 2) the initial film is deposited on glass and therefore may have different nanostructure than those films deposited on a-Si substrate as in an n-i-p type solar cell. In order to characterize the thin p-layer in a solar cell, HRTEM was performed and the results are presented below.

HRTEM



Figure 2 HRTEM images of p layer deposited at low  $T_s$  and high H dilution. Fig 2A and 2B are HAADF (Highangle annular dark-field ) and SAED (Selected-area electron diffraction) images of the Sample A with a H<sub>2</sub>plasma treatment on i-layer; Fig 2C and 2D are HAADF and NED (Nano-electron diffraction) images of the Sample B which has a slightly less V<sub>oc</sub>.

HRTEM was performed on a 15-nm thick p-layer grown on a 15-nm intrinsic a-Si:H layer, which is the exactly the same as i-p interface in device fabrication. Additional H<sub>2</sub>-plasma treatment on i layer is carried out for some of the samples. Sample A went though H<sub>2</sub>-plasma treatment (Fig 2A and Fig 2B) and Sample B did not (Fig 2C and Fig 2D). Figure 2A shows a high-angle annular dark-field (HAADF) image, exhibiting many separated bright dots which are characteristics of nc-Si:H. Most of these bright dots, the nc-Si:H grains, have a size of around 3 to 5 nm, which is larger than the size estimated from Raman measurement. Several large white dots in Figure 2A are the clusters of 3 or 4 crystalline grains. Figure 2B is the selected-area electron diffraction (SAED), showing a diffraction pattern with crystalline feature for the area probed.

Sample B was deposited under the same conditions as Sample A except that it did not go through H<sub>2</sub>-plasma treatment that promotes nc-Si:H growth [3]. Such a p-layer usually leads to an a-Si:H solar cell with approximately 20mV less in Voc, as described below. Figure 2C shows a HAADF image of Sample B. exhibiting smaller volume fraction of nc-Si:H grains. 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. 2C (a grain in Sample B) and the result is shown in Fig. 2D. The interference fringes near the center indicate the white dots correspond to crystalline structure. Comparing the HAADF images of Samples A and B shown in Figures 2A and 2C, respectively, it is concluded that H<sub>2</sub>-plasma treatment leads to a higher volume fraction of nc-Si:H phase in p-layer.

Another p-layer, Sample C, was deposited under a similar condition as Sample A but with higher rf power. (HRTEM result is not shown here). Raman spectrum measured from both the front and backside on glass shows that this p-layer material is amorphous without any observable nc-Si:H phase. When this p-type material is used in a nip a-Si:H solar cell, it leads to a  $V_{oc}$  of 0.98V, less than that with the p-type materials containing fine-grained nc-Si:H.

#### **IV Performance Comparison**

In order to investigate the impact of nanocrystalline p-layer on solar cell devices, we incorporate above-described nc-Si:H p-layers into a-Si:H nip solar cells, which are fabricated on stainless steel substrates coated with a Al/ZnO back reflector. Since the  $V_{oc}$  is less than 1 V for those cells made with a-Si:H p layer, the comparison here is limited between the Sample A conditions and Sample B conditions described above.

Table 1. Comparison of  $V_{oc}$  of a-Si:H solar cells with different p layers.

P layer conditions	Highest V <sub>oc</sub> (V)
Sample A	1.042
Sample B	1.018

P layer with Sample B condition has fewer nc-Si:H grains than Sample A, so it is closer to a-Si:H to nc-Si:H transition. Its corresponding V<sub>oc</sub> is about 20mV less than that made under Sample A condition. Therefore, some nc-Si:H formation in p layer is needed to improve the V<sub>oc</sub> of a-Si:H solar cells. However, at much higher volume fraction of nc-Si:H in p layer the V<sub>oc</sub> drops. The optimum p layer for obtaining high V<sub>oc</sub> is to have a mixed-phase material with fine grained nc-Si:H embedded in a-Si:H network. Figure 3 shows the IV curve of the solar cell having V<sub>oc</sub>=1.042V.



Figure 3 IV characteristics of the a-Si:H solar cell with  $V_{oc}$ =1.042V (AM1.5, 100mW/ cm<sup>2</sup>).

## CONCLUSION

The p-layer used at UT to obtain high- $V_{oc}$  a-Si solar cells is a mixed–phase material that contains nc-Si:H grains, ~3-5 nm in size, embedded in an a-Si:H matrix. Comparing HAADF images of two samples (Samples A and B), it is concluded that the mixed phase p-layer with a higher volume fraction of nc-Si:H phase, within the range studied, leads to a higher V<sub>oc</sub>.

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#### REFERENCES

[1] X. Deng, Annual Subcontract Progress Report submitted from UT to NREL under Thin Film Partnership Program NDJ-2-30630-08, Phase I Report (2002) and Phase II Report (2003).

[2] S. Guha, J. Yang, P. Nath, and M. Hack, *Appl. Phys. Lett.* **49**, 1986, pp. 218- 220.

[3] R. J. Koval, Chi Chen, G. M. Ferreira, A. S. Ferlauto, J. M. Pearce, P. I. Rovira, C. R. Wronski, and R. W. Collinsa, *Appl. Phys. Lett.* **81**, 2002, pp. 1258-1260.

[4] X. Liao, W. Wang and X. Deng, *Proc. 29th IEEE-PVSC*, 2002, pp. 1234-1237

[5] W. Wang, H. Povolny, W. Du, X. Liao and X. Deng, *Proc. 29th IEEE-PVSC,* 2002, pp. 1082-1085.

[6] J. Zi, H. Buescher, C. Falter, W. Ludwig, K. Zhang and X. Xie, *Appl. Phys. Lett.* **69**, 1996, pp. 200-202.

[7] V. Paillard, P. Puech, R. Sirvin, S. Hamma and P. Roca i Cabarrocas, *J. Appl. Phys.* **90**, 2001, pp. 3276-3279.