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# Improved emitter performance of RIE black silicon through the application of in-situ oxidation during POCl<sub>3</sub> diffusion

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#### Abstract

Nano-texture has the potential to reduce the optical losses of crystalline silicon solar cells. RIE fabricated black silicon enables near zero reflectance across a broad range of wavelengths and the angular dependence has been shown to be superior to existing technologies. However, in front-contact cells which are the current industrial mainstream architecture, the emitter is located on the front textured side and is typically realized by POCl<sub>3</sub> diffusion. The interaction of this process with the nano-texture is complex, which makes it challenging to optimise the electrical performance of the phosphorus emitter. This paper studies the impact of in-situ oxidation during emitter formation to the electrical performance of a POCl<sub>3</sub> diffused RIE nanotextured emitter surface. Additional corona charge was applied on the ALD SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> stack to avoid the limitation on the emitter performance due to non-ideal surface passivation conditions. After saturation with surface charge, the results demonstrate in-situ oxidation to be an effective technique to improve the electrical performance. An emitter recombination factor of 147 fA/cm<sup>2</sup> was achieved for a 127  $\Omega/\Box$ emitter formed on reactive-ion etched sample with surface area enhancement factor and effective slope index of 4.19 and 1.63, respectively. Further paths for improvement are identified, particularly relating to the collection of carriers generated by short wavelength light and how that relates to the shape of the texture used.

Keywords: Phosphorus diffusion; In-situ oxidation; Field effect passivation; Emitter recombination; Black silicon

# **1. Introduction**

In recent years, nano-scaled texturing has been used to reduce the optical loss of c-Si solar cells resulting in improved cell efficiency [1,2]. For example, RIE based texturing has been applied to large area mc-Si front junction solar cells to achieve world record results [3,4]. Furthermore, a shallower form of black silicon formed via chemical etching has been used to address manufacturing problems related to diamond wire sawing [5], to improve cell efficiency [6] and has become standard in production lines [7]. However, to integrate these types of textures with front junction solar cells, the size and shape of the features tend to be compromised to balance the optical and electrical performance, an approach that has been applied to RIE formed textures in numerous works [8-11]. To further improve the cell efficiency it would be beneficial to integrate black silicon textures into solar cells without the need to compromise the near-zero broadband reflectance that has been achieved [12–14].

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Whilst these textures have been used successfully on rear junction cells [2], their integration into the more standard cell architectures has been difficult.

The initial challenge was to develop a technique to passivate large surface area, heavily n-type diffused silicon, since traditional PECVD based depositions of  $SiN_x$  were considered incompatible with such extreme surface features [15,16]. A solution to this was found in the form of a positively charged  $SiO_2/Al_2O_3$  stack deposited by atomic layer deposition (ALD) [17]. However, initial attempts at integration into a front junction cell resulted in relatively high emitter recombination due to the presence of excess phosphorous in the emitter region [18]. That work concluded that to achieve further improvements it would be necessary to reduce the phosphorous concentration, thus enabling less recombination and better field effect passivation at the surface.

In-situ oxidation during thermal diffusion has previously been demonstrated as a technique to improve the electrical quality of an emitter region on samples textured with upright random pyramids [19,20]. The increased flow of oxygen compared to a more traditional process was found to limit the flux of phosphorous atoms into the silicon, thus reducing the overall dopant concentration and reducing the surface concentration. The benefits of reducing the amount of phosphorous within a solar cell emitter has been demonstrated by many good studies [21,22]. The enhanced surface area to volume ratio of black silicon presents an additional complication when optimising the diffusion process. Previous studies have demonstrated an enhancement in doping concentration, attributed to the enhanced surface area and a likely increased reaction between silicon and PSG [8,10,11,17,23–25], however in some cases the enhancements were marginal [8,24]. An example of strong enhancement was observed for a previous attempt to produce RIE textured selective emitter cells which unintentionally resulted in an emitter with  $R_{sh}$  of 40  $\Omega/\Box$  (rather than the target of 100  $\Omega/\Box$ ) due to the deep nano-features on the surface [26]. Such results indicate the need for a systematic approach to optimise the POCl<sub>3</sub> doping process for extreme black silicon samples.

In this work we address that limitation by applying known high efficiency cell processing techniques to reduce the amount of doping within the emitter. Specifically, we systematically study the effects of in-situ oxidation during thermal diffusion on the quality of P emitters formed on RIE produced ~1 um tall upright needles with an effective slope index of 1.63, which is about 4 times higher than random upright-pyramid. The electrical characterisation includes the first demonstration on black silicon of the application of a photoluminescence-based technique to measure the emitter collection efficiency. With the reduction in surface concentration achieved we then apply positive corona charge to the surface atomic layer deposited films and demonstrate its ability to further improve the performance. The results demonstrate the lowest recombination P emitters ever achieved on this type of texture and have implications for other types of textures that incorporate nano-scale features.

## 2. Material and methods

## 2.1 Fabrication

The process flow of this work is outlined in Figure 1. A batch of 250  $\mu$ m thick, double-sided polished 4-inch p-type float zone (FZ) silicon wafers with 1  $\Omega$ .cm base resistivity was used for RIE texturing. The b-Si nanostructure was fabricated using a process described in [14] with an Oxford Instruments Plasmalab 100. The wafers were subsequently cleaned with the standard cleaning procedure [27]. Random pyramid samples were acquired through industry. The random pyramid samples were made on diamond-wire sawed 6-inch p-type mono-Si with a 1.6  $\Omega$ .cm base resistivity and a thickness of ~180  $\mu$ m.

POCl<sub>3</sub> diffusion was done using a Tempress tube furnace and the recipes were based on those described in [20]. Random pyramid samples and nanotextured samples were diffused in separate runs due to the differences in wafer dimensions. Polished control samples were loaded in the same run as the nanotextured samples. Pre-deposition for all samples was done at 795 °C for 25 mins with a fixed POCl<sub>3</sub>/O<sub>2</sub> ratio = 450/600. Prior to the drive-in step, the temperature was ramped to 855 °C with a fixed ramp rate of 10 °C/minute and a fixed O<sub>2</sub> concentration of 8.33 % v/v. The drive-in step was done at 855 °C for 30 mins with a fixed total nitrogen gas flow of 7.25 slm. The oxygen gas flow was varied to reach the specified O<sub>2</sub> concentration (v/v). For more details, see [20].

Nanotextured and polished samples were passivated with a SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> stack deposited with a Beneq TFS-500. Prior to ALD deposition, a 30 second hydrofluoric acid (HF) dip (1%) was used to remove the native oxide on the surface. A SiO<sub>2</sub> layer (n = 1.49 at 633 nm, thickness = 20 nm) was first deposited by plasma-enhanced ALD at 200 °C using 120 cycles of oxygen and a commercial silicon precursor. Subsequently, an Al<sub>2</sub>O<sub>3</sub> layer (n = 1.62 at 633 nm, thickness = 33 nm) was deposited at the same temperature by a thermal ALD process consisting of 270 cycles of H<sub>2</sub>O and TMA precursors. The Al<sub>2</sub>O<sub>3</sub> deposition was performed in the same chamber with the first run without breaking the vacuum in between. During every cycle, a double-pulse of each precursor was used to ensure conformal deposition on the entire deep-RIE surfaces. After ALD deposition, the samples were annealed at 425 °C for 30 mins in nitrogen ambient to activate surface passivation [18]. Contactless capacitance-voltage measurements were done on an n-type non-diffused polished reference sample passivated with the same ALD stack. The fixed charge density (Q<sub>f</sub>) and interfacial trap density (D<sub>it</sub>) was extracted to be 2 x 10<sup>11</sup> cm<sup>-2</sup>eV<sup>-1</sup> and 3 x 10<sup>11</sup> cm<sup>-2</sup>, respectively.

Random pyramid samples were passivated with  $SiN_x$ :H (n = 2.08, thickness = 75 nm) deposited by a Meyer Burger MAIA remote plasma enhanced chemical vapour deposition (PECVD) tool at 400 °C [28]. The samples were subsequently fired on a belt furnace with a peak temperature of 740 °C.



Fig. 1. Process flow chart for random pyramid sample, reactive-ion etched sample and polished reference sample.

## 2.2 Characterization

SEM images were measured by using a FEI Nova NanoSEM 450. AFM scans were performed by using a Bruker ICON in tapping-mode with 512 line scans. A diamond-like carbon coated silicon probe (TESPD) with a nominal tip radius of 18 nm was used for the random pyramid sample. A minimum 5:1 high-aspect ratio probe (TESPA-HAR) with a nominal tip radius of 10 nm was used specifically for the nanotextured samples. The sampling interval for the random pyramid sample was 78 nm, while the sampling interval for the random pyramid sample was 19 nm. The front surface reflectance of all samples was measured using a commercial spectrophotometer (Perkin Elmer 1050) with an integrating sphere.

The sheet resistance was measured by a 4 point-probe scanner (Sunlab Sherescan). The difference in sheet resistance measured between both forward and reverse current direction for all samples was less than 1  $\Omega/\Box$ . For random pyramid samples, the sheet resistance was measured at 9 points, whilst only the centre point was measured on nanotextured samples to avoid excessive damage of fragile nano-scale features.

The defect density, fixed charge density and surface potential were measured by a Semilab PV-2000A instrument following the standard analysis procedures [29]. A Semilab LCC-300 linear corona charger was used to generate corona charges on the wafer surface for studying the field-effect passivation. After corona charging, the surface potential of the samples was immediately measured every 5 mm across the whole wafer by Semilab PV-2000A using Kelvin probe. The uniformity of the inspected area was confirmed by surface voltage maps. The effective minority carrier lifetime of all samples was measured by quasi-steady-state photo-conductance (QSSPC) via the generalised technique using Sinton WCT-120 [30]. Auger recombination was corrected by using the Richter model [31]. The emitter recombination factor was extracted by the Kane & Swanson method at an injection level of 1

 $-2 \times 10^{16}$  cm<sup>-3</sup>. The emitter recombination factor (J<sub>0e</sub>) was monitored by an ex-situ carrier lifetime measurement done between each step of corona charging.

The quantum efficiency of the samples was measured by a photoluminescence-based spectro-response (PL-SR) method [32,33]. Prior to the measurement, a calibrated photo-diode was placed at the sample position to calibrate the photon-flux from the LED array at different wavelengths. This calibration was used for a fixed photo-diode that was placed next to the samples. During the measurement, the intesity of the LED array was adjusted to obtain a constant PL signal for all wavelengths in order to avoid the possibility of injection dependent quantum efficiency at low injection. The wavelength-dependent photoluminescence quantum efficiency ( $PL_{QE}$ ) was normalized to the value at 660 nm.

# 2.3 Calculations

The surface characteristics were extracted from the measured AFM data using the Gwyddion software [34]. The root-mean squared roughness ( $\sigma_{rms}$ ) and surface-area-to-projected-area ratio ( $f_{surf}$ ) were extracted based on the standard definition. The correlation length ( $\tau_L$ ) was extracted by first plotting the data from the AFM scans using a built-in Auto-Correlation Function (G(x)) in Gwyddion. Then, the G(x) was fitted by the equation:

$$G(x) = \sigma_{rms}^2 \exp\left(-\frac{x^2}{\tau_L^2}\right) + g_o \#(1)$$

where  $\sigma_{rms}$  is the root-mean squared roughness, x is the horizontal distance,  $\tau_L$  is the correlation length and  $g_o$  is a vertical offset to account for the fact that G(x) could drop below zero for coarse surfaces. Facet angles were extracted by local plane fitting over 2 pixels. The facet angle and surface area were both extracted by using the built-in algorithm provided in Gwyddion. No additional image processing was used except for levelling the data by mean plane subtraction.

The emitter recombination factor  $(J_{0e})$  was extracted by the Kane & Swanson method using the equation below [35]:

$$\frac{1}{\tau_{corr}} = \frac{1}{\tau_{bulk}} + \frac{2J_{0e}(N_D + \Delta n)}{qWn_i^2} \#(2)$$

where  $\tau_{corr}$  is the Auger-corrected effective lifetime,  $\tau_{bulk}$  is the bulk lifetime,  $J_{0e}$  is the emitter recombination factor [36],  $N_D$  is the base doping,  $\Delta n$  is the excess carrier density, q is the elemental charge, W is the wafer thickness and  $n_i$  is the intrinsic carrier density.

## 3. Results and Discussion

## 3.1 Surface characteristics

The SEM images of the sample surfaces, shown in Figure 2, demonstrate the fundamental physical differences between the RIE formed needle-shaped nanostructures and the chemically etched upright random pyramids. Note the different scales used for the SEM images. The wavelength dependent reflectance of the front surfaces, shown in Figure 3,

highlights the optical advantage of the nanostructured texture, which has less reflectance at all wavelengths, despite the incorporation of an additional anti-reflection coating on the random pyramid sample. The superior optical properties of RIE texture results in a gain of  $0.64 \text{ mA/cm}^2$  photogenerated current over the Rp texture, under the AM 1.5G spectrum from 300 nm to 950 nm. The difference is expected to be bigger if the parasitic absorption within the SiN<sub>x</sub> film on Rp texture is taken into account. Note however that for photovoltaic applications some of this lost light will be trapped and reflected back onto the cell by the encapsulation layers in a module.



Fig. 2. Tilted (75°) and top view SEM images for random pyramid texture (a and b) and RIE nanotexture (c and d).



Fig. 3. Front surface reflectance of silicon nitride coated random pyramid texture and uncoated (bare silicon) RIE nanotexture from 300 nm to 950 nm.

Surface statistics extracted from the AFM scans (Table 1) quantify the differences in surface topography. As expected, both  $\sigma_{rms}$  and  $\tau_L$  are significantly higher for random pyramid textures compared to the RIE nanotextures. Note that this may have implications for the scattering of light from the nanotexture [37]. The effective slope index, expressed as the ratio between  $\sigma_{rms}$  and  $\tau_L$  [38], and the peak angle ( $\theta_{peak}$ ) were far greater for the nanotexture. This results in the  $f_{surf}$  of the nanotexture being ~3 times higher than that of the random pyramid sample. Later in the paper we will demonstrate some correlation between this ratio, the

enhancement in emitter doping and the amount of recombination within the doped texture regions. It is also worth noting that the random pyramid texture exhibits two dominant peaks in surface angle at 47° and 50°. This result is in good agreement with the literature and smaller than the common misconception of the pyramid angle being 54.7°, which assumes the texture as an ideal {111} bound pyramid resulted by the ratio of etch rate of {111} and {100} orientation being infinite [39,40]. As a result, the measured surface area enhancement factor ( $f_{surf}$ ) of the random pyramid is about 1.44 instead of 1.7.

TABLE ISURFACE CHARACTERISTICS OF RANDOM PYRAMID (RP) AND<br/>REACTIVE-ION ETCHING (RIE) TEXTURE

Texture	$\sigma_{rms}(nm)$	$\tau_L(nm)$	$\sigma_{rms'}\tau_L$	$\Theta_{\text{peak}}(^{\circ})$	$f_{ m surf}$
Rp	481	1213	0.39	47, 50	1.44
RĨE	224	137	1.63	75	4.19

## **3.2 Electrical Properties**

The front surface of a solar cell must provide adequate lateral conduction of majority carriers, limit the amount of recombination of minority carriers (at both open-circuit and short-circuit conditions) and provide good ohmic contact to metal contacts. In general, the ideal front surface would have a low sheet resistance and exhibit very low recombination (low  $J_{0E}$  and high collection efficiency). However, it is necessary to make a trade-off since the high doping concentration required to minimise resistive loss also results in higher recombination [22,41]. In this section we examine the first two of these and demonstrate processing that improves the performance of the nanotexture.

# 3.2.1 Impact of in-situ oxidation on the emitter doping

Increased oxygen concentration during diffusion resulted in increased sheet resistance (i.e. lighter doping) for all samples (see Figure 4). This is consistent with the results seen in other studies utilising oxygen during drive-in [20]. In the case of the nanotexture a much higher O<sub>2</sub> concentration was required to reach the desired R<sub>sh</sub> range  $(100 \ \Omega/\Box - 140 \ \Omega/\Box)$  and for any specific oxygen concentration the doping was enhanced by the nanotexture. This enhancement is likely related to the increased surface area of the nanotexture (i.e. the increased  $f_{surf}$  shown in Table 1) which provides much more silicon per unit volume for the deposited phosphosilicate glass (PSG) to react with. This results in an increased release of P atoms as well as overall more source being provided by the increased surface area. Beyond 3% oxygen concentration the change in sheet resistance begins to flatten out. Given this was observed on both polished samples and nanotextured samples it is more likely related to a process limitation (e.g. the oxide thickness may limit the supply of P). From the point of view of resistive loss, it would be better to have an emitter with lower sheet resistance, however the next section will demonstrate that these higher sheet resistance emitters provide more benefit through lower recombination than they lose through less conductivity.



Fig. 4. Effect of in-situ oxidation during drive-in step on the sheet resistance of different textures.

Further insight into the junction formation on the different textured surfaces is revealed by means of cross-sectional SEM dopant contrast imaging (SEMDCI) of the postdiffusion nanotextured and Rp samples (Figure 5). SEMDCI relies on a reduced acceleration voltage during SEM imaging, which causes phosphorous-doped regions to appear darker while boron-doped regions appear brighter [42–45]. Although the regions with highest contrast in the images have been shown to be correlated to the junction depth, the exact position of the junction would need further calibration [45]. Nevertheless, the relation between the surface topography and the dark regions are drastically different. On the random pyramid texture, the dark regions (i.e. emitter region) is conformal with the surface morphology. This results in a uniform junction depth (from the surface) and the centre volume of the pyramid remaining non-diffused. On the other hand, all the needles in the RIE texture appear dark and this extends into the region beneath the needles. This indicates that the entire volume of each needle is doped by phosphorous and that the electrical junction is formed in a somewhat parallel plane below the surface. This results in a non-uniform junction depth, with different points on the surface located at different distances from the junction.



Fig. 5. Cross-sectional SEM doping contrast images for (a) random pyramid sample and (b) RIE sample. The phosphorus-diffused region appears darker whilst the boron-doped region appears brighter.

The reason for the formation of different junction depths may be explained by considering the details of the diffusion process. During thermal diffusion, a PSG layer is deposited conformally on the nano-texture and as a result, phosphorus atoms are introduced into the needles from all sides. The junction depth of >400 nm is larger than the width of the

nanofeatures (~100 nm). Therefore, phosphorus atoms diffusing from one side of the needles are expected to reach the other side and cause enhanced doping throughout the needles. Yet, no substantial contrast was observed within the nanowire as compared to deeper in the bulk. This observation could be limited by the imaging parameters used in the SEMDCI technique, which requires further optimization and studies. Nevertheless, the PSG deposited in the valleys introduces dopant down to the bulk of the silicon forming a rather homogeneously doped region underneath the RIE textures (appearing as a dark layer in the SEMDCI image). In contrast, the  $\tau_L$  of the Rp texture is much larger than the junction depth. Therefore, no enhanced-doping effect is observed at the centre of the pyramids. It should be noted that an enhanced doping effect has been observed at the tips of Rp texture [46], however the total volume of those regions is not great and therefore is not expected to have any significant impact on overall doping.

The implications of this difference in junction formation on solar cell performance is complex. On the one hand a smaller total junction area is good since it potentially minimises junction recombination. Under open circuit conditions the high recombination surface being located at a distance from the junction is also good since it allows the emitter profile to shield bulk carriers from recombining there. However, for short-wavelength photons there exists much longer distances between carrier generation and junction collection. This has implications for the collection of light absorbed in the needles, particularly at shorter wavelengths. Furthermore, it is likely that the total amount of dopants incorporated into the needles is enhanced since phosphorous atoms may enter from all sides [10,17,47]. This will result in higher surface concentration and higher doping concentration within the emitter, both of which will increase recombination in those regions.

# 3.2.2 Emitter recombination

In addition to emitter optimization via in-situ oxidation, further improvements were also made to the surface passivation by means of corona deposition of additional surface charge. It is challenging to accurately measure the exact amount of charge successfully deposited onto a nano-textured surface and as such the results presented in this section refer to the amount of charge generated by the corona tool. The reduction in emitter recombination factor (J<sub>0e</sub>) for three nanotextured samples (spanning the range of emitter strengths) is shown in Figure 6 (left). Initially the 67  $\Omega/\Box$  emitter had the lowest recombination factor, whilst the  $\Omega/\Box$  emitter had the highest with the 127  $\Omega/\Box$  emitter positioned between them. This demonstrates the complex balance between doping induced recombination and shielding of carriers from surface recombination. In all cases the J<sub>0e</sub> of the nanotextured emitters was reduced by the corona deposition of charge. Once this improvement saturated the emitter with the least amount of doping had the lowest J<sub>0e</sub> and the heaviest emitter was the highest. Similar behaviour was also observed for the set of polished reference samples: the J<sub>0e</sub> for all samples was reduced with additional corona charge deposited (Figure 6, right). Since the initial  $J_{0e}$  of the polished samples was much lower compared to the RIE samples, the improvement in  $J_{0e}$ as a result of corona deposition of charge was less prominent. In addition, the total amount of generated charge required for the polished samples to reach saturation of J<sub>0e</sub> was significantly less compared to the RIE samples. This could be related to the difference in surface area

between these two set of samples, which is further discussed in supplementary material. Nevertheless, the best performing  $J_{0e}$  achieved on the polished samples is close to value reported in the literature for an industrial high efficiency passivated emitter and rear cell with selective emitter (27 fA/cm<sup>2</sup> vs 31 fA/cm<sup>2</sup>) [48]. This result highlights the quality of emitter formation and surface passivation employed in this work.



Fig. 6. Evolution of emitter recombination factor under corona charge deposition for reactive-ion etched silicon samples (left) and polished reference samples (right). The dash lines serve as a guide to the eye.

It is interesting to understand the roles of surface charges further since it clearly provides one path to further performance improvement. Unfortunately, in this experiment it is only possible to study the impact of generated charge (i.e. not deposited charge) onto the emitters. The impact on emitter recombination is convoluted by two effects, the first is the efficiency of the deposition itself (i.e. what fraction of generated charge remains on the surface) and secondly how the different emitter doping reacts to the deposition of that charge. The former effect has been discussed in more details in the supplementary section.

The impact of generated charge onto the emitter recombination factor of RIE samples are summarized in Figure 7. The results reveal that the total reduction in  $J_{0e}$  increases as the emitter  $R_{sh}$  increases. Since all the nanotextured samples have the same dielectric layers and the corona charges were deposited in identical fashion, this difference in the  $J_{0e}$  reduction  $(\Delta J_{0e})$  should be attributed to the difference in emitter doping density and the interaction of different surface charge with different surface doping concentration. When surface doping density reduces, additional corona charge on the dielectric layer can progressively cause more significant band-bending near the surface. This repels minority carriers away from the trapping sites at the silicon/dielectric interface and hence surface recombination reduces. As a result, the larger reduction in  $J_{0e}$  through corona charging for the nanotextured samples with higher  $R_{sh}$  may be explained by the enhanced field effect passivation on the surface in combination with the reduction in emitter recombination due to less doping concentration. As a result, the final  $J_{0e}$  reduces with increasing  $R_{sh}$ , reaching 147 fA/cm<sup>2</sup> for a 127  $\Omega/\Box$  emitter formed on reactive-ion etched surface.



Fig. 7. Effect of corona charge deposition on the emitter recombination factor of RIE samples with different emitter sheet resistance.

The best values of emitter recombination factor  $(J_{0e})$  measured on the nanotextures is shown in Figure 8 (left). The heaviest emitter doping of ~65  $\Omega/\Box$  had a J<sub>0e</sub> of 179 fA/cm<sup>2</sup> which was then progressively reduced via in-situ oxidation to 147 fA/cm<sup>2</sup> for the ~127  $\Omega$ / $\Box$ emitter. Comparison to previous results in the literature (Figure 8, right) demonstrates this to be a significant improvement compared to previous studies with the J<sub>0e</sub> roughly halved for similar levels of sheet resistance. The selected literature data were chosen from studies that also employed deep RIE textures (weighted reflection less than 1%) with nominally the same ALD passivation stack as used in this study. It should be noted that [P] ion implantation was used in Van De Loo et al. and gas-phase diffusion was used in Pasanen et al [17,49]. The  $J_{0e}$ improvement achieved in this work is attributed to the reduction in doping concentration both at the surface and within the bulk of the emitter on the nanotextured samples. These reduced doping levels also allowed the deposition of surface charge to play a greater role in reducing the overall recombination within the emitters. Compared to the J<sub>0e</sub> measured on the random pyramid sample with similar  $R_{sh}$  (~ 130  $\Omega/\Box$ ) there was a factor of ~3 for the best performing RIE sample. This has an interesting similarity to the surface area ratio between these two textures, which may indicate that the surface area remains critical for the conditions investigated in this study. For the polished reference samples, the J<sub>0e</sub> after corona deposition of charge remains relatively unchanged irrespective to different strength of emitters.



Fig. 8. (left) The best emitter recombination factor for RIE samples with different sheet resistance after saturation with corona charging, (right) Summary of emitter recombination for RIE samples and random pyramid samples fabricated in this paper and RIE samples reported in the literature [17,49].

#### **3.2.3 Carriers collection**

The reduction in emitter recombination demonstrated above was also found to result in an improvement in the collection of carriers. Under short-circuit conditions, carriers generated within the emitter region must diffuse to the junction and be collected to contribute to the light generated current. Measurement of the normalised external quantum efficiency (EQE<sub>PL, norm</sub>) of the nanotextured and Rp samples (Figure 9, left) demonstrates in both cases an improvement with reduced sheet resistance. In the case of the nanotexture the EQE<sub>PL</sub> at 365 nm improved from 0.24 to 0.42 by increasing R<sub>sh</sub>. It should be noted that this result is normalised to the performance at 660 nm and any absolute reduction there would result in an overall reduction in the absolute amount of carrier collection. Comparison to the RP sample reveals that there remains further scope for improvement. The random pyramid samples EQE<sub>PL</sub> (0.64 - 0.74) is superior to the nanotexture despite being reduced by the sub-optimal reflection and parasitic absorption within the SiN layer. The internal collection efficiency of these samples is 0.8 to 0.95 which is common in finished solar cells [20]. The nanotextured samples do not have parasitic absorption in any surface layers and it is likely the reduced EQE<sub>PL</sub> is the result of the deep junction, as shown in the SEMDCI image of Figure 5. Under illumination, carriers generated at the valleys of the RIE texture need only travel 400 nm to be collected (similar to the distance in the RP sample). However, carriers generated within the needles need to travel an extra distance (up  $\sim 800$  nm further) before reaching the junction. In addition, these needle regions are more heavily doped, and carriers must travel within 60 nm of the silicon surface where they are exposed to the trapping sites at the silicon/dielectric interface. Since the absorption depth for photons with 500 nm wavelength is about 1 µm, photons with shorter wavelengths were mainly absorbed within the needles. As a result, the generated carriers from short wavelength were strongly influenced by the geometry of the nano-scaled needles and its interaction with thermal diffusion described above. This result highlights collection efficiency as a key metric for the performance of nanotextures and one that should be considered during further optimisation. The application of contact-less PL techniques provides a very useful means of measuring this on samples with extreme textured features where the formation of contact schemes may be difficult to achieve and/or may complicate the result.



Fig. 9. (left)  $EQE_{PL}$  for random pyramid samples and RIE smaples as a function of illumination wavelength. (right)  $QE_{PL}$  at 365 nm for random pyramid samples and RIE samples with different sheet resistance

## 4. Conclusion

In this paper, the electrical properties of emitters formed on RIE nanostructures were investigated and compared to upright random pyramid samples. Emitter sheet resistance  $(R_{sh})$ on the nanotextured samples ranging from 67 – 127  $\Omega/\Box$  were achieved by adjusting the oxygen concentration during the drive-in step. It was found that increased levels of oxygen were required to account for the increased doping caused by the additional surface area of the nanotexture. After applying ALD passivation layers and additional corona charge, the J<sub>0e</sub> was found to reduce with increasing oxygen concentration, reaching 147 fA/cm<sup>2</sup> for a surface area enhancement factor of ~4.2, representing a significant improvement compared to previous studies. This result highlighted the effectiveness of in-situ oxidation as a strategy to improve the emitter quality, particularly when forming a junction on deep RIE textures. It also highlighted the need for an ALD film with higher positive fixed charge density. The lowest J<sub>0e</sub> achieved on deep RIE texture was found to be approximately three times higher than the random pyramid sample with similar R<sub>sh</sub>. This factor is suggested to be correlated to the surface area ratio between these two textures, as confirmed by atomic force microscopy. The internal quantum efficiency (measured using photoluminescence-based techniques) of the deep RIE samples was also improved by increasing the strength of in-situ oxidation process. Further scope for improvement was identified since values extracted were significantly lower than the random pyramid samples. Cross-sectional SEMDCI images revealed that the interaction between nano-scaled texture and thermal diffusion process causes doping throughout the whole RIE needles. It is suggested that the increased travel distance before being collected by the electrical junction combined with the higher exposure to the trapping sites within the needles, are responsible for the reduced collection efficiency within the emitter formed on deep RIE samples.

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#### Supplementary

Results in Figure 6 shows that the amount of generated charge required for the emitter recombination factor to reach saturation is significantly higher for RIE samples, as compared to the polished reference samples. The following discussion aims to provide further insight for such observation.

The surface potential measured with the Kelvin probe was converted into a density of charge on the surface by using the equation [18]:

$$\frac{\Delta Q_c}{A} = \epsilon_o \left( \frac{\epsilon_S \epsilon_A}{\epsilon_S t_A + \epsilon_A t_S} \right) \Delta V_{surf} \#(S1)$$

where  $\Delta Q_c$  is the total amount of charge (C), A is the surface area (cm<sup>-2</sup>),  $\varepsilon_o$  is the permittivity of free space,  $\varepsilon_s$  and  $\varepsilon_A$  are the dielectric constant of silicon dioxide and aluminium oxide respectively, t is the thickness and  $\Delta V_{surf}$  is the change in surface potential before and after corona charging. The dielectric constant value used for the silicon dioxide and aluminium oxide are 3.9 and 7, respectively. The chosen values were based on literature for the same materials deposited at the same temperature and employing the same methods [50,51]. It should be noted that accurate, quantitative measurements of deposited charge onto a surface with the extreme features of a nano-texture is challenging and care should be taken in interpreting too much from the absolute numbers presented here.

The result in Figure 6 demonstrates that beyond a certain point, further generation of charge did not result in more charge deposited on the surface. Measurements of the surface voltage as a function of generated charge (Figure S1, summarised in Table S1) appear to confirm this. For the polished reference sample, the surface voltage increased linearly with the generated corona charge, reaching ~ 16 V with ~ 1800 nC/cm<sup>2</sup> of generated charge. In contrast, the nanotexture required a much higher amount of corona charge to increase the surface voltage as compared to the polished sample. After normalizing the amount of charge by  $f_{\text{surf}}$  (~ 4.19), the change in surface voltage shows a logarithmic relationship with generated charge as opposed to a linear relationship. Furthermore, the final saturated voltage only reached  $\sim 10$  V (below the 16 V of the planar sample). The amount of deposited charge on the polished sample calculated from surface voltage showed good agreement with the generated charge reported from the corona charger, until reaching  $\sim 16$  V where the dielectric layer may have started to become leaky. Applying the same calculation on the nanotexture yielded a final charge of  $4.96 \times 10^{12} \text{ cm}^{-2}$ , which is an order of magnitude higher than the initial number of charges in the ALD SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> stack however still less than that deposited on the polished sample.



Fig. S1. Evolution of surface voltage under corona charge deposition for polished sample (green squares) and reactive-ion etched sample before (blue circles) and after (cyan circles) surface area normalization

TABLE S1GENERATED AND MEASURED CORONA CHARGE ON PLANAR AND NANOTEXTUREDSAMPLE

Planar			Deep RIE			
Generated charge <sup>1</sup> (cm <sup>-2</sup> )	Deposited charge <sup>2</sup> (cm <sup>-2</sup> )	Relative ∆ (%)	Generated charge <sup>1</sup> (cm <sup>-2</sup> )	Deposited charge <sup>2</sup> (cm <sup>-2</sup> )	Relative ∆ (%)	
$1.87 \ge 10^{12}$	$1.78 \ge 10^{12}$	4.81	$1.34 \ge 10^{12}$	$9.73 \times 10^{11}$	27.3	
$3.75 \times 10^{12}$	$3.46 \ge 10^{12}$	7.73	$2.53 \times 10^{12}$	$1.78 \ge 10^{12}$	29.6	
$1.12 \times 10^{13}$	$8.40 \ge 10^{12}$	25	$4.91 \times 10^{12}$	$3.13 \times 10^{12}$	36.3	
\	\	\	$7.29 \ge 10^{12}$	$3.77 \ge 10^{12}$	48.3	
\	\	\	1.21 x 10 <sup>13</sup>	4.34 x 10 <sup>12</sup>	64.0	
\	\	\	$2.69 \times 10^{13}$	4.96 x 10 <sup>12</sup>	81.6	

<sup>&</sup>lt;sup>1</sup> Displayed from Semilab LCC-300 linear corona charger, <sup>2</sup> measured using kelvin probe in Semilab PV-2000A

One explanation for this difference in effective deposition of surface charge is the impact of the different surface morphology. Since the nanotexture has needle-like features, the initial generated charges might be deposited near the tips. As the corona charging proceeds, more charges may be localized in that same region and possibly create a shield to prevent subsequent charge from reaching the side walls and valley of the features. Therefore, the saturated surface voltage is much lower than in the case of the polished reference sample. Similar speculation has also been suggested in a study where post-annealing of an ALD layer (forming conformal negative charge) was found to provide better passivation than applying corona charge on silicon nano-wire prior to annealing [52]. Nevertheless, the non-linear corona charging effect and the interpretation of surface voltage on nanotexture requires improved understanding. This result has implications for the use of corona charging in the study of the quality of surface passivation layers formed on such extreme surface features, including the use of corona-based contact-less capacitance-voltage measurement for textured surfaces.

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