Reducing Interface Traps with High Density Hydrogen Treatment to Increase Passivated Emitter Rear Contact Cell Efficiency

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Abstract

In this work, a high-density hydrogen (HDH) treatment is proposed to reduce interface traps and enhance the efficiency of the passivated emitter rear contact (PERC) device. The hydrogen gas is compressed at pressure (~ 70 atm) and relatively low temperature (~ 200 °C) to reduce interface traps without changing any other part of the device’s original fabrication process. Fourier-transform infrared spectroscopy (FTIR) confirmed the enhancement of Si–H bonding and secondary-ion mass spectrometry (SIMS) confirmed the SiN/Si interface traps after the HDH treatment. In addition, electrical measurements of conductance-voltage are measured and extracted to verify the interface trap density (Dit). Moreover, short circuit current density (Jsc), series resistance (Rs), and fill factor (F.F.) are analyzed with a simulated light source of 1 kW M⁻² global AM1.5 spectrum to confirm the increase in cell efficiency. External quantum efficiency (EQE) is also measured to confirm the enhancement in conversion efficiency between different wavelengths. Finally, a model is proposed to explain the experimental result before and after the treatment.

Keywords: High-density hydrogen treatment (HDH), Solar cell, Interface traps, SiN, Passivation layer

Introduction

Solar cells are one of many renewable energies in the world and are considered the most capable to replace transitional petrochemical energy. There are several types of solar cells based on different material systems, such as silicon [1–3], perovskite [4, 5], or III–V compounds [6, 7]. Among them, the silicon-based solar cell is commonly used for its low cost, high stability, and excellent efficiency up to 26% [8–10]. The passivated emitter rear contact (PERC) device is regarded as one of the potential devices to replace back surface field (BSF) solar cells [11, 12]. In 1983, Prof. Martin Green first proposed a PERC cell at the University of New South Wales (UNSW), the concept of which was to combine the emitter and rear passivation layer to reduce the interface defects and increase cell efficiency. Although the PERC emitter and rear passivation layer can passivate the interface defects, the film quality of either the emitter or anti-reflection coating (ARC) layer affects the interface [13–15].

According to previous work, other than improving thin film quality to reduce interface traps, post annealing treatment is another method to decrease defects [16–18]. A post treatment that of forming gas annealing in nitrogen (95%) and hydrogen (5%) at 400 °C is used to reduce interface traps with hydrogen and enhance cell efficiency. Unfortunately, such a treatment requires reaction at approximately 400 °C, a temperature too high for solar cells such as heterojunction with intrinsic thin layer (HIT) which are fabricated at temperatures under 200 °C.

In this work, we propose a suitable high-density hydrogen (HDH) treatment to reduce the interface traps between the emitter passivation layer and the n-type Si layer without the necessity to alter any additional element of device fabrication. Similar to previous research, HDH treatment is used to passivate the defects using hydrogen ions. The experimental result suggests an enhancement of the Si–H bond after the HDH treatment, according to the Fourier-transform infrared spectroscopy (FTIR) measurement secondary-ion mass...
spectrometry (SIMS). In addition, electrical measurements including conductance, short circuit current density (Jsc), series resistance (Rs), and fill factor (F.F.) are extracted to confirm the reduction of density of state (Dit) and the increase of cell efficiency. Finally, we also proposed a model to further illustrate the effects of HDH treatment on the PERC solar cell.

**Experimental Methods**

**PERC solar cell fabrication**
The PERC fabrication process is illustrated below. The p-type Czochralski silicon is used as the substrate with a thickness of approximately 150 μm. The KOH solution is
used to etch the Si substrate surface and form the pyramid-texture morphology of the surface. In order to form the p-n junction, POCl₃ is used to diffuse into the Si substrate surface and form the n-type layer. Then, the emitter SiN passivation layer is deposited via chemical vapor deposition (CVD) as an anti-reflection coating (ARC) layer. After the ARC layer is deposited, HF solution is used to remove the rear side n-type layer. Then, the Al₂O₃ layer is deposited as the rear passivation layer with a thickness of 25 nm by atomic layer deposition (ALD). The 95-nm-thick SiN layer is then deposited by CVD. After the rear passivation process is finished, laser ablation is applied to cut grooves for the preparation of the screen printing process of the silver (Ag) top electrode used on the ARC layer, while aluminum (Al) is used for the bottom electrode. Finally, the device is heated in a firing process in order to ensure proper contact between metal and semiconductor. The structure of the PERC device is shown in Fig. 1.

**HDH Treatment**

The HDH treatment is then applied to the PERC device. The process of HDH treatment is as depicted in Fig. 2. The hydrogen gas is used as the treatment source and is pumped into the reaction chamber containing the PERC device. Then, the gas is compressed to 70 atm and the reaction temperature is set at 200 °C for 1 h. The gas is then pumped out to finish the HDH treatment.

**Material Characterization**

Bruker VERTEX 70v FTIR is used to analyze Si–H bonding before and after treatment and ION-TOF, TOF-SIMS V is used to analyze hydrogen ratio at SiN/Si interface.

**Electrical Characterization**

I-V and G-V characteristics are measured with an Agilent B1500 semiconductor analyzer and Cascade M150 probe station in a dark box for both light and dark conditions. The parameters of efficiency (Jsc, Rs, and fill factor) are extracted at a simulated light source of 1 kW M⁻² global AM1.5 spectrum at 25 °C. QEX10 Solar Cell external quantum efficiency (EQE) is used to analyze the efficiency from 300 to 1200 nm.

**Result and Discussion**

The emitter SiN passivation layer with and without the HDH treatment is examined using a FTIR analysis. As shown in Fig. 3, the SiN with and with HDH
treatment both exhibit 3350 cm$^{-1}$ of the N–H stretching bond and 2165 cm$^{-1}$ of the Si–H stretching bond [19–21]. However, the absorption peak intensity ratios of N–H and Si–H bonding are both enhanced after the treatment, which implies that hydrogen is injected into the SiN layer.

In order to confirm that the HDH treatment reduces the SiN/Si interface traps, secondary-ion mass spectrometry (SIMS) is used to confirm the hydrogen distribution [22, 23]. In Fig. 4, because the SiN layer is deposited using CVD, the hydrogen intensity in this SiN layer is higher than in the Si. After the treatment, while the hydrogen intensity is not obviously increased in bulk, the intensity is clearly enhanced at the SiN and Si interface, and this result indicates that the HDH treatment reacts at the SiN/Si interface.

To further confirm the difference in Dit between the emitter SiN layer and p-Si substrate after HDH treatment in Fig. 5, the Al/SiN/p-Si/Al metal-insulator-semiconductor (MIS) structure is fabricated. Since the SiN and p-Si interface has a large amount of defects, the G-V result can be applied to extract the interface trap density (Dit) [24]. The conductance equation is given as:

$$\frac{G_p}{\omega} = \frac{D_{it}\omega^2\tau_{it}}{1 + \omega^2\tau_{it}^2}$$

(1)

where $\omega$ is angular frequency, $\tau$ is the carrier lifetime, and $G_p$ is the frequency-dependent conductance. To simplify Eq. 1, the Dit is related to conductance, and the conductance peak is reduced after the treatment, which suggests the HDH treatment can reduce the PERC interface traps.

Next, electrical measurements are carried out on the PERC cell device in both light and dark conditions. The device bias is applied to the Al bottom electrode, while the top electrode is ground. The sweeping range of the voltage is from $-1$ to $0.75$ V. Figure 6 shows the I-V characteristic under dark conditions. The current leakage is reduced significantly after HDH treatment, with the ratio of the decrease being about 0.5 orders. In addition, on the right side of the I-V characteristic, the hump of the on current

![Fig. 6 Analysis of I-V characteristics under dark conditions with current leakage and ideal factor.](image-url)
is found to be reduced after the treatment. We also extract the I-V curve and convert it as the ideal factor following the diode current equation:

\[ I = I_s \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right] \]  

(2)

where \( I_s \) is the saturation current, \( q \) is the electronic charge, \( V \) is the applied voltage, \( n \) is the ideal factor, \( k \) is the Boltzmann constant, and \( T \) is the absolute temperature. Equation 2 can be further simplified into \( I = I_s \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right] \); when the \( n \) value is close to 1, the on current is close to the diffusion current. When the \( n \) value is close to 2, this means that the on current is close to the combination current [25]. After the treatment, the slope of the on current is reduced from 1.5 to 1.42, which means that the on current is close to the diffusion current after treatment due to the decrease in the number of defects.

To further examine the electrical characteristics, the parameters of efficiency (Jsc, Rs, and fill factor) are extracted at a simulated light source of 1 kW M\(^{-2}\) global AM1.5 spectrum at 25 °C. After the HDH treatment, the average efficiency is enhanced from 17.3 to 18.2%, as shown in Fig. 7a. The Jsc also increases from 37.6 to 38.2 mA, as shown in Fig. 7b. In addition, the Rs has been reduced from 0.712 to 0.487 after treatment, as in Fig. 7c. As for the fill factor, it increases from 70.5 to 73.3, as shown in Fig. 7d.

In order to confirm the conversion efficiency at different wavelength ranges, the external quantum efficiency (EQE) is used to analyze the wavelength from 300 to 1200 nm [26, 27]. As shown in Fig. 8, the quantum efficiency before HDH treatment has an average EQE of 94% between 400 and 600 nm. However, after the HDH treatment, we can obtain an even higher EQE result. The results show an increase to 97% between 400 and 600 nm, which is induced by the suppression of the emitter SiN/Si interface traps.

Finally, we propose a model to explain the effects of HDH on the PERC device. The PERC emitter of Ag/SiN/n-type Si structure and the relationship to SiN/Si interface trap structure are demonstrated in Fig. 9.
When the electron-hole pair is generated in the p-n junction, induced by light, the electron moves to the Ag top electrode. If there are interface traps at the SiN/Si interface, they will assist electron recombination with holes. To reduce the interface traps, HDH treatment is applied to the PERC device, with high-pressure gas being used to injected hydrogen into the device and react with the interface. After the treatment, hydrogen bonds with the dangling bond at the SiN/Si interface and interface traps are reduced. Therefore, recombination decreases, which reduces current leakage and enhances the Jsc and cell efficiency.

Conclusion
In this study, HDH treatment is successfully proposed to reduce interface traps and enhance device efficiency. The FTIR spectrum shows that Si–H bonding is enhanced and conductance-voltage peak decreases after the treatment. Therefore, the reduced number of interface traps leads to a reduction in current leakage, and the ideality factor value is also decreased. Moreover, the efficiency is enhanced after the treatment, and Jsc, Rs, and fill factor are increased. Finally, the EQE result demonstrates an enhancement of short wavelength, which is evidence of a reduction in emitter interface traps.

Abbreviations
HDH: High-density hydrogen treatment; PERC: Passivated emitter rear contact cell; FTIR: Fourier-transform infrared spectroscopy; SIMS: Secondary-ion mass spectrometry; Dit: Interface trap density; Jsc: Circuit current density; Rs: Series resistance; F.F.: Fill factor; EQE: External quantum efficiency; BSF: Back surface field; UNSW: University of New South Wales; ARC: Anti-reflection coating; CVD: Chemical vapor deposition; ALD: Atomic layer deposition; MIS: Metal-insulator-semiconductor structure

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Authors’ Contributions
CCY, PHC, WCS, SYC, and HCH performed the measurements. TCC and TMT were involved in planning and supervised the work. CCY, YFT, CCL, and PYW processed the experimental data, performed the analysis, drafted the manuscript, and designed the figures. SYC and SCL manufactured the samples. All authors discussed the results and commented on the manuscript. All authors read and approved the final manuscript.

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Availability of Data and Materials
All data is available from the authors via a reasonable request.

Competing Interests
The authors declare that they have no competing interests.

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References
1. Yang CC, Chiang HC, Chen PH, Su YT, Su WC, Lin CC, Huang SP, Zheng HK, Huang HC, Chen SY, Lin CC, Huang JW, TsaI TM, Chang TC (2018) Integrating a charge trapping layer in passivated emitter rear contact cell to enhance efficiency. IEEE Electron Device Lett. 39(7):983–986
2. Chen HL, Chen PH, Chang TC, Young TF, Wang MC, AI CF, TsaI TM, Chang KC, Chen MC, Su YT, Yang CC, Lin CC (2017) Super critical fluid technique to enhance current output on amorphous silicon-based photovoltaic. IEEE Electron Device Lett. 38(10):1401–1404
3. Wang MC, Chang TC, Tsao SW, Chen YZ, Tseng SC, Hsu TC, Jan DJ, AI CF, Chen JR (2011) n(+)-Doped-layer free amorphous silicon thin film solar cells fabricated with the CuMg alloy as back contact metal. Solid-State Electronics 57(1):73–75
4. Liu M, Johnston MB, Snailth HJ (2013) Efficient planar heterojunction perovskite solar cells by vapour deposition. Nature 501(747):395
5. Green MA, Anita HB, Snailth HJ (2014) The emergence of perovskite solar cells. Nat Photonics 8(7):506
6. King RR, Karam NH, Ermer JH, Haddad N, Colter P, Ishikii T, Yoon H, Cotal HL, Joslin DE, Krut DO (2000) Next-generation, high-efficiency III-V multijunction solar cells in Conference Record of the Twenty-Eighth IEEE Photovoltaic Specialists Conference-2000 998-1001
7. Essig S, Allebé C, Remo T, Geisz JF, Steiner MA, Horowitz K, Barraud L, Ward JS, Schnabel M, Descoeudres A (2017) Raising the one-sun conversion efficiency of III–V/Si solar cells to 32.8% for two junctions and 35.9% for three junctions. Nature Energy 2(9):17144
8. Green MA, Blakers AW, Shi J, Keller EM, Wenham SR (1984) 19.1-percent efficient silicon solar-cell. Appl Phys Lett. 44(12):1163–1164
9. Blakers AW, Wang A, Milne AM, Zhao JH, Green MA (1989) 22.8-percent efficient silicon solar-cell. Appl Phys Lett. 55(13):1363–1365
10. Green MA (2015) The passivated emitter and rear cell (PERC); from conception to mass production Sol. Energy Mater Sol Cells 143:190–197
11. Fossum JG (1977) Physical operation of back-surface-field silicon solar cells. IEEE Trans Electron Devices 24(4):322–325
12. Narasimha S, Rohatgi A, Weeber AW (1999) An optimized rapid aluminium back surface field technique for silicon solar cells. IEEE Trans Electron Devices 46(7):1363–1370
13. Duerinckx F, Szufuck D (2002) Defect passivation of industrial multicrystalline solar cells based on PECVD silicon nitride. Solar Energy Mater Solar Cells 72(1–4):231–246
14. Yekudah V, Rohatgi A, Jeong JW, Gabor AM, Hanoka JI, Wallace RL (2000) PECVD SiN/sub x/Induced hydrogen passing in string ribbon silicon (solar cells) in Conference Record of the Twenty-Eighth IEEE Photovoltaic Specialists Conference-2000 91–94
15. Santana G, Morales-Acevedo A (2000) Optimization of PECVD SiN: H films for silicon solar cells. Solar Energy Mater Solar Cells 60(2):135–142
16. Alnaimi IK, Nayfeh A (2013) Reduction of interface traps at the amorphous-silicon/crystalline-silicon interface by hydrogen and nitrogen annealing. Solar Energy 98:236–240
17. Oh SI, Choi G, Hwang H, Lu W, Jang JH (2013) Hydrogenated KGZ thin-film transistors using high-pressure hydrogen annealing. IEEE Trans Electron Devices 60(8):2537–2541
18. Cai L, Rohatgi A (1997) Effect of post-PECVD photo-assisted anneal on multicrystalline silicon solar cells. IEEE Trans Electron Devices 44(1):107–103
19. Kim KS, Kim KH, Ji YJ, Park JW, Shin JH, Ellingsboe AR, Yeom GY (2017) Silicon nitride deposition for flexible organic electronic devices by VHF (162 MHz)-PECVD using a multi-tile push-pull plasma source. Sci Rep 7(1)
20. Januś A, Kyzioł A, Konfal-Góral J, Malek A, Jonas S (2015) Plasma assisted chemical vapour deposition—technological design of functional coatings. Arch Metallurgy Mater 60(2):909–914
21. Zaghloul L, Papaioannou GJ, Bhushan B, Wang H, Cocetti F, Pons P, Plana R (2011) Effect of deposition gas ratio, RF power, and substrate temperature on the charging/discharging processes in PECVD silicon nitride films for electrostatic NEMS/MEMS reliability using atomic force microscopy. J Microelectromechanical Syst 20(6):1395–1418
22. Kluska S, Granek F (2011) High-efficiency silicon solar cells with boron local back surface fields formed by laser chemical processing. IEEE Electron Device Lett. 32(9):1257–1259
23. Hahn G, Geiger P, Fath P, Bucher E (2000) Hydrogen passivation of ribbon silicon-electronic properties and solar cell results. In Conference Record of the Twenty-Eighth IEEE Photovoltaic Specialists Conference-2000 95-98
24. Martens K, Wang W, Keersmaecker KD, Borghs G, Groeseneken G, Maes H (2007) Impact of weak Fermi-level pinning on the correct interpretation of III-V MOS CV and GV characteristics. Microelectronic Eng 84(9-10):2146–2149
25. Sze SM, Ng KK, Physics of semiconductor devices. John wiley & sons, 2006.
26. Zhang S, Pan X, Jiao H, Deng W, Xu J, Chen Y, Altermatt PP, Feng Z, Verlinden PJ (2015) 335-W world-record p-type monocrystalline module with 20.6% efficient PERC solar cells. IEEE J Photovoltaics 6(1):145–152
27. Kray D, Dicker J, Osswald D, Leimenstoll A, Glunz SW, Zimmermann W, Tentscher KH, Strobl G (2003) Progress in high-efficiency emitter-wrap-through cells on medium quality substrates in 3rd World Conference on Photovoltaic. Energy Conversion 2:1340–1343

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