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Improvement in the light conversion efficiency of silicon solar cells by pure hydrogen annealing

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ABSTRACT

In this report, the effects of pure hydrogen gas annealing on series resistance (R_s), shunt resistance (R_{sh}), open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor, and efficiency were investigated systematically using standard, commercially available polysilicon solar cells. Improvements on the electrical characteristics, fill factors, and efficiency of the solar cells were observed after annealing by pure hydrogen gas at 350 °C for 15 min. In the best case, the conversion efficiency was raised by nearly 1% point. Judging from our experimental evidences, the improvement on cell performance could be mostly attributed to the reduction of R_s and improvement in Ag grid/emitter contact resistance in the cells during the annealing process.

1. Introduction

Cost reductions on the development solar cells can be achieved either by a reduction of manufacturing costs or by an increase in solar cell efficiency. Silicon (Si) is a dominant material used in the commercial production of low-cost solar cells, and various cost competitive, relatively cheaper processing steps have been developed to make these solar cells more energy efficient. The lifetime of minority charge carriers is a widely accepted material parameter, which influences the conversion efficiency of the p–n junction silicon solar cells [1]. The main factors responsible for reducing the lifetime of the charge carriers are defects and impurities present in silicon wafers. Dangling bonds on the surface are the main trapping centers for the charged carriers. Hydrogen atoms play a vital role in the deactivation of those recombination centers. There are numerous established methods of hydrogen passivation, such as hydrogen ion implantation [2], hydrogen plasma injection [3], plasma enhanced chemical vapor deposition (PECVD) of hydrogenated silicon nitride [4] and forming gas (mixture gas of H_2 and N_2) annealing (FGA). Among all these, FGA is a much simpler and cost effective method for hydrogen passivation.

For enhancing conversion efficiency in solar cell applications, the treatment using hydrogen forming gas at an appropriate temperature can interact with impurities and improve the grain boundary to achieve better efficiency. There have been several reports on the enhanced conversion efficiency of low-cost solar cells after annealing in forming gas at elevated temperature [5–10]. Improvements in solar cell efficiency after FGA on silicon nitride-coated surfaces have been readily demonstrated by Kishore et al. [10] and Hanoka et al. [11]. The behavior of silver film contacts on n-type silicon after nitrogen post-metallization annealing was investigated in [12,13]. The beneficial effect of the FGA on the fill factor of Si solar cells with screen-printed Ag contacts has been found to be thermally activated at a temperature above 300 °C; this effect has also been found to be irreversibly stable in time [14]. It has been shown that the annealing method affects the current

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path between silver crystals and fingers, and lower contact resistance is suggested as the mechanism for improving efficiency.

In this report, we did not study how hydrogen passivation affected the SiN_x:H layer during or after the PECVD process. Instead, the effects of pure hydrogen gas anneal on series resistance (R_s), shunt resistance (R_{sh}), open circuit voltage (V_{oc}), short circuit current (I_{sc}), fill factor, and efficiency were investigated systematically using standard and commercially available polysilicon solar cells. Improvement on the electrical characteristics, fill factors, and efficiency of solar cells were observed after the hydrogen annealing process at 350 °C.

2. Materials and methods

Our studies were performed using standard, commercially available industrial solar cells on six-inch p-type Cz-polysilicon wafers. Cell surfaces were roughened using HF and HNO_3 saw damage etch with no additional texturisation. A $POCl_3$ diffusion process was carried out to obtain sheet resistance of 65 Ω/sq. The SiO_2 residues on the cell surfaces were removed through Phosphorus Glass (PSG) etching system. A SiN_x anti-reflection coating was deposited on the cells with a plasma enhanced chemical vapor deposition (PECVD) system. The front and rear side finger and bus bar contacts were screen-printed with a standard, commercially available lead containing Ag paste, Al paste, and Ag+Al paste. After drying at 200 °C, the cells were fired in a fast firing conveyor belt furnace at an optimal firing temperature of 850 °C to make fingers and bus bars come in contact with the N- and P-type regions for maximum performance. Finally, the cell edges were isolated using laser cutting.

The finished cells were then annealed in a belt furnace under hydrogen atmosphere at different temperatures ranging from 200 to 600 °C for 15 min. After annealing, samples were first isolated from the heat source to cool them down slowly in order to reduce the thermal shock. At the second stage, the temperature of the samples was further reduced to ambient temperature with cooling water. The performance parameters of the sample cells were again determined from *I–V* characteristic curves under illuminated condition using an AM 1.5 Global spectrum. The data from the comparative analysis of the performance parameters of a group of samples before and after hydrogen gas annealing are presented in the next session.

3. Results and discussion

In order to understand the effects of the H_2 annealing temperature on the conversion efficiency of the cells, the temperature was varied during the hydrogen gas annealing although the dwell time was kept at 15 min throughout the entire experiment. The development of the efficiency of solar cells, fired at optimal temperature of 850 °C for the screen-printed contacts, was plotted versus the hydrogen annealing temperature (Fig. 1). Efficiency did not show significant improvement until a temperature of 300 °C was reached. When the annealing temperature reached above 400 °C, cell performance began to degrade, and the average efficiency dropped by 0.62% at a temperature of 450 °C. This indicates that pure hydrogen gas annealing worked best at 350 °C. Above that temperature, the efficiency of the cells began to decrease due to the increase in surface dangling bonds and surface recombination loss at higher temperature. In addition, dwell time longer than 15 min did not improve the cell performance. On the contrary, annealing processes performed in nitrogen atmosphere under the same experimental conditions only show deteriorated or no improvement in cell performance, which indicate that the hydrogen gas indeed plays an important role in annealing.

In Fig. 2, we plot the efficiency rates before and after H_2 annealing at 350 °C for 15 min of 24 sample cells with efficiency rates ranging from 14.4% to 15.6%. Although some of the samples' efficiency rates were greatly improved, not all of them were improved after H_2 annealing. The reason for this will be discussed later. The gains of the V_{oc} and I_{sc} of the samples tested are also plotted in Figs. 3 and 4, respectively. Although we observed a slight increase in both V_{oc} and I_{sc} after annealing, the amount of increase was neither proportional nor strongly correlated to the increase in efficiency. Hydrogen is well known to have the ability to diffuse in Si

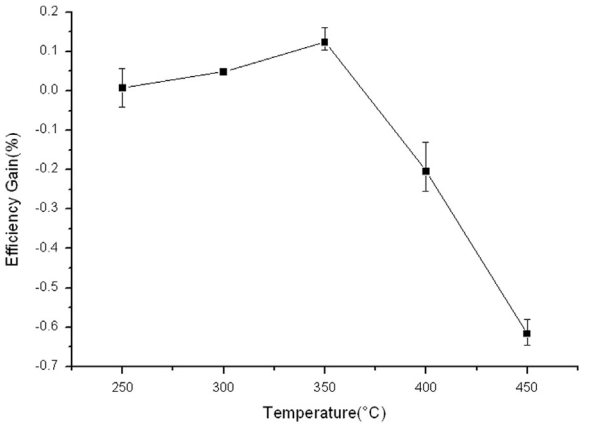

Fig. 1. Temperature dependence of the averaged efficiency gain of solar cells at temperatures ranging from 250 to 450 °C.

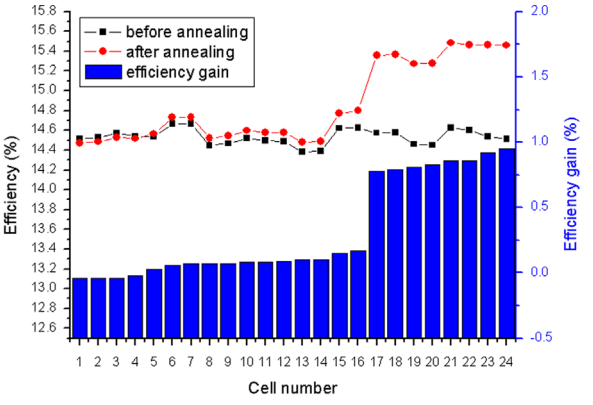

Fig. 2. Plots of efficiency and efficiency gain before and after H_2 treatment.

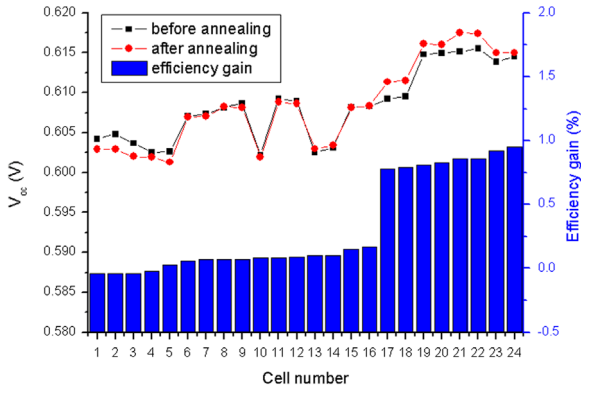

Fig. 3. Open circuit voltages and efficiency gains of solar cells before and after H_2 treatment.

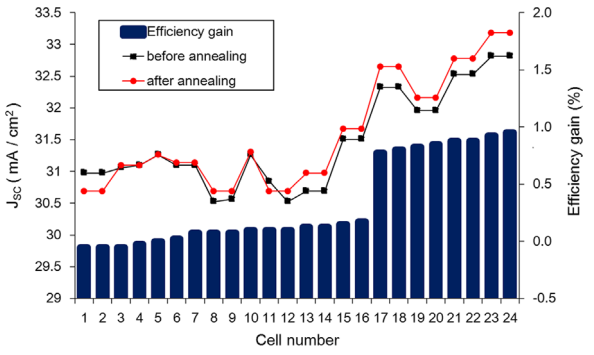

Fig. 4. Short circuit current density and efficiency gains of solar cells before and after H_2 treatment.

and in particular to bond to dangling bonds, resulting in a passivation of defects, reduced surface recombination loss, and an enhancement in cell efficiency. However, our studies show that annealing does not influence the V_{oc} and I_{sc}. This indicates that hydrogen passivation of defects and grain boundaries are not responsible for the observed efficiency improvement.

The gain of the fill factor of the samples after annealing is also shown in Fig. 5, in which the efficiency gain has been plotted in parallel for comparison. We found that the fill factor gain and the efficiency gain were strongly correlated. After determining the values of the R_s and R_{sh}, we then studied the changes in these parameters after H_2 annealing. The results are shown in Figs. 6 and 7. We found a strong correlation between R_s and increment of efficiency, but not with the R_{sh}. Thus, it is apparent that the increase in efficiency after the annealing process is mostly due to the reduction of the R_s. Since the value of R_s is composed of the specific contact resistance (ρ_c) between the Ag grids and the emitters, the grid resistance, and the emitter resistance, measurements of above individual resistance are performed by the three-point probe method before and after annealing. The results show that the grid resistance and the emitter resistance are not affected by annealing. However, in Fig. 8, ρ_c shows a strong correlation to the improvement in R_s. Therefore, the reduction in the R_s is solely resulted from the improvement in the ρ_c.

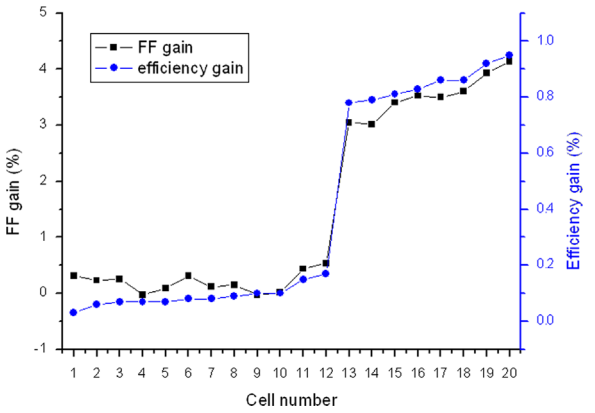

Fig. 5. Fill factor gains and efficiency gains of solar cells before and after H_2 treatment.

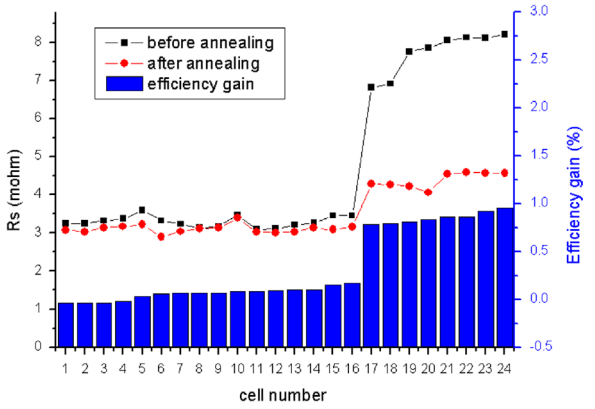

Fig. 6. Series resistance and efficiency gains of solar cells before and after H_2 treatment.

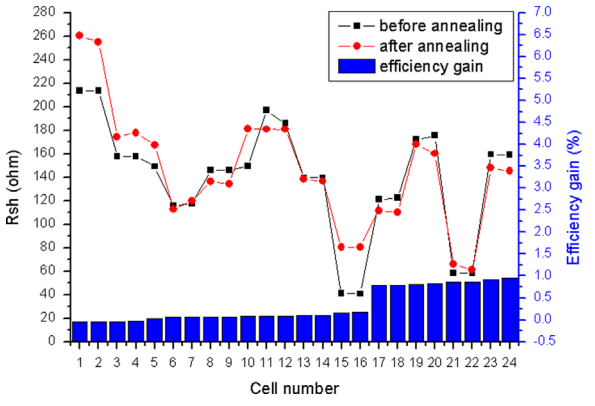

Fig. 7. Shunt resistance and efficiency gains of solar cells before and after H_2 treatment.

In the next experiments, we began our tests on cells with different conversion efficiency rates. In the first set of samples we identified 10 solar cells with higher efficiency rates ranging from 15.8% to 16.0% and with R_s values ranging from 3.38 to 5.02 MΩ. For the second set, we used another group of 10 samples with lower efficiency rates ranging from 14.5% to 14.7% and with R_s values ranging from 3.03 MΩ to 9.96 MΩ. All the samples were annealed

in a belt furnace under hydrogen atmosphere at a temperature at 350 °C for 15 min. Again, we found that annealing had an insignificant effect on V_{oc}, I_{sc}, and R_{sh}. However, the improvement on R_s was proportional to the increase in efficiency (Figs. 9 and 10). Moreover, the gain of the fill factor totally resembled the curve of the efficiency gain (Fig. 11). Based on the results, it can be said that the H_2 annealing process for gaining conversion efficiency and fill factor through the improvement on R_S works for cells with either higher or lower efficiency rates. It works even better for cells with an initial higher R_s. The Ag grids/emitters contact interface and microstructures were studied by Lin et al. [15] by using transmission electron microscopy and scanning electron microscopy. It was found that even in optimal fired contacts, there are at least three different microstructures in the thin glass-layer. The Ag grids/emitters interface was greatly influenced by glass-phase layer and dissolved metal atoms, and consequently, the current transport across the interface was also affected. We speculate that samples with different initial R_s have different microstructures which lead to different annealing results after pure hydrogen annealing.

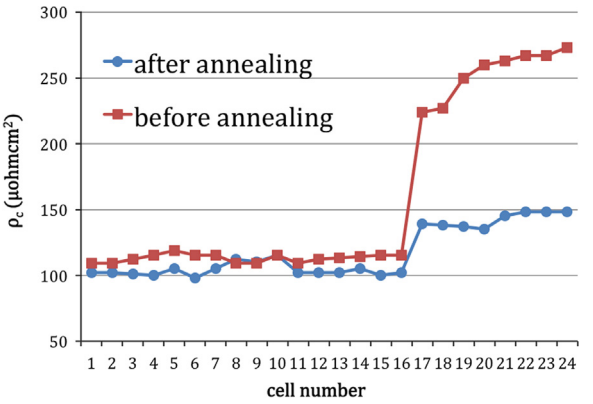

Fig. 8. Specific contact resistance (ρ_c) between the Ag grids and the emitters of solar cells before and after H_2 treatment.

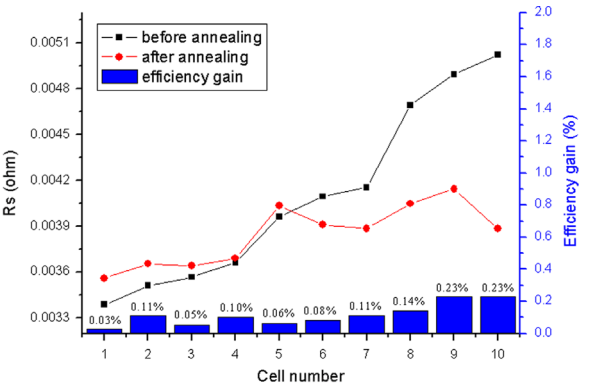

Fig. 9. Series resistance and efficiency gains of solar cells with slightly higher efficiency ranged from 15.8% to 16.0% before and after H_2 treatment.

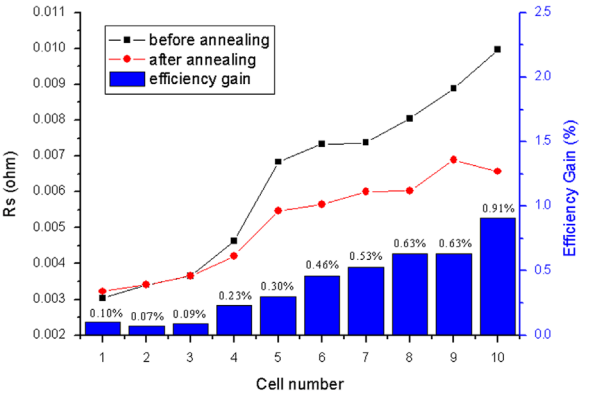

Fig. 10. Series resistance and efficiency gains of solar cells with lower efficiency ranged from 14.5% to 14.7% before and after H_2 treatment.

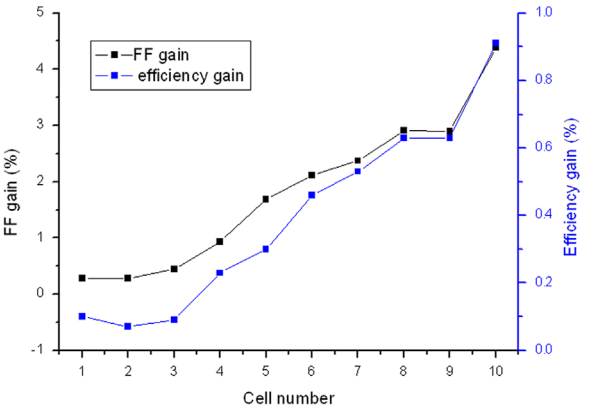

Fig. 11. Fill factor gains and efficiency gains of solar cells with lower efficiency before and after H_2 treatment.

Analyzing our *I–V* characteristics revealed that the increase in the fill factor can only be attributed to the decrease in series resistance which, in turn, can be traced back to the reduction in the contact resistivity as reported in [16]. A model of current transport through screen-printed contacts of a forming gas anneal on solar cells has been proposed by Schubert et al. [17], in which current flow can take place via three channels: direct interaction at isolated spots between the Ag crystallites and the Ag grid [18,19], tunneling through the thin glass region [20], and conduction through the glass layer by tunneling through metallic precipitates in the glass layer [16,21]. Our H_2 gas annealing method worked best at $T=350$ °C. We speculate that the H_2 gas annealing is able to improve the Ag/emitter interface during the annealing process. Therefore, current transport between emitter and the bulk silver fingers was enhanced due to the reduction in contact resistance. However, due to the complicate and non-uniform features of the contact interface, more evidence and further microstructure investigation is still needed.

4. Conclusions

We presented a simple and low-cost method to increase conversion efficiency of commercially available polysilicon solar cells using pure H_2 annealing at an ideal temperature. It has been shown that the investigated solar cells increased

in conversion efficiency by nearly 1% point after H_2 annealing due to lower R_s and improved Ag grid/emitter contact. Other parameters, such as shunt resistance, open circuit voltage, and short circuit current were less or not at all influenced. We speculate that it is possibly due to a reducing reaction in the glass layer with H_2 gas which enhances current transport at Ag/emitter interface and leads to the decrease in contact resistance.

Acknowledgment

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