

Research Article

Efficiency Improved by H₂ Forming Gas Treatment for Si-Based Solar Cell Applications

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The photovoltaic (PV) effects have been investigated and improved using efficient treatments both on single-crystalline (sc) and on multicrystalline (mc) silicon (Si) solar cells. The major effect of forming gas (FG) treatment on solar cell performance is the fill-factor values, which increase 3.75% and 8.28%, respectively, on sc-Si and mc-Si solar cells. As for the optimal 15%-H₂ ratio and 40-minute FG treatment, the conversion efficiency (η) values drastically increase to 14.89% and 14.31%, respectively, for sc- and mc-Si solar cells. Moreover, we can measure the internal quantum efficiency (IQE) values increase with H₂-FG treatment under visible wavelength (400~900 nm) radiation. Thus based on the work in this research, we confirm that H₂ passivation has become crucial both in PV as well as in microelectronics fields. Moreover, the developed mc-Si solar cell by proper H₂ FG treatment is quite suitable for commercial applications.

1. Introduction

Due to high price of fossil energy source and huge pollution of environmental issue in recent years, the development of renewable energy regains our attention. The development of the solar energy industry is one of the most popular technologies in renewable energy. For the solar energy becoming a practical renewable energy, it is widely accepted that we must have efficient ways to convert radiation into electricity as called photovoltaic (PV) effect. Nowadays, however, the unit price of converting power by solar energy is much higher than that of the traditional energy source. Thus, how to enhance the overall efficiency and reduce the manufacturing cost is an important subject for developing the solar energy industry [1, 2].

The crystalline silicon-based (Si-based) solar cell is not only still heavily dependent on the materials base of

the semiconductor industry but also features an excellent stability, technology maturity, and an easy acquisition. It also fulfils these requirements for the rapidly expanding solar energy market [3, 4]. For a Si crystalline growth, if any grain boundary exists inside the crystal, the dangling bond will be formed by the breaking interface in a Si atom. In any *pn*-junction of the solar-cell process, meanwhile, the emitting electrons inside the crystalline Si are highly active and easily combined with other elements [5, 6]. For the dangling bond in the band gap, the excess of positively charged states in dangling bond gives rise to energy level deep, thus enhancing *n* types Si crystalline by irradiating the material, or by extrinsic doping.

It is well known that cost reductions of the developed solar cell can be achieved either by a reduction of manufacturing cost or by an increase in solar cell efficiency and defects in the bulk of Si to remove the band-gap

levels into the valence or conduction bands [5–8]. Among the types of Si-based crystalline, single crystalline (sc-Si), multicrystalline (mc-Si), and amorphous (a-Si), the mc-Si wafer owns the highest growth rate and the lowest fabrication cost [3, 4]. Unfortunately, the mc-Si contains a large number of defects and dislocation suffered from lattice mismatch, thus yielding to the least conversion efficiency on the PV applications [4].

For enhancing the conversion efficiency in the solar-cell application, the treatment with hydrogen (H_2) forming gas (FG) at appropriate temperature can interact with impurities. The passivation effect of H_2 gas can also be used for improving the grain boundary of the mc-Si to achieve a better efficiency [9, 10]. It is widely accepted that the FG treats with H_2 gas in the recent Si-based solar cells from the viewpoint of fabrication cost and performance.

Practically all PV devices incorporate a pn -junction in a semiconductor across which the photo voltage is developed. At first in this paper, we simulate the phosphorus (P) diffusion process on a p -type Si substrate and obtain the optimal parameters for developing the solar cell. Then, the H_2 FG treatments on sc- and mc-Si solar cells are used for improving their performance parameters. Solar-cell operation can be modeled by considering the ideal equivalent scheme [11], consisting of a current source and two diodes in parallel. The current source models include the light-generated (I_L) or short-circuit (I_{SC}) current density. The first solar-cell diode models the diffusion current from base and emitter regions and the second diode represents generation-recombination (GR) current in the junction space-charge region.

The illuminated current-voltage (I-V) characteristics in our developed solar cell are described by [11]

$$I = I_{sc} - I_0 \left\{ \exp \left[\frac{q(V + R_S I)}{nkT} \right] - 1 \right\} - \frac{V + IR_S}{R_{sh}}, \quad (1)$$

where I_0 represents the saturation current with a constant value, k is Boltzmann's constant and T is temperature in degrees Kelvin. In a real device, the dissipating power effects electrically to two parasitic resistances in series (R_s) and in parallel (R_{sh}) with our developed solar cell.

Two of the most figures of merit to evaluate the designed solar-cell performance are the conversion efficiency (η , in %) and the internal quantum efficiency (IQE), which can be expressed as [12]

$$\begin{aligned} \eta &\equiv \frac{P_{out}}{P_{in}} = [FF] \times \left(\frac{V_{OC} \times I_{SC}}{P_{in}} \right) \\ &= \left[\left(\frac{P_{max}}{V_{OC} \times I_{SC}} \right) \times 100\% \right] \times \left(\frac{V_{OC} \times I_{SC}}{P_{in}} \right), \end{aligned} \quad (2)$$

$$IQE = \frac{I_{electron}}{I_{photon}(1 - R)}, \quad (3)$$

where FF (in %) is the fill factor, V_{OC} is the open-circuit voltage, and I_{SC} is the short-circuit current, in the ideal equivalent scheme. $I_{electron}$ is the induced electron current of solar cell, I_{photon} is the incident photon current and R is reflection coefficient on the absorbed layer.

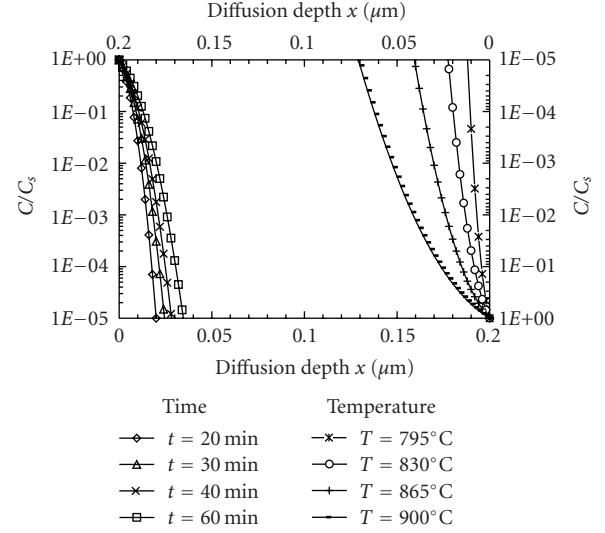


FIGURE 1: The profile curves of dopant concentration ratio (C/C_s) on the corresponding diffuse distance (x) with changing time (on bottom-left axis) and temperature (on top-right axis) respectively, for the phosphorus diffusion.

To measure the PV effect, the I-V curves are displayed on a curve tracer (Wacom, WXS-220S-L2). For simplification of terrestrial solar-cell characterization, the induced photocurrents (I) of the developed devices are measured under the air mass (AM 1.5 G) with a standard value of 1000 W/m^2 . The quality of the surface passivation was revealed by light beam-induced current measurements, which were obtained by Semilab WT-2000. We also measured the sample's IQE by PV Measurement (Model: QEX7).

2. Solar Cell Design and Fabrication

The main structure of a solar cell design is first to diffuse the P doped on a p -type Si substrate. Assume that the simple one-dimensional diffusion process in our developed solar-cell model, the dopant concentration ($C(x, t)$, in cm^{-3}), and the diffusion coefficient (D) solved by the Fick equation under constant surface concentration (C_s) at the diffusion length ($x = 0$) can be expressed by [11]

$$\begin{aligned} C(x, t) &= C_s \operatorname{erfc} \left(\frac{x}{2\sqrt{Dt}} \right), \\ D &= D_0 \exp \left(\frac{-E_a}{kT} \right), \end{aligned} \quad (4)$$

where erfc is the complementary error function, $\sqrt{Dt} \cdot E_a$ (in eV) is the activation energy of diffusion, and k is the Boltzmann constant.

The above critical diffusion parameters of temperatures (T) and time (t) were determined by a computer with a MATLAB program (version 6.X). For simulating the P and drive-in diffusion, Figure 1 shows the profile curves of dopant concentration ratio (C/C_s) on the corresponding diffuse distance (x) with changing time (on bottom-left axis) and temperature (on top-right axis), respectively. The

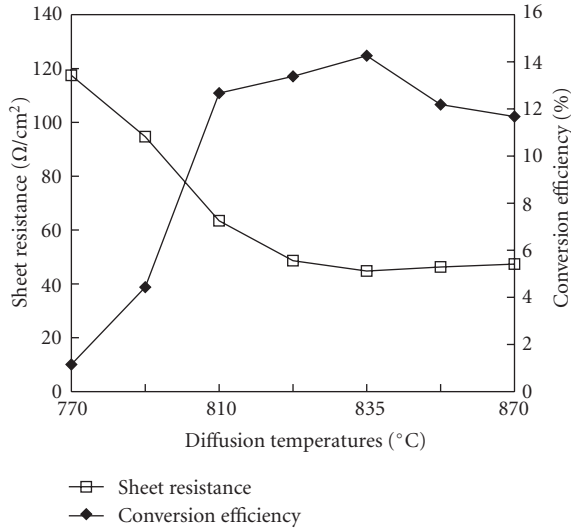


FIGURE 2: The sheet resistance (in Ω/cm^2) and conversion efficiency (in %) with respect to temperatures (from 770°C to 900°C) of the solar-cell prototypes with and without drive-in diffusion processes.

diffusion time and temperature are varied from 20 minutes to 60 minutes, and from 790°C to 900°C , respectively. In these curves of Figure 1, we can clearly observe that the diffusion profile of changing temperature influences more than those of changing diffusion time. For more precise investigation on a optimal condition, therefore, we select the 30-minute diffusion time to fabricate the solar-cell prototypes with fine trimming the diffusion temperatures.

During the P-doped process, we select the *p*-type sc-Si substrate with/without the drive-in diffusion to form the solar-cell prototype. Figure 2 illustrates the sheet resistance (in Ω/cm^2) and the conversion efficiency (in %), respectively, as a function of different temperatures (from 770°C to 900°C) of the solar-cell prototypes with and without drive-in diffusion processes. Among the diffusion processes described above, the maximum conversion efficiency value (14.26% calculated from (2)) of the prototype is at 835°C diffusion temperature, thus causing efficiency decreases as further increases in the diffusion temperature beyond 835°C . The sheet resistance decreases initially with increasing the diffusion temperatures and reaches a minimum value at 835°C -diffusion temperature. With this optimal diffusion parameters at 835°C for a solar-cell prototype, the sheet resistance is measured to be $44.7 \Omega/\text{cm}^2$, and its corresponding conversion efficiency is 14.26%.

In general diffusion process, the heavily doped ($\geq 10^{18}\text{cm}^{-3}$) region which contains a dead layer near the top surface usually decreased the PV characteristics of a solar cell [13, 14]. The creation of an emitter by diffusion of P from a POCl_3 (phosphorus oxy-chloride) ambient at high temperature (above 800°C) is a standard drive-in process in industry [15]. During the diffusion process, we first predeposit a diffusion layer on the surface and then perform the drive-in (redistribution) diffusion at the fixed total impurity mass.

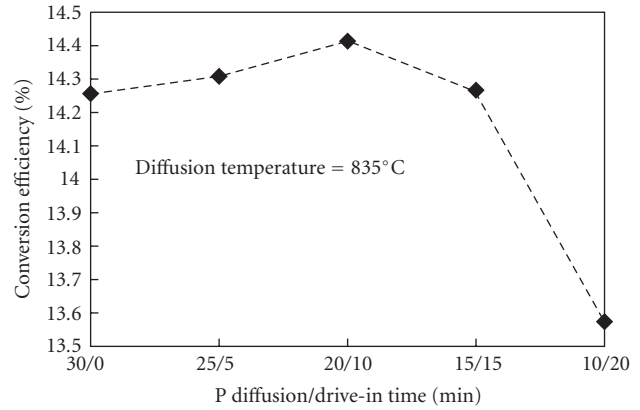


FIGURE 3: The conversion efficiency of the sc-Si prototype using same total 30-minute diffusion with the different drive-in times.

Under the total 30-minute time with predeposit and drive-in diffusion (at 835°C), Figure 3 shows the most improved 14.41% conversion efficiency for 20 minutes and 10 minutes, respectively, on predeposit and drive-in diffusion. As described previously, this improved PV phenomenon is attributed to the fact that drive-in process diffused by POCl_3 ambient can eliminate the dead layer and enhance the solar-cell performance.

In the future development of PV materials, most important is efficiency, and not to be neglected, lowest possible cost. Today the market is dominated by crystalline Si in its mc- and sc- form. Even though the mc-Si material is the least cost for manufacturing a solar cell [5], the developed mc-Si solar cell still owns less conversion efficiency than that of an sc-Si prototype ($\eta = 14.41\%$ at Figure 3). The low-efficiency reason is that the grain boundary effect may increase series resistance, reduce lifetime, and increase dark (leakage current) of a dependent photocurrent [11]. Among the treatment methods for enhancing the PV performance, the passivation effect of H_2 FG is commonly used to remove the band-gap levels into the valence or conduction bands [5–8].

3. Treatment Result and Discussion

Before any treatment of the mc-Si solar cell upon predeposit P and drive-in diffusion, a 100-nm Si_xN_y and SiO_2 antireflection coating was deposited on the front at 200°C by plasma enhanced chemical vapor deposition as described in our previously work [16–20]. When the metallization of both sides was finished, the samples were immediately fired in the belt furnace at 950°C . This was followed by the FG process. It was used by introducing H_2 FG (mixed gas, $\text{N}_2:\text{H}_2 = 85\%:15\%$) with 3600 sccm for 10 to 40 minutes at 400°C in atmosphere.

Both the I_{SC} (in Amp) and the V_{OC} (in Volt) of the developed solar cells all with respect to different H_2 FG time (in minutes) on the sc- and mc-Si substrates for comparison are illustrated in Figure 4. This figure illustrates axes with the different scale, in which the bottom and top axes annotate

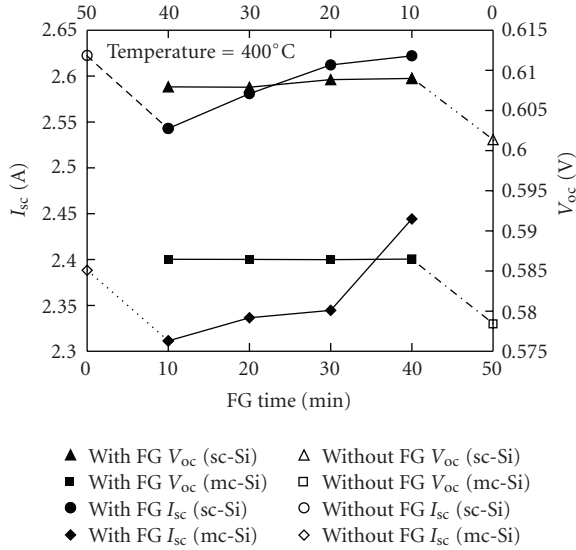


FIGURE 4: The open-circuit voltages (V_{OC}) and the short-circuit currents (I_{SC}) of sc- and mc-Si solar cells without ($t = 0$ min) and with different H_2 FG treatment time.

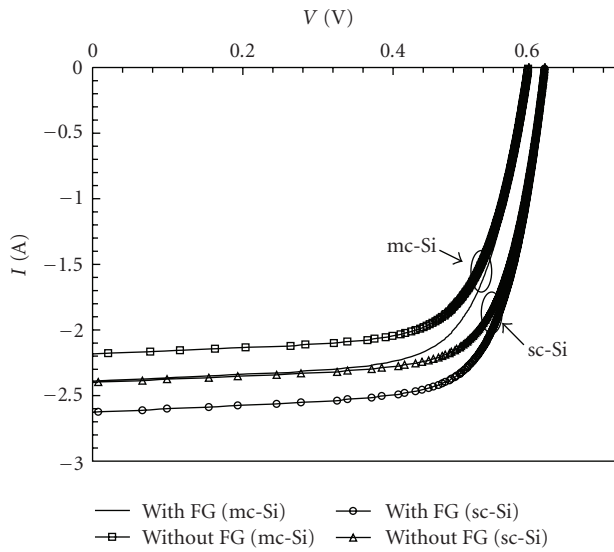


FIGURE 5: Improved Fill Factor of sc- and mc-Si Solar Cells at H_2 FG Treatment: 40 minutes (sc-Si: 69.92% \rightarrow 73.93%, mc-Si: 59.43% \rightarrow 72.63%).

FG time with opposite approaching direction, while the left and right axes denote I_{SC} and V_{OC} , separately. In both sc- and mc-Si solar cells without FG treatment (at $T = 0$ minute as reference value), I_{SC} values are 2.622 A and 2.388 A. Values of V_{OC} are 0.6013 V and 0.5784 V, respectively, for sc- and mc-Si solar cells. Among the H_2 FG times, the I_{SC} values decrease initially and then increase with respect to the bottom-left axis, while the V_{OC} values with respect to the top-right axis vary not much after 10-minute treatment. These values imply that there exist two competing effects during the H_2 treatment. One is degradation effect which decreases the shunt resistance and increases the leakage

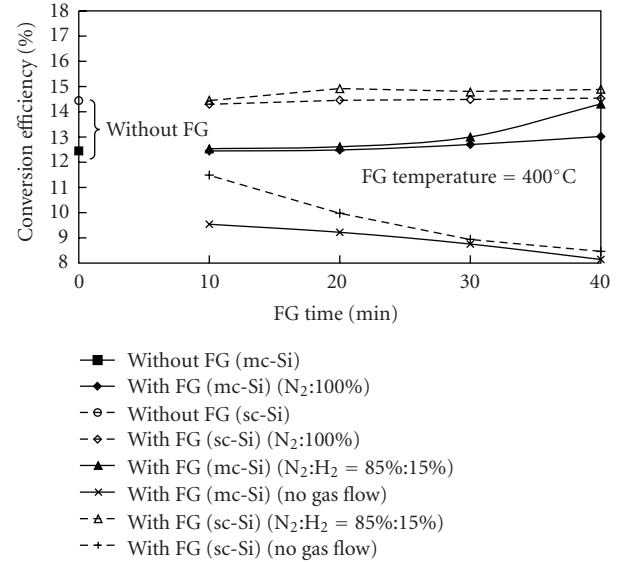


FIGURE 6: Improved energy conversion efficiency (η) of sc-Si and mc-Si solar cells with/without different H_2 FG (for mixed gas ratios) treatment time.

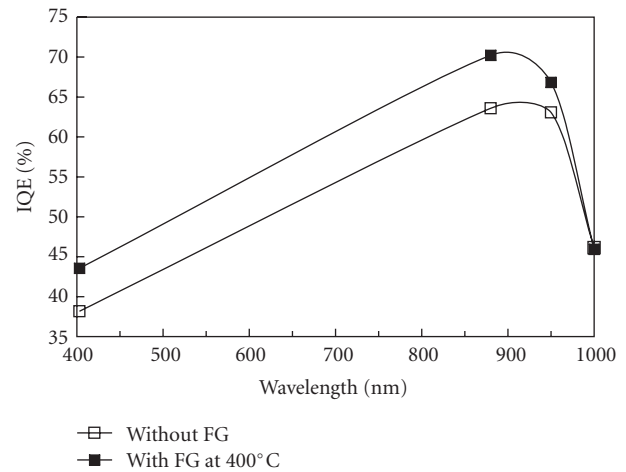


FIGURE 7: Improved internal quantum efficiency (IQE) of the mc-Si solar cells with/without by H_2 FG treatment.

current at the high temperature of 400°C. The other is H_2 FG effect which passivates the defects in the device [21]. The degradation effect dominates at the first 10 minutes and then the passivation effect takes control for longer treatment time. The decrement is still large for 30-minute H_2 treatment for mc-Si solar cell. This could be due to the grain boundaries of the mc-Si and takes longer time to passivate them [21]. The I-V curves shown in Figure 5 can evaluate the PV effect on the developed solar cells. The FF values after 40-minute H_2 FG treatment can be improved by 3.75% and 8.28%, respectively, for the developed sc- and mc-Si solar cells.

Figure 6 shows the η values (calculated by (2) from Figures 4 and 5) of the sc- and mc-Si solar cells with/without H_2 FG treatment time at different gas ratios. The η values without FG treatment on sc- and mc-Si solar cells are also

shown at zero FG treatment time. There are low conversion efficiencies without any gas flow both on sc- and mc-Si solar cells. Since the sc-Si material has few impurity and grain boundary as mentioned previously, there is very small space for improvement on FG treatment. This is the reason why these efficiency values on mc-Si solar cell show the increasing effect on a longer FG time (between 30 and 40 minutes) while there is no significant effect on the sc-Si solar cells.

This figure also illustrates the passivation effect on the different FG H₂-ratio of our developed sc- and mc-Si solar cells. For safety consideration the 15%-H₂ ratio is the maximum value to avoid the H₂ explosion. As for the optimal H₂ ratio of 15% on FG treatment, the η values drastically increase to 14.89% and 14.31% at 40 minutes, respectively, for sc- and mc-Si solar cells. Note that these two values at 40-minute H₂ FG have only 0.58% difference on the sc- and mc-Si solar cells. Thus, we prove that the conversion efficiency can be improved by H₂ FG treatment (with optimal 15%-H₂ at 40-minute treatment time) for the cheaper mc-Si solar cell.

Moreover, we can measure the IQE values increase with H₂-FG treatment under visible wavelength (400~900 nm) radiation (as shown in Figure 7). However, the measured IQE value under long wavelength (about 1000 nm) is basically the same for samples with and without H₂ FG treatment. This suggests that H₂ FG treatment provides better passivation in the area near the surface. For these deeper areas which H₂ atoms cannot reach, the passivation effect is not obvious. This is why the quantum efficiency under long wavelength remains the same (or even worse) after H₂ treatment. Because H₂ atoms cannot travel very deep in the developed device, the region deep in the device was not well passivated. Therefore, the developed solar cell was even degraded at long wavelength with H₂ FG treatment.

4. Conclusion

The effects on sc-Si and mc-Si solar cells are investigated. The η values are increased with the H₂ FG treatment. The increment is larger for the mc-Si solar cell than that of the sc-Si solar cell. Probably due to the existence of grain boundaries as well as high concentration of impurities, the FG treatment with the optimal 40-minute time and 15%-H₂ ratio has more impact on mc-Si compare to that on sc-Si. The V_{OC} is also increased for the both cases. The increment saturates for 10-minute FG time for the both cases, which suggests that it could be due to the quality improvement of the metallization. There are two effects during the H₂ treatment. The degradation effect dominates at the first 10 minutes and the passivation effect dominates for the longer treatment time, which results in the change of the decrement of the I_{SC}. The LBIC measurements show that the IQE values improved with FG treatment, especially in the visible radiation (wavelength range from 400 nm to 900 nm). Therefore, increasing the H₂ FG treatment time (40 minutes) is an applicable method to improve the developed sc-Si and mc-Si performance for solar cell applications. It should be recognized that the P diffusion deep into the bulk of a solar

cell is a prerequisite for efficient passivation and concomitant improvement in the solar-cell performance. Based on the work in this research, the developed mc-Si solar cell by proper H₂ FG treatment is quite suitable for commercial applications.

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