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LASER ASSISTED HONEYCOMB-TEXTURING ON MULTICRYSTALLINE SILICON FOR INDUSTRIAL APPLICATIONS

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ABSTRACT:
In this study we investigated a manufacturing process for Honeycomb-texturing. An optimized masking dielectric layer, the opening of the mask via laser and an industrially applicable under-etching process lead to a homogeneous hexagonal structure with etch holes of 15 µm depth and a width of 31.5 µm. The reflection is dependent on the honeycomb structure or the surface roughness. It has been shown that by a short etching time the honeycomb texture is not completed, the surface is covered with too small honeycomb cavities; the unetched surface contributes with a reflection of 23 % to an increased total reflection at the surface. An optimum by etching time of 78 s (minimum reflection) was achieved, with a honeycomb width W_d = 31.5 µm and a depth honeycomb W_h = 15 µm, which lead to the best reflection of 17.5 % and even the highest lifetime of 604 µs after passivation.

Keywords: Honeycomb-texture, single side texture, multicrystalline silicon, Etching, Laser ablation, dielectric layer

1 INTRODUCTION

Multicrystalline silicon solar cells have a high market share in the production volume of solar cells because of its low cost combined with quite high reachable energy conversion efficiency.

One of the essential tasks of a texture is to reduce the reflection of light via multiple reflections of rays at outer surfaces of the wafer. Industrial-standard acidic textured surfaces on multicrystalline substrates still have a relatively high reflection value between 30 % and 23 % [1]. This type of texture is created using an isotropic etching process in an acidic solution of hydrofluoric acid (HF) and nitride acid (HNO_3). A low reflection value is accompanied by a rough surface, which leads to a low surface passivation quality. Achieving low reflection values while keeping the surface area low remains one of the main issues of multicrystalline solar cells. A method to lower the reflection is by utilizing a Honeycomb (HC)-texture instead of the standard isotropic acidic texture. These textures can be created in various ways, for example by masking with lithography [2], Inkjet [3][4], Nanoimprint [5] or by direct laser ablation texturing [6] and consecutive etching.

The main focus of this paper is a detailed description of the fabrication process for the laser assisted Honeycomb-texture. We give an insight into the mask fabricated followed by a detailed analysis of the development of the honeycomb morphology during the etching. The first part of this paper deals with the application “single side” wet chemical etching processes to produce HC-texture. To achieve an optimal surface morphology of a HC-texture, a variation of etching times was performed.

The next step was to analyze the honeycomb-texture morphology by different etching times.

Characterization methods of the surface morphology of HC-texture morphology were based on Scanning Electron Microscope and a Laser Scanning Microscopy. To analyze the surfaces weighted reflection, a spectral photometer with integrating sphere is used. In this context it was examined how the different honeycomb structures affect the surface reflection.

In order to assess the quality of the passivation, we prepared passivated samples to measure carrier lifetime and thus get information about the passivation quality.

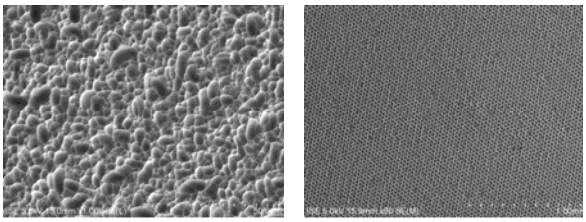


Figure 1: SEM picture of a multicrystalline silicon wafer

Comparison of an acidic etched surface morphology (left) and a honeycomb surface morphology (right) on a multicrystalline silicon wafer (fig. 1).

2 FABRICATION OF HONEYCOMB-TEXTURE

The experiments were performed using p-type mc silicon wafers with an area of 156 x 156 mm², a thickness of 200 µm and with a resistance of 3 Ωcm. The basic process flow for the generation of the used honeycomb-structure is shown in figure 2.

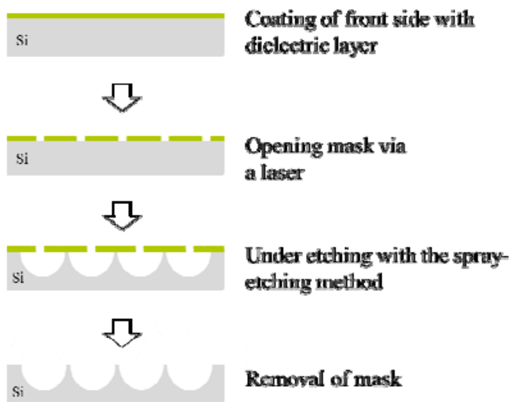


Figure 1: Process flow for fabrication the honeycomb-texture with laser ablation

After a full-area coating of the wafer with the masking layer, the layer is partially opened using a picosecond-laser system. The following chemical etching leads to the final structure of etching holes, which become visible after the removal of the masking layer.

2.1 Masking layer

The front side of the wafer was coated with a PECVD-silicon nitride with a thickness of 200 nm. In previous experiments, we compared sputtered silicon nitride layers with PECVD layers. Concerning the compatibility to the used etching solution, there was no difference but due to the significant higher etching rate of PECVD silicon nitride in pure HF, used in the mask removal process, the PECVD process was used.

2.2 Laser technology

The laser that was used to ablate the mask is a Lumera Super Rapid with a pulse duration of 12 picoseconds and a wavelength of 355 nm.
The laser process was optimized for the masking layer to provide reproducible openings of minimal diameter. The primary laser parameters for the HC-texturing process are summarized in Table 1.

Table I: Laser ablation parameters for etch resist structuring.

Wavelength	355 nm
Power	200 mW
Pulse repetition frequency	50 kHz
Pulse duration	10 - 12 ps

A hexagonal structure was created by local removal of the full-area masking layers by means of laser ablation. The depth and the width of the opened holes were measured with confocal microscopy.

2.3 Chemical Etching systems

In this paper we used an inline etching tool, where the wafers were transported horizontally while they were sprayed with the etching solution. During the etching process a thin film of etching solution is deposited on the front side of the wafers.
For the wet chemical treatment, a mixture of HF (40 % (w/w)) and HNO_3 (69 % (w/w)) (1:4) at room temperature was used. A solution from the HNO_3-rich regime was selected in order to avoid a rough texture inside the honeycombs structure as it could appear for HF-rich solutions. This acidic solution etches very quickly and is often used for polishing. The isotropic etch mechanism etches all crystal planes with the same etch rate and thus forms the hemispherical wells [9].
For the inline spray-etching, a spray system has been developed ensuring a controllable mask under-etching in order to form the honeycomb surface structure. To achieve an optimal surface morphology of a HC-texture, a variation of etching times was performed.

2.4 Mask removal

Following the under-etching process, the wafers were immersed in a solution of buffered hydrofluoric acid at room temperature and etched for 10 min using manual agitation. They were then removed from the solution, rinsed in DI water and dried with nitrogen.

2.5 Surface characterization

The surfaces morphology of the HC-textured wafers was characterized by confocal microscopy, weighted reflection and scanning electron microscopy (SEM). The weighted reflection was measured before and after the under etching process.
The reduction of reflection was characterized by measuring the effective reflection as defined in equation (1)

$$R_{eff} = \frac{\int_{250}^{1200} R(\lambda)N(\lambda)d\lambda}{\int_{250}^{1200} N(\lambda)d\lambda} \qquad (1)$$

where $R(\lambda)$ is the total reflection , $N(\lambda)$ the number of photons incident on a unit area for a given wavelength in one second for the solar spectrum AM1,5.

2.5 Minority Carrier lifetime samples

Lifetime samples of different texturing schemes were prepared to evaluate charge carrier lifetime effects of the HC-texture.
For the lifetime experiment, as-cut float zone (Fz-Si) p-type wafer with a thickness of 250 µm and a bulk resistivity of 3 Ωcm were used. The samples were produced asymmetrically since the spray process can be applied only on one side.
The first group was a reference group textured with the standard acidic texturing process at Fraunhofer ISE. This group will be used to benchmark the performance of the honeycomb lifetime samples. The second group contained samples with a HC-texture, which was created using a masking SiNx layer.
Then all groups were cleaned and subsequently deposited with a PECVD stack of silicon-rich oxynitride (SiriON) [7] and a SiN_x capping layer on both sides. The resulting effective carrier lifetime of honeycomb-textured samples has been determined by means of quasi steady state photoconductance (QSSPC) [11] technique at an injection level of $\Delta n = 1*10^{15}$ cm^{-3}. Figure 6 shows the process flow.

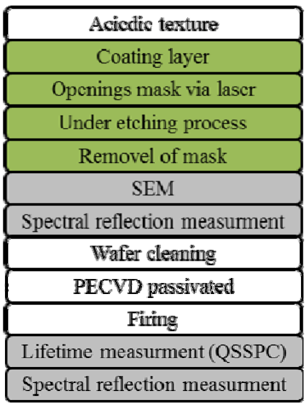


Figure 6: Process scheme for lifetime samples in this work.

3 RESULT

The first experimental part was to characterize the spot diameter after ablation. The homogeneity of the hexagonal pattern and the resulting spot diameter was analysed using confocal microscopy. The important feature is a triangular alignment of the etch pits to achieve a good surface coverage when the etching is completed. The analysis has revealed that the triangles were equilateral. The triangles should have an angle of 60 °. Figure 2 show that an angle of 60 ° ± 1.04 ° could be reached.

The average distance between the holes (number of measurements n = 33) was 34.3 µm ± 1.5 µm the measurement was carried out at the center of the circle described by the opening in the mask. The images show a homogeneous hole pattern, with uniformly distributed openings (fig. 2) of 8.0 µm. The standard deviation of the holes diameters was calculated to be of ± 0.3 µm (n=11). In conclusion, we can say that a homogeneous hexagonal pattern was fabricated with the laser ablation process. The homogeneous hexagonal pattern is an important point for the further process step.
Figure 2 shows a confocal microscopy image of a SiN_x mask on multicrystalline silicon wafers after laser ablation.
With irregularities in the laser pattern, the honeycomb cannot grow together optimally, which can increase the reflection of the texture by the under etching process.

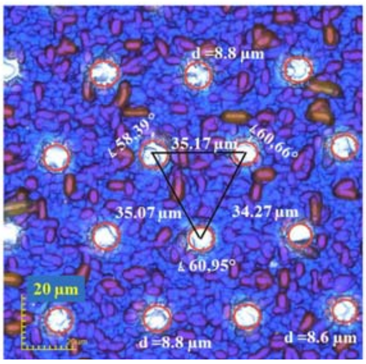


Figure 2: Optical microscopy image of a laser-patterned SiN_x layer after laser ablations process. A good regularity of the pattern can be seen. A spot diameter of d = 8 µm was achieved.

3.2 Characterization of the surface morphology
The next characterizations step is to analyse the weighted surface reflection and the aspect ratio of the resulting texture after different etching times.
The aspect ratio is an important parameter for the honeycomb morphology. Nishimoto [8] comes to the conclusion that reflection of an isotropically etched structure which consists of spherical segments depends strongly on the aspect ratio

$$A = \frac{h}{d} \qquad (2)$$

with the height h and width d. The minimal reflection is reached for A = 0.5. For perpendicularly incident light of 600 nm the surface reflection is then reduced to 15 % [8].
The investigation of the weighted reflection by different etching times has revealed the following correlation between etching time and weighted reflection, shown in Figure 3 (reflection and aspect ratio) and Figure 4 (SEM-pictures). For the shortest etching time the honeycomb-texture was not yet fully developed, the area covered with etch holes was too small; shown in fig. 4a. The honeycomb morphology has a width of ~21 µm and holes depths of ~11 µm. The etch holes area is too small, the unetched surface still covers 82.9% of the surface and contributes with a reflection of 29% to an increased total reflection of the surface.

An excellently formed honeycomb structure was obtained at an etching time of 78 s, where an aspect ratio of 0.5 could be achieved. The weighted reflection of 17.5 % (at a wavelength of 600 nm on multicrystalline silicon) is hence considerably lower than most other honeycomb-textures (see picture 4 c).The etch holes have a depth of 15 µm and a width of 31.5 µm.
A lower aspect ratio of 0.2 was achieved using an etching time of 144 s, which causes the reflection to increase to 29 % as can be seen in Figure 3. The reason for the low aspect ratio is that the neighboring holes overlap and the inclined area is partially lost (see picture 4d). The surface is now dominated by nearly flat regions in the middle of the etching holes and gently sloping parts in the region, where the etching holes overlapped.

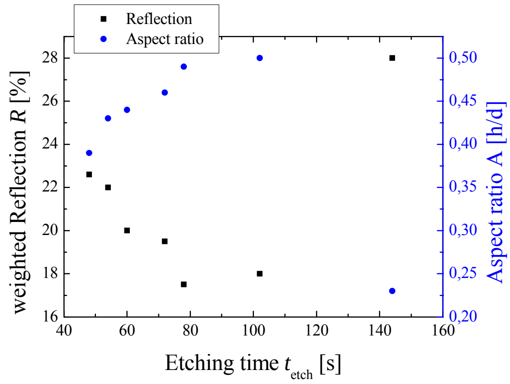
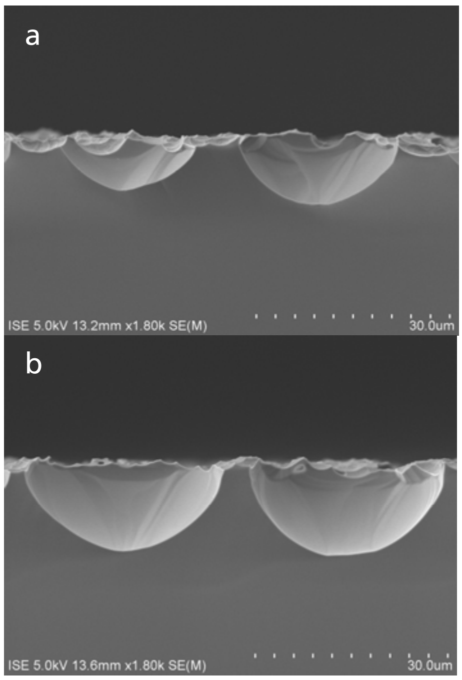


Figure 3: Weighted reflection vs. the etching time of the samples and the aspect ratio of the under etching holes. The squares symbols show the reflection after etching process. The circles symbols describe the weighted reflection after the spray-etching process.

SEM pictures of the resulting textures are shown in figure 4. The images show the differences in surface morphology caused by different etching times. The samples are the same samples as in fig. 3.



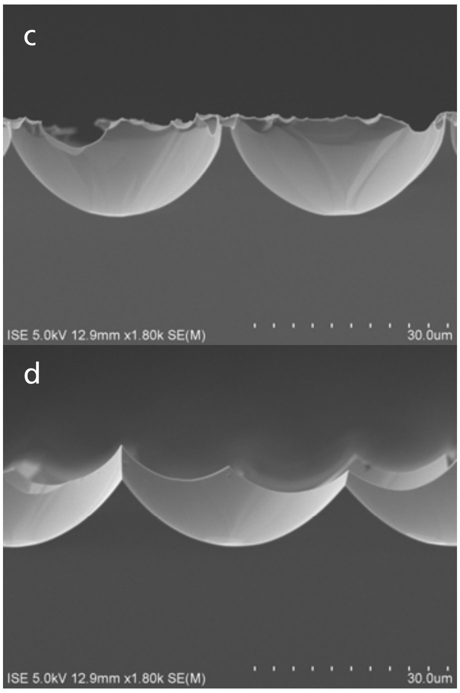


Figure 4: SEM images of the honeycomb-texture with the hexagonal structure samples after etching process. For manufacturing the honeycomb texture various etching time (a) t_{ech}=48 s, (b) t_{ech}= 60 s, (c) t_{ech}= 78 s, (d) t_{ech}= 144 s were used.

3.4 Excess carrier lifetime results

Figure 7 shows the lifetime results of passivated samples with HC-textures using different etching times as well as that of a reference with an acidic texturization. The lifetime results illustrate that the final silicon surface is free of measurable laser damaged material.

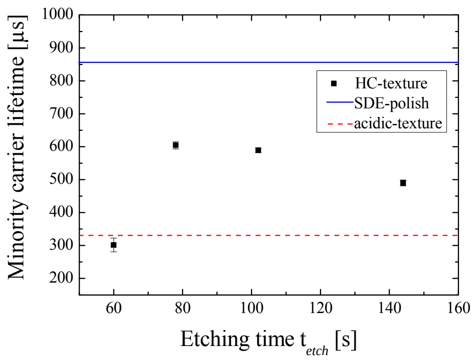


Figure 7: Investigation of different etching times for the manufactured HC-textured process with subsequent SiriOn deposition on asymmetrically processed lifetime test samples (p-type Fz-Si wafer, 3 Ωcm, and thickness 250 µm). For comparison, an acidic texture sample was used. The lifetimes were measured after firing step at an injection level of with $\Delta n = 1{*}10^{15}$ cm^{-3}QSSPC [10].

The measurement was performed on four measurement points in the middle of the wafer surface. From the measured lifetime values the mean value was calculated. Compared to the reference, the honeycomb lifetime samples show significantly higher lifetimes, shown in Figure 7.

Using an etching time of 78 s, which lead to the best reflection value, the highest lifetime of 604 µs was achieved. The reason might be the better passivation of the microscopically smoother surface in the honeycombs and better accessibility to the coating process since there are no deep trenches which often arise on acidic textured surfaces. The lifetime at an etching time of 60 s which was found to be etched too shortly, can be explained with the unfinished honeycomb structure as shown in Figure 4b. While the surface is covered to 82.9 % with smooth honeycomb structures, the remaining17.1 % covered with an acidic texturization dominate the passivation quality of the surface. Regarding the overetched sample (etching time: 144 s), the surface passivation quality stays unchanged, since the surface is still covered with a smooth structure.
As conclusion, it can be stated that the honeycomb texture can be better passivated due to the smoother surface morphology compared to the acidic texture.

4 SUMMARY

In this paper, we presented a process route to a honeycomb-texture by means of silicon nitride masking, laser structuring, etching in HF/HNO_3 and mask removal with buffered HF.
It was found that the laser processing produces a homogeneous hexagonal pattern which is an important point for the quality of the applied texture.
The etching process can be adjusted to optimize the honeycombs surface morphology. A homogeneous honeycomb-structure with a low etching time of less than 80 seconds could be achieved. It was found that selecting a longer etching time the honeycombs overlap and therefore result in a high reflectivity; while a shorter etching time results in a only partially covered surface with even higher refection.
Conducted lifetime measurements show that the incomplete texture leads to a significant lower passivation quality that the samples that were completely covered with honeycombs.
The optimal etched samples as well as those, where the overlapping etching structures form a higher reflecting surface showed significant higher lifetimes of 590 - 600 µs, which is nearly the mean value between the lifetime of an acidic textured sample (334 µs) and that of a shiny etched sample (850 µs).

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