Presented at the 26th European PV Solar Energy Conference and Exhibition, 5-9 September 2011, Hamburg, Germany

INCREASED ION ENERGIES FOR TEXTURING IN A HIGH-THROUGHPUT PLASMA TOOL

Peter Piechulla, Johannes Seiffe, Marc Hofmann, Jochen Rentsch, Ralf Preu
Fraunhofer Institute for Solar Energy Systems (ISE), Heidenhofstrasse 2, D-79110 Freiburg, Germany
Tel: +49-761-4588-5654. Fax: +49-761-4588-9250, email: peter.michael.piechulla@ise.fraunhofer.de

ABSTRACT: Plasma texturing is a promising alternative to wet chemical texturing of solar cells. Processes using increased ion energies have previously been shown to be advantageous on single wafer tools. In this work, the microwave plasma of an inline tool is enhanced by a radiofrequency field, which leads to a DC self bias and thus increased ion energies. A high-throughput process suitable for monocrystalline cells has been developed and characterized by weighted reflection and excess carrier lifetime on float zone material. Additionally, experiments on shiny etched wafers with <111> and <100> orientation have been shown to be a promising approach to finding parameters for etching independent of crystal orientation.

Keywords: dry etching, plasma texturing, lifetime, inline processing, crystal orientation, isotropic etching, microwave, RF plasma, RIE

1 INTRODUCTION

Creating light trapping structures on the surface of a solar cell is an effective way to increase its efficiency and thus to reduce the costs per watt-peak. Up to now, mostly acidic or alkaline wet chemical etching processes were used for texturing, namely potassium hydroxide (KOH) and isopropanol (IPA) for crystalline silicon or nitric acid (HNO_3) and hydrofluoric acid (HF) for multicrystalline silicon. Usually the damage resulting from wire sawing is removed in the same step. These wet chemical texturing processes have several flaws for current as well as for future solar cell technologies and production schemes:

1) Acidic solutions do not produce satisfactorily low values for reflection.
2) Alkaline solutions depend on crystal orientation, so they can only be applied on monocrystalline silicon.
3) Creating a texture only on one side of a wafer, as is preferable for rear-passivated cells, is difficult.
4) Acidic texturing depends on a roughness resulting from saw damage, which may not be present when new wafering techniques are used.
5) Concentrations of chemicals in the etch baths change over time and large amounts of deionised water are consumed.

A mask-free plasma texturing process is a way to overcome these drawbacks. However, for an industrial production line, only high-throughput inline or batch plasma tools are attractive. The texturing process can be combined with other plasma processes, such as PECVD of a dopant source, in the same plasma tool.

Many articles have been published on plasma texturing processes on single wafer tools as well as on inline plasma tools (for example [1-4]). Most authors used a mixture of sulfurhexafluoride (SF_6) and oxygen as process gasses and low ion energies when using inline tools. The addition of oxygen to the plasma leads to formation of SiO_xF_y adsorbate layers and causes the self-masking effect necessary for texturing [5].

Low ion energies are advantageous in terms of low defect rates on the surface. On the other hand, ion energy has been proved to be a useful parameter to increase etch rates and control the texture features' size and aspect ratio on single wafer tools. In this work, the use of increased ion energies for texturing is investigated on an inline plasma tool. Articles about texturing on single wafer tools have been a source of inspiration, but parameter sets can not just be transferred to an inline tool. Inline tools are different from single wafer tools in many ways. For example parameters such as the temperature or electrical grounding of samples are hard to control due to the fact that samples are placed on a moving carrier for the etching process.

In this work the advantages of both low and variable ion energy are combined in a two step process. In the first step, samples are textured in an RF-enhanced microwave plasma. In a second step, the surface damage is reduced by etching in a pure microwave plasma, without leaving the vacuum chamber between steps.

2 EXPERIMENTAL

Experiments in this work have been performed in a modified semi-inline SiNA system by Roth&Rau. A linear copper antenna is used for plasma excitation over a width of 0.9 m, using microwaves of 2.45 GHz (Figure 1).

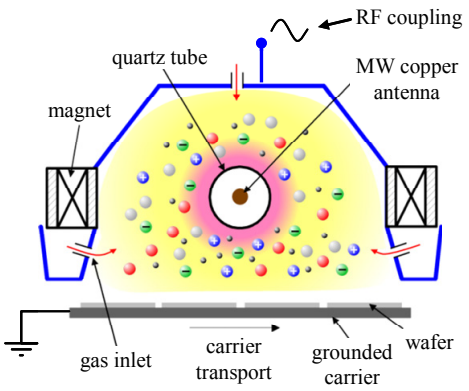

Figure 1: Cross section of a linear microwave plasma source with additional RF excitation

Additionally, a 13.56 MHz radio frequency field is capacitively coupled to the source's enclosure. The carrier serves as grounded electrode, so that a positive plasma potential is established. To give an idea of the kinetic energies of ions incident on the samples, measurements with a retarding field analyzer have been performed. The results are presented in Section 3.

Saw-damage-free float zone wafers with (100) crystal orientation were used for this work. The wafers were textured on only one side. The process sequence is displayed in Figure 2. The etch time given in the RESULTS section is the time needed for one point on the carrier to pass the plasma source at a certain carrier velocity. For the two step processes, the process is stopped in between and the carrier is returned to the initial position, without leaving the vacuum. Spectral reflection has been measured using an integrating sphere (Varian Cary 5000) and then weighted with the AM1.5 spectrum and the internal quantum efficiency (IQE) of typical cells [6]. For electrical passivation of the surface, a stack of silicon-rich oxynitride (SiON) and a SiN_x capping layer is applied on both sides (SiriON stack [7]).

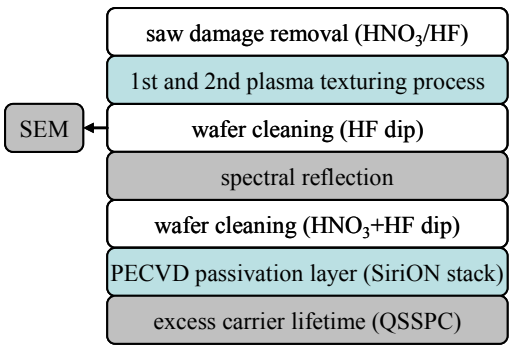

Figure 2: Process sequence for samples in this work

Untextured reference samples as well as KOH-textured samples have been passivated for comparison of excess carrier lifetimes. These were measured via QSSPC, using the generalized method described by Cuevas et al [8].

For the entire plasma texturing process, oxygen content, overall gas flow, pressure and microwave power have been kept constant. The plasma texturing process was separated in two parts, both applied sequentially without leaving the vacuum. In the first step of the process RF power has been varied, while carrier velocity (process time) has been kept constant. For the second step, only microwave excitation has been used and carrier velocity has been varied.

As mentioned above, temperature of samples is hard to control when using the inline plasma tool. Measurements using change-of-state sensors have been made. These sensors are labels that change their colour when a certain temperature is exceeded. Temperatures of over 100° C have been measured for a sample being exposed to the plasma for only 15 seconds.

3 MEASUREMENT OF ION ENERGY

To characterize the conditions in the RF-enhanced microwave plasma, a retarding field analyzer was used. This device was centrally arranged under the plasma source (see Figure 1) surrounded by wafers so that it is exposed to the same conditions as a sample. The process parameters were the same as in the experiments for this work.

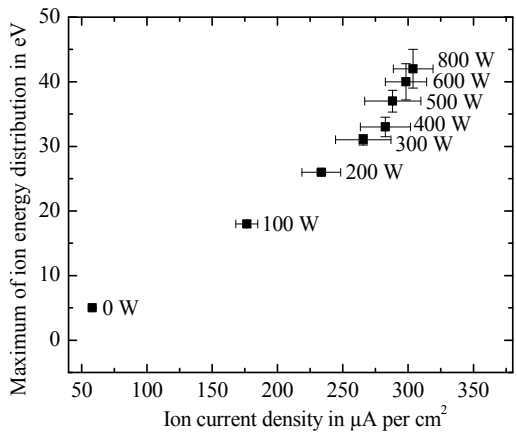

Figure 3: Ion current density and ion energy for various power outputs of the RF generator. The 0 W value has been arbitrarily set to 5 eV in this graph since the ion energy distribution has its maximum at 0 eV and is decreasing to 0 within 10 eV.

As can be seen in Figure 3, both ion energy and current increase with RF power output. For higher RF power outputs the differences are quite small.

4 RESULTS

In Figure 4 (top), weighted reflection values are displayed over etch time for various RF power outputs. After being exposed to the RF-enhanced plasma for 120 s, the samples show different reflection values than those etched without RF. The results are sensitive to even small changes in ion energy, considering the results from section 3. For example the difference in ion energy between 400 W and 600 W power output is rather small, while differences in reflection are bold. However, there is

no clear tendency indicating that better textures are produced at higher RF power outputs.

As mentioned above, electrical grounding of samples is an issue. Repeatability may be considered in this context (Figure 4, bottom). From Figure 3 one can find that the ion current density is much lower for MW excitation only. This implies that proper grounding of samples is not as important as for higher RF power outputs. Longer etch times for the second etching step (MW only) thus lead to better repeatability.

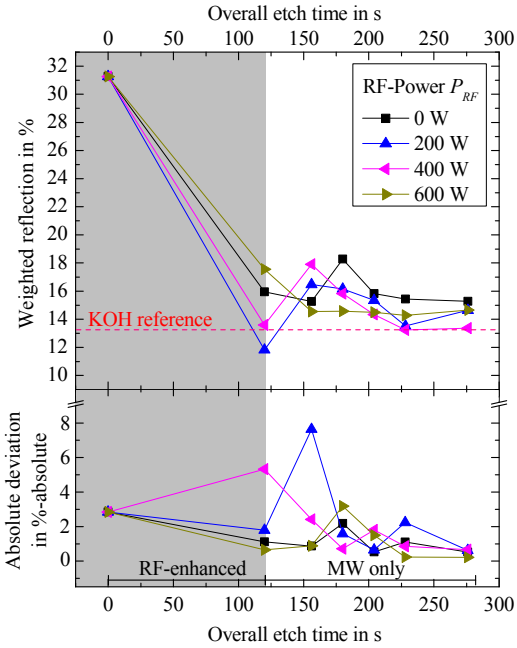

Figure 4: Weighted reflection (top) and absolute deviation (bottom) over etch time for various RF power outputs, starting with saw-damage-free surfaces. After 120 s only MW excitation is used.

Especially for 200 W and 400 W the weighted reflection drastically increases after 120 s when samples are etched with MW excitation only. SEM pictures indicate that a fine needle-like structure is present on the surface which is removed when process conditions are changed (Figure 5). A concurrent effect may be due to the fact that the process is stopped at 120 s. Hence, the reaction equilibrium of deposition and etching of adsorbate layers is disturbed. This explains why reflection also increases for the 0 W trace in Figure 4.

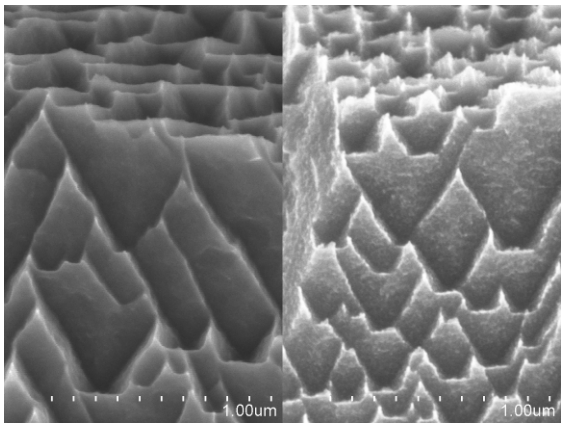

Figure 5: Fine overlaying structure when etched with RF enhancement (right) and cleaner structure after second etching step (left). The SEM acceleration voltage was 5 kV, the working distance was 10.9 mm.

Even after longer etch times for the second step without RF, a more effective structure for reduction of reflectance is created. The weighted reflection reaches values down to about 13 %, which are similar to those of KOH-textured surfaces. In Figure 6, reflection and corresponding lifetime values are displayed for the same samples. Electrical properties of the surface are restored within 60 s when etching with MW excitation, whilst low reflectance is reached after longer etch times.

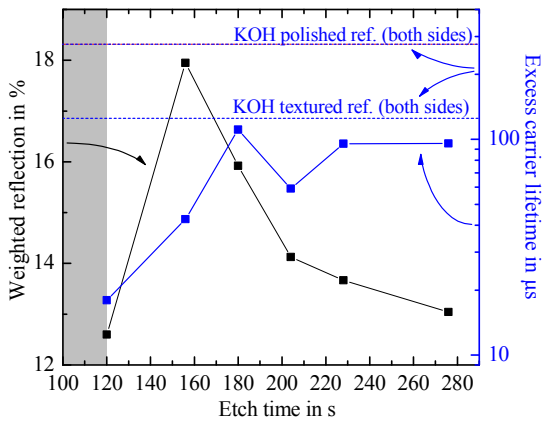

Figure 6: Weighted reflection and excess carrier lifetime in the second etching step. The samples have previously been etched for 120 s at 400 W RF.

For comparison, KOH damage-etched Czochralski and multicrystalline samples, as well as HNO_3/HF-etched samples have been plasma-textured (Figure 7). The reflection values are similar for KOH and HNO_3/HF-etched samples when RF enhancement is used. For multicrystalline samples, the values are slightly higher than for <100> silicon.

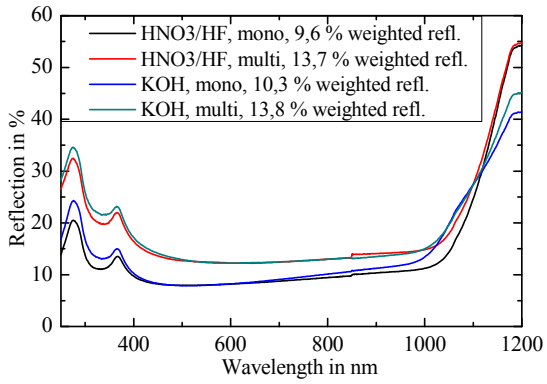

Figure 7: Spectral reflection when mono- or multicrytalline and acidic or alkaline damage etched material is plasma textured subsequently.

The traces for KOH and HNO_3/HF damage etched samples are of similar shape, except for the infrared region. This is probably due to reflection on the rear side.

5 OUTLOOK

As can be seen in Figure 5, the structures are not entirely random. Though plasma etching is often assumed to be independent of crystal orientation, this does not apply here. Similar to a KOH-texture, <111>-planes are preserved and inverted pyramids are formed. Yet, this process and related processes have been proved to work on multicrystalline silicon, which is probably due to the smaller dimensions of structures compared to KOH-textures [2]. At small dimensions, the shape of a structure becomes less important for its optical properties. On the other hand, for increasingly small structures with low aspect ratio, optical properties approach those of a polished surface [9]. Hence, larger structures and processes independent of crystal orientation are desirable. Results of Moreno et al. indicate that sufficiently high ion energies can lead to etching independent of crystal orientation [10]. Figure 8 shows the results of an approach with higher ion energies using the inline tool.

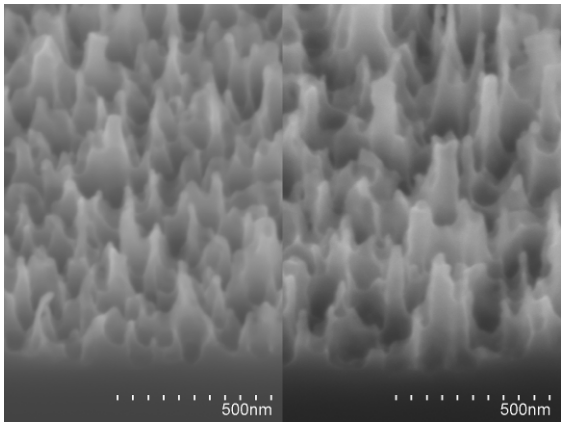

Figure 8: Structures created on shiny etched <100> wafers (left) and <111> wafers (right) created at higher ion energies on the inline tool (800 W RF power output). The SEM acceleration voltage was 5 kV, the working distance was 14.7 mm.

This leads to needle-like structures with reflection values as low as 3 %, similar to "Black Silicon" as described by Jansen et al [5]. Formation of structures does not seem to depend on crystal orientation. However, these structures are too fragile for use in solar cells. Effective electrical passivation and screen-printing of contacts would prove difficult.

6 SUMMARY

So far, a process has been developed that produces surfaces of low reflectance on monocrystalline silicon (13 %) and acceptable electrical properties (96 µs for one side of the sample being textured). Relatively low etch times of about 3 minutes allow industrial scale throughput in principle when 18 plasma source pairs would be used leading to approximately 3600 wafers per hour. In another approach, it has been shown that higher ion energies allow etching independent of crystal orientation, which is a promising perspective for multicrystalline silicon.

7 ACKNOWLEDGMENTS

The authors would like to thank Rainer Neubauer for the wet chemical cleaning, as well as Jutta Zielonka and Katrin Birmann for their support in taking SEM pictures.

This work has been supported by the German Federal Ministry of Education and Research (BMBF) under contract no. 13N11838.

8 REFERENCES

[1] H.F.W. Dekkers, et al., Proceedings of the 17th European Photovoltaic Solar Energy Conference, Munich, Germany (2001) 1678.

[2] J. Rentsch, et al., Proceedings of the 31st IEEE Photovoltaic Specialists Conference, Orlando, Florida (2005) 1316.

[3] H.F.W. Dekkers, et al., Proceedings of the 19th European Photovoltaic Solar Energy Conference, Paris, France (2004) 412.

[4] D.S. Ruby, et al., Solar Energy Materials and Solar Cells 74 (2002) 133.

[5] H. Jansen, et al., J. Micromech. Microeng. 5 (1994) 115.

[6] W. Sparber. in Fachbereich Technische Physik, pp. 113, Technische Universität Graz, Graz 2003.

[7] J. Seiffe, et al., Journal of Applied Physics 109 (2011) 034105.

[8] A. Cuevas, et al., Solar Energy 76 (2004) 255.

[9] F. Llopis, et al., Progress in Photovoltaics: Research and Applications 13 (2004) 27.

[10] M. Moreno, et al., Solar Energy Materials & Solar Cells 94 (2010) 733.