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Hybrid laser-etching-process for wafer texturing

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Abstract

An approach of a texturing process combining surface modification by ultra-short pulsed laser radiation and etching techniques is developed. The hybrid process is divided into two steps: Firstly, the surface of a silicon wafer is modified by laser radiation. For this purpose, the influence of several laser parameters, e.g. wavelength, pulse duration and energy density, have been analyzed. Secondly, the surface texture is fabricated by an etching process. The modification threshold of the laser treatment is determined for different silicon materials. Different surface modifications occur for different materials after applying the laser treatment. No significant influence of the pulse duration or focus radius is found. Furthermore, the influence of laser processing and plasma etching on reflectivity spectra is compared and interactions between laser and etching parameters are investigated. The developed hybrid process results in smooth and fine surface microstructures. First results show a reduction of the reflectivity in the range of 30% compared to the reflectivity of unstructured wafers.

Keywords: Laser; Etching; Plasma; Diamond wire; Silicon wafer; Texture; Surface; Reflectivity; Light trapping

1. Introduction

The development of a silicon wafer texturing process combining laser modification by ultra-short pulsed (USP) laser radiation and etching techniques aims for low reflectivity at the silicon surface. The light trapping properties will be improved by an optimized microstructure. The development of this process aims to enhance the use of diamond wire slicing in silicon solar cell production.

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The hybrid laser-etching-process developed in this work is divided into two steps: Firstly, the surface of a silicon wafer is modified by laser radiation. The influence of several laser parameters will be analyzed. Wavelength, pulse duration and energy density of the laser radiation are expected as key parameters. Secondly, the surface structure is finalized by an etching process. Besides the comparison of the wet-chemical and plasma etching techniques, the interaction between laser and etching parameters will be investigated. Different types of silicon wafers (monocrystalline, polycrystalline, slurry sliced, diamond wire sliced) are treated with the hybrid process.

For the production of highly efficient solar cells it is important to achieve very high light trapping rates. Therefore, the realization of a low reflectivity of the light facing wafer surface is an important challenge. Optimized microstructures manufactured by the developed texturing process offer the potential to improve light trapping properties.

In the case of slurry sliced wafers, light trapping properties are obtained by using well-established wet-chemical etching processes [1, 2]. A more efficient way of wafer sawing than slurry slicing is the diamond wire cutting. Higher cutting speeds and smaller cutting kerfs are achieved with this method [3, 4]. The well-established wet-chemical etching processes depend on characteristic damages of the crystalline lattice at the wafer surface. The large number of fine defects caused by slurry slicing serves as etching seeds to generate a light absorbing microstructure. The initial roughness of the surface is crucial for this etching mechanism. Long etching-times can increase the reflectivity but at the same time it causes several disadvantages for the production process [5].

For diamond-wire sliced wafers, the etching mechanism is different due to a low number of exposed defects. In the last years, different approaches to optimize surface texturing of diamond-wire sliced wafers were followed. In the case of monocrystalline material, the characteristic pyramidal structure could be achieved after a pre-polishing step [6]. For polycrystalline silicon, it is difficult to remove saw marks by a wet-etching process. In most cases, the groove-like surface structure caused by the diamond wire slicing is still visible. However, textured surfaces with low reflectivity and high cell efficiency could be reached by a treatment with sulfuric acid-rich mixtures of HF-HNO₃-H₂SO₄ [7]. Another approach to remove saw marks on diamond-wire sawn polycrystalline wafers is vapor blast etching [8].

Polycrystalline silicon is a cost-efficient material in solar cell production. Hence, there is still a need to establish an efficient method of surface texturing, especially for diamond-wire sliced wafers. Compared to etching processes, the initial material structure has a lower impact on laser processes. These can be adapted to almost any material and condition. Using this powerful tool a pre-conditioning of the wafer surface is realized. Different approaches of combining laser and etching processes were already pursued [9, 10, 11]. A honeycomb like texture was generated with a nanosecond-laser and a plasma etching cleaning step. The reflectivity of the resulting silicon surface was reduced by a factor of three compared to the standard alkaline plain etching process. But the minority carrier lifetime reached with the used laser-plasma-process was significantly lower than for standard wet-etching processes. Furthermore the feasible process speed was uneconomic for the employed laser system [9].

In the presented work, the wafer surface is treated by USP laser radiation. This allows a more heterogeneous illumination at higher pulse intensities and steeper temperature gradients compared to short pulsed laser processing (ns-regime). Thus, the laser treatment serves as pre-conditioning of the surface and induces a high density of defects
which serve as etching seeds. The laser modification is followed by an etching step that removes the debris causes by the laser treatment and generates the final surface structure.

2. Experimental

Four different kinds of silicon wafer are treated: monocrystalline silicon with a plain etched surface (material A), monocrystalline silicon with slurry sliced surface (material B), polycrystalline silicon with diamond wire sliced surface (material C) and polycrystalline silicon with slurry sliced surface (material D).

The surface modification is performed by USP laser radiation of the solid-state laser source “Pharos” from the company Light Conversion. The pulse duration \( \tau \) can be chosen in the range of 0.2 to 12 ps. The applied wavelength is 513 nm and the repetition rate is set to 100 kHz. The laser radiation is deflected by a galvanometric scanning system. Different f-theta objectives are used to achieve three different focus radii \( (1/e^2) : r = 15, 30 \) and \( 60 \) \( \mu m \).

The fluence \( F \) is defined as the ratio of the pulse energy and the illuminated area in the focus. The modification threshold \( \Phi \) is determined by the method introduced by Liu [12]. This threshold is the lowest fluence to fabricate a modification of the surface. In these experiments the fluence \( F \) is varied from 0.01 to 3 J/cm\(^2\). The modification threshold is analyzed for different spatial overlap \( \rho \) (in the following: spot overlap) of the radii of subsequent pulses \( (\rho = 0, 0.5, 0.75 \) and 0.88).

For the hybrid process, the subsequent etching is done with microwave-driven plasma. A 2.45 GHz microwave plasma etching process with low residual damage has been employed for dry etching of the wafer surface. A mixture of CF\(_4\) and O\(_2\) is used as process gas at a pressure of 0.6 mbar. The microwave power is set to 600 W and the process time is 60 to 120 s. Sets of different laser parameters are applied to material D to modify the surface in areas of 20x20 mm\(^2\). The laser fluence \( F \) is varied from 0.07 to 0.7 J/cm\(^2\) and the spot overlap \( \rho \) as mentioned above.

The textured surfaces are analyzed with a confocal laser scanning microscope (LSM) and a scanning electron microscope (SEM). The reflectivity of the surfaces is measured with a UV-VIS-NIR spectrometer.

3. Results & discussion

3.1. Laser texturing

The modification threshold of the USP laser treatment is determined from material A to D. Different surface modifications are observed at low fluences \( (F < 250 \text{ mJ/cm}\(^2\)) \) for different surfaces, see fig. 1. A higher contrast is

![Fig. 1. LSM images of laser modification of different materials, \( \tau = 5 \text{ ps}, F = 180 \text{ mJ/cm}\(^2\), separated illuminated areas (\( \rho = 0 \)).](image)
measured by the LSM in the illuminated areas of material A and B compared to the untreated surface. No change of the surface roughness is detected. But for material C and D a reduction of the intensity measured by the LSM is observed in the illuminated areas. In addition the surface roughness increases. For high fluences (F >250 mJ/cm²) the surface modification of material A gets more and more similar to the one of material C and D, see fig. 2. No significant influence of the pulse duration τ or focus radius r on these effects is found. Thus this is not an intensity-but fluence-driven effect.

The topography of the surface structure of a standard material (material D) generated by USP radiation does not differ by using different pulse durations τ (ps or fs regime) for all applied spot overlaps ρ, see fig. 3. The higher the spot overlap, the more the sharp ridges become smoother due to heat accumulation. The surface roughness increases as well with higher spot overlap. For ρ>0.7 all edges and ridges are molten. No significant influence of the pulse duration is observed here.

The modification thresholds of different materials at different applied laser parameters are summarized in table 1. Material D shows a high roughness. Thus the determination of the modification thresholds is not applicable for that material. No significant influence of the pulse duration τ, spot overlap ρ or the initial surface topology is found. Therefore all shown values of the modification threshold are the arithmetic average of the values for parameter sets
with several spot overlaps $\rho$. The values vary mostly in the range of $50 < \Phi_X < 115 \text{ mJ/cm}^2$. The arithmetic average is $83 \text{ mJ/cm}^2$.

<table>
<thead>
<tr>
<th>Pulse duration [ps]</th>
<th>Focus radius [(\mu\text{m})]</th>
<th>$\Phi_A$ [mJ/cm$^2$]</th>
<th>$\Phi_B$ [mJ/cm$^2$]</th>
<th>$\Phi_C$ [mJ/cm$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>9</td>
<td>73</td>
<td>82</td>
<td>91</td>
</tr>
<tr>
<td>0.2</td>
<td>15</td>
<td>60</td>
<td>51</td>
<td>27</td>
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<tr>
<td>0.2</td>
<td>30</td>
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<td>5</td>
<td>9</td>
<td>80</td>
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The high variation of the modification threshold $\Phi$ for different focus radii $r$ at a pulse duration $\tau = 220 \text{ fs}$ is observed and discussed in detail below. The laser modification appears similar in LSM intensity images, see fig. 4. Thus the conclusion is drawn that the focus radius has no significant influence on the modification threshold $\Phi$. The value of the modification threshold of material C for $\tau = 0.2 \text{ ps}$ and $r = 15 \mu\text{m}$ will be re-examined.

![Fig. 4. LSM images of laser modification of material C at different focus radii $r = 18$ (a), 30 (b) and 60 (c) \(\mu\text{m}\), $F = 100 \text{ mJ/cm}^2$, $\rho = 0$.](image)

### 3.2. Hybrid process

The microstructures generated by the laser modification are compared to those generated by plasma etching. Another aspect is the influence of the observed effects on the subsequent etching step of the hybrid process.

The surface of materials B and D is treated with different processing sequences (only laser, only plasma etching and hybrid process). The corresponding laser parameters are: pulse duration $\tau = 220 \text{ fs}$, fluence $F = 0.67 \text{ J/cm}^2$ and spot overlap $\rho = 0.8$. The conditions of the plasma etching are set to: $\text{CF}_4/\text{O}_2$ gas, pressure 0.6 mbar, microwave power 600 W and etching time 60 s. In Fig. 5 SEM images of the generated microstructures are shown. The laser treatment induces melting of ridges due to accumulation of extant heat for high spot overlap. Furthermore, the ultra-short laser pulses cause much debris which covers the surface. The produced particles are smaller than 1 \(\mu\text{m}\) (fig. 5, left). The employed plasma etching process makes the surface clean but jagged (fig. 5, middle). This process removes the debris from the laser treatment and generates a smooth and fine microstructure (fig. 5, right).
In the following the influence of the generated microstructures on the reflectivity is analyzed. Reflection spectra of material D at a fixed spot overlap $\rho = 0.3$ for a wavelength range from 300 to 1100 nm are shown in fig. 6. The black dotted reference line represents the reflectivity of the untreated material. The modification of the surface is performed at two different fluences, 0.27 and 0.67 J/cm² (blue/red). The reflectivity spectrum right after the laser process is shown by the dashed lines, while reflectivity after the etching is shown by the solid lines.

The influence of the laser modification on the reflectivity is different for these two fluences: While the reflectivity increases for the lower fluence, it decreases for the higher fluence. Nevertheless, the reflectivity is significantly reduced for both applied fluences after the plasma etching step compared to the unstructured wafer. The hybrid treatment at the lower fluences ($F = 0.27$ J/cm²) leads to a lower reflectivity than $F = 0.67$ J/cm², even though reflectivity is increased after the laser process. Thus a relative reduction of reflectivity up to 20% in the wavelength range 450-1000 nm could be achieved by using the hybrid process, so far.

Fig. 6. Reflectivity spectra of material D after the laser-etching process at different fluences $F$ and fixed spot overlap $\rho = 0.3$, etching time 120 s.
In Fig. 7 the reflection spectra for different pulse overlaps $\rho$ at a fixed laser fluence of $F = 0.67 \text{ J/cm}^2$ are shown. For a spot overlap of 30% the reflectivity is decreased by the laser process as well as the subsequent etching process. Applying only the laser process with a spot overlap of $\rho = 0.8$, a relative reduction of the reflectivity between 35% and 50% is observed in the visible spectral region. A subsequent etching of these laser modified surfaces leads to higher reflectivity but the overall reduction of the reflectivity is still in the range of 30%.

From the results of these experiments is concluded that the combined laser-etching process can be controlled by a set of different parameters, which can be adjusted and optimized for achieving a specific surface texture and associated reflectivity.

4. Summary & conclusion

A hybrid process for silicon wafer texturing is developed. This process combines laser modification and etching techniques to generate microstructures optimized for high efficient light trapping. This helps to enhance the use of diamond wire slicing in silicon solar cell production. As the initial material structure has a low impact on laser processes, the presented texturing method offers especially for diamond-wire sliced and polycrystalline silicon new perspectives.

We observe different laser modifications for different surface topography. The modification threshold $\Phi$ is independent from pulse duration $\tau$, focus radius $r$ and spot overlap $\rho$. By this the conclusion is drawn that the presented laser modification is a robust process. The overall arithmetic average of the modification threshold $\Phi$ is 83 mJ/cm².

The hybrid process removes the debris generated by a large spot overlap and results in smooth and fine microstructures. First results show a reduction of the reflectivity in the range of 30% compared to the reflectivity of unstructured wafers. The conclusion is drawn that there are different effects which can be influenced by the adequate choice of the process parameters. Further examinations aim for optimization of the relevant process parameters.

5. Outlook

In further experiments these effects will be exploited to gain a more detailed understanding and to derive well adapted process parameters. Therefore, the damage mechanism of the laser treatment will be analyzed. To examine the impact of thermal and non-thermal effects, pulse duration as well as wavelength will be varied. Special emphasis will be given to the investigation of the influence of the etching parameter on the generated surface structure and the influence of defect type on the etching behavior. In addition the examination of the reflectivity will be extended to
the other types of silicon wafers (material A to C). The reflectivity achieved with the laser-etching process will be compared to the reflectivity of standard wet-chemical textured wafers. Finally, other important characteristics, such as the minority carrier lifetime, will be studied to further assess the suitability of the presented laser-etching-process for the fabrication of high-efficiency solar cells.

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