# Effect of Novel Surface Treatment on Large-Area Low-Cost SOD Diffused Monocrystalline Silicon Solar Cells

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Non-uniformity in the sheet resistance and difficulty in removing the spin glass and other contaminants on wafer surfaces are two major problems confronted after spin-on-doping (SOD). This paper reports a surface treatment process as a possible solution to key problems. The wettability of the silicon surface was enhanced before SOD by maintaining the hydrophilic nature of the surface with a native oxide layer on it, and a novel treatment with hot hydrochloric acid (HCl) was employed as an intermediate step to remove the contaminants easily. Monocrystalline silicon solar cells were fabricated on a large area (103 mm × 103 mm) by using the approach of this study and employing spin-on doping and IR lamp furnace annealing. Uniform sheet resistance, easy removal of surface contaminants after SOD, better performance parameters, and low leakage current were the results of the surface treatment approach of this study. Monocrystalline silicon solar cells with conversion efficiencies of 11.9 % and 13.1 % were fabricated on large area monocrystalline silicon wafers with and without a PECVD silicon-nitride antireflection coating.

## I. INTRODUCTION

The competitiveness of the solar cell technology in energy production strongly depends on price. Research groups have been working to develop solar cell performance without substantial increasing the cost involved during solar-cell fabrication and to reduce the cost of the solar cells from the present level. Industries are struggling to find new technologies that could lower the prices of highly efficient solar cells. Spin-on doping (SOD) and short-time furnace annealing [1–6] directly address the issue of fabrication cost by reducing the processing time in comparison with conventional furnace processing using phosphorous oxy-chloride (POCl$_3$) source [7–10], but without significant degradation in performance parameters of the solar cell. In the conventional solar cell fabrication process, an additional oxide passivation step is required to reduce the surface recombination velocity [11].

Recently, rapid thermal diffusion from SOD has emerged as a promising method for shallow junction formation. The rapid thermal processing (RTP) technique uses halogen lamps or arc-lamps to heat up the dopant-coated wafer at very high ramps of up (100 – 400 °C/sec) so that the temperature can be raised in very short time. As a result, the thermal budget is reduced, and the junction depth of the created p-n junction can be very shallow while the surface concentration is still high. A shallow junction with a depth of less than 20 nm was first reported by Usami *et al.* [12]. They found that the RTD (rapid thermal diffusion) of P and B was enhanced with the heating rate. This was ascribed to the stress field induced in the heating stage. The RTD from SOD has further been studied and applied to solar cells by Ventura and co-worker [13]. They showed that the efficiency of RTD from phosphorus SOD films deposited on Si wafers depended on the source composition and its thickness. Solar cells obtained by using this technique have shown promising characteristics, which confirms the use of the remaining thin doped spin-on-glass (SOG) layer as being suitable for good surface passivation without inducing minority-carrier diffusion-length degradation in the base of the solar cell.

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A high-efficiency mono-crystalline silicon solar cell fabricated by using RTD from SOD has been realized by Ruby *et al.* [14]. However, diffusion with SOD may often lead to a reduced conversion efficiency of large-area solar cells due to non-uniformity in the diffusion in monocrystalline silicon wafers. This non-uniformity problem can be solved by some chemical treatment [15]. Other problems of SOD when applied to textured surfaces are bubble damage and film cracks for SOD film thicknesses exceeding 6000 Å.

A phosphorous-doped SOD source is normally used for $n^+$ emitter-layer formation. However, even after baking the samples spin coated at 120 °C for 20 min, not all of the organic solvents present in the SOD film are totally evaporated. During the high temperature treatment, organic residuals adhere strongly to the silicon surface as a result of which the spin-coated layer is very difficult to remove after the diffusion, even by buffered hydrofluoric acid (BHF) treatment. Actually, BHF cannot etch out organic residuals on the silicon surface after diffusion even though the same solution can remove silicon dioxide at a rate of ~100 nm/min.

Spin-on glass residuals are unacceptable for solar cell fabrication because they shadow light, obstruct ohmic contact formation, and increase the leakage current significantly. Normally, RCA1 and RCA2 cleaning methods are used for residual-layer removal. These chemical cleaning methods are expensive and time consuming. The objective of this paper is to establish a simplified low-cost treatment with hot hydrochloric acid for short time after removal of the phosphosilicate glass (PSG) layer. Our method eliminates the organic contamination and leads to a reduced leakage current in large-area monocrystalline solar cells. We also report a uniformity in the sheet resistance after SOD diffusion of textured wafers at different peaks of temperature using IR lamp furnace at a fixed peak annealing time.

## II. EXPERIMENT

The fabrication of solar cells on monocrystalline silicon (BAYSIX) was done by using cost-effective techniques, such as spin-on doping, rapid thermal processing (RTP), plasma enhanced chemical vapor deposition (PECVD), and screen printing. The complete process sequence is comprised of the following steps:
· Removal of saw damages followed by wet texturization of the wafer surface
· Spin-on coating of phosphosilicate glass on the front surface
· RTP diffusion
· Removal of the PSG
· Wet Edge isolation
· Novel hot hydrochloric acid (HCl) treatment
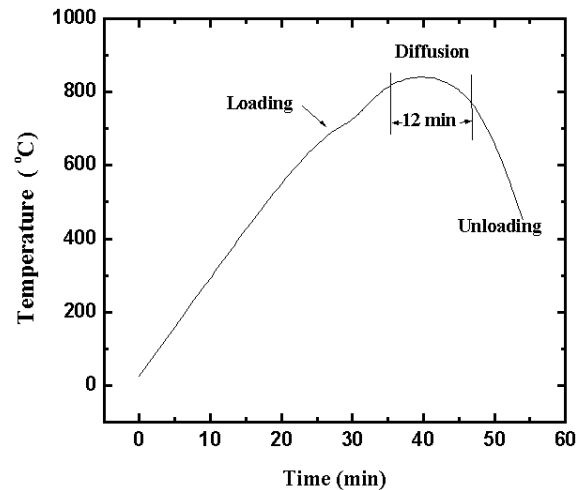· PECVD silicon-nitride coating (ARC)



Fig. 1. Typical RTP profiling during SOD emitter diffusion.

· Screen printing on the back and the front surfaces, followed by baking after each printing
· Co-firing

In the saw damage removal step, about 25-$\mu$m of silicon is etched out with a NaOH solution at 70 °C. Then, alkali etching is carried out for texturing by dipping the wafers in a 1.9 % NaOH solution at 80 °C for 45 min, which is followed by a 2- to 3-min rinsing in hot deionized (DI) water at 80 °C and spin drying. The conventional step of diluted HF dipping after texturing the wafers in alkali solution is not carried out before SOD diffusion in order to increase the wettability of the silicon wafer surface. The silicon surface is then coated with phosphorus dopant P509 (Filmtronics, USA) by dropping the dopant on the surface and spinning at 2500 RPM for 30 s, followed by baking at 120 °C for 10 min in a hot-air oven. The SOD diffusion process is carried out at two different temperature plateaus (850 °C and 900 °C) and two fixed time-interval plateaus. Fig. 1 shows the typical doping temperature profile used during SOD diffusion.

### 1. Diffusion Uniformity

The calculation of the standard deviation of the sheet resistance of the dopant SOD-diffused silicon surface at different points is a good measure of the uniformity of diffusion and of the quality of junction formation. This assumes further importance in the case of SOD diffusion where the thickness of the SOD layer is relatively nonuniform [8]. For a textured surface, the criterion of uniformity is still critical. Fig. 2 and 3 show the sheet resistance distribution and the standard deviation of diffused sheet resistance of three SOD-diffused samples. For the standard deviation calculation, we used a four-point probe system to measures the sheet resistances of 103
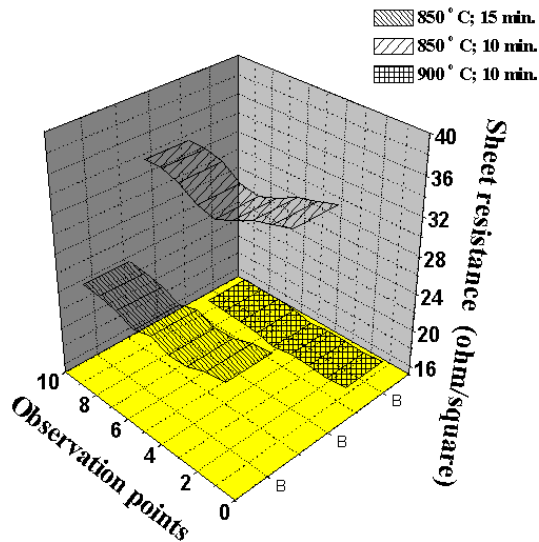
Fig. 2. Sheet resistance distribution of three different SOD diffused mono-crystalline silicon wafers without HF treatment.
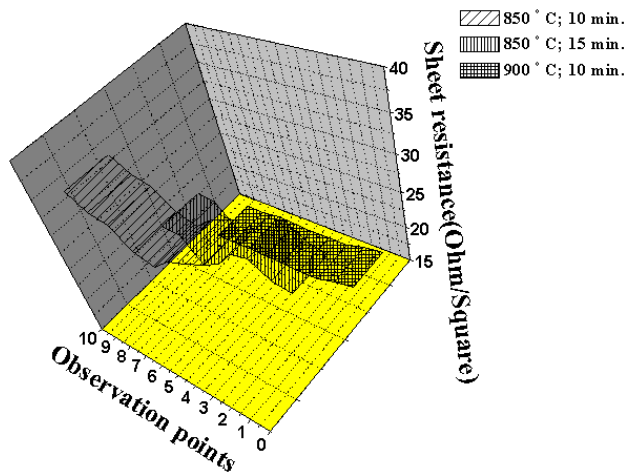


Fig. 3. Sheet resistance distribution of three different SOD diffused mono-crystalline silicon wafers with HF treatment.

mm × 103 mm diffused silicon wafers at nine different geometrical locations. The sheet resistance is a measure of the number of electrically active phosphorus atoms in the emitter and depends on the RTP conditions. After removal of the PSG by hydrofluoric acid, the sheet resistances of SOD-diffused wafers for different doping conditions were measured using four-point probes.

## 2. Surface Treatment of Textured and Diffused Wafers

The problem of organic contamination associated with the SOD technique becomes more acute for textured surfaces. In order to remove the organic residues completely during BHF treatment, pretreated the wafers with 50 % hydrochloric acid (HCl) at 60 °C for 10 min, followed by dipping for 15 sec in 10 % BHF, rinsing for 2 min in DI water and spin drying. This novel hot HCl treatment greatly increased the performance of SOD-diffused, monocrystalline silicon solar cells as compared to untreated ones. Fourier transformation infrared (FTIR) analysis was carried out to find contamination of post-diffused, PSG removed wafers with and without hot HCl treatment in order to investigate the role of the surface treatment with hot HCl.

## 3. Solar-cell Fabrication

To examine our method in terms of effectiveness in low-cost cell fabrication process, we prepared solar cells with and without simplified chemical treatment, keeping all other processes the same. All PSG-removed SOD-diffused wafers were edge isolated by dipping for 1 – 12 min in a 1 HF + 4 HNO$_3$ + 1 CH$_3$COOH solution, followed by rinsing in running DI water and spin drying. For the antireflection coating, a 70-nm-thick layer of SiN$_x$ with a refractive index 2.1 was deposited on the front side of the wafer by means of PECVD at 300 °C. The back and the front metallizations of the SOD diffused wafers with and without SiNx coating were done by using standard Al-paste (product no. FX 53-038, Ferro Electronic Materials) and Ag-paste (product no. 3349, Ferro Electronic Materials), respectively, and screen printing, followed by baking after each printing. The wafers were then co-fired in conveyer belt furnace, and the fabricated cells were characterized.

## III. RESULTS AND DISCUSSION

The sheet resistance distribution of the SOD-diffused samples is good enough without any HF dipping prior to SOD, as shown in Fig. 2, and the sheet resistance of the SOD wafer after HF dipping is shown in Fig. 3 for comparison. The sheet resistance of the silicon wafer varied within the rage of 15 to 40 $\Omega/\square$, depending upon the annealing temperature and time. From the sheet resistance distribution curves shown in Fig. 2, the uniformity of sheet resistance is observed to increase with temperature because at comparatively higher temperatures, impurity atoms throughout the large area of the silicon surface have sufficient thermal energy to diffuse into the silicon lattice. Also, increasing time of diffusion helps impurities to settle into the crystal lattice, ultimately improving the sheet resistance distribution. The annealing time and temperature determine the redistribution of the diffusing tracer. The average diffusion displacement (*i.e.*, diffusion length) $X_D$ of the tracer can
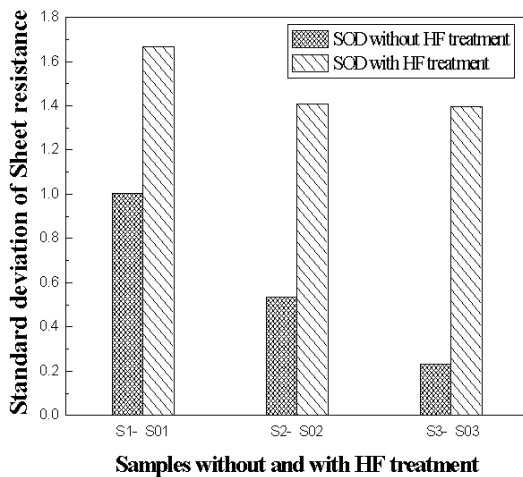
Fig. 4. Standard deviation of the sheet resistance of the silicon wafers doped with and without HF treatment.

Fig. 5. Dark IV characteristics of monocrystalline silicon solar cells (a) with and (b) without post-diffusion HCl treatment.

be calculated by using

$$X_D = \sqrt{4Dt}$$

where $D$ is the diffusion coefficient at the annealing temperature and $t$ is the annealing time. The value of $X_D$ sets the characteristic distance of the experimental depth profile has to exceed the depth resolution, but not the accessible depth range of the profiling technique. The proper adjustment of $X_D$ requires an initial guess for $D$ and often takes several attempts to find the proper annealing parameters for successful depth profiling.

The surface concentration and the sheet resistance realized with these materials also depend upon the atmosphere in which the diffusion is carried out. In an oxidizing atmosphere, the growth of $SiO_2$ at the silicon surface will eventually prevent the access of dopant atoms from the doped oxide to the silicon. The standard deviation of the sheet resistance of the SOD-diffused samples without prior HF treatment is noted to be much lower than that of SOD-diffused samples with HF treatment due to the uniform sheet resistance distribution all over the diffused silicon surface, as shown in Fig. 4. This implies that the thickness of the diffused $n^+$ layer is uniform. In our study, no additional 10 % HF treatment before SOD diffusion (normally used for conventional $POCl_3$ diffusion) was used. Actually, a thin hydrophilic oxide layer was formed during a 5-min dipping in a hot DI-water bath at 80 °C, leading to an improvement in wettability of the silicon surface. This led to a higher uniformity of the thickness of the SOD film and may be the cause of the lower standard deviation of the sheet resistance of the wafer doped by annealing at a particular temperature for a fixed time without HF treatment, as shown in Fig. 4, which improves the quality of the diffused junction in SOD-diffused samples. The method of this study simplifies the fabrication process steps and improves the doping uniformity. A thin thermal oxide layer could also be grown as an alternative technique to the approach of
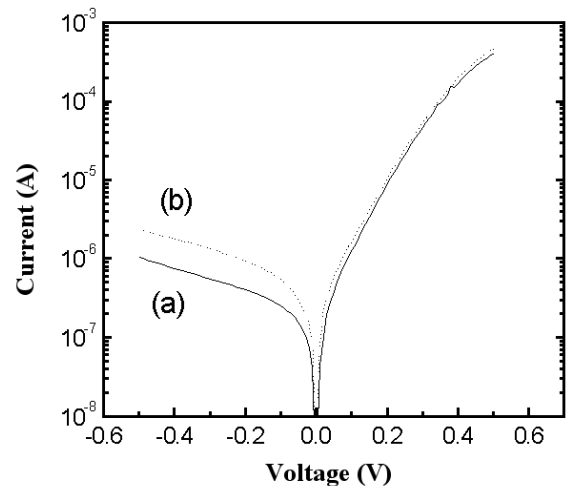
this study, but that process requires a higher temperature and a longer process time.

Reduction of unwanted impurities present on the SOD-diffused surface plays an active role in reducing junction leakage. These unwanted impurities are not removed completely during removal of the PSG layer with a diluted HF solution. Organic contaminants, such as amines, may be present in the diffused-SOD layer. Such organic contaminants create a layer along the edge of the diffused wafer and the layer cannot be removed completely during a short-time etching for edge isolation. However, an increase in the edge etching time is not possible beyond a certain limit due to the possible risk of the etchant penetrating through the p-n junction isolation regions towards the active solar-cell area. This ultimately gives rise to a leakage path after screen-printed metal formation. In addition, these contaminants on the surface contribute significantly to increasing the series resistance ($R_s$) of the fabricated solar cell. Table 1 shows the values of different electrical parameters of SOD-diffused solar cells with and without a hot HCl treatment. The open circuit voltage ($V_{oc}$) of the hot-HCl-treated cell is greater than that of the cell without HCl treatment by 3 mV. Similarly, for the HCl-treated cell the series resistance ($R_s$) is less than that of the cell without treatment, as a result of which the short-circuit current ($I_{sc}$) is improved by 0.05 Å. HCl treatment leads to a major difference in the fill factor (FF) of the cell. The FF was found to be 77 % in the cell with hot HCl treatment whereas it was only 66 % in the cell fabricated without hot treatment. Such a great difference in the FF must be due to better metal-semiconductor contact due to the removal of contaminants from the silicon surface during hot HCl treatment before metallization.

Fig. 5 shows the dark I-V (DIV) characteristics of the SOD-diffused solar cell with and without hot HCl

Table 1. Comparison of performance parameters of solar cells with and without HCl treatment.

| Surface treatment | $V_{oc}$ (V) | $I_{sc}$ (A) | FF | $E_{ff}$ (%) | $R_s$ (m$\Omega$) | $I_{0e1}$ (A) | $I_{0e2}$ (A) |
|---|---|---|---|---|---|---|---|
| Without hot HCl | 0.596 | 2.90 | 0.66 | 11.0 | 39 | $1.6 \times 10^{-5}$ | $3.05 \times 10^{-7}$ |
| With hot HCl | 0.599 | 2.95 | 0.77 | 11.9 | 28 | $6.1 \times 10^{-6}$ | $3.05 \times 10^{-7}$ |

$V_{oc}$- open-circuit voltage, $I_{sc}$- short-circuit current, FF - fill factor, $R_s$ -series resistance, $E_{ff}$ - efficiency, $I_{01}$ - injection current, and $I_{02}$ -recombination current.

Table 2. Parameters of SOD diffused solar cells on different surfaces.

| Front surface condition | $V_{oc}$ (V) | $I_{sc}$ (A) | $V_m$ (V) | $I_m$ (A) | FF | $F_{ff}$ (%) |
|---|---|---|---|---|---|---|
| Textured without SiN$_x$ ARC | 0.599 | 2.95 | 0.483 | 2.55 | 0.70 | 11.9 |
| Textured with SiN$_x$ ARC | 0.593 | 3.25 | 0.469 | 2.90 | 0.71 | 13.1 |

$V_{oc}$- open-circuit voltage, $I_{sc}$- short-circuit current, $V_m$- voltage at maximum power point, $I_m$- current at maximum power, FF - fill factor, and $E_{ff}$ - efficiency.

treatment. In our experiment, the DIV characteristics were extracted as two different leakage current components ($I_{0e1}$ and $I_{0e2}$), which are given in Table 1. The improvement of the injection current component ($I_{0e1}$) for the hot-HCl-treated cell from $1.6 \times 10^{-5}$ Å to $6.1 \times 10^{-6}$ Å is significant compared to that in untreated diffused solar cells. This verifies the reduction in contaminants after hot HCl treatment. Hydrochloric acid enters into chemical reactions characteristic of the chloride ion, such as reactions with various inorganic and organic compounds in which hydrochloric acid is used as a chlorinating agent and reactions with metals and their oxides in which complex chloride-containing ions are formed. Liquid-liquid extraction is one of the most used methods for isolating an organic compound from a mixture. Organic bases, amines, are converted to their corresponding cationic salts by reacting with acids. These salts are then soluble in water and can be separated from the organic mixture. The following chemical equation represents the reaction of hot HCl molecule with one of the possible contaminants on the silicon surface:

$$N(CH_2CH_3)_3 \xrightarrow{HCl} H-N(CH_2CH_3)_3^+ + Cl^-$$
$$Cationic salt - water soluble$$
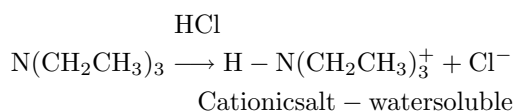
Hot HCl treatment might have removed such residuals with organic contaminants that are not removed by diluted HF dipping, leading to an improved in $I_{0e1}$ component of the dark current and improved electrical parameters of solar cells. The decrease in the series resistance ($R_s$) of the HCl-treated (at 60 °C, 10 min) solar cell also indicates a reduction in the contamination present
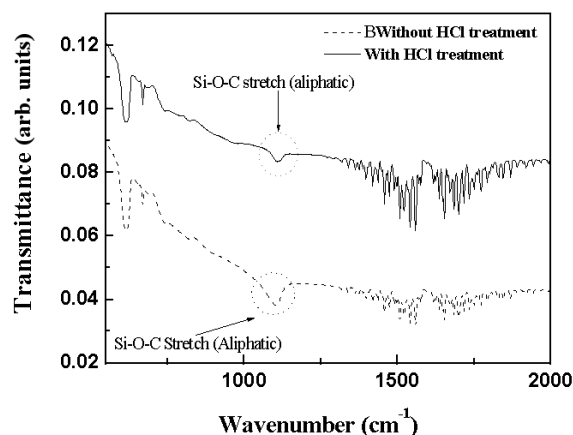


Fig. 6. FTIR analysis of SOD diffused samples with and without hot HCl treatment.

on the solar cell's surface. Actually, the series resistance and other electrical parameters of solar cells strongly depend on the front and the back contacts. Thus, surface treatment with HCl at 60 °C for 10 min improves all the electrical parameters of SOD-diffused solar cells.

The decrease in the peak at 1110 cm$^{-1}$ for the HCl-treated sample compared to that of the sample without hot HCl treatment is shown in the FTIR analysis in Fig. 6, which indicates a reduction in the organic contaminant (Si-O-C, aliphatic) after treatment. Fig. 6 shows a typical light I-V (LIV) characteristic of large-area (103 mm × 103 mm) SOD-diffused solar cells with and without a PECVD silicon-nitride coating, and Table 2 shows the different electrical parameters of the fabricated solar
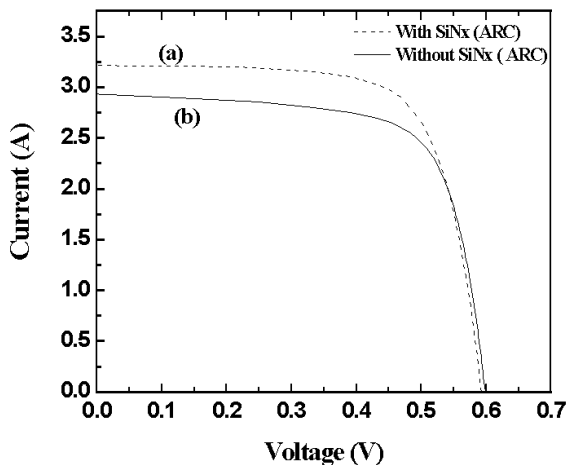
Fig. 7. Illuminated I-V (LIV) characteristics of large-area (104 cm$^2$) SOD monocrystalline silicon solar cells (a) with and (b) without PECVD silicon nitride.

cells. From Fig. 7 and Table 2, we observe that the short-circuit current density, the open-circuit voltage, and fill the factor of a typical SOD-diffused large-area (104 cm$^2$) solar cell with a PECVD silicon-nitride antireflection coating are 31.25 mA/cm$^2$, 593 mV, and 0.71 respectively. This is mainly due to uniform SOD diffusion and good electrical contact formation during screen printing and co-firing. In this way, the hydrophilic nature of the textured surface without HF treatment improves the uniformity of diffusion and leads to an improved open circuit voltage. Additional HCl treatment at 60 °C for 10 min helps to remove the residual organic contaminants and leads to an enhanced electrical contact behavior for the solar cell.

## IV. CONCLUSIONS

Spin-on diffusion is a convenient low-cost technique for the diffusion of large-area solar cells. However, since the solar cells are usually textured in order to lower the reflection loss and to improve the collection efficiency, the spin-on film becomes nonuniform in thickness, leading to a poor-quality junction. Direct use of textured wafers for spin-on coating after several treatments with DI water leads to an improvement in the wettability of the silicon surface, resulting in a uniform sheet resistance (standard deviation <1). Spin-on glass residues

formed during IR lamp furnace annealing generate recombination centers, high resistances, and increase leakage currents ($I_{0e1} = 1.6 \times 10^{-5}$ Å), thereby lowering the solar-cell efficiency. A novel hot HCl treatment of PSG-removed samples ensures the removal of organic contaminants after SOD-diffusion and improves the SOD diffused solar cell's performance parameters, which is reflected in an improved solar-cell conversion efficiency. Using our novel approach, we have successfully achieved a 0.9 % conversion efficiency gain for SOD-diffused large-area monocrystalline silicon solar cells.

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