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SILICON SOLAR CELLS TEXTURED BY REACTIVE ION ETCHING WITH NATURAL LITHOGRAPHY

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ABSTRACT: Several groups have demonstrated that Reactive Ion Etching (RIE) can texture multi-crystalline silicon very well. Moreover RIE texturing can be integrated quite easily into existing process sequences. Whether this can be done cost effectively is still uncertain.

In this work we apply RIE etching after deposition of a mask. The mask is a well defined microscopic mask that is created by self-organised processes. The mask geometry and etch conditions can be varied to create different kinds of periodic textures. Using these techniques we achieved a reproducible and homogeneous RIE texture on full size multi-crystalline silicon wafers.

We achieved a .24% absolute efficiency gain by RIE over non-textured cells. RIE textured cells with an efficiency of 14.8% were made using an industrial type process sequence.

Keywords: Silicon - 1: Multi-Crystalline - 2: Texturisation - 3: RIE -4

1 INTRODUCTION

For improved efficiencies multi-crystalline silicon solar cells must be textured. Mono-crystalline (100) oriented wafers can be textured easily and cheaply in alkaline solutions. Alkaline solutions expose (111) crystallographic planes and produce pyramids on (100) oriented material. On multi-crystalline silicon, alkaline solutions are much less effective due to the varying crystallographic orientation.

For multi-crystalline silicon mechanical grooving is an interesting and possibly cost-effective texturing method. Etches based on HF-HNO₃, or more generally an oxidising agent with oxide removal by HF can texture multi-crystalline silicon [1]. These etches have several disadvantages. Defects and crystallographic boundaries are etched much faster than other areas. In addition these etch processes are hard to control and reproduce. Anodic oxidation ([2], [3]) can be controlled but may be difficult to implement on a large scale.

Several groups have demonstrated that Reactive Ion Etching (RIE) can texture multi-crystalline silicon very well. RIE has the advantage over alkaline etches that it is insensitive to the crystallographic orientation. RIE has the advantage over acid etches that it can be controlled more easily. Kyocera ([4],[5],[6]) reported 17.1% cell efficiency on RIE textured cells with evaporated metal contacts and emitter diffusion in tube furnaces. Recently Kyocera [7] reported 16.0% conversion efficiency on 15x15 cm² with a screen printing firing through scenario. In this paper however there is no direct comparison with non-RIE textured cells. Ruby [8] uses RIE after metallisation and elegantly combines a self-aligned emitter etch back with texturing. We used [9] RIE in combination with screen printing on multi-crystalline silicon wafers. Processing proved not to be a problem. However in that work the RIE equipment had limited capabilities, so that we were only able to process small numbers of cells and only a limited area of the cell could be textured.

In 1998, RWTH Aachen and ECN joined forces to upscale the process developed so far by ECN. Several options to do so are discussed in this paper, including a literature review on Reactive Ion Etching methods. Also, a possible industrial processing scheme will be discussed and results of first experiments according to this scheme will be presented, including the morphology of the texturisation and cell results. Suggestions for further improvements will be presented.





2 RIE TEXTURING

Reactive Ion Etching is widely used in micro-machining and micro electronic technology to etch well-defined structures into silicon or other materials. RIE [10] uses a gas flow discharge to dissociate and ionise relatively stable molecules forming chemically reactive and ionic species. The chemistry is chosen such that these species react with the solid to be etched (silicon in our case) to form volatile products. A widely used gas mixture in RIE consists of SF₆, O₂ and CHF₃. Figure 1 shows a schematic lay-out of a RIE reactor.



Figure 1: Schematic lay-out of a setup for Reactive Ion Etching.

In order to achieve texture with RIE two routes can be used. The first is to use so called automasking At certain etch conditions the RIE process itself creates a random mask [11]. This route is also known as the "Black Silicon Method" ([12]). We used this route in our own earlier work [9]. We believe that automasking may be difficult to achieve reliably on a larger scale.

Another approach is to combine RIE with some kind of masking process. Winderbaum [13] uses lithography of an SiO₂ layer. Zaidi [14] employs interferometric lithography.

We have looked into natural lithography [15]. In natural lithography self-organised processes are used to create a well defined mask. At RWTH Aachen a method has been developed in which a multi-crystalline wafer can be coated densely, uniformly and reliably with a mono-layer of small spheres. A dense hexagonal packing of the spheres is realised. The spheres can be used subsequently as a mask in a conventional RIE step. After RIE etching the spheres are removed. Using this technique we were able to achieve a reproducible and homogeneous RIE texture over a full size multicrystalline silicon wafer. This approach avoids the use of a more complex type of lithography. Figures 2 and 3 show two examples of the resulting textures.



Figure 2: Texture produced by RIE and natural lithography using recipe 3a



Figure 3: Texture produced by RIE and natural lithography using recipe 2b

3 PROCESSING

In figure 4 we present the process sequence used. Processing was carried out on 10x10cm² wafers. Sawdamage is removed by etching in a concentrated NaOH solution. We do RIE texturing after saw-damage removal prior to emitter diffusion. The experiment described here was a neighbour experiment with three groups of 15 wafers. The reference group had no RIE texture. The two other groups were textured with recipes 3a (2) and 2b (3), respectively. A phosphorous emitter of 50 Ω/\Box is diffused into the wafer in a belt furnace. We did expect some problems with the removal of the phosphorous glass since one might expect the glass to adhere more strongly to such microscopically textured surfaces. However no problems were encountered. A silicon nitride coating was applied at ISFH by remote plasma enhanced CVD. The front- and rear side metallisation is applied by conventional screen print-





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Figure 4: Process sequence used. The reference group was processed without RIE.

ing. The metallisation is fired through the silicon nitride. The processing on RIE textured cells was successful. The texture proved to be mechanically stable. We could use the same processing sequence as in our standard baseline process without any problems.

4 RESULTS



Figure 5: Reflection curves for wafers #6 of the three different groups

Figure 5 shows reflection curves of cells with- and without RIE texture. The RIE cells have a lower reflectance for all wavelengths.

Table 1 shows the average I-V characteristics of three groups of 15 wafers in an experiment with neighbouring wafers. Table 2 shows the differences of the neighbouring wafers with the standard deviations. The efficiency increase comes from an increase in short circuit current. Open circuit voltage and fill factor for the RIE cells are comparable to the reference groups. Ta-

Group	RIE	$I_{ph}(A)$	$V_{oc}(mV)$	FF	η
1	-	3.035	605	76.3	14.02
2	3a	3.105	605	76.2	14.26
3	2b	3.090	605	76.2	14.13

Table 1: Average I-V measurements of the 3 groups of 15 cells

Group	RIE	I_{ph}	V_{oc}	FF	η
2	3a	+.05(.03)	-0.3(1)	1(.8)	+.24(.2)
3	2b	+.04(.02)	-0.2(1)	1(1)	+.11(.2)

Table 2: Difference of RIE groups with the reference groups

ble 3 details the calibrated I-V results of the best two neighbour sets.

Figure 6 gives the relative internal quantum efficiencies. It is clear that the cells with the RIE texture have a reduced quantum efficiency compared to the reference group for wavelengths below 500 nm. There may be several reasons for this:

Recombination of carriers generated in the needles Short wavelength light is absorbed in the first few nanometers. Carriers generated here have a large chance of recombining at the surface of the needles and will not reach the p-n junction.

- **RIE induced damage** One problem with RIE may be that the energetic ions can introduce damage in the silicon material. This may be another reason for the reduced IQE at short wavelengths. One future direction of research is to look into RIE recipes that induce less damage [16].
- **Highly doped needles** Perhaps the needles become very highly doped during diffusion. This does not manifest itself in a reduction of the sheet resistance since the needles do not contribute to the lateral sheet resistance. High doping may reduce the diffusion length for minorities generated in the needles.

5 CONCLUSIONS

Reactive Ion Etching can be integrated quite easily in a standard process sequence. We achieved an efficiency

Group	RIE	I_{ph}	V_{oc}	FF	η
1#5	-	3.090	609.4	77.3	14.55
2#5	3a	3.162	608.4	77.1	14.84
1#9	-	3.072	612.9	77.1	14.51
2#9	3a	3.152	611.9	76.4	14.74

Table 3: Calibration measurements of 4 best cells



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Figure 6: IQE relative to group 1 for wafers #5 of groups 2,3

gain in our lab by RIE of .2%. 10x10cm² cells with a conversion efficiency of 14.8% have been obtained. A good quality nitride coating appears to be essential to obtain an efficiency gain since in an accompanying experiment with a low-frequency PECVD batch reactor we did not see an efficiency gain.

We do see a reduction in internal quantum efficiency for short wavelengths. We see two possible routes to improving the IQE. One route is to use RIE etch conditions that give less crystallographic damage. Another route is to use emitters of higher sheet resistance in combination with good surface passivation.

An interesting question is whether RIE texturing is upscalable and how upscaling of RIE compares to mechanical grooving. Kyocera [6] plans to have a RIE reactor with sufficient throughput available this year. Surface passivation with Plasma Enhanced Chemical Vapour Deposition (PECVD) is a process comparable to RIE in the sense that it involves vacuum technology and plasmas. For PECVD high throughput equipment is becoming more widely available. In our process sequence RIE and nitride deposition are not performed consecutively. If RIE and PECVD could be combined into a single reactor however, the RIE process may well be cost effective.

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REFERENCES

- D. Sarti, Q.N. le, S. Bastide, G. Goaer, and D. Ferry. 13th EC Photovoltaic Solar Energy Conference, Nice, France, pages 25–8, 1995.
- [2] S. Bastide and S. Strehlke. 13th EC Photovoltaic Solar Energy Conference, Nice, France, pages 1280–3, 1995.
- [3] A. Krotkus and K. Grigoras. Solar Energy Materials and Solar Cells, 45:267–273, 1997.
- [4] Y. Inomata, K. Fukui, and K. Shirasawa. Solar Energy Materials and Solar Cells, 48(1-4):237– 42, 1997.
- [5] K. Fukui, K. Okada, Y. Inomata, H. Takahashi, S. Fujii, Y. Fukawa, and K. Shirasawa. Solar Energy Materials and Solar Cells, 48(1-4):219–228, 1997.
- [6] K. Shirasawa, K. Fukui, K. Okada, Y. Inomata, H. Takahashi, and S. Fujii. 14th EC Photovoltaic Solar Energy Conference, Barcelona, Spain, pages 384–387, 1997.
- [7] S. Fujil, Y. Fukawa, H. Takahashi, Y. Inomata, K. Okada, K. Fukui, and K. Shirasawa. 11th Int. Photovoltaic Science and Engineering Conference, Sep. 20-24, 1999, Sapporo, Japan, Technical Digest, 1999.
- [8] D.S. Ruby, P. Yang, S. Zaidi, S. Brueck, M. Roy, and S. Narayanan. Second World Conference on Photovoltaic Energy Conversion, Vienna, 1998, pages 1460–63, 1998.
- [9] A.R. Burgers, C.J.J. Tool, J.D. Hylton, A.W. Weeber, A.G.B.J. Verholen, J.G.E. Gardeniers, M.J. de Boer, and M.C. Elwenspoek. 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion, Vienna, 1998, pages 1531– 34. 1998. ECN-RX-98-037.
- [10] Henri Jansen, Han Gardeniers, Meint de Boer, Miko Elwenspoek, and Jan Fluitman. J. Micromech. Microeng., 6:14–28, 1996.
- [11] R. Lüdemann, S. Schaefer, U. Schubert, and H. Lautenschlager. 14th EC Photovoltaic Solar Energy Conference, Barcelona, Spain, pages 131–134, 1997.
- [12] Henri Jansen, Meint de Boer, Rob Lichtenberg, and Miko Elwenspoek. J. Micromech. Microeng., 5:115–20, 1995.
- [13] S. Winterbaum, O. Reinhold, and F. Yun. Solar Energy Materials and Solar Cells, 46(3):239– 248, 1997.
- [14] S.H. Zaidi and S.R.J. Brueck. 26th IEEE Photovoltaic Specialists Conference, Anaheim, United States, pages 171–4, 1997.
- [15] H. Deckman and J. Dunsmuir. Appl. Phys. Lett., 41(4):377 – 379, 1982.
- [16] S. Schaefer and R. Lüdemann. J. of Vac. Sci. and Technol. A, 17(3):749–54, 1999.

