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Making silicon solar cells in a green, low-hazardous, and inexpensive way

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ABSTRACT

A facile, green, and low-cost process for fabricating silicon solar cells safely at home or in school is presented. In the process, we not only prepare a H₃PO₄-based nontoxic spin-on diffusion source, but also replace the hazardous HF with KOH for removal of the residual silica glass after diffusion. Furthermore, for enhancing the efficiency of solar cells, we employ a simple and low toxic sol-gel method to fabricate the TiO₂ antireflection layer on the solar cell. Experimental results show that KOH not only effectively removes residual silica glass, it also etch back the dead layer, resulting in the reduced minority carrier recombination. However, as KOH can also etch away silicon, caution should be made to prevent over-etching of the silicon that damages the p-n junction. Si solar cells prepared with our approach reaches 12.1% in efficiency. To test if our HF-free process also works on an optimized production process, we test our KOH etching step in an optimized solar cell process in a production line. An averaged cell efficiency of 17.5% was attained, which is comparable to that of 17.8% with cells fabricated in the traditional production process employing HF etching. This fact evidences the future potential of producing HF-free green solar cells.

Keywords: Solar cell, spin-on-dopant, HF-free, KOH

Introduction

Despite the advancement in non-silicon¹⁻⁴ based and organic solar cell technologies,⁵⁻⁸ silicon solar cells are still the mainstay of the photovoltaic (PV) industry. Even though crystalline (c-) Si solar cells attained high conversion efficiencies (η 's) of ~25%,^{9, 10} the widespread use of the solar PV is still limited by the high cost and toxic nature of some key process chemicals as well as waste products.

For example, according to the 2014 annual report of US Energy information Administration (EIA),¹¹ the average estimated total system levelized cost of electricity (LCOE, in 2012\$/MWh) of a solar power plant to enter service 5 years after the report is estimated to be 130.0 \$/MWh. This cost is quite expensive as compared to that of power plants utilizing nuclear (96.1 \$/MWh) or fossil fuels (coal: 95.6 \$/MWh; natural gas: 66.3 \$/MWh), not to mention the intangible costs raised by the hazard, waste, and environmental pollution in solar cell production. Encouragingly, as shown in Fig. 1, the estimated LCOE of a PV power plant has reduced from 210.7 \$/MWh in 2011, to 130.0\$/MWh in 2014. Additional cost reduction routes and efforts could bring down the LCOE of solar PV to a competitive level with that of a conventional coal fired or a nuclear power plant. Such cost benefits would result in wider market suitability and help accelerate the process of projected gradual phase-out of the conventional power plants. The coal fired plants are known to emit the most greenhouse gases per unit generated power, while safety issue of the nuclear power plant is evident since the 3/11 nuclear disaster in Japan. In addition to the costs, a green process is desirable to make the PV industry commercially and environmentally sustainable.

Currently, unless otherwise assisted, making Si solar cells at home or in school are almost impossible, because the conventional PV cell production strongly relies on hydrofluoric acid (HF), silane, and POCl₃ in processes of substrate cleaning, antireflection, and diffusion, respectively. However, HF is a deadly corrosive, silane is an explosive, and POCl₃ is toxic. Solar cell manufacture would be impossible in schools or in cottage-scale industries using these hazardous chemicals. Moreover, facilities, such as diffusion furnaces and plasma enhanced chemical vapor deposition (PECVD) systems, used in the conventional large scale process are quite expensive and requires expert handling that impedes the idea of widespread manufacture and use.

In our previous report¹², we have demonstrated the use of a low-hazardous H₃PO₄-based spin-on dopant (SOD) applied to silicon nanowires (SiNWs) for facile radial p-n junction formation in SiNWs solar cells prepared by a sol-gel method.¹³ The radial junctions were shown to relax the costly requirement of Si purity. Additionally, SiNWs offered inherent antireflection, which render the extra antireflection layer redundant. However, HF was still used both in oxide removal and electroless etching for SiNWs. In 2000, Szlufcik *et al.*¹⁴ suggested a "HF-free cleaning" idea for reduction of chemical waste and cost. However, their approach was solely not to remove the residual silica glass (or phosphosilicate glass, PSG) after diffusion during solar cell fabrication; it relied heavily on using a PECVD system for forming a good SiN_x antireflection and a passivation layer. Very recently, we noted that Basu et al.¹⁵ have filed an application in World Intellectual Property Organization (WIPO), claiming the use of a solution including KOH (or NaOH) and sodium hypochlorite (NaOCI) for PSG removal as well as etch-back on the doped pyramids of

Sophisticated technologies in c-Si, though good in certain aspects like development and future avenues, would result in marginal increase in efficiency but coupled with unaffordable costs. Instead, we propose an alternative strategy of using a facile and green process of solar cell manufacture that would allow setting up of low-scale cottage PV industry with easy access to and understanding of technology in addition to the existing heavy industries. Higher production volumes, less intimidating technologies, and competition would help bring down the LCOE substantially to enable widespread usage of solar PV. In this report, we present a low-cost, green process of making c-Si solar cells safely at home or in school with efficiencies reaching 12.1%. Costly PECVD, and sputtering machines are replaced by sandpaper grinding, KOH etching, H₃PO₄-based SOD, sol-gel prepared TiO₂ layer and so on. A PV cell with 12.1% efficiency can be completed within one hour which could still be improved after minor optimization. In the production line, the HF free process resulted in average cell efficiency of 17.5% compared to 17.8% obtained with HF processing.

Experimental

Testing KOH etching rate

KOH etching rate of SiO₂ is shown in Fig. 2(a). A commercially available SiO₂/Si substrate (E-light Tech. Inc., Taiwan) was rinsed in KOH (1M, 70°C, Showa, dissolved in deionized (DI) water) for 30 min. The initial SiO₂ film thickness was determined by a spectroscopic reflectometer (K-mac ST2000 DLXn, Korea) to be 305nm. Post etching, the thickness of the etched SiO₂ (Fig. 2(b)) was again determined and the etching rate was estimated from the decrease in SiO₂ thickness per minute.

Solar cell fabrication

Alongside a conventional process shown in Fig. 3(a), the proposed green process for solar cell fabrication is depicted in Fig. 3(b). Following Fig. 3, we will depict the two processes as follows.

1. Solar cells prepared with the green process (Fig. 3(b))

- (1) Native oxide removal and texturing: A 1-10 ohm cm (100) p-Si substrate (2cm×2cm, double side polished, E-light Tech. Inc.) was first grinded gently on one side for about 30 seconds using a 1200 grit sand paper (3M 734) for removal of the native surface oxide. A rinse in KOH (1M, 70°C, Showa) for 1 min, results in pyramid-like texturing of the ground side of the substrate. Any grinding induced surface damage is also removed. Instead of using KOH for the texturing, we have also tried the widely used KOH/IPA recipe. Similar cell performances were obtained using both types of etching processes. However, the conventional KOH/IPA requires a longer etching time (at least ~10 minutes) to get similar texturization.
- (2) SOD preparation and diffusion: After the formation of the pyramids, a homemade H₃PO₄-based SOD

was prepared as the diffusion source^{12, 13}. Two solutions were prepared. Solution A consisted of a mixture of 0.306 mL of tetraethoxysilane (TEOS, Showa, Japan) and 0.702 mL of isopropyl alcohol (IPA, Tedia, US). Solution B consisted of a mixture of 1 mL phosphoric acid solution (H₃PO₄, 85wt%, Scharlau, Spain), 0.902 mL of IPA, and 0.8 mL DI water. The SOD was completed by mixing solution A and B together. For diffusion, a 1 mL portion of the SOD source was spin-coated (600 rpm 10 s followed by 1000 rpm 20 s) on the Si substrate to form a doping layer. Drive-in of the dopant into the surface was achieved by sending the substrate into a quartz tube furnace at a controlled temperature followed by pulling it out after a predetermined time. After several tries, the optimized annealing thermal budget was found to be 7 min at 980°C. With this thermal budget, the total diffusion time can be completed in 10 min.

- (3) PSG removal and etch-back: After diffusion, removal of the remnant PSG was accomplished by rinsing the substrate in KOH (70°C, 1M, dissolved in DI water) for a predetermined time ranging from 8~60 sec. The easy PSG removal can be reasoned by the cracks formed on the PSG, allowing KOH to reach the underneath Si pyramids, resulting in effective lift-off of the PSG. Since KOH etching on Si tends to form pyramids, revealing Si {111} surfaces, this 2nd KOH etching on the diffused pyramids would automatically etch-back the Si{111} surfaces of the pyramids in a conformal way, resulting in successful removal of the dead layer, which is heavily doped and of high recombination rate.
- (4) ARC and Passivation: We have employed a colloidal solution of TiO_2 as the antireflection coating (ARC) as described by Shi et al.²² In brief, 5 mL Ti(OBu)₄ (Acros, US), 0.5 mL ethyl acetate (Acros, US) and 23 mL ethanol (Echo Chemical Co., Taiwan) were mixed in a flask as precursors. Then a solution containing 1.5 mL HNO₃ (0.1 M), 12 mL ethanol and 1.5 mL de-ionized water was added dropwise (1 mL/min) into the precursor solution. With continuous stirring for 12 h at 800 rpm, the mixture was aged at room temperature before use. After several tries (by varying annealing temperature and time), we found that an optimized TiO_2 ARC can be formed by spin coating the solution at 2000 rpm followed by air annealing at 450°C for 5 min. Here, we only report the cell prepared with the optimized ARC. At the TiO₂/Si interface, we expected a thin layer of SiO₂, which could help passivating the silicon surface. According to literature ²³, TiO₂ deposition followed by a 950°C annealing will form a thin SiO_2 layer at the TiO₂/Si interface, which would be beneficial in passivation, enhancing the cell performance. In this case, a much lower optimum annealing temperature of 450°C was used. We believe that the high temperature annealing could have degraded the junction quality. Alternatively, after KOH etching, we tried to passivate the Si surface intentionally under different temperatures in air after the KOH etching step. Currently, we found the highest efficiency cell (12.1% in efficiency, with ARC) can be attained under 850°C passivation for 5 min.
- (5) Screen printing the electrodes: The front and rear electrodes were completed by screen-printing Ag paste (followed by 700°C sintering for 30s), and Al paste (600°C sintering for 4 min), respectively. The front electrodes had a finger width of 0.2 mm, and a finger spacing of 2.4 mm. The electrodes can also be co-fired as done conventionally. It only requires further tuning of the sintering conditions. For this reason, a co-firing step is depicted in the green process of Fig. 3.

- (6) Sintering electrodes: The sintering conditions for both electrodes were already mentioned in the previous step. The sintering was carried out by sending the substrate into a quartz tube furnace at the controlled temperature followed by pulling it out after a predetermined time.
- (7) Mechanical isolation: After manual cleavage of the substrate for cell isolation, a solar cell of 1.0 cm
 × 1.0 cm size, was prepared using a simple, non-HF, and green process within approximately one hour.

2. Solar cells prepared in a KOH-based conventional production line (Fig. 3(a))

With scope for further improvements in the green process, we wanted to evaluate the efficiency of the green process (particularly, the KOH PSG removal step) with the inclusion of optimized diffusion, passivation, ARC, and electrode co-firing steps. For this, we employed a conventional production line (see the process flow shown in Fig. 3(a)) with optimized process steps resulting in cells with 18 % efficiencies reproducibly. Several solar cells were fabricated following the 'production line' route, by using a KOH aided PSG removal (with different etching times) instead of HF. The initial oxide removal and texturing were also done by KOH/IPA solution. As no HF was used, this step did require a longer time (30min). For comparison, control cells were produced with the 'production line' using HF for PSG removal.

The substrates use in the 'production line' were 12.5 cm \times 12.5 cm p-type Si (100) (1~10 Ω ·cm, unpolished). For texturing purpose, the substrates were rinsed in a solution of KOH (45% in water, or 11.7M, Showa): IPA: DI water =1:2:4.35, at 80°C for 30 min. HF was not applied prior to texturing, as mentioned. The dopant diffusion was performed in a standard diffusion furnace using POCl₃. The PSG removal, if with HF, was carried out by rinsing the substrate in 1% HF for 2 min, whereas non-HF PSG removal was done by rinsing the substrate in KOH solution (45% in water, 80°C) for a predetermined time. The passivation and ARC were completed by SiN_x deposition (90 nm, 450°C) using a PECVD system. A front electrode finger spacing of 1.8 mm were employed. After both electrodes were screen-printed, the cell was co-fired at 780°C for 3 min. Finally, the cell fabrication was completed after laser edge isolation.

3. Cell performance characterization

The solar cell performances were characterized by the current-voltage (J-V) curves measured using a Keithley 2400 source meter under AM 1.5G illumination from a 500 W solar simulator (Sciencetech, SS0.5KW). A reference cell (PVM201, PV Measurements Inc.) was used to calibrate the illumination intensity.

Results and discussion

In order to demonstrate a fully 'green' process for solar cell fabrication, the efficacy of HF and KOH etching of SiO₂ had to be understood and compared, where the latter was seldom adopted in the industry presumably due to its slow etching rate. Thus a test of KOH etching of SiO₂ should be studied to begin with. After rinsing the SiO₂/Si in KOH (1M, 70°C) for 30min, the apparent purple color of the SiO₂ changed to yellow (Fig. 2(b)) visually indicating that KOH etching did take place. From the thickness reduction, the etching rate was determined to be 1.00 nm/min. This etching rate is small, compared to HF etching, but helpful in the removal of PSG as we will describe later.

J-V curves for Si solar cells prepared with different lengths of KOH etching time, for PSG-removal

and emitter etch-back, but without the ARC are shown in Fig. 4(a). Also shown are the performances of a cell coated additionally with the ARC and a cell treated both with the ARC and the intentional passivation (850°C, 5 min). Note that the PSG removal time of the former was 20s, but that of the latter was only 8 sec. Fig. 4(b) summarizes the η , open circuit voltage (V_{oc}), short circuit current density (J_{sc}), and fill factor (FF) as functions of the KOH etching time for different cells. It is evident that η , V_{oc} and FF all decrease with increased KOH etching time. A maximum efficiency of 9.0% was obtained for the cell, without the ARC, treated with 20s KOH etching. The J_{sc} followed a similar trend with KOH etching time, however, the high J_{sc} observed for 45s of etching was actually due to leakage. The V_{oc} and FF of the cell (20s KOH etching) with and without the TiO₂ ARC were similar. However, J_{sc} of the cell with the ARC (20s KOH etching) increased by 8.2% compared to the cell without it. The increased J_{sc} is responsible for the increased η which reaches 9.4%. After many efforts, as already shown in Fig. 4, we found an even higher efficiency (12.1%) can be achieved if a short time (8 sec) KOH etching followed by an intentional passivation in air at 850°C for 5 min was employed.

The reason for the decreased η with increased KOH etching time (Fig. 4(b)) is worth exploring and illustrated in Fig. 5. Since the walls of the Si pyramids (Fig. 5(d)) are Si {111} planes, having the highest atomic density, they demonstrate the slowest etching rates. After diffusion, there is a PSG layer, a dead layer (an area of very high carrier recombination), and an n⁺ doped layer formed on the pyramid (Fig 5(a)). When immersed in KOH for a suitable time, the PSG would be lifted off and the dead layer was conformally etched away, resulting in a near-perfect n⁺-p junction on the pyramids (Fig. 5(b)). However, if the etching time is too long, the KOH would continue to etch away the n⁺ layer, leading to junction failures in some region (Fig. 5(c)). Therefore, by suitable optimization of the KOH etching time, not only the PSG but also the dead layer on the pyramids could be removed efficiently. As the dead layer provides for the high carrier recombination, its removal ensures efficient carrier generation by the ultra violet light and carrier collection at the surface.

The experimental results in Fig. 4 gives us more confidence that our green approach can compete with the conventional process. Note that, conventionally, the dead layer problem can be solved mainly in two ways. A simple way but with increasing production duration is to add an additional step that rinses the diffused substrate in a mixture containing HF and HNO₃. In the mixture, a complex chemical reaction occurs²⁴:

(1)

 $3Si + 4HNO_3 + 18 HF \rightarrow 3 H_2SiF_6 + 4NO + 8 H_2O_7$

which results in a conformal removal of the dead layer on Si surfaces. Another way which is more favorable is to fine tune the diffusion steps²⁵, such as optimizing the flow rate of oxygen²⁶ or POCl₃²⁷ during diffusion, to minimized the dead layer formation. While using KOH, our green approach accomplishes dead layer removal in an alternative way. First of all, note that the dead layer is formed on the surface of pyramids, which reveal only Si {111} planes for the far lower KOH etching rate along Si {111} planes compared to that along other planes. Revealing only Si {111} planes, the pyramid surfaces, when etched again in KOH, can only be slowly etched along their Si {111} planes. Thought complex in detail steps²⁸, the overall reaction generally accepted in literature²⁹⁻³¹ is described as follows.

 $\text{Si} + 2 \text{ H}_2\text{O} + 2 \text{ OH}^- \rightarrow 2 \text{ H}_2 + \text{Si}(\text{OH})_2\text{O}_2^{-2}$.

Within a suitable etching time, the desired conformal removal of the dead layer can be achieved, exposing underneath the clean active n^+ -Si {111} planes whose quality can be comparable to that prepared in the conventional ways.

(2)

In view of the above, the 9.4 (with ARC) to 12.1% (with ARC and passivation) efficiency solar cell fabricated by the green process is by no means satisfactory. More efforts on tuning the process parameters of diffusion, ARC, passivation, and electrode co-firing of the cell were required. Since KOH etching for PSG removal as well as etch-back comprised the key feature of our green process, we wanted to use it in an optimized conventional production line, replacing the original HF etching (for PSG removal) process. In this way, the optimized process conditions of diffusion, passivation, ARC, and electrode co-firing would be retained, but the toxic part of the process would be avoided. In addition, it would give us an idea of the highest efficiencies attainable by the fully green process. The results are summarized in Fig. 6, with Fig. 6(a) showing the J-V curves, and Fig. 6(b) showing the characterized parameters as functions of KOH etching time. From Fig. 6, we can see clearly that solar cells produced with the optimized conventional process (with HF etching) showed a representative efficiency of 17.8%. If the process of PSG removal is only a 2 % drop from the optimized value. In principle, as illustrated in Fig. 5, a further reduction in the KOH etching time may help prevent the 2% drop from the optimized efficiency value. To prove this, further investigations should be well worthwhile.

Apparently, there is still an efficiency gap between the homemade cell (12.1%, with ARC and passivation) and the production line cell (17.5%). For improving the homemade cell efficiencies, several approaches would be required. First of all, there should be still some room for optimization of the passivation step in our process. Secondly, the optimal diffused reflectivity (not shown) of our TiO₂ ARC remained high as ~30% (2000 rpm, averaged in the visible range), which is three times higher than the ~10% reflectivity of Si₃N₄ ARC on the production line cells. The high reflectivity could be due to the poor conformal coating of the TiO₂ ARC on the Si pyramids. Should the ARC be improved from 30% to 10%, the increased absorption (70% to 90%) with an optimistic estimate could already push the efficiency from the present achieved level of 12.1% to 15.6%. Even with a conservative estimate, the efficiency value could still be enhanced through many ways such as optimization of the front electrode finger width and spacing, diffusion profile, and crystal quality.

From Fig. 6, as the KOH immersion time increased, the efficiency reduced until junction failures occurred. This behavior is understandable from Fig. 4. From Fig. 6(b), we observe that as the KOH etching time was increased from 30 to 90s, the V_{oc} was nearly unchanged, but the J_{sc} decreased. The decrease in J_{sc} can be understood by the photocurrent (I_L) equation derived from an ideal photodiode model described in the textbook³², i.e.

$$I_L = J_{sc}A = qAG(L_e + W + L_h), \tag{3}$$

where W and q represents the junction width and electronic charge, respectively; A, G, L_e , and L_h denotes the junction area, generation rate, electron diffusion length, and hole diffusion length of the diode,

respectively. When the n⁺ layer was thinner than L_e , less photo-generated electrons in the n₊ region would be collected, which would lead to a reduced J_{sc} . If the n⁺ layer is etched further (>90s), V_{oc} would eventually decrease (Fig. 6), which is an indication of the occurrence of junction failures as shown in Fig. 5(c).

In light of the above, we claim that this green process of solar cell fabrication has the potential of a common household technology but still maintaining a high performance as evident from nearly matching efficiency value. Further optimization can promote it further. Importantly, the chemicals used in this process are all environmentally friendly, easily recycled leaving minimum or no toxic waste. For example, KOH, when mixed with phosphorous acid (H₃PO₃), forms potassium phosphite, which is a water soluble fertilizer widely used in controlling microbial plant diseases. Likewise, H₃PO₄, when reacted with NH₃, can be turned into diammonium phosphate ((NH₄)₂HPO₄), which is also a commonly used fertilizer.

With a substantial lowering of the technological and cost threshold of the solar cell production unit as described above, we believe that a variety of cottage industries could make their own powerhouse. These powerhouses would not only provide electricity for their everyday life but also power their cottage industries, enabling a wide spread usage of the PV-cells but with no environmental concerns. Dedicated small scale solar power production units can be realized with increasing density for penetrating commercial and geographical barriers presented by the rural and inaccessible areas of the country. This is especially helpful for the resource-poor people living in the tropics. The vision of widespread usage of solar power, projected several decades back, may move a step forward.

Conclusion

In conclusion, a low-cost, environmentally friendly, and green process promises at least 12.1 % efficient silicon solar cells to be fabricated safely at home or in schools. A simple home-made H₃PO₄-based nontoxic spin-on diffusion source, and use of KOH etching, for the removal of the residual silica glass after diffusion, could replace the highly hazardous HF from the whole process. Experimental results show that KOH not only effectively removes residual silica glass, it also etch back the dead layer, resulting in the reduced minority carrier recombination. A sol-gel method has been adopted to fabricate the TiO₂ antireflection layer on the solar cell to enhance the efficiency. The proposed green process when integrated in a conventional production line, replacing the HF based process by KOH, resulted in average cell efficiency of 17.5% against a 17. 8% HF based traditional technology.

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Figure captions

Fig. 1 Levelized costs of electricity of various power plants reported by EIA in recent years.

- Fig. 2 A simple test of etching rate of SiO₂ in 1M KOH (70~75°C). The schematic diagram of the test was shown in (a). After 30min etching, the photograph in (b) showed a clear color change after etching.
- Fig. 3. Process flows of Si solar cells produced using (a) the conventional process and (b) a suggested green process (this work). Note, some steps are marked with graphs, which meaning were denoted in (c). Note also that, those steps that were toxic, explosive and costly in the conventional process are replaced by facile, low-hazardous, and environmentally friendly steps in the green process.
- Fig. 4. Performances of Si solar cells prepared with different lengths of KOH etching time for PSG-removal and emitter etch-back. Also shown are the performances of a cell coated additionally with TiO₂ ARC and a cell treated both with ARC and passivation (850°C, 5 min). Note that the latter was etched in KOH for only 8 sec. (a) J-V curves of the different cells. (b) Efficiencies, V_{oc}'s, J_{sc}'s and FF's of the cells. Note that the lines connecting the data points in (b) are only guide for eyes.
- Fig. 5 Schematic diagrams showing KOH etching effects on doped pyramids. (a) After SOD diffusion, PSG is spread on the doped pyramids, on top of which a heavily doped region called "dead layer" is shown.(b) After KOH etch-back for a suitable time, the PSG as well as the dead layer is removed. (c) If the etch-back is carried out too long, parts of the doped region can be etched away, resulting in junction failures. (d) SEM image of typical pyramids formed by KOH etching.
- Fig. 6 Performances of Si solar cells prepared on an optimized conventional production line with the PSG removal step replaced by KOH etching at different lengths of time. The results of two cells prepared with conventional HF etching, as control samples, were also shown. (a) J-V curves of the different cells.
 (b) Efficiencies, V_{oc}'s, J_{sc}'s and FF's of the cells. Note that the lines connecting the data points in (b) are only guide for eyes. Note also, for clarity, data points in (b) have excluded the poor performance samples noted as KOH120s#2 and KOH150s#2 in (a).

Table of Content entry

Making silicon solar cells in a green, low-hazardous, and inexpensive way

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A facile, green, HF-free process for fabricating silicon solar cells safely at home or in school is presented.









Fig. 4





