

Improvement of multicrystalline silicon wafer solar cells by post-fabrication wet-chemical etching in phosphoric acid

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Abstract. In this study, we have improved electrical characteristics such as the efficiency (η) and the fill factor (FF) of finished multicrystalline silicon (*mc*-Si) solar cells by using a new chemical treatment with a hot phosphoric (H_3PO_4) acidic solution. These *mc*-Si solar cells were made by a standard industrial process with screen-printed contacts and a silicon nitride (SiN) antireflection coating. We have deposited SiN thin layer (80 nm) on *p*-type *mc*-Si substrate by the mean of plasma enhanced chemical vapour deposition (PECVD) technique. The reactive gases used as precursors inside PECVD chamber are a mixture of silane (SiH_4) and ammonia (NH_3) at a temperature of 380°C. The developed H_3PO_4 chemical surface treatment has improved η from 5.4 to 7.7% and FF from 50.4 to 70.8%, this means a relative increase of up to 40% from the initial values of η and FF. In order to explain these improvements, physical (AFM, EDX), chemical (FTIR) and optical (spectrophotometer) analyses were done.

Keywords. Silicon; PECVD; passivation; AFM; H_3PO_4 etch.

1. Introduction

Silicon nitride (SiN) thin films are widely used in various microelectronic and optoelectronic devices (Ino *et al* 1994). It is used as gate dielectric in MOS components (Tsvividis 1999) and also applied in the fabrication of microelectromechanical systems (MEMS) (Kaushik *et al* 2005). In photovoltaic field, SiN has the function of defects passivation (Sopori *et al* 1996) and light anti-reflection (Barrera *et al* 2008). SiN is applied as anti-reflective coating (ARC) to minimize reflections and ensuring a higher photocurrent (El Amrani *et al* 2008). It is also known that the hydrogen introduced in SiN film has a crucial role in the bulk and surface passivation (Duernickx and Szlufck 2002; Sopori *et al* 2005). Generally, for solar cells metallization a standard screen printing process is applied. Initially, this process was first developed for monocrystalline silicon solar cells and then adapted for multicrystalline silicon substrate. The application of this process on *mc*-Si wafers results in lower performance solar devices. A classical hydrofluoric acid (HF) dipping is well known for enhancing the efficiency (η) and the fill factor (FF) and for long time was applied on monocrystalline silicon solar cells. Unfortunately, HF immersion was found to be less effective in enhancing

the electrical characteristics (η and FF) of the *mc*-Si solar cells. By contrast, we show in this paper that we can boost *mc*-Si solar cells performances with our new and cost effective chemical H_3PO_4 treatment.

2. Experimental

Solar cells used in this study were based on structure of n^+/p junction. The structure of this n^+/p multicrystalline silicon cell is given in figure 1.

The starting material was a *mc*-Si wafer of *p*-type (boron-doped) with $\sim 3 \Omega \text{ cm}$ resistivity and having an initial thickness of 380 μm . These wafers were dipped into NaOH (30% at 85°C) polishing solution until a final thickness of 350 μm was reached; followed neutralization and RCA decontamination stages by putting them in a bath made of $\text{H}_2\text{O}_2/\text{NH}_4\text{OH}/\text{DI H}_2\text{O}$ at 70°C, then etched in diluted HF (5%) immediately (Kern and Puotinen 1970).

We started by the diffusion of *n* donor atoms (phosphor) made by a gas source of POCl_3 mixed with oxygen (O_2) gas and injected into a LYDOP[®] furnace tube at 875°C, leading to 40 Ω/\square emitter resistance, thus conducting to a shallow n^+ junction with about $2.7 \times 10^{20} \text{ cm}^{-3}$ doping. For the device to function well, elimination of n^+ diffusion on lateral sides of solar cells was necessary. A plasma etching was made to remove the parasitic junc-

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tion. Phosphor silicon glass (PSG) layer resulting from the diffusion step was removed by dipping in diluted HF (10%) solution. The next step was the deposition of SiN thin film by PECVD technique (SEMCO Engineering furnace). We used an industrial low frequency (LF) direct plasma pulsed reactor operating at 430 kHz using a gas mixture of silane (SiH₄) and ammonia (NH₃). Finally, Ag and Ag–Al paste screen printing contacts on the front and back sides, respectively were done. The front contact consisted of a grid formed by parallel strip lines connected to 2 busbars. The back contact was a uniform layer of Ag–Al composite covering the whole *mc*-Si surface. The purpose of using an Ag/Al mixture paste was to eliminate the backside parasitic *n*⁺ junction. A firing step with a BTU furnace was applied in order to allow diffusion of Ag front contact through the SiN layer (known as firing through process). Also, this firing step permitted the diffusion of Ag/Al paste in the back side of *mc*-Si wafer and gave a good ohmic contact. The obtained cells were tested under normalized conditions of AM1.5 (1000 W/m²) by a Fraunhofer *I*–*V* solar simulator to extract the electrical parameters. Then, these cells were etched in H₃PO₄ solution and we extracted the new electrical parameters (η and FF) by *I*–*V* measurement.

The thickness of SiN layer was determined by ellipsometry (EL X-1, Dr Riss Ellipsometer *bau* GmbH). The reflectance was measured using a Varian Cary 500 UV–VIS–NIR spectrophotometer. The chemical etch was done by an acidic solution of H₃PO₄ (68%) at a temperature of 85°C. In order to study the influence of H₃PO₄ solution in passivating both SiN/Si interface and Si bulk, several samples were etched at two different times of 20 and 30 min. The conditions of SiN deposition inside PECVD chamber are summarized in table 1.

3. Results and discussion

The H₃PO₄ treatment was applied to *n*⁺/*p* standard solar cell that has been realized by the process described above. Conceding that, the initial efficiency (η) and fill factor (FF) were as low as 5.4% and 50.4%, respectively

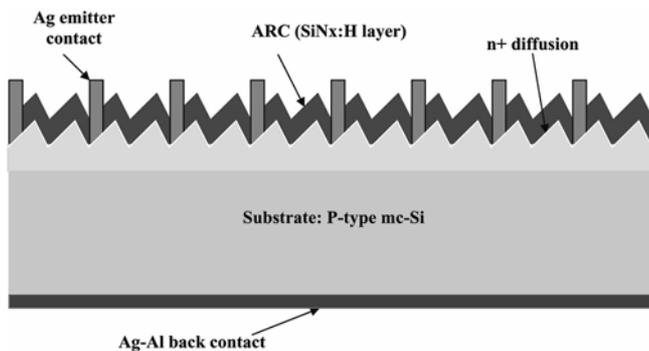


Figure 1. Schematic view of *mc*-Si *n*⁺/*p* photovoltaic device.

for sample S1. Nevertheless, after H₃PO₄ treatment for 30 min at 85°C, we observed an improvement of η and FF as shown in figure 2. The η reached 7.7% and FF 70.8%, this means a relative increase of about 40% up from the initial values. In order to demonstrate the reproducibility of this process we have etched a second sample (S2). Figure 3 shows the amelioration of η and FF.

Table 1. PECVD parameters for SiN deposition on *mc*-Si substrate.

PECVD parameters	Parameter values
Temperature inside the chamber	380°C
Gases ratio SiH ₄ /NH ₃	1/6
Deposition time	150 s
Film thickness	80 nm
Pressure	1700 mTorr

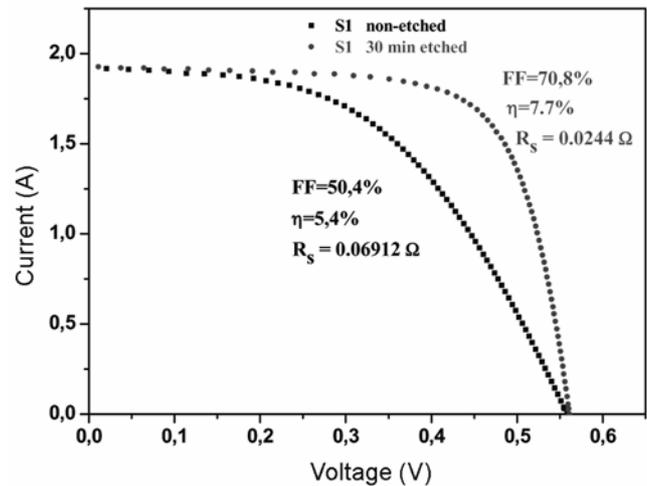


Figure 2. *I*–*V* of S1 solar cell.

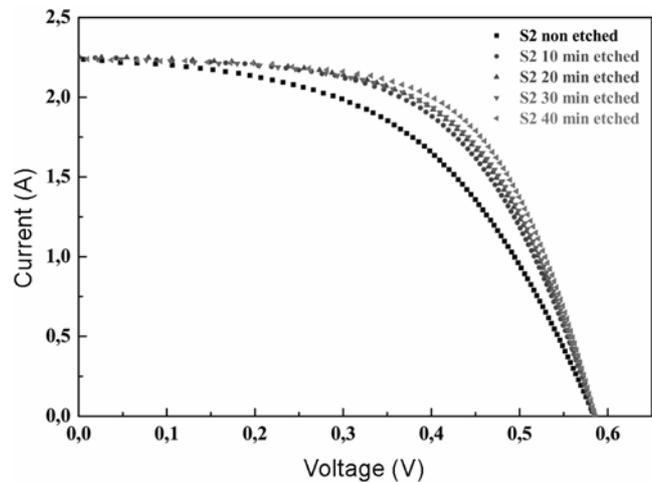


Figure 3. *I*–*V* of S2 solar cell.

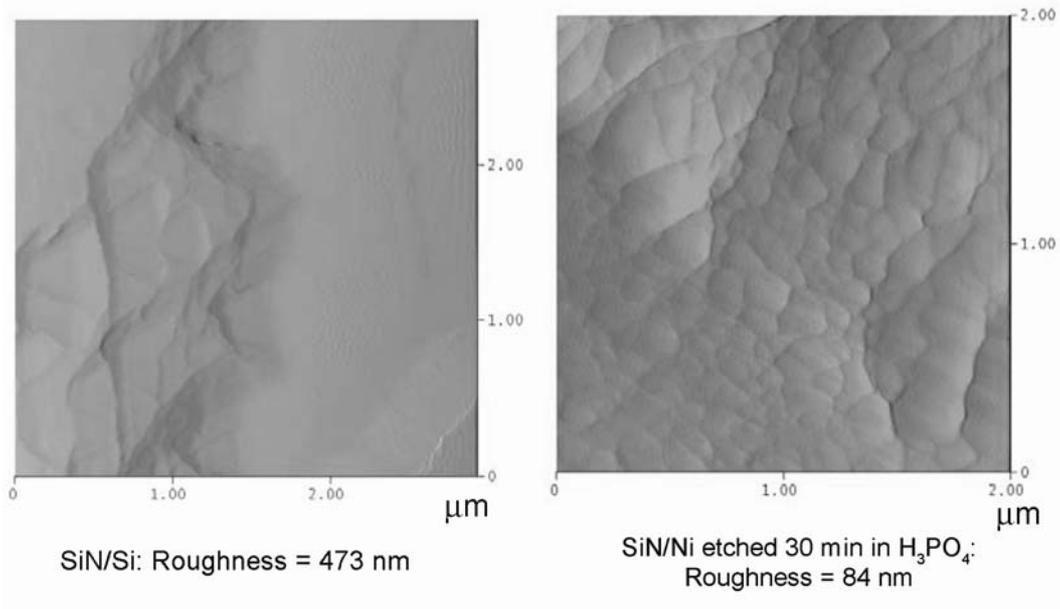


Figure 4. AFM view of SiN surface.

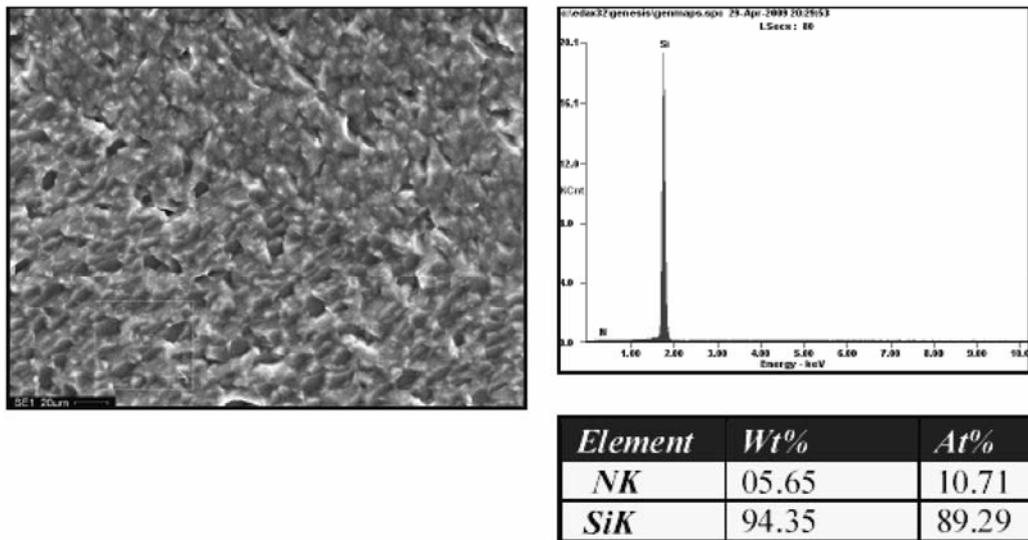


Figure 5. SEM-EDX analysis of SiN thin layer etched by H₃PO₄ for 30 min.

the S2 solar cell, we have chosen the etching times: 10, 20, 30 and 40 min. Series resistance was calculated and found to be decreasing after chemical attack as shown in figure 2. In order to understand the physics behind the boosting of η and FF, we made a full analysis of the chemical composition of SiN thin layer before and after etching.

Our first interpretation of the roughness evolution by atomic force microscopy (AFM) analysis (figure 4) is that the final roughness of 84 nm is equal to the thickness of SiN layer (80 nm). This means that the layer is starting to be locally etched and more preferentially at grain boundaries, which facilitates the acidic solution penetration to

the SiN/Si interface. Thus, the passivation by hydrogenation becomes more probable.

On the other hand, we have done the SEM-EDX analysis. We found that following the chemical etch by H₃PO₄ solution, the Si content of SiN layer increases. Figure 5 shows SEM micrograph and EDX analysis of a 30 min etched sample. Figure 6 summarizes all SEM-EDX studies for grain regions i.e. small grain, large grain and grain boundaries. We found that in the small grain region the SiN layer is Si rich. The explanation to this phenomenon is that for the small grain region, the density of grain boundaries and crystalline defects becomes higher and the number of free Si pending bonds increases (on the

mc-Si substrate). This facilitates the Si atoms fixation during PECVD SiN deposition in these regions which leads to a Si rich area. Globally (as shown in figure 6), etching in H_3PO_4 solution for 30 min increases the Si content in all regions (small grains, large grains and grain boundaries) of *mc*-Si wafer and thus ameliorating the passivation effect. Also, the PECVD SiN deposition process is accomplished with a relatively high ration of SiH_4/NH_3 gas and these lead to a Si rich thin SiN layer (Sopori 2003).

The H_3PO_4 etch leads to an increase of Si content in all regions (small grain, large grain and grain boundaries) of the SiN layer as shown in figure 6. This can explain observed $I(V)$ and improved electrical performances of the solar cells (figures 2 and 3).

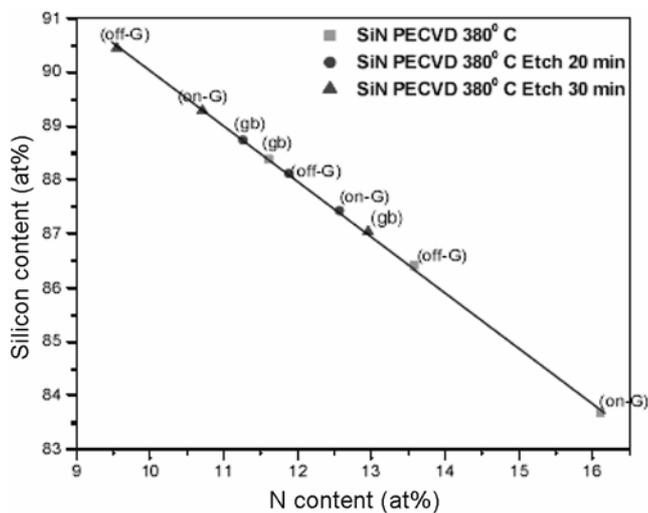


Figure 6. N/Si content with different H_3PO_4 etching times.

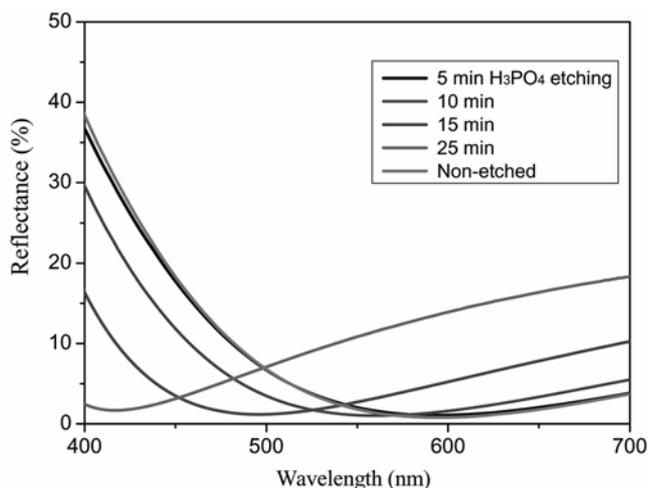


Figure 7. Reflectance of SiN coated solar cells.

Finally, we used a Varian Cary 500 spectrophotometer to extract the reflectance of thin SiN layer. The reflectance was measured for each of the samples that were etched for different times. We can see from figure 7 that a non-etched SiN layer is highly reflective in the visible range as well as the near-UV. In contrast, the sample etched for 25 min displays a low reflectance behaviour in the near-UV range. The sample etched for 15 min in H_3PO_4 possesses the best reflective characteristics in the 400–700 nm range i.e. it absorbs more light than the other samples on a broader spectral array.

4. Conclusions

We have shown an effective amelioration of $I(V)$ characteristics resulting from a new H_3PO_4 chemical treatment. A boosting up to 40% of efficiency and fill factor has been successfully accomplished by this treatment. AFM study shows that SiN layer is starting to be locally etched after 30 min of H_3PO_4 etch which facilitates the acidic solution penetration to the SiN/Si interface. Thus, the passivation by hydrogenation becomes more probable. Finally, SEM–EDX study showed that after this chemical treatment, the rate of Si content increases in all regions (small grains, large grains and grain boundaries) of the SiN thin layer and thus ameliorating the passivation effect. Phosphoric acid passivation is an effective way to make a better passivation of SiN/*mc*-Si interface at low temperature.

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