



Heat treatment of amorphous silicon p-i-n solar cells with high-pressure H₂O vapor

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ABSTRACT

We report improvement in characteristics of hydrogenated amorphous silicon (a-Si:H) p-i-n structured solar cells by high-pressure H₂O vapor heat treatment. a-Si:H p-i-n solar cells were formed on glass substrates coated with textured SnO₂ layer. P-, i-, and n-type a-Si:H layers were subsequently formed by plasma enhanced chemical vapor deposition. Finally an indium-tin-oxide layer was coated on the n-type a-Si:H surface. Heat treatment at 210 °C with 2×10^5 Pa H₂O vapor for 1 h was applied to the a-Si:H p-i-n solar cells. Electrical characteristics were measured when samples were kept in dark and illuminated with light of AM 1.5 at 100 mW/cm². The heat treatment with H₂O vapor increased fill factor (FF) and the conversion efficiency from 0.54 and 7.7% (initial) to 0.57 and 8.4%, respectively. Marked improvement in solar cell characteristics was also observed in the case of a poor a-Si:H p-i-n solar cell. FF and the conversion efficiency were increased from 0.29 and 3.2% (initial) to 0.56 and 7.7%, respectively.

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1. Introduction

Hydrogenated amorphous silicon (a-Si:H) solar cells have been widely investigated and used for several devices as electrical power source [1]. a-Si:H has excellent properties. Hydrogen and silicon network had realized wide optical band gap and low density of states in the mid-gap [2]. Moreover, activation of impurities succeeded in doped silicon formation. P, intrinsic i, and n (p-i-n) type solar cells have been successfully fabricated using plasma enhanced chemical vapor deposition (PECVD) [3]. An effectively direct band gap property results in high absorption coefficient in visible wavelength regions. This is an advantage of thin film solar cells [4]. However, a-Si:H films have still substantial localized tail states near valence and conduction band edges because of Si–Si bonding disordering. Those states strongly depend on fabrication conditions and can play a role of recombination site of photo-induced carriers.

In this paper, we report improvement in solar cell characteristics of a-Si:H p-i-n solar cells by high-pressure H₂O vapor heat treatment [5]. We first describe characteristics of defect reduction in silicon films by high-pressure H₂O vapor heat treatment. We then report application of high-pressure H₂O vapor heat treatment to a-Si:H p-i-n solar cells and changes in their characteristics. We will discuss suitable conditions of high-pressure H₂O vapor heat treatment to improvement in solar cell characteristics.

2. High-pressure H₂O vapor heat treatment to silicon films

High-pressure H₂O vapor heat treatment was developed to reduce the density of defect states in SiO₂, a-Si, and poly-Si films and their interfaces [5–9]. H₂O vapor molecules incorporate into those films and effectively terminate electrical active silicon dangling bonds. In our previous studies on a-Si [6], the dark conductivity of low pressure chemical vapor deposited amorphous silicon (LPCVD a-Si) films remarkably decreased from the order of 10^{−8} to 10^{−12} S/cm and their photoconductivity increased from the order of 10^{−8} to 10^{−7} S/cm when they were heated with H₂O vapor pressure up to 2×10^6 Pa at temperatures between 190 and 270 °C, as shown in Fig. 1. Those characteristics are comparable to conventional a-Si:H formed by PECVD. LPCVD a-Si films have a high density of band-gap defect states. Those defects caused highly electrically hopping conduction in dark field and have low photoconductivity because of high carrier recombination due to the defects. The results of Fig. 1 show H₂O vapor molecules effectively decreased the density of band gap states. However, optical absorption spectra were hardly changed by high-pressure H₂O vapor heat treatment. The estimation with Tauc resulted in an optical band gap of 1.5 eV. Change in hydrogen concentration was lower than the detection limit of 1 at.% of Fourier transform infrared spectroscopy (FTIR). These results showed that high-pressure H₂O vapor heat treatment did not incorporate substantial amounts of hydrogen or oxygen atoms in LPCVD a-Si. No change in optical absorption spectra of a-Si:H films formed by PECVD was also observed in the case of 2.1×10^6 -Pa H₂O vapor heat treatment at 270 °C for 1 h, as shown in Fig. 2. The optical band gap was estimated as 1.67 eV. Raman scattering spectroscopy measurement revealed that the density of hydrogen atoms was decreased by 20% of initial value, as shown in Fig. 3. In our previous report, the secondary ion mass

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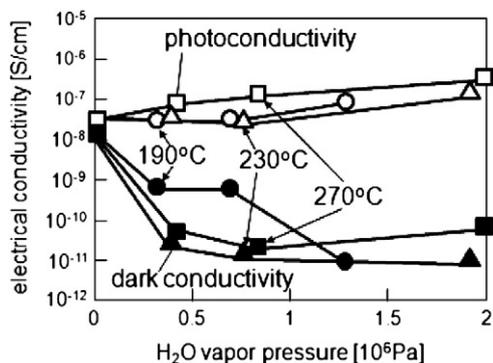


Fig. 1. Dark conductivity and photoconductivity of LPCVD a-Si as a function of H_2O vapor pressure with different temperatures from 190 to 270 °C for 1 h.

spectrometry (SIMS) also revealed that the density of hydrogen atoms decreased by about $1 \times 10^{20} \text{ cm}^{-3}$ and the density of oxygen atoms was slightly increased by $1 \times 10^{19} \text{ cm}^{-3}$ for laser crystallized silicon films heated at 260 °C with 1.3×10^6 -Pa H_2O vapor for 1 h [8]. The spin density of laser crystallized silicon films was decreased from $2 \times 10^{18} \text{ cm}^{-3}$ to $6.5 \times 10^{16} \text{ cm}^{-3}$ by 1.3×10^6 Pa H_2O vapor heat treatment at 260 °C for 6 h. Those results mean that high-pressure H_2O vapor heat treatment effectively reduced electrical active dangling bonds. The density of oxygen atoms incorporated into silicon by that treatment was very low so that optical properties did not change.

3. Experimental

a-Si:H p-i-n cells with an area of 1.08 cm^2 were fabricated on glass substrates coated with a textured SnO_2 layer. p-type, 350-nm-thick i-type, and n-type a-Si:H layers were subsequently formed at 190 °C by PECVD. Seventy-nanometer-thick indium-tin-oxide (ITO) layer was then coated onto the n-type a-Si:H surface. Finally, a-Si:H p-i-n cells were heated at 150 °C for 2 h. An air mass 1.5 (AM 1.5)-type solar simulator at 100 mW/cm^2 was used for the measurement of solar cell characteristics. Fig. 4 shows an equipment of high-pressure H_2O vapor heat treatment for solar cells. Five 6-inch-sized solar cell wafers can be simultaneously heated with 9×10^5 Pa and at 280 °C at maximum. Errors in estimation of times of H_2O vapor heat treatment were about 3 min, which was limited by the duration of melting and evaporating of an H_2O ice pellet, which was dropped from the top of the tower located right edge into the chamber. In this paper, we concentrated low temperature treatment at 180 and 210 °C and a low pressure of 2×10^5 Pa to avoid high thermal and pressure stress to solar cells.

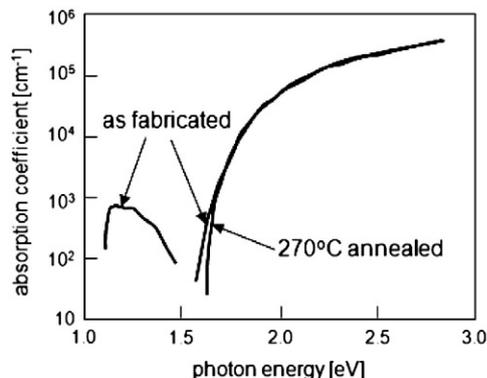


Fig. 2. Change in optical absorption spectra of PECVD a-Si:H with heat treatment at 2.1×10^6 -Pa H_2O vapor at 270 °C for 1 h.

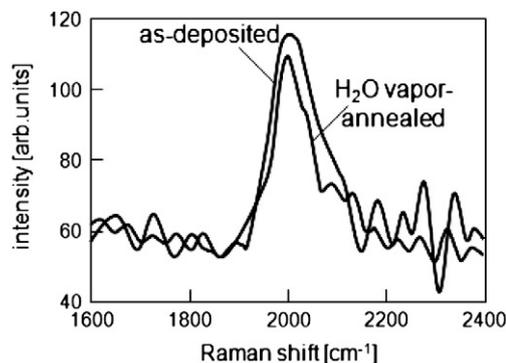


Fig. 3. Raman scattering spectra of Si-H resonant scattering peaks of as deposited a-Si:H and annealed with 1.3×10^6 Pa H_2O vapor at 260 °C for 3 h.

4. Results

Fig. 5 shows the absolute electrical current per unit area as a function of voltage (a) and solar cell characteristics (b) for samples of initial a-Si:H p-i-n cell and a-Si:H p-i-n cell treated with 2×10^5 -Pa H_2O at 210 °C for 1 h, when they were kept in dark and illuminated with light. The electrical current increased as the voltage increased in dark condition for the both a-Si solar cells. Fig. 5(a) clearly showed that 2×10^5 -Pa H_2O heat treatment at 210 °C for 1 h decreased the electrical current in a low voltage region. Light illumination remarkably increased the electrical current for the both solar cells. A substantial current at 0 V indicating the short circuit current density (J_{sc}) was observed. The voltage giving no electrical current meaning the open circuit voltage (V_{oc}) was almost the same between initial and high-pressure H_2O vapor heated samples. Good and typical solar cell characteristics were obtained for the both a-Si:H p-i-n cells, as shown in Fig. 6(b). H_2O vapor heat treatment (2×10^5 Pa) at 210 °C for 1 h increased the fill factor FF from 0.54 (initial) to 0.57. The conversion efficiency was therefore increased from 7.7 (initial) to 8.4% by 2×10^5 -Pa H_2O vapor heat treatment at 210 °C for 1 h. Interesting results were obtained in the case of poor initial a-Si cell characteristics, as shown in Fig. 6, that shows the absolute electrical current per unit area as a function of voltage (a) and solar cell characteristics (b) for samples of an initial cell and a cell treated with 2×10^5 Pa H_2O at 210 °C for 1 h, when they were kept in dark and illuminated with light. The initial a-Si:H cell had a high electrical dark current, a low J_{sc} of $1.3 \times 10^{-2} \text{ A/cm}^2$ and a high series resistance of $65 \Omega \text{ cm}^2$, as shown in Fig. 6. On the other hand, 2×10^5 -Pa H_2O vapor heat treatment at 210 °C for 1 h decreased the electrical dark current, increased J_{sc} to $1.6 \times 10^{-2} \text{ A/cm}^2$, and decreased the series resistance to $17.5 \Omega \text{ cm}^2$. Therefore, FF and conversion efficiency were increased from 0.29 and 3.2% (initial) to 0.56 and 7.7%, respectively, by high-pressure H_2O vapor heat treatment. On the other hand, no change in J_{sc} , V_{oc} , and FF was observed by heat treatment at 210 °C for 1 h in dry atmosphere.

Fig. 7 shows the absolute electrical current per unit area as a function of voltage (a) and solar cell characteristics (b) for samples of

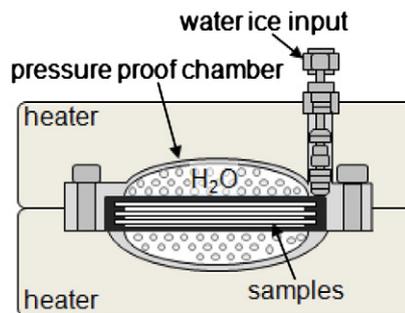


Fig. 4. Equipment of high-pressure H_2O vapor heat treatment for solar cells.

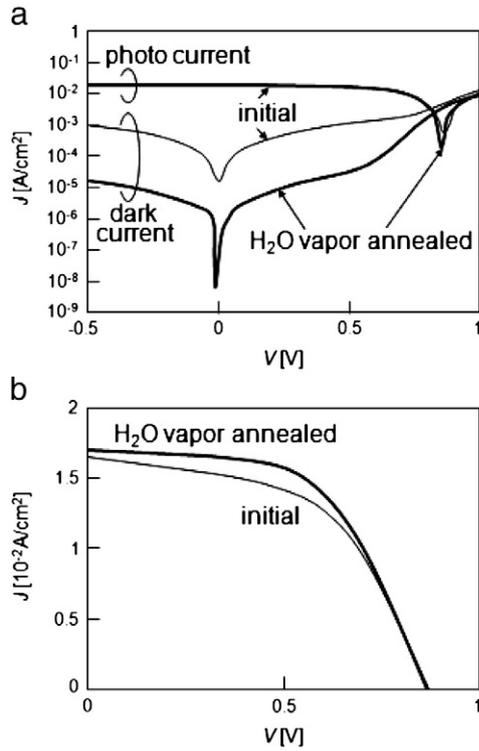


Fig. 5. Absolute electrical current per unit area as a function of voltage (a) and solar cell characteristics and (b) for samples of initial a-Si:H p-i-n cell and a-Si:H p-i-n cell treated with 2×10^5 -Pa H₂O at 210 °C for 1 h, when they were kept in dark and illuminated with AM 1.5 at 100 mW/cm².

initial a-Si:H p-i-n cell and a-Si:H p-i-n cell treated with 2×10^5 Pa H₂O at 180 °C for 1 h, when they were kept in dark and illuminated with light. In contrast to 210 °C heat treatment case shown in

Figs. 5 and 6, high-pressure H₂O vapor heat treatment increased the electrical current in dark and slightly decreased photo-induced current as show in Fig. 7(a). FF and conversion efficiency therefore decreased from 0.57 and 8.1% (initial) to 0.36 and 4.6%, respectively, as shown in Fig. 7(b).

5. Discussion

Improvement in solar cell characteristics was observed by 2×10^5 -Pa H₂O vapor heat treatment at 210 °C for 1 h. Marked decrease in current in the dark field shown in Fig. 5(a) indicates that the density of carrier recombination sites was decreased in the p-i-n a-Si:H layered structure by 2×10^5 -Pa H₂O vapor heat treatment at 210 °C for 1 h. This probably results from decrease in the density of gap states, which was also demonstrated by decrease in dark conductivity and increase in photoconductivity for LPCVD a-Si films, as shown in Fig. 1. We believe that decrease in the density of gap states especially at the depleted *i* region resulted in increases in J_{sc} and FF, as shown in Fig. 5(b). Hasumi et al. previously reported that 2×10^5 -Pa H₂O vapor heat treatment at 210 °C improved solar cell characteristics crystalline silicon with increasing J_{sc} and the conversion efficiency [10]. No serious gap states must exist in crystalline silicon. Many vacancies, which may play a role in carrier recombination, would localize near PN junction formed by dopant diffusion. We believe that vacancies were also effectively reduced by high-pressure H₂O vapor heat treatment for both cases of a-Si as well as crystalline silicon solar cells. Marked improvements in FF and conversion efficiency were also obtained 2×10^5 -Pa H₂O vapor heat treatment at 210 °C for 1 h, as shown in Fig. 6. The poor initial characteristic probably indicates a high density of carrier recombination center at a-Si:H p-i-n region. The high-pressure H₂O vapor heat treatment effectively made carrier recombination sites inactive. However, high-pressure H₂O vapor heat treatment at 180 °C was not effective to improve solar cell characteristics. Although physics is not clear yet, 180 °C probably was too low to reduce defects because of low thermal

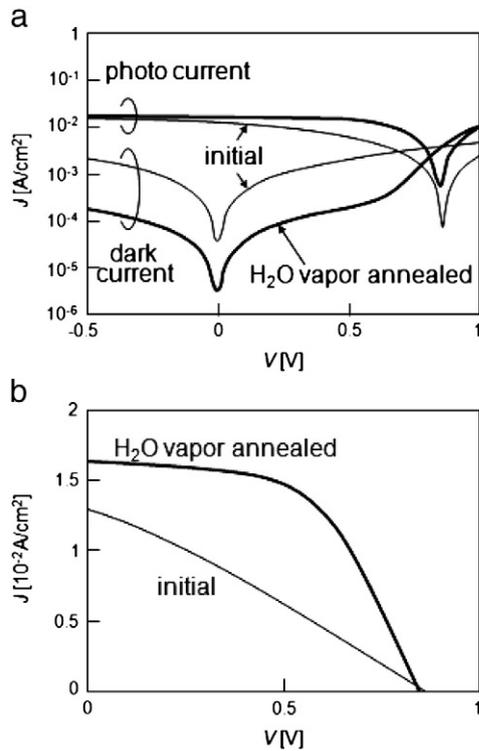


Fig. 6. Absolute electrical current per unit area as a function of voltage (a) and solar cell characteristics and (b) for samples of poor characteristic initial a-Si:H p-i-n cell and a-Si:H p-i-n cell treated with 2×10^5 -Pa H₂O at 210 °C for 1 h, when they were kept in dark and illuminated with AM 1.5 at 100 mW/cm².

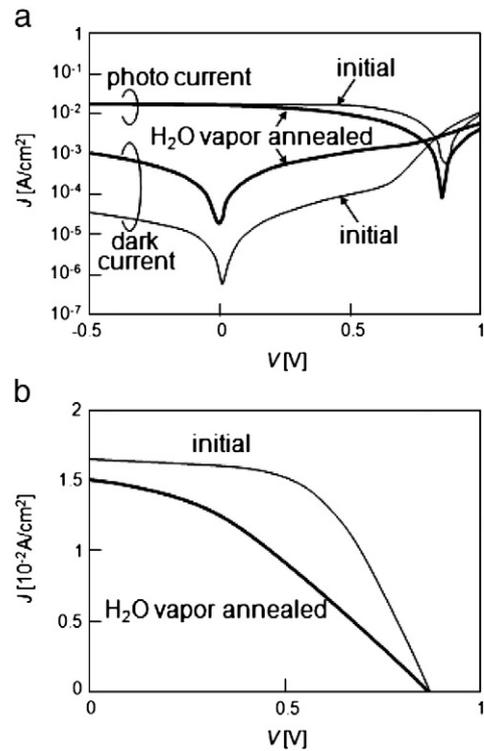


Fig. 7. Absolute electrical current per unit area as a function of voltage (a) and solar cell characteristics and (b) for samples of initial a-Si:H p-i-n cell and a-Si:H p-i-n cell treated with 2×10^2 -Pa H₂O at 180 °C for 1 h, when they were kept in dark and illuminated with AM 1.5 at 100 mW/cm².

energy. Moreover, H₂O molecules probably stay in the a-Si:H p-i-n region. They would play a role of photo-induced carrier recombination.

6. Summary

We investigated improvement in characteristics of a-Si:H p-i-n solar cells by high-pressure H₂O vapor heat treatment. a-Si:H p-i-n solar cells were formed on glass substrates coated with textured SnO₂ layer. P-, i-, and n-type a-Si:H layers were subsequently formed by PECVD. Finally an ITO layer was coated on the n-type a-Si:H surface. Heat treatments at 210 and 180 °C with 2×10^5 Pa H₂O vapor for 1 h were applied to the a-Si:H p-i-n solar cells. Electrical characteristics were measured when samples were kept in dark and light illuminated with AM 1.5 at 100 mW/cm². H₂O vapor (2×10^5 Pa) at 210 °C for 1 h decreased the electrical dark conductivity probably because the carrier recombination probability was decreased. FF and the conversion efficiency were increased 0.54 and 7.7% (initial) to 0.57 and 8.4%, respectively, by 2×10^5 Pa H₂O vapor at 210 °C for 1 h. Marked improvement in solar cell characteristics was also observed by the same treatment condition at 210 °C in the case of a poor a-Si:H p-i-n solar cell. FF and the conversion efficiency were increased from 0.29 and 3.2% (initial) to 0.56 and 7.7%, respectively. However, 2×10^5 -Pa H₂O vapor at 180 °C for 1 h decreased FF and the conversion efficiency from 0.57 and 8.1% (initial) to 0.36 and 4.6%, respectively. Those experimental results indicate that high-pressure H₂O vapor heat treatment has a capability of improvement in solar cell characteristics of a-Si:H p-i-n solar cells. The carrier recombination probability was probably decreased in p-i-n a-Si:H

regions by high-pressure H₂O vapor heat treatment. Heating temperature is important. The present results revealed that 210 °C is necessary at least.

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