Short Communication

Low Temperature Deposition of Boron Doped P-type Si:H Window Layers for Amorphous Silicon Solar Cells

Zhihua Hu, Shurong Wang, Zhaohui Yao

Key Lab. of Advanced Technology & Preparation for Renewable Energy Materials, Ministry of Education, Solar Energy Research Institute, School of Energy and Environmental Sciences, Yunnan Normal University, Kunming, Yunnan, 650092, P.R. China
*E-mail: 1049173841@qq.com

Received: 26 February 2021 / Accepted: 6 April 2021 / Published: 30 April 2021

In this paper, boron doped Si:H p-layers were prepared at a low substrate temperature of 60°C by using a PECVD technique with varied a hydrogen gas dilution ratio of 50, 100 and 150. A detailed investigation was employed on as-deposited films by using Transmission and Raman spectra measurements. The crystalline fractions in volume of these films were estimated as ~16%, 52% and ~73% respectively. These p-layers had been incorporated into single junction a-Si:H solar cells with configuration of Glass/TCO/p-i-n/Al. It was found that a p-layer prepared with a hydrogen gas dilution ratio of 50 is more benefit for device performances. A dot cell with an area of 0.1256 cm$^2$ had been made and an energy conversion efficiency of 9.0% has been achieved.

Keywords: P-I-N a-Si solar cells; p-type Si:H window layers; low temperature deposition

1. INTRODUCTION

The p-type window layer is critical to hydrogenated amorphous silicon (a-Si:H) alloy solar cells[1]. One of the most great milestone in a-Si:H solar cell technology was Carbon incorporation in the p-type window layer[2]. Meanwhile, considerable effort had focused on alternating this alloy p-layer from amorphous a-SiC:H to “nanocrystalline” Si:H[3,4]. However, incorporation of nano-Si:H p-layers without carbon addition to amorphous silicon solar cells has not been greatly successful[5,6], although significant progresses have been achieved by Hamma and Roca[7]. Challenge here is to develop a homogeneous p-layer with a wide optical band gap and a high electrical conductivity on transparent conductive oxides (TCO) for pin solar cells. One possible way to achieve this like film is to deposit p-layers under a high hydrogen dilution ratio, a high power density at a low substrate temperature, with a expectation for increasing hydrogen content and/or decreasing Si crystallites grain size in a-Si network.
This work explores the possibility of deposition of Si:H p-layers at low temperature (~60°C) using hydrogen dilution technique and it’s incorporation into single junction solar cells with amorphous silicon i-layers deposited at a higher substrate temperature (~170 °C) in a superstrate sequence.

2. EXPERIMENTAL

Ultra thin boron doped Si:H thin layers were prepared with a conventional RF-PECVD system using a mixture of B₂H₆, H₂ and SiH₄ at a low temperature (~60°C) under a RF power density of 1W/cm², a pressure of 200 Pa and a varied hydrogen dilution ratio (H₂/SiH₄) of 150, 100 and 50. Films were deposited on GZO coated glasses. Since the subsequent i-layer and n-layer in solar cells were deposited at a higher temperature of 170°C, all of the samples have been heated from 60°C to 170°C and kept in vacuum for 2 hours before cooling down and taking out for investigation. The bandgap in the visible spectral range was estimated by using an UV–VIS–NIR double beam spectrophotometer measurement. Raman scattering was used to detect the crystallinity. The power of the laser was kept small to prevent crystallization during Raman spectroscopy measurements.

Table 1. PECVD conditions for pin solar cells

<table>
<thead>
<tr>
<th>Substrate temperature (°C)</th>
<th>rf power density (mW/cm²)</th>
<th>Chamber pressure (Pa)</th>
<th>H Dilution rate (H₂/SiH₄)</th>
<th>Deposition time (min)</th>
<th>Doping gas concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-nc-Si:H</td>
<td>60</td>
<td>1000</td>
<td>200</td>
<td>150,100,50</td>
<td>2</td>
</tr>
<tr>
<td>i-a-Si:H</td>
<td>170</td>
<td>70</td>
<td>70</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td>n-nc-Si:H</td>
<td>170</td>
<td>70</td>
<td>70</td>
<td>60</td>
<td>5</td>
</tr>
</tbody>
</table>

Single junction solar cells were fabricated on GZO coated glasses under conditions presented in Table1. The p-layers were deposited at 60°C and then heated to 170°C. For deposition of intrinsic active layers, standard conditions were used with a power density of 70 mW/cm², a pressure of 70 Pa, a hydrogen dilution ratio of 10 and a substrate temperature of 170°C. A higher hydrogen dilution ratio of 60 was employed for the n-layer deposition. The area of solar cells was defined by a mask-evaporation of Aluminum rear dots with an area of 0.1256 cm². The solar cell produced has a configuration of Glass/TCO/p(20nm) /i (350nm) /n (30nm) /Al (200nm), TCO here was Gallium doped Zinc Oxide (GZO). The dot solar cells were measured under a condition of AM1.5, 100mW/cm² at 25°C.

3. RESULTS AND DISCUSSION

Fig.1 shown the Transmission spectra of Si:H p-layers (~50nm) prepared on GZO coated glasses. Curve (a), (b) and (c) in Fig.1 represent spectrum of thin film deposited under different hydrogen dilution ratio (H₂/SiH₄) of 150, 100 and 50 respectively. It is noted from Fig.1 that the absorption spectra of the Si:H films is monotonically shifted towards longer wavelength with
increasing hydrogen dilution ratio. However, the absorption behavior of Fig.1(c) in the shorter wavelength region is markedly different from Fig.1(a) and (b), which show remarkable bending. The curve bending could have originated from the dual band gap nature of thin films prepared under higher hydrogen dilution ratio, 150 for (a) and 100 for (b), which facilitates the formation of Si crystallites. The effective optical bandgaps calculated from the Tauc’s plot are 1.68 eV for (a), 1.78 eV for (b) and 1.90 eV for (c). The optical band gap for the Si:H films decrease with increasing hydrogen dilution ratio.

![Transmission spectra of Si:H p-layers prepared on ZnO:Ga with hydrogen dilution ratios of 150 (a), 100 (b) and 50 (c)](image)

**Figure 1.** Transmission spectra of Si:H p-layers prepared on ZnO:Ga with hydrogen dilution ratios of 150 (a), 100 (b) and 50 (c)

Fig. 2 presents the Raman spectra recorded in the range of 100 to 650 cm\(^{-1}\) taken from annealed Si:H p-layers with different hydrogen dilution ratios deposited on GZO coated glass substrates. In order to obtain the parameters such as peak position, FWHM and area, a sum of four Gaussian and two Lorentzian line-shapes with a constant baseline were used to fit Raman spectra. It is noted that, in Fig.2, the TO mode of Si film broadens, and the peak position shifts towards lower wavelength with increasing hydrogen dilution ratio in comparison with that of bulky crystalline silicon (521 cm\(^{-1}\) not shown in Fig. 2).
Figure 2. Fitted Raman spectra of Si:H p-layers prepared on ZnO:Ga with hydrogen dilution ratios of 150 (a), 100 (b) and 50 (c)

Fig. 2 also shows five broad bands around 135, 330, 440, 480 and 500 cm$^{-1}$ which originated from a-Si TA, LA, LO, TO modes and one either grain boundary (GB) phase, a silicon Wurzite phase, or even smaller crystallites [9] that could result from twinning defects. These assignments are clearly labeled in Fig.2(b). The increase of a-Si TA, LA, LO and TO modes intensities also suggests the reduction of Si nanocrystallites volume fraction in the a-Si:H matrix[10]. These changes in Si nanocrystallites in a-Si:H could be the reason for the notable difference in transmission spectra in the short wavelength region (see Fig. 1).

This ultra thin p-type Si:H films have been incorporated into single junction solar cells in a superstrate structure. The intrinsic layers were directly deposited on top of a p-layer at 170 °C under standard conditions with a hydrogen dilution ratio of 10 (see Table 1). No buffer layer has been intentionally inserted into the p/i interface. Fig.3 displays the illuminated J-V characteristics of solar cells with p-layers prepared under different hydrogen dilution ratios from 150 to 50 as in (a) to (c). It is observed that the overall performances are improved while hydrogen dilution was decreased from 150 to 50. Efficiency (Eff) of 7.7 % with an open circuit voltage (Voc) of 0.82 V and a fill factor (FF) of 0.63 (see curve c in Fig 3) has been achieved for a slightly crystallized p-layer (Xc ~16%). However, the Voc and FF are 0.50, 0.69 and 0.56, 0.60 respectively for (a), (b). This drop in the solar cell parameters is due to the defects and band edge discontinuities at the p/i interface, which might cause recombination of photocarriers at the junction while highly crystallized p-layers are used. This initial result is in agreement with Hamma and Roca [7] who intended that the optimum crystalline volume fraction of p-layer should be around 30 % when a-Si:H is used as i-layer for p-i-n solar cells.
In order to achieve a high quality p/i interface, a hydrogen plasma treatment for the underlying p-layer surface was employed prior to deposition of the i-layer [11]. This treatment could improve the material quality of the i-layer, because there are possible weak bonds on the p-layer surface [12]. Fig. 4 gives the light J-V characteristics of a-Si:H p-i-n solar cell with a slightly crystallized nano-Si:H p-layer and a H2-plasma treatment incorporated, which shows an Eff of 9.0 % with a short circuit current density (Jsc) of 15.2 mA/cm², an open circuit voltage (Voc) of 0.90 V and a fill factor (FF) of 0.65 (AM1.5, 25°C). As can be seen, although the Voc and Jsc are acceptable, the FF value is relatively low, indicating that the material quality and the optimization of process need further improvements.

4. CONCLUSIONS

Boron doped Si:H p-layers were deposited by PECVD technique using a gas mixture of SiH4, H2 and B2H6 at a low substrate temperature (~60°C). Visible transmission and Raman scattering
spectra were employed for optical and microstructural characterization. Incorporation of as developed p-layers into single junction a-Si:H solar cells shows a slightly crystallized Si:H p-layer perform the best. Applying these slightly crystallized Si:H p-layers, together with an initial H₂-plasma treatment of the p-layer prior to deposition of the i-layer, an efficiency of 9.0% with an open circuit voltage of 0.90 V, a fill factor of 0.65 and a short circuit current density of 15.2 mA/cm² has been achieved.

ACKNOWLEDGMENTS
We are thankful for the Project Supported by National Foundation of Science, China, No. 61941401.

© 2021 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).

References

© 2021 The Authors. Published by ESG (www.electrochemsci.org). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/).