Journal of Non-Crystalline Solids 358 (2012) 2324–2326

Contents lists available at SciVerse ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Enhanced spectral response by silicon nitride index matching layer in amorphous silicon thin-film solar cells

C.H. Hsu *, Y.P. Lin, H.J. Hsu, C.C. Tsai

Department of Photonics, National Chiao Tung University, Hsinchu, Taiwan

ARTICLE INFO

Article history:
Received 10 September 2011
Received in revised form 9 December 2011
Available online 9 February 2012

Keywords:
Hydrogenated amorphous silicon thin-film solar cell;
Plasma enhanced chemical vapor deposition;
Hydrogenated amorphous silicon nitride

ABSTRACT

We employed the low temperature hydrogenated amorphous silicon nitride (a-SiN_x:H) prepared by plasma-enhanced chemical vapor deposition as a refractive index (n) matching layers in a silicon-based thin-film solar cell between glass ($n=1.5$) and the transparent conducting oxide ($n=2$). By varying the stoichiometry, refractive index and thickness of the a-SiN_x:H layers, we enhanced the spectral response and efficiency of the hydrogenated amorphous silicon thin-film solar cells. The refractive index of a-SiN_x:H was reduced from 2.32 to 1.78. Optimizing the a-SiN_x:H thickness to 80 nm increased the J_{SC} from 8.3 to 9.8 mA/cm^2 and the corresponding cell efficiency increased from 4.5 to 5.3%, as compared to the cell without the a-SiN_x:H index-matching layer on planar substrate. The a-SiN_x:H layers with graded refractive indices were effective for enhancing the cell performance.

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) has received much attention [1,2] for thin-film solar cell applications due to the following properties. The bandgap of approximately 1.75 eV makes it suitable for the effective absorption of the solar spectrum. The high absorption coefficient of a-Si:H allows it to absorb light with less material. The low process temperature also realizes the use of low cost glass as substrate, and the material is scalable for large area manufacturing. However, the Staebler–Wronski effect (SWE) [3] induces defects resulting in a decrease in the cell efficiency [4,5]. The degree of degradation due to SWE is related to the material quality and the film thickness [6]. The SWE can be reduced by limiting the thickness of a-Si:H absorber, which makes light management more crucial in improving cell efficiency.

The difference in refractive indices causes optical reflection in an electro-optical device. The surface with proper texture can reduce the total reflection which was suggested to be due to the profiled refractive index at the rough interface [7]. Moreover, studies have also reported the improvement of optical reflection by depositing titanium oxide or silicon oxide at the interface between the transparent conducting oxide (TCO) and Si [8,9]. In this work, we employed the low temperature hydrogenated amorphous silicon nitride (a-SiN_x:H) prepared by plasma enhanced chemical vapor deposition (PECVD) as a refractive index-matching (or anti-reflective, AR) layers between glass ($n=1.5$) and TCO ($n=2$). The refractive index of a-SiN_x:H can be easily changed in PECVD through varying the deposition conditions. Moreover, the deposition of a-SiN_x:H and the TCO films can be carried out at low temperature. The a-SiN_x:H can also act as a passivation layer which allows the use of low cost substrates containing certain levels of mobile ions. By varying the stoichiometry, refractive index and thickness of the a-SiN_x:H layers, the improved cell performance were obtained and discussed.

2. Experimental

The a-SiN_x:H films were deposited on 4 mm glasses by a PECVD system at a frequency of 27.12 MHz. It is a commercial load-lock system with a maximal substrate size of 20×20 cm^2. Gas mixtures of SiH_4, NH_3 and H_2 were used and the substrate temperature was kept at 200 °C. The NH_3-to-SiH_4 ratio, rf power and hydrogen flow rate were varied to obtain different stoichiometry and refractive index of a-SiN_x:H. This a-SiN_x:H layer was deposited to have single or graded refractive index. Then, a flat TCO layer with a thickness of 900 nm was deposited by RF sputtering, followed by a p-i-n a-Si:H solar cell. The a-SiN_x:H and all three layers (p-i-n) were prepared in a single deposition chamber. The thickness of the a-Si:H absorber layer was 300 nm, followed by a TCO/Ag back reflector. The optical reflection was obtained from the UV/VIS/IR spectrometer. The refractive index was measured by an n&k analyzer and was determined at 632.8 nm. The cells had an area of 5×5 mm^2 were patterned for I–V measurement. The J-V characteristic and the spectral response were measured by an AM1.5 illuminated I–V system and an external quantum efficiency (EQE) measurement, respectively.

---

* Corresponding author.
E-mail address: sean.c.hsu@gmail.com (C.H. Hsu).

0022-3093/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2011.12.102

3. Results

Fig. 1 shows the refractive index as a function of the hydrogen dilution ratio (defined as the H_2 flow rate divided by the SiH_4 flow rate) with different NH_3-to-SiH_4 flow rate ratio (R_{NH3}). The R_{NH3} is one of the dominant factors which influence the refractive index of a-SiN_x:H. Depending on the hydrogen dilution ratio, the refractive index was reduced approximately from 1.9 to 1.8, with R_{NH3} increased from 5 to 8.3. Moreover, the refractive index was also affected by the hydrogen dilution ratio. Hydrogen is generally introduced to assist the dissociation of reactant gas during deposition. At a smaller R_{NH3}, the introduction of H_2 significantly increased the refractive index. For a larger R_{NH3}, hydrogen still increased the refractive index slightly. As a result, the minimum refractive index as low as 1.78 was prepared in this study, using R_{NH3} of 8.3 and no additional hydrogen flow.

Since the refractive index can be changed in-situ by the deposition conditions, the a-SiN_x:H with graded refractive index was achieved to further reduce the optical reflection. Base on the experimental results, the films with same thickness had refractive indices of 1.78, 1.86, 1.9, and 1.97 were sequentially deposited on the glass. To investigate the optical characteristics, samples with graded or constant *n* of the a-SiN_x:H AR layers were deposited on 4 mm glasses, followed by a 0.9 μm-thick TCO. The samples were also confirmed to have negligible roughness by scanning probe microscopy. Fig. 2 shows the transmittance with different thicknesses of a-SiN_x:H AR layers. Due to the thickness dependent optical interference, the curve of transmittance appears as a periodic fluctuation. With the increasing thicknesses of a-SiN_x:H films, the periodic fluctuation of the transmittance shifted toward long wavelength. The average transmittance of the samples with 80 and 100 nm a-SiN_x:H layers was higher than that of the samples with 0 and 40 nm a-SiN_x:H layers in both single or graded case. The samples with single refractive index showed a smaller fluctuation and a slightly higher transmittance as compared to the samples with graded refractive index.

Fig. 3 illustrates the performance of the a-Si:H thin-film solar cells with different thicknesses of a-SiN_x:H having graded refractive index. The open circuit voltage (V_{OC}) and fill factor (FF) showed no significant change when increasing the thickness of a-SiN_x:H. In contrast to the cell without a-SiN_x:H, the J_{SC} increased from 8.3 to 9.8 mA/cm^2 and the corresponding efficiency increased from 4.5% to 5.3%. The scattering was arising from the experimental error due to the incomplete absorption. The results still indicate a better performance as the thickness of a-SiN_x:H film was 80 nm.

The external quantum efficiency (QE) of a-Si:H solar cells is shown in Fig. 4. Because there was no front surface texturing in the devices, the QE in the long-wavelength region fluctuated due to optical interference. With the addition of a-SiN_x:H layers, the shorter wavelength response slightly increased. As the thickness of the a-SiN_x:H was 40 nm, the QE at wavelengths of 500 and 580 nm had steep decrease. As a result, the current density was even lower than the device without a-SiN_x:H. As the thickness was 100 nm, the QE decreased at the wavelength of 600 nm but increased in the 470–510 nm region. There was an optimized thickness of 80 nm showing a smoother response in the 500–600 nm region. Although there were drops at the wavelengths of 600 and 690 nm, a much

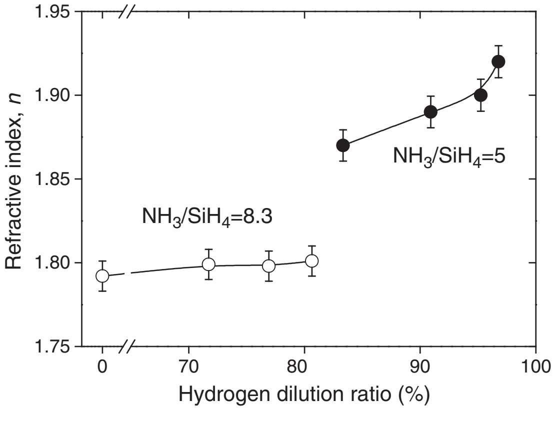

Fig. 1. Effects of hydrogen dilution ratio and NH_3-to-SiH_4 flow rate ratio on the refractive index of a-SiN_x:H film.

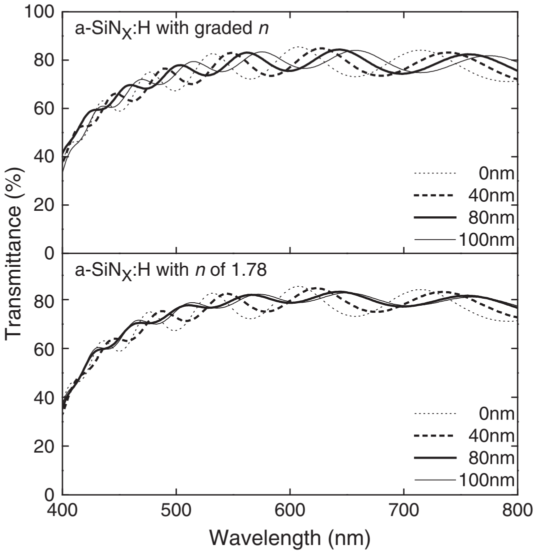

Fig. 2. Transmittance of the samples with different thicknesses of a-SiN_x:H AR layer. The upper and lower figures show the dependence of graded and single refractive index, respectively.

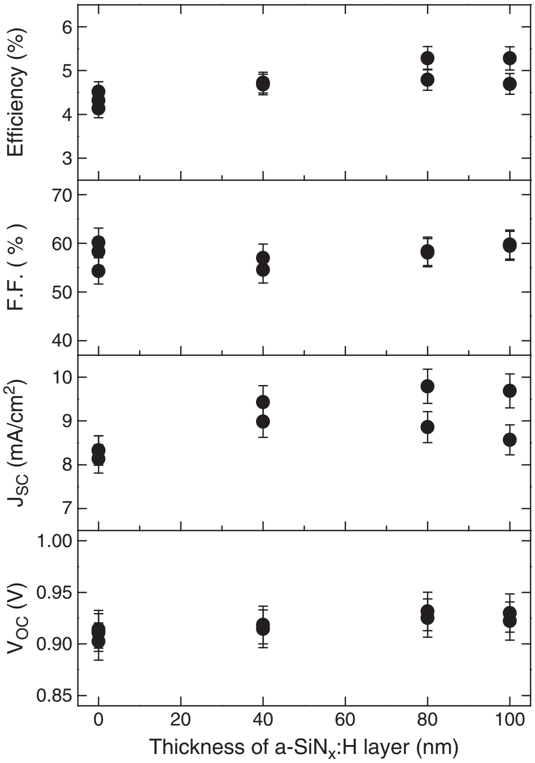

Fig. 3. J-V characteristics of the cells with different thicknesses of the graded a-SiN_x:H layer.

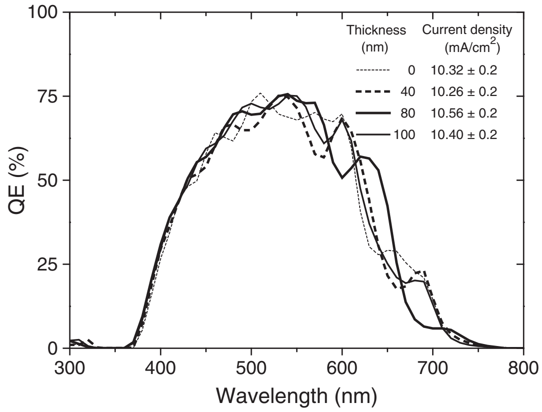

Fig. 4. External quantum efficiency of a-Si:H thin-film solar cells with different thicknesses of a-SiN$_x$:H layers having graded refractive index.

better response in the 600–650 nm region resulted in a higher current density of 10.56 mA/cm^2.

4. Discussion

The refractive index of glass (n_0) is 1.5 and that of TCO (n_2) is approximately 2. According to the equation, $n_1 = (n_0\ n_2)^{1/2}$, the theoretically ideal refractive index (n_1) of a-SiN$_x$:H as an antireflective layer is 1.73. The refractive index of a-SiN$_x$:H is determined by the concentration of N in the film, which is significantly affected by the deposition conditions. Studies [10,11] have reported the refractive index of a-SiN$_x$:H deposited at low temperature by PECVD can be adjusted in the range from 1.7 to 2.4. By controlling the power, pressure, and the flow rate ratio of the feeding gas, low refractive indices of a-SiN$_x$:H can be obtained. As shown in Fig. 1, as the R$_{NH3}$ increased, the N content in a-SiN$_x$:H film increased which resulted in a decreased refractive index. The addition of H$_2$ also affects the film content and the resulting refractive index. The H$_2$ may increase the dissociation in the plasma, but also increase the etching on the surface. The preferential etching of the N–H bonding by the hydrogen plasma was proposed to increase the refractive index [12]. As a result, the lower hydrogen dilution ratio would further lowered the refractive index. A minimum refractive index of 1.78 was obtained when there was no hydrogen in the feeding gas.

The glass used in this study had no particular treatment to reduce the iron content. Therefore, the transmittance in the shorter wavelength region was significantly lower (Fig. 2) because of the absorption due to charge transfer process [13]. Although the practical transmittance would be affected by the following p-i-n device, this still indicated that the reflection of the devices with AR coating can be minimized at certain particular wavelengths, and could have higher reflection at others. As can be seen in Fig. 2, the transmittance of the samples with a-SiN$_x$:H AR layers having *n* of 1.78 have a similar trend to that of the samples with a-SiN$_x$:H having graded *n*. The average transmittance of the samples with constant *n* was slightly higher than that with graded *n*. However, the solar cells consisted of these AR layers showed no significant difference. This may be due to the further influence of the p-i-n device which reduced the small transmittance difference. Moreover, the difference of refractive index between glass and TCO may also be too small, so that the refractive index of 1.78 was already effective in improving the cell performance. To further improve the index matching by graded *n*, materials such as silicon oxide (SiO$_x$) or silicon oxynitride (SiO$_x$N$_y$) can also be deposited by PECVD. The materials can have refractive indices as low as approximately 1.5 which is closer to the refractive index of glass.

A same device process carried out on a textured SnO$_2$:F glass can achieve an efficiency of 9.45% with V$_{OC}$ = 0.91 V, J$_{SC}$ = 14.42 mA/cm^2 and FF = 72.36% [14]. In this study, planar substrates were used to investigate the effect of a-SiN$_x$:H index-matching layers. The results in Fig. 3 showed a higher V$_{OC}$ of the device than the one on the above mentioned textured SnO$_2$:F glass, which may be due to the less interface recombination from the planar structure. The improvement of J$_{SC}$ contributed by the AR layer was the main factor for enhancing the performance of the a-Si:H solar cells. An optimized thickness of 80 nm of the graded a-SiN$_x$:H AR layer was observed from the J-V characteristics.

The QE measurement also showed an optimized current density as the thickness was 80 nm, which is shown in Fig. 4. A relative increase of 2.3% (from 10.32 to 10.56 mA/cm^2), as compared to the device without a-SiN$_x$:H on planar substrate was obtained, owing to the increases in the wavelength region of 510–560 nm and 610–660 nm. Considering the standard AM1.5 solar spectrum, a higher irradiance was located in the range from 480 to 600 nm. According to the equation of quarter-wavelength ($d = \lambda/4n$), a corresponding ideal thickness from 67 to 82 nm was attained for the a-SiN$_x$:H having refractive index of 1.78. The calculated value was close to the experimental result of 80 nm. The disadvantage of the QE in the long wavelength region may be able to be improved through further texturing of the substrates.

5. Conclusions

We were able to deposit the a-SiN$_x$:H layer with refractive index as low as 1.78 through varying the deposition conditions. By optimizing the thickness and the refractive index of the a-SiN$_x$:H index-matching layer, we have achieved an enhanced absorption in the range of 500–600 nm, where the solar spectrum has a higher intensity. The results showed improvements of the J-V characteristics, mainly due to the increasing short-circuit current. Compared to the cell without a-SiN$_x$:H layer on non-textured substrate, the cell with 80 nm a-SiN$_x$:H AR layer increased the J$_{SC}$ from 8.3 to 9.8 mA/cm^2, and the corresponding cell efficiency was increased from 4.5 to 5.3%. A relative improvement of 2.3% in current density as measured by QE was also confirmed.

Acknowledgement

This work was supported by the Center for Green Energy Technology at the National Chiao Tung University, the National Science Technology Program-Energy of National Science Council and the Nexpower Technology Corporation in Taiwan.

References

[1] B. Rech, H. Wagner, Appl. Phys. A. 69 (1999) 155.
[2] P. Roca i Cabarrocas, Curr. Opin. Solid State Mater. Sci. 6 (2002) 439.
[3] D.L. Staebler, C.R. Wronski, Appl. Phys. Lett. 31 (1977) 292.
[4] J. Yang, S. Guha, Appl. Phys. Lett. 61 (1992) 2917.
[5] M. Ito, M. Kondo, Jpn. J. Appl. Phys. 45 (2006) L230.
[6] R.J. Koval, J. Koh, Z. Lu, L. Jiao, R.W. Collins, C.R. Wronski, Appl. Phys. Lett. 75 (1999) 1553.
[7] J. Springer, A. Poruba, M. Vanecek, J. Appl. Phys. 96 (2004) 5329.
[8] T. Fujibayashi, T. Matsui, M. Kondo, Appl. Phys. Lett. 88 (2006) 183508.
[9] C. Das, A. Doumit, F. Finger, A. Gordijn, J. Huepkes, J. Kirchhoff, A. Lambertz, T. Melle, W. Reetz, Sol. Energy Mater. Sol. Cells 93 (2009) 973–975.
[10] T. Lauinger, J. Moschner, A.G. Aberle, R. Hezel, J. Vac. Sci. Technol., A 16 (1998) 530.
[11] T.M. Klein, T.M. Anderson, A.I. Chowdhury, G.N. Parsons, J. Vac. Sci. Technol., A 17 (1999) 108.
[12] Y. Kuo, Appl. Phys. Lett. 63 (1993) 144.
[13] T. Uchino, K. Nakaguchi, Y. Nagashima, T. Kond, J. Non-Cryst. Solids 261 (2000) 72.
[14] P.H. Cheng, S.W. Liang, Y.P. Lin, H.J. Hsu, C.H. Hsu, C.C. Tsai, Mater. Res. Soc. Symp. Proc. 1321 (2011) 39.