Formation of a Porous Silicon Layer by Electrochemical Etching and Application to the Silicon Solar Cell

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SiN_x thin film grown by plasma-enhanced chemical vapor deposition (PECVD) has conventionally been used as an antireflection layer of the silicon solar cell. In this work, a porous silicon (PS) layer formed by electrochemical etching was shaped on the surface of a crystalline silicon wafer for a simple alternative of anti-reflection coating (ARC). The etching solution was prepared by mixing HF and ethanol for efficient bubble elimination on the silicon surface during the etching process. The anodization of the silicon surface was performed under a constant current, and the process parameters, such as current density and etching time including volume fraction of HF to ethanol in the solution, were carefully tuned to minimize the surface reflectance of the CZ silicon wafer with sheet resistance of 35–40 Ω/□. The PS layer as an anti-reflection coating in the solar cell was compared with conventional PECVD SiN_x thin film by measuring the surface reflectance of the cell. Also, Photovoltaic *I*–*V* properties and the quantum efficiencies of the cells with PS layers were measured.

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1. Introduction

In order to enhance the performance of a solar cell, it is very important to reduce the reflection loss from the surface of the cell. The deposition of SiN_x layer on a bulk crystalline silicon wafer as an anti-reflection coating has been the most common method used at the solar cell production lines. Particularly, the screen-printing process based on a firing-through metallization with PECVD SiN_x ARC seems to be extremely beneficial for improving the efficiencies of industrial silicon solar cells.^{(1),(2)} In spite of the advantages of the PECVD SiN_x, it may impose an additional cost and increase the cell price.

Instead of PECVD SiN_x, it is now well established that porous silicon layer is a promising candidate for reducing surface reflectance and passivating silicon surface.^{(3)–(5)} A PS ARC is formed by an electrochemical or stain (chemical) etching of the silicon surface in an HF-based solution. The refractive index of the porous silicon can easily be controlled by varying the porosity of the silicon material, which is strongly dependent on etching conditions such as additives in the solution, HF concentration, and current density in the case of electrochemical etching. The porous layer on top of the silicon wafer may play an efficient role in diminishing the amount of reflected light from the cell if the PS thickness and refractive index are optimized along the etching time and other etching conditions.

In this work, porous silicon layers were formed by electrochemical etching on top of the *p*–*n*⁺ junctions to confirm the applicability of the PS layer to a common solar cell production line. The porosities and the reflectances of the PS layers were determined for various etching conditions and the efficiency of the solar cell with PS ARC was confirmed by an *I*–*V* test as well as a measurement of the quantum efficiency. The effectiveness of the PS layer on the reflectance and the quantum efficiency of the cell was compared with that of conventional PECVD SiN_x thin film.

2. Experimental procedure

2.1 Substrate

In this work, two kinds of (100)-oriented silicon wafers

with different resistivities were employed. A silicon wafer with lower resistivity was used for the observation of the PS etching behavior, and the applied current density during electrochemical etching was up to 40 mA/cm². On the other hand, a silicon wafer with higher resistivity was chosen to manufacture the solar cell with a PS layer, and the applied current density ranged between 0.5–3.0 mA/cm².

P-type, CZ (Czochralski) silicon wafers with resistivities of 0.5–1.7 Ω·cm were used to produce the solar cell with PS layers. The *n*⁺ emitter layers were formed by phosphorus diffusion from a POCl₃ source to confirm the applicability of the PS layer to the solar cell and to flow more current to the silicon surface during electrochemical etching. The diffusion process was carried out so as the sheet resistance of the wafer was to be in the range of 35–40 Ω/□, which made the thickness of the top *n*⁺ layer to be in the range of 0.38–0.41 μm. Then, the wafer with the *p*–*n*⁺ junction was cut to the size of 2.5 cm × 2.5 cm to fit into the Teflon bath.

2.2 Formation of PS layer

The etching solutions (electrolyte) were prepared by mixing HF, H₂O, and C₂H₅OH with volume fractions between 1 : 1 : 1 and 1 : 1 : 5. Absolute ethanol, which is most widely used as a surfactant in the case of PS formation, efficiently eliminates the bubbles on the etched surface and improves the uniformity of the PS layer. The Teflon bath in which the silicon surface was etched is shown in Fig. 1. The metal contact was made at

Fig. 1. Schematic diagram of a Teflon bath for electrochemical etching.

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the back side of the wafer and sealed so that only the front side of the wafer was exposed to the etching solution.

Porosities and thicknesses of the samples were obtained through the simulation of the ellipsometry data with a Maxwell-Garnett effective medium theory in which we assumed that voids are in crystalline silicon. Those simulation results were compared with SEM and/or reflectance data to confirm the reliability of thicknesses and refractive indices of the PS layers. Since a highly conductive silicon wafer can offer more carriers than a resistive wafer during electrochemical etching, a higher current density can be applied to the conductive wafer at the same potential. In this work, a p^+ FZ (float zone) silicon wafer with a low resistivity of $0.01\text{--}0.02\ \Omega\cdot\text{cm}$ was initially used to test the etching solution and reliability of the etching system.

2.3 SiN_x deposition

A hydrogenated SiN_x layer was deposited on the same wafer as that for the PS layer using a PECVD system manufactured by Centrotherm. A small-sized Si wafer was put on a horizontal tray in the tube furnace and the deposition temperature was set to 450°C . The gas flow rate of SiH_4 and NH_3 were 500 and 3,700 sccm, respectively, while the gas pressure in the tube was fixed at 150 mTorr.

2.4 Cell manufacturing procedure

In order to obtain the photovoltaic properties of the cells with PS layer, metal electrode must be formed on the front and rear surfaces of the cell. A silver paste was directly screen-printed on the PS layer as the front metal and aluminum paste was used for the rear metal printing. An electrical ohmic contact was completed through co-firing the pastes in the belt furnace at 700°C . The performance of the solar cell with PS layer was confirmed using a solar simulator at AM1.5 condition ($100\text{ mW}/\text{cm}^2$) and a quantum efficiency measurement system.

3. Results and discussion

The microstructure and the optical properties of the PS layers are strongly dependent on the various etching conditions. In this work, the electrical charge was supplied to the wafer in galvanostatic (constant current) mode with current densities between $0.5\text{--}3.0\text{ mA}/\text{cm}^2$ for the $p\text{--}n^+$ junction wafers and with current densities up to $40\text{ mA}/\text{cm}^2$ for the p^+ Si wafers. Generally, the pore size in the PS layer increases with an increase of the current density, and large pore sizes can cause problems during the screen-printing process. Thus, the porosities of the etched layers were limited to smaller values with a controlling current density when the PS layer was applied to the solar cell. On the other hand, the applied current density was increased to $40\text{ mA}/\text{cm}^2$ to observe etching behavior using the lower resistive wafer.

Figure 2 shows the SEM (scanning electron microscopy) cross-sectional images of the porous silicon layers etched under current densities of $3\text{--}30\text{ mA}/\text{cm}^2$ on p^+ FZ silicon wafers for 100 seconds. In the figure, it was clear that the porosity as well as the thickness of the etched layer increased with the increase of the current density. The morphology of the PS layer shows that the electrochemical etching of the Si occurred uniformly within the wafer and made the granular structure in a columnar shape, as shown in **Fig. 3**. In addition, it must be noted that small holes with sizes of $5\text{--}10\text{ nm}$ could be observed at the surface of the PS layer etched at $30\text{ mA}/\text{cm}^2$. It may be thought that the size of the hole also increased with the increase of the current density. The silver paste for front electrode can penetrate through those holes during the screen-printing process and might cause shunting problems in

Fig. 2. SEM cross-sectional views of the PS layers on FZ silicon wafers. The current densities during electrochemical etching were (a) 3, (b) 5, (c) 10, (d) 20, and (e) $30\text{ mA}/\text{cm}^2$, respectively. The photographs on the right of (c), (d), and (e) are inclined views of the same PS layers as that on the left.

Fig. 3. Close SEM image of the PS layer on an FZ silicon wafer etched electrochemically with a current density of $30\text{ mA}/\text{cm}^2$.

the cell. This means that the current density should be limited to a lower value for the PS layer to be applied to the solar cell.

From a rough estimate of the SEM image, the thickness of the PS layer was obtained as shown in **Fig. 4**. The thickness did not linearly increase as the current density, but the growth rate of the PS layer slightly decreased. The amount of

Fig. 4. Thickness of the PS layer on the p^+ FZ Si wafer as a function of the current density.

Fig. 5. Porosities and refractive indices of the etched layers on the p^+ FZ Si wafer as a function of the current density.

Si materials etched at the surface was proportional to the supplied total charge, and the thickness of the PS layer itself was not linear to the current density.

Figure 5 shows the porosities and the refractive indices of the etched layers along the current density. The refractive index of the PS layer was calculated using Eq. (1) based on the Bruggeman effective medium approximation theory:⁶⁾

$$f_{\text{void}} = 1 - \left[\frac{(1 - n_{\text{PS}}^2)(n_{\text{c-Si}}^2 + 2n_{\text{PS}}^2)}{3n_{\text{PS}}^2(1 - n_{\text{c-Si}}^2)} \right] \quad (1)$$

where $n_{\text{c-Si}}$ and n_{PS} are the refractive indices of crystalline Si and PS, respectively. In the calculation, the refractive index of the Si was substituted by 3.84, which is the value at a wavelength of 650 nm. The optimal refractive index of the ARC (n_{ARC}) must satisfy the following relation:⁷⁾

$$n_{\text{ARC}} = \sqrt{n_{\text{c-Si}}} \quad (2)$$

where it is assumed that the ambient medium is air and the refractive index of air is 1. In that case, the reflected light from the interface between air and the ARC fully cancels the reflected light from the interface between the ARC and Si wafer, and the minimum reflectance, R_{min} , can reach zero. In order to fit with this condition, n_{PS} must be 1.96, which means that f_{void} is 60%. Figure 5 reveals that the current density during electrochemical etching must be set to a value higher than 40 mA/cm² to obtain an optimal refractive index of the PS layer on the p^+ Si wafer, yet we found that, for the Si wafer with the $p-n^+$ junction on the highly resistive Si wafer a much lower value of the current density could form the PS layers with optimal refractive indices.

Fig. 6. Reflectance of the PS layers on $p-n^+$ junctions as a function of the current density. The volume fraction of the etching solution and the etching time were 1:1:1 and 200 s. Reflectance of the PS layer was compared with that of the SiN_x layer.

As stated above, the PS layer was formed on the higher resistive Si wafer in the case of the cell manufacturing process. To confirm the suitability of the PS layer as an ARC, the integrated reflectance measurements were performed with a spectrometer fitted with an integrating sphere in the wavelength between 400 and 1000 nm. Figure 6 shows the dependency of the reflectance of the PS layers on $p-n^+$ junctions to the current density during electrochemical etching. The volume fraction of the etching solution was $[\text{HF}]:[\text{H}_2\text{O}]:[\text{C}_2\text{H}_5\text{OH}] = 1:1:1$ and the etching time was fixed to 200 s. As stated above, the current density necessary to obtain an optimal anti-reflective PS layer on $p-n^+$ junction wafer was much lower than that on the p^+ Si wafer. A decrease of the reflectance as the current density originated from the fact that the refractive index of the PS layer was lowered and its thickness increased. Figure 6 also shows the reflectance of the SiN_x layer compared with that of the PS layer. In the view point of anti-reflective ability, the PS layer was more competitive than the SiN_x layer for the silicon solar cell.

The overall behavior of the refractive indices of the PS layers along the various etching conditions are shown in Fig. 7 (a). The higher current density made the PS layer more porous and the refractive index decreased as with an increase of current density. A similar tendency was also found when the ethanol ratio in the etching solution was increased. Since the role of the ethanol is to remove the bubbles on the etched surface during electrochemical etching, there may be a non-etched surface blocked from the etching solution for a small volume fraction of ethanol. On the other hand, the amount of ethanol did not affect the thickness of the PS layer. As shown in Fig. 7(b), the thickness of the PS layer increased almost linearly with the current density and the etching time. This means that only the total charge determines the thickness of the PS layer. The small deviation from the linear increase and the difference in the refractive index with the etching time may result from the fact that as the electrochemical etching reaction proceeds, the silicon material far from the surface must be etched, and consequently the etch rate decreases. Thus, the etch rate and the surface porosity varied slightly as the electrochemical etching proceeded.

For an optimal ARC layer, the optical thickness of the layer must be close to a quarter of the wavelength of incident light such as:⁸⁾

$$n_{\text{ARC}}d_{\text{ARC}} = \lambda_{\text{min}}/4 \quad (3)$$

Fig. 7. (a) Refractive indices and (b) thicknesses of the PS layers along the current density, the etching solution, and the etching time.

where d_{ARC} is the thickness of the ARC layer and λ_{min} is the wavelength at which the reflectance becomes a minimum value. To obtain a minimum reflectance between 600 and 650 nm, the thickness of the ARC layer is required to be 77–83 nm. Figure 7 shows that the Eqs. (2) and (3) could be satisfied if the PS layer was etched with conditions such as $[\text{HF}]:[\text{H}_2\text{O}]:[\text{C}_2\text{H}_5\text{OH}] = 1:1:3$, current density of 1.5 mA/cm², and an etching time of 400 s. The reflectance of that PS layer averaged in the wavelength ranged between 400–1000 nm was 10.3%, which, compared with the averaged reflectance of 15.0% of the conventional SiN_x ARC layer, was rather small value as shown in Fig. 6.

Figure 8 shows the light I - V curves of the solar cells with the varying etching times of the PS layers under the current density of 2.5 mA/cm² and $[\text{HF}]:[\text{H}_2\text{O}]:[\text{C}_2\text{H}_5\text{OH}] = 1:1:5$. The thickness and refractive index of the PS layer were 60 nm and 1.85 for 200 sec-etching, and 85 nm and 1.80 for 280 sec-etching, respectively. Photovoltaic parameters obtained from the I - V measurement was $\eta = 7.7\%$, $V_{\text{oc}} = 0.594$ V, $J_{\text{sc}} = 28.8$ mA/cm², and $\text{FF} = 0.449$ for the cell with the PS layer etched for 200 sec. In case the etching time was 280 s, the performance of the cell increased to $\eta = 10.6\%$, $V_{\text{oc}} = 0.584$ V, $J_{\text{sc}} = 35.0$ mA/cm², and $\text{FF} = 0.519$. This increase in the efficiency was largely due to the decrease in the reflectance which appeared in the increase in the short-circuit current density. In order to estimate the efficiency of the solar cell using the PS layer as an ARC, metal electrodes were formed at the front and rear side of the cell. However, direct contact of the metal on the front PS layer may shunt the cell during the heat treatment of the screen-printed paste. Also, the series resistance was still low from the non-optimized metal process. Those two unsolved factors brought a low fill factor and efficiency to the I - V curve of the solar cell with the PS layer in

Fig. 8. Light I - V curves of solar cells with PS layers varying etching times under a current density of 2.5 mA/cm². The shape of the I - V curves showed that metal contact was very resistive and the shunt resistance was low.

Fig. 9. Internal quantum efficiencies of the cells with PS layers as functions of the wavelength calculated from the measured external quantum efficiency and the reflectance of the cell varying etching time under the current density of 2.5 mA/cm². The IQE of the cell with the SiN_x layer is also shown in the graph.

spite of a high short-circuit current density.

Figure 9 shows the internal quantum efficiencies of the cells with PS layers as functions of the wavelength. Internal quantum efficiency (IQE) was obtained from the measured external quantum efficiency (EQE) such as:

$$IQE(\lambda) = \frac{EQE(\lambda)}{1 - R(\lambda)} \quad (4)$$

where λ is the free-space wavelength and R the reflectance if there is no absorption of the light in the ARC layer. Considering the recombination loss of the carrier at the non-passivated surface of the cell, the IQE of the cell with the low-cost PS layer was comparable to that of the cell with the SiN_x ARC layer. Hereafter, a modified process for metal contact, for example plating a metal electrode,⁹⁾ must be introduced to minimize the recombination loss at the surface and the shunting effect in the cell with the PS layer.

4. Conclusions

Porous silicon layers were formed on p^+ FZ silicon and CZ silicon with a p - n^+ junction by an electrochemical etching method for ARC layers of a silicon solar cell. The porosity of the PS layer increased with the current density and volume fraction of ethanol in the etching solution. The optimal PS

layer on $p-n^+$ junction to fit with the minimum reflectance for solar cell application was obtained for $[\text{HF}]:[\text{H}_2\text{O}]:[\text{C}_2\text{H}_5\text{OH}] = 1:1:3$, a current density of 1.5 mA/cm^2 , and an etching time of 400 s. The reflectance averaged between 400–1000 nm was 10.3% for the optimal PS layer, which was much lower than that of the conventional SiN_x ARC layer. The photovoltaic I–V curve showed that the short circuit current density could be obtained up to 35.0 mA/cm^2 . On the other hand, the solar cell with the PS layer still showed low efficiency due to the low fill factor. An analysis of the quantum efficiency confirmed that the cell with the PS layer as an ARC was comparable to the cell with the SiN_x ARC layer.

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References

- 1) Shirasawa, K., Fukui, K., Okada, K., Inomata, Y., Takakashi, H., Fukawa, Y. and Fujii, S., Proc. 14th EPVSEC, Jun. 3–Jul. 4, Barcelona, Spain (1997) pp. 384–387.
- 2) Duercks, F., Szulc, J., Ziebakowski, A., Nijs, J. and Mertens, R., Proc. 14th EPVSEC, Jun. 3–Jul. 4, Barcelona, Spain (1997) pp. 792–795.
- 3) Strehlke, S., Bastide, S., Guillet, J. and Levy-Clement, C., *Mater. Sci. Eng.*, Vol. 69, pp. 81–86 (2000).
- 4) Aroutiounian, V. M., Maroutyan, K. R., Zaikyan, A. L. and Touryan, K. J., *Thin Solid Films*, Vol. 403, pp. 517–521 (2002).
- 5) Yerokhov, V., Hezel, R., Lipinski, M., Nagel, H., Mylynych, A. and Panek, P., Proc. 17th EPVSEC, Oct. 22–26, Munich, Germany (2001) pp. 335–338.
- 6) Pickering, C., Beale, M. I. J., Robbins, D. J., Pearson, P. J. and Greef, R., *Thin Solid Films*, Vol. 125, pp. 157–163 (1985).
- 7) Goodman, A. M., *Appl. Optics*, Vol. 17, pp. 2779–2787 (1978).
- 8) Sopori, B. L. and Pryor, R. A., *Solar Cells*, Vol. 8, pp. 249–261 (1983).
- 9) Kim, D. S., Lee, E. J., Kim, J. and Lee, S. H., *J. Korean Phys. Soc.*, Vol. 46, 1208–1212 (2005).