High-Pressure H_2O Vapor Heat Treatment for Characteristic Improvement in Crystalline Silicon Solar Cells

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Abstract. Improvement in characteristics of commercial single crystalline silicon solar cells was demonstrated by high-pressure H_2O vapor heat treatment. The short circuit current, open circuit voltage and conversion efficiency increased from 10.6 to 11.4 mA/cm^2, 0.515 to 0.526 V, and 11.6 to 12.5%, respectively by the heat treatment at 210^{o}C in 2.0 x 10^5 Pa H_2O vapor for 30 min. This result indicated that high-pressure H_2O vapor heat treatment effectively modified the passivation layer of silicon solar cells and reduced the defects of photo induced carrier recombination. However, the degradation of conversion efficiency from 13.7 to 12.2% was observed by the heat treatment at 210^{o}C in 1.0 x 10^6 Pa H_2O vapor for 30 min because of the increase in serial resistance loss by the oxidation of silver electrode.

Introduction

Solar cells are promising devices for producing electrical powers without increasing the density of carbon dioxide in the atmosphere, and the markets of solar cell have been expanded due to these demands rapidly. Especially, crystalline silicon solar cells have been most promising because of their high conversion efficiency, reliability and the use of safe materials. Technical developments aiming at increasing the conversion efficiency and decreasing manufacturing cost are important. For example, there have been developments on surface texture for introducing sunlight into silicon solar cells with no significant reflection loss, multi band gap engineering for carrier generating from sunlight with wide spectra, defect reduction in crystalline silicon bulk for decreasing carrier recombination probability, and transparent electrodes with a low resistivity for decreasing joule heating loss [1].

We have developed high pressure H_2O vapor heat treatment as a technology for defect passivation of polycrystalline silicon thin film transistors (poly-Si TFTs) [2]. The improvement in TFT characteristics was achieved by simple process applied to the samples with 1.3 x 10^6 Pa H_2O vapor environment at temperatures ranging from 200 to 300^{o}C, with duration for 180 min [3, 4]. This treatment is also attractive for low-cost process. Moreover defect passivation of layered structures of silicon and silicon oxide is achieved. Metal electrodes do not block passivation effect of high pressure H_2O vapor heat treatment. Therefore, most people have used high pressure H_2O vapor heat treatment at a process steps after fabricating TFT structures. We therefore take an interest in applying high pressure H_2O vapor heat treatment to crystalline silicon solar cells with transparent electrodes, metal wires and passivation insulators for simple and low cost defect passivation.

In this study, we propose the high-pressure H_2O vapor heat treatment as a novel and simple method for the improvement in characteristics of commercial crystalline silicon solar cells by the passivation of defects in the surface and grain boundary of solar cells. The improvement is achieved by the reduction of photo induced carrier recombination loss. Through investigation of different conditions, we propose effective conditions of high pressure H_2O vapor heat treatment for improvement in solar cells characteristics. In addition, we discuss the subject to apply the H_2O vapor annealing to the solar cell fabrication process.

Experimental

Commercial single crystalline silicon solar cells with an official conversion efficiency of 13.5 %, with a structure of SiN_x/ITO/n+Si/p-Si/Al were prepared for the investigation. Front surface electrode wires were made by silver paste printing and that of back surface was silver/aluminum [5]. The solar cells were divided into small pieces with area ranging from 1 to 2 cm^2. Conversion efficiency distributed from 8.4 to 16.3 % for the divided samples with average conversion efficiency of 12.4 %. This result has suggested that a distribution of efficiency exists in one sheet of solar cell. In order to prevent the variation in the treatment resulting by the variation in the initial solar cell characteristics, 16 samples were treated simultaneously for each H_2O vapor annealing condition.

High-pressure H_2O vapor heat treatment was applied to the samples placed in a pressure proof chamber with ice made from purified water. By heating the chamber, the water evaporated and the pressure inside the chamber increased. The treatment temperature was varied in the range of 170 to 230^{o}C. The pressure inside the chamber changed from 1.0 x 10^5 to 1.0 x 10^6 Pa by controlling the ice volume. The duration was changed from 10 to 180 min.

Electrical properties of initial and the H_2O vapor heat treated samples were measured by Agilent 4156C parameter analyzer. A light emitting diode array with a wavelength of 590 nm at an intensity of 24 mW/cm^2 was used for the light illumination source. The open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor and conversion efficiency were experimentally measured.

Results and Discussion

Improvement in solar cell characteristics was achieved by the high-pressure H_2O vapor heat treatment on specific conditions. For example, Fig. 1 shows the solar cell characteristics observed in a sample with and without heat treated at 210^{o}C in 2.0 x 10^5 Pa H_2O vapor environment for 30 min. V_{oc}, I_{sc} and conversion efficiency increased from 10.5 to 11.5 mA/cm^2, 0.525 to 0.544 V, and 12.4 to 13.7%, respectively by the H_2O vapor heat treatment. Those improvements in solar cell characteristics are assumed to be caused by the passivation of defects and the decrease in the probability of photo induced carrier recombination in the solar cell.

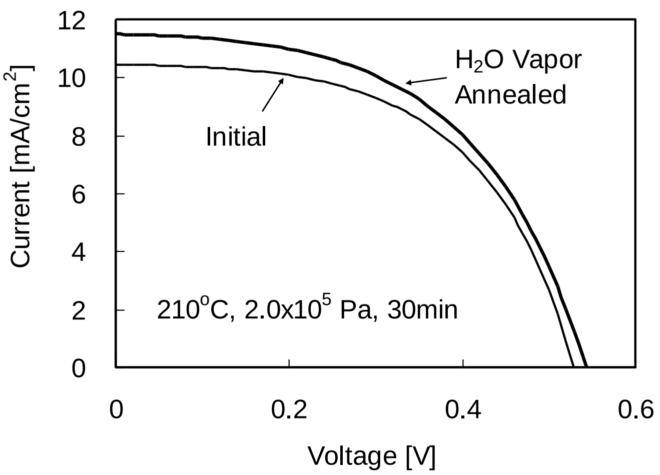

Fig. 1 Solar cell characteristics of initial and H_2O vapor annealed single crystalline silicon solar cell.

Figure 2 shows V_{oc} of 16 samples heat treated simultaneously, for annealing temperature of (a) 190°C, (b) 210°C and (c) 230°C. Initial V_{oc} is in horizontal axis and those for H_2O vapor heat treatment at 2.0 x 10^5 Pa for 30 min in vertical axis. V_{oc} increased by H_2O vapor heat

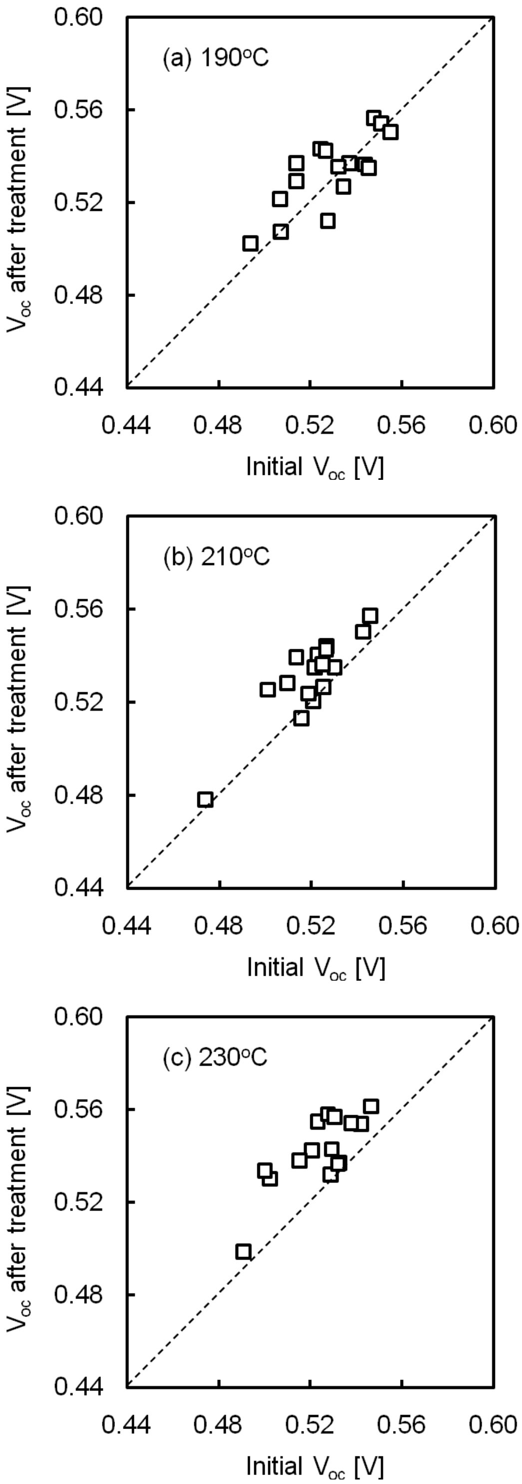

Fig. 2 V_{oc} for initial samples in horizontal axis and those for H_2O vapor treated samples with 2.0 x 10^5 Pa for 30 min at (a) 190°C, (b) 210°C and (c) 230°C in vertical axis.

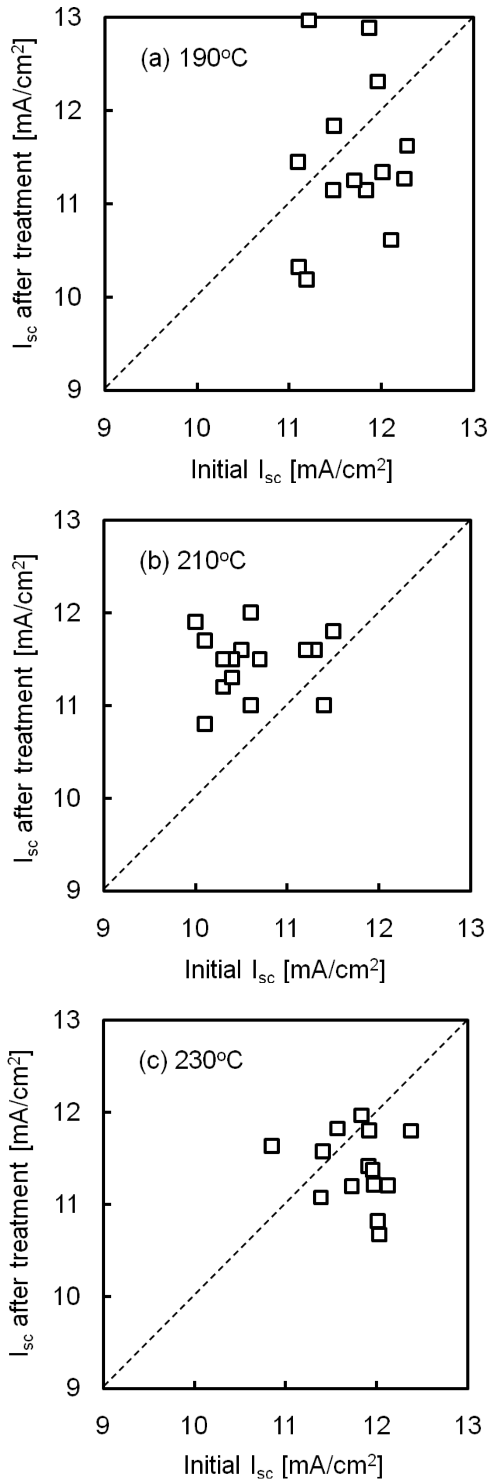

Fig. 3 I_{sc} for initial samples in horizontal axis and those for H_2O vapor treated samples with 2.0 x 10^5 Pa for 30 min at (a) 190°C, (b) 210°C and (c) 230°C in vertical axis.

treatment at 210°C and 230°C for most of the samples. The initial average V_{oc} varied slightly in the ranging from 0.520 to 0.529 V for the samples prepared for each annealing condition. Increment in average V_{oc} were 0.004, 0.011 and 0.018 V, respectively by the high pressure H_2O vapor heat treatment at 190, 210 and 230°C. Those increment increased as the treatment temperature increased from 190 to 230°C.

Figure 3 shows I_{sc} of 16 samples heat treated simultaneously for annealing temperature of (a) 190°C, (b) 210°C and (c) 230°C. Initial I_{sc} in horizontal axis and those for H_2O vapor heat treatment at 2.0 x 10^5 Pa for 30 min in vertical axis. The average I_{sc} increased from 10.6 to 11.4 mA/cm^2 by heat treatment at 210°C. On the other hand, it decreased from 12.0 to 11.6 mA/cm^2 for the samples treated at 230°C. The decrease in I_{sc} was concerned with the degradation of fill factor. The average fill factor decreased as the treatment temperature increased to 230°C. The origin of fill factor degradation is discussed later. The increment in I_{sc} by the H_2O vapor annealing at 210°C was larger for samples with lower initial I_{sc}, as shown in Fig. 3. This result suggests that the H_2O vapor heat treatment is capable of making I_{sc} uniform by reducing carrier annihilation sites.

Simultaneous increases in V_{oc} and I_{sc} for the samples shown in Figs. 2(b) and 3(b) clearly indicate that the H_2O vapor treatment at 210°C increases the density of photo-induced carriers and the effective minority carrier lifetime. The change in solar cell characteristics as a function of effective minority carrier lifetime were numerically calculated using Silvaco Co. Ltd. Luminous device simulator. Increase in V_{oc} and I_{sc} by the increase in effective minority carrier lifetime were confirmed by the calculation [6].

Conversion efficiency was improved by the H_2O vapor treatment at 210°C. Figure 4 shows the distribution of conversion efficiency for initial and H_2O vapor annealed samples with 2.0 x 10^5 Pa for 30 min at 210°C. The initial average conversion efficiency of 11.7 % improved to 12.5 % by the heat treatment at 210°C. The improvement in conversion efficiency by H_2O vapor heat treatment was achieved mainly by the increase of V_{oc} and I_{sc} through decrease in the probability of photo induced carrier recombination and the increase in the minority carrier lifetime. However, average conversion efficiency for the samples H_2O vapor heat treated at 230°C decreased from 13.3 to 12.9 %. The origin of decrease in conversion efficiency is the rapid degradation of fill factor by the H_2O vapor heat treatment.

For each treatment pressure, the ratios of averaged solar cell characteristics after H_2O vapor treatment to the initial were obtained (hereinafter average ratio). Figure 5 shows the average ratios of V_{oc}, I_{sc}, fill factor and conversion efficiency as a function of H_2O vapor pressure for samples H_2O heat treated at 210°C for 30 min. Solar cell characteristics were not changed for the samples annealed in 1.0 x 10^5 Pa H_2O vapor. The samples treated in 2.0 x 10^5 Pa H_2O vapor showed the highest improvement with average ratios of V_{oc}, I_{sc} and conversion efficiency of 1.02, 1.08 and 1.08, respectively. However, at higher pressure of 1.0 x 10^6 Pa, the improvements in V_{oc} and I_{sc} were low and fill factor and conversion efficiency decreased to 0.86 and 0.89, respectively.

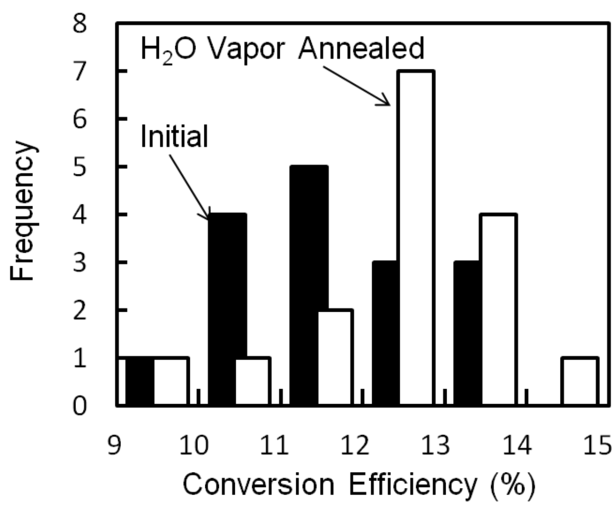

Fig. 4 Distribution of conversion efficiency for initial and H_2O vapor annealed samples with 2.0 x 10^5 Pa for 30 min at 210°C.

Dependence of average ratios of

solar cell characteristics on duration of H_2O vapor heat treatment is shown in Fig. 6. H_2O vapor heat treatment was applied simultaneously for 16 samples at 210°C in 2.0 x 10^5 Pa for 10, 30 and 180 min. It is insufficient for 10 min duration to improve the solar cell characteristics, though I_{sc} was slightly increased. The V_{oc}, I_{sc} and conversion efficiency were improved by the H_2O vapor heat treatment for 30 min. On the other hand, the average ratios of fill factor and conversion efficiency decreased to 0.90 and 0.93, respectively in the case of 180 min duration.

Degradation of fill factor and conversion efficiency for the H_2O vapor heat treated samples were observed in the cases of treatment temperature at 230°C, pressure in 1.0 x 10^6 Pa H_2O vapor and duration for 180 min. We discuss possible origin of those degradations. Fill factor decreased from 0.57 to 0.42 by H_2O vapor annealing at 210°C in 1.0 x 10^6 Pa for 30 min. It is well known that such a degradation of fill factor can be explained by the increase in the serial resistance loss. Simple model calculation was made by a conventional equivalent circuit model with serial resistance (R_s) connected to the equivalent circuit of initial solar cell. Figure 7 shows the solar cell characteristics of initial and heat treated samples at 210°C in 1.0 x 10^6 Pa H_2O vapor environment for 30 min (bold lines) and calculated current voltage characteristics for R_s of 5, 12 and 25 Ω (thin lines). The calculated solar cell characteristics shows good agreement with the curve of H_2O vapor annealed sample for R_s = 12 Ω. The color of silver electrode lines pasted on the surface changed from white to gray by the H_2O vapor heat treatment at 210°C in 1.0 x 10^6 Pa for 30 min. Moreover, the resistance of silver electrode lines after the treatment increased by 8 times. These observations suggest that degradation of solar cell characteristics by high pressure H_2O vapor heat treatment was caused by the oxidation of silver electrodes resulting in increase of R_s. This suggests that high pressure H_2O vapor heat treatment should be carried out before silver electrode pasting in order to look for much more improvement in solar cell characteristics. The defects of poly-Si TFT are more effectively reduce by H_2O vapor heat treatment at temperatures ranging from 200 to 300°C in 1.3 x 10^6 Pa. The possibility of further improvement in characteristics of crystalline silicon solar

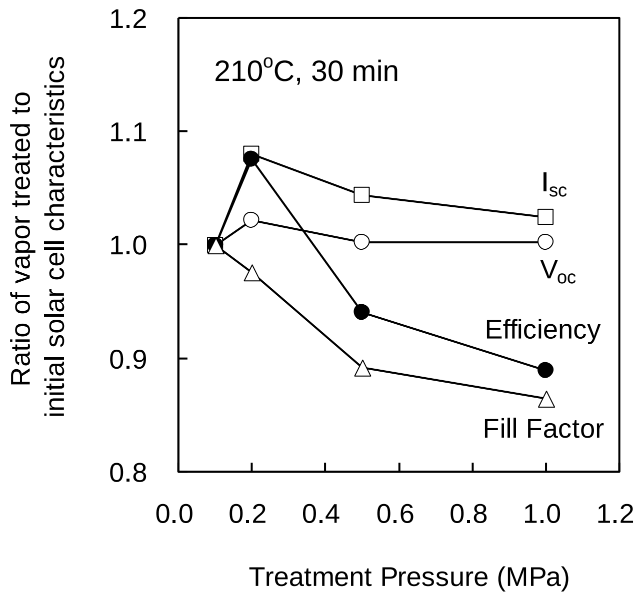

Fig. 5 Average ratios of V_{oc}, I_{sc}, fill factor and conversion efficiency of the samples H_2O vapor treated to initial as a function of treatment pressure.

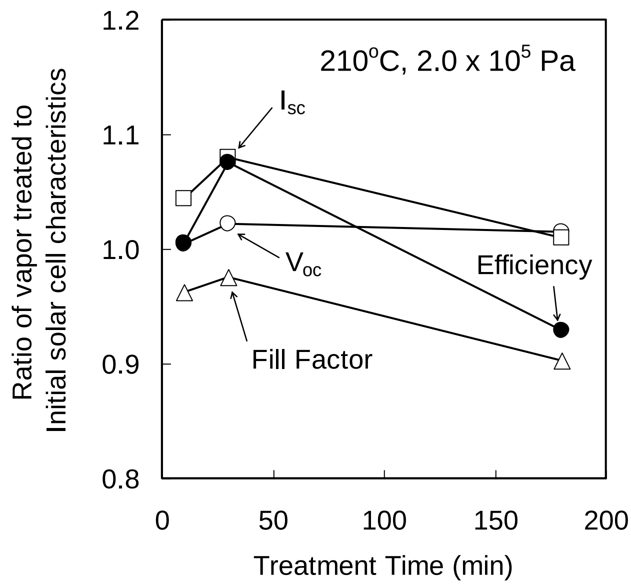

Fig. 6 Average ratios of V_{oc}, I_{sc}, fill factor and conversion efficiency of the samples H_2O vapor treated to initial as a function of duration.

cells by H_2O vapor treatment is still remained.

Summary

Improvement in characteristics of commercial single crystalline silicon solar cells was demonstrated by high-pressure H_2O vapor heat treatment. The characteristics of crystalline silicon solar cells improved by 2.0 x 10^5 Pa H_2O vapor heat treatment at 210^{o}C for 30 min. Average I_{sc}, V_{oc} and conversion efficiency of simultaneously H_2O vapor heat treated 16 samples were increased from 10.6 to 11.4 mA/cm^2, 0.515 to 0.526 V, and 11.6 to 12.5%, respectively. By appling the H_2O vapor heat treatment, steam penetrated into the solar cell and defects were effectively passivated. The improvement of solar cell characteristics is assumed to be caused by the decrease in the probability of photo induced carrier recombination, and then the increase in the minority carrier lifetime.

On the other hand, degradation of fill factor and conversion efficiency was observed by the 1.0 x 10^6 Pa H_2O vapor heat treatment at 210^{o}C for 30 min and 2.0 x 10^5 Pa H_2O vapor heat treatment at 210^{o}C for 180 min. The degradation of solar cell characteristics was caused by the increase of serial resistance loss according to the oxidation of silver electrodes. It is easily avoidable by modifying the process of electrode fabrication. These results suggest that the characteristics of crystalline silicon solar cells may be easily improved by the low temperature and low cost process i.e. by the high-pressure H_2O vapor heat treatment. Moreover, this treatment has a potential for further improvements in characteristics of crystalline silicon solar cells.

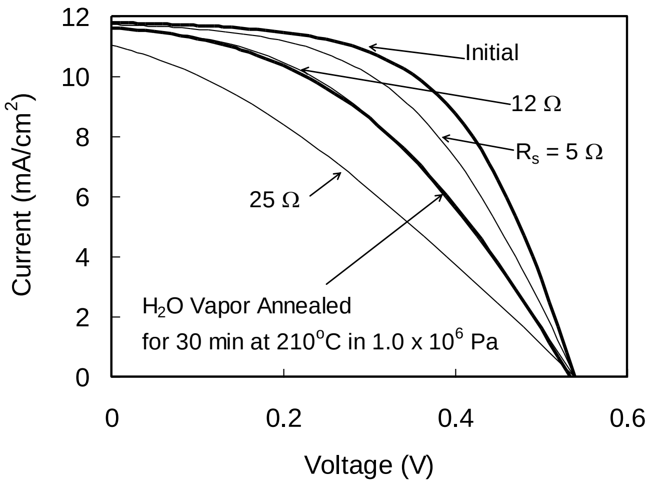

Fig. 7 Solar cell characteristics observed in a sample as fabricated and heat treated at 210^{o}C for 30 min in 1.0 x 10^6 Pa H_2O vapor environment (bold lines) and calculated current-voltage characteristics for serial resistance (R_s) of 5, 12 and 25 Ω (thin lines).

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