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Investigation of ablation mechanisms for selective laser ablation of silicon nitride layers

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Abstract

In this work SiN\textsubscript{X} deposited on silicon was locally ablated using laser irradiation. The focus was set on the investigation of the ablation mechanisms where a picosecond (ps) pulse laser is used with three wavelengths 1064, 532, 355 nm. The ablated areas were characterized by light microscopy and the threshold fluences were determined for various layer thicknesses. Furthermore, four-probe sheet-resistance and Suns\textsubscript{V\textsubscript{oc}} measurements were conducted. Light microscopy images were taken and compared to simulated color maps, which were calculated from spectral reflection coefficients.

The results of sheet resistance and Suns\textsubscript{V\textsubscript{oc}} measurements show an influence on the underlying silicon for all three wavelengths used. However, light microscopy images reveal for the first time a change from indirect ablation (lift-off) to partial lift-off for a thin a-SiN\textsubscript{X}:H-layer (n \approx 2.1, t \approx 75 nm) by using a VIS picosecond laser. Thus, a first step towards selective laser ablation was made of dielectrics.

Keywords: Laser processing; ablation; ultra-short pulse laser; Si solar cells

1. Introduction

Recently, patterning processes of dielectrics are more and more introduced into the production process of crystalline silicon solar cells. Reasons for this trend are advanced solar cell structures like Passivated-Emitter-and-Rear-Cell (PERC) or selective emitter processes [1]. For patterning a dielectric layer, laser processes became increasingly attractive, because they are fast, accurate and contact-free. However,
conventional diode pumped solid-state lasers (pulse duration ~ nanoseconds) damage [2] and change the structure of the silicon beneath [3]. The absorption starts in silicon if the photon energy is above the band gap energy of silicon and below the band gap energy of the dielectric. Hence, the silicon melts locally and lifts off (indirect ablation Fig. 1 c)) the dielectric layer induced by mechanical stress inside the layer. This occurs because of increasing vapor pressure of the molten silicon at high fluences [4] and different coefficients of thermal expansion of substrate and layer at lower fluences. Note that the mass density of liquid silicon is higher than the dense of solid silicon [5]. A crater in SiNx with sharp edges is so created.

In the case of ultra short laser pulses (pulse duration ~ picoseconds, femtoseconds) typically a high number of photons are incident on the sample within a short time. The probability increases, that multiple photons are absorbed at the same time to excite an electron into the conduction band: This intensity dependent multi-photon absorption [6] is bound to a high energy source and can lead to a high electron concentration in the conduction band. A comparable effect of increased absorption is the avalanche-like absorption: With a high initial number of excited electrons, even more photons can be absorbed, what can be compared to an avalanche effect [6]. This occurs at high laser intensities leading to a direct absorption in the dielectric as well as to an ablation of the layer after the end of the laser pulse (direct ablation in Fig. 1 a)). A Gaussian-like crater in SiNx is so created by using a Gaussian laser beam profile.

If the intensity decreases through absorption in the dielectric (below a material dependent value), only absorption of single photons is possible. As a consequence the dielectric appears transparent to the photons that are finally absorbed in the silicon substrate. The heat-affected dielectric layer volume breaks off induced by mechanical stress generated by molten silicon at lower fluences (partial lift-off in Fig. 1 b)). A crater in SiNx with sharp edges at the top and a Gaussian-like profile at the bottom is so created by using a Gaussian laser beam profile.

Molten silicon resolidifies but the crystalline structure is affected by amorphization and recrystallization.

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One set of six wafers was prepared to determine the threshold fluence \( F_{th} \), which is depend on the SiN<sub>x</sub> thickness. The threshold fluence is the pulse energy density at which the complete SiN<sub>x</sub> is removed. For

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these experiments, a PECVD layer of a-SiNₓ:H (n ≈ 2.1) of varying thickness (30, 50, 75, 100 nm) was deposited on the samples. The thickness and the refractive index of the SiNₓ-layer were measured by means of ellipsometry. \( F_{\text{th}} \) of the silicon nitride was determined by visual inspection using light microscopy and by plotting the opened area over the logarithmic pulse energy [7].

2.2. Laser induced damage

On a set of six wafers a phosphorus emitter was diffused. The sheet resistance was varied in the range of 40 – 80Ω/sq. All wafers were coated with 75 nm PECVD SiNₓ (n ≈ 2.1) on one side and metallized on the other side by aluminum screen printing and firing. The dielectric layer was partially laser ablated with different fluences and cut into 20 samples.

The SunsVₜₙc [8] measurement was used to extract the implied \( V_{\text{oc}} \). Hence, information about the laser induced damage could be determined. Furthermore the samples were characterized by means of emitter sheet resistance measurements (four point probe) to determine the influence of the doping profile.

3. Simulation

The ablated areas and depth profiles shown in Fig. 1 (last row) were simulated to compare them with the light microscopy images in sec. 4.1. Therefore, the spectral reflection coefficient of SiNₓ with varying thicknesses on silicon in the wavelength range of 380-780 nm was calculated by using the transfer matrix method [9]. The refractive index and the absorption coefficient for the silicon nitride used were determined by spectral ellipsometry and for silicon extracted from literature [10]. Then the spectral reflection coefficient was converted into a color, which depends on the SiNₓ thickness.

The ablated areas after one single laser pulse with a Gaussian laser beam profile for a direct, an indirect ablation and a partial lift-off of SiNₓ (thickness 95 nm) are shown in Fig. 2. These figures show that absorption in the dielectric generate a color gradient (Fig. 2 a) and Fig. 2 b)). Differences between 2 a) and 2 b) occur from the defined edges in case of the crater profile in Fig. 1 b). In the case of indirect ablation only bare silicon is visible in the ablated area (Fig. 2 c)).

4. Results

4.1. SiNₓ thickness dependent threshold fluences

Fig. 3 a) summarizes the observed images of the laser ablated areas in the order of the wavelength and SiNₓ thickness used. For IR all images show bare silicon, also at lower fluences (not shown here) as well as ripple structures in Fig. 3 b) [11] which is indicating in an indirect ablation (see Fig. 2 b)). In the cases of the VIS and UV wavelength for SiNₓ thickness above 50 nm a color gradient is visible. The color gradient differs from the estimated one in Fig. 2 a) for direct ablation: The dark blue halo (corresponding
to a layer thickness of approx. 75 nm) was not observed in the microscopic pictures. A partial lift-off occurred as shown in Fig. 2 b) because the heat-affected layer volume breaks, induced by mechanical stress generated by the melting of the underlying silicon. It is obvious that the silicon nitride (in addition to the silicon) absorbs a part of the pulse energy at the VIS wavelength. The corresponding photon energy of 2.3 eV is lower than the band gap energy of 3.5 eV [2]. Therefore, non-linear absorption is very likely. The layer thickness in the spot centre corresponds to approx. 50 nm. An increase of the fluence generates a complete removal of the silicon nitride (not shown here). In the cases of the VIS and UV wavelengths for SiNx thicknesses less than 50 nm no color gradient is visible because the silicon nitride is colorless for a layer thickness of less than approx. 20 nm.

Fig. 3 Representative optical microscope images of the laser ablated areas according to the wavelengths and SiNx thicknesses used for fluences ~ $F_{th}$ (a) and a more detailed image with ripple structures for a layer thickness of 50 nm by using an IR-ps pulse (b)

$F_{th}$ was determined for all wavelengths and layer thicknesses used. The result is shown in Fig. 4 a). For IR the highest energy of > 600 mJ/cm² is necessary, for VIS and for UV the determined fluences are lower with < 500 mJ/cm² and < 300 mJ/cm², respectively.

Fig. 4 Determined threshold fluence as a function of layer thickness without (a) and with reflection correction (c) by subtracting the reflected pulse energy from simulated spectral reflection coefficients (b)
As already shown by Hermann et al. for silicon dioxide [4], the actually absorbed pulse energy has to be determined by subtracting the fraction of reflection. Applying this method, Fig. 4 c) shows that the threshold fluence for IR is independent of the layer thickness because of the indirect ablation mechanism mentioned above. On the other side the threshold fluences for VIS and UV are still dependent on the layer thickness corresponding to the partial lift-off. For a thickness of 75 nm the values are given in Table 1.

Table 1 threshold fluences $F_{th}$ for PECVD deposited SiNx with a thickness of 75 nm

<table>
<thead>
<tr>
<th>Wavelength</th>
<th>IR (1064 nm)</th>
<th>VIS (532 nm)</th>
<th>UV (355 nm)</th>
</tr>
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<tbody>
<tr>
<td>$F_{th}$ [mJ/cm²]</td>
<td>646 ± 20</td>
<td>293 ± 15</td>
<td>112 ± 12</td>
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</table>

4.2. Laser induced damage

Fig. 5 a) highlights laser-dependent evolutions of the sheet resistance ratios before and after irradiation ($\Delta R_s$). For all wavelengths used, $R_s$ increases as soon as $F_{th}$ is reached until a saturation value is attained due to limited size of the ablation diameter. Gall et al. [12] presented the same dependences on $R_s$ by using a UV-picoseconds-laser and determined only a small modification (surface depletion and small redistribution of P atoms in the depth range of 40-80 nm) of the initial phosphorous emitter by comparing secondary ion mass spectroscopy (SIMS) profiles before and after irradiation. In our interpretation for low fluences above $F_{th}$ silicon melts and evaporates partially. The other fraction of the molten silicon creates an amorphous phase near the surface due to fast resolidification (about $10^{13}$ K/s) [13]. Thus, phosphorus atoms are electrically inactive. Note that using SIMS only the entire phosphorus concentration is measured (electrically active and inactive). In the case of higher fluences a deeper puddle of silicon is created. Long after the end of the laser pulse (ns range) this puddle finally cools and resolidifies. The cooling rate during solidification is then sufficiently low so that a single crystal grows back epitaxially on the substrate. Thus, initially inactive P atoms will be activated and compensate inactivated P atoms in the amorphous region. Fig. 5 c) displays the different cases.

Fig. 5 Ratios post/pre laser irradiation for sheet resistances (a) and open circuit voltages (b). c) shows a schematic for the reaction of amorphous and recrystallized regions through low and high fluences.
The result of the SunsV_{oc} measurement is displayed in Fig. 5 b) as the open circuit voltage ratio before and after irradiation (ΔV_{oc}). For UV a decrease in V_{oc} for significantly higher fluences compared to the increasing sheet resistance was obtained. For VIS and IR a decrease in V_{oc} already at fluences below F_{th} was observed. These different behaviors could be explained by the different optical penetration depths (\alpha^{2}). For the investigated wavelengths the optical penetration depths are \approx 900 \mu m for IR, 1.2 \mu m for VIS and 0.01 \mu m for UV [10]. A high fraction of the IR and VIS photons at fluences under F_{th} could reach the space-charge region (SCR) and modify the crystalline structure by defect generation. Above F_{th} additional to the defect generation in the SCR, occurred a removal of evaporated silicon and the creation of a surface near amorphous phase. For UV, only a surface near absorption takes place. At higher fluences the removal of evaporated silicon and the size of the amorphous phase increase. This leads to a decrease in V_{oc}.

5. Conclusion

In this paper the laser ablation of PECVD SiN_{x} layers on silicon using a picoseconds laser was investigated. A color gradient in the SiN_{x} layer (thickness > 50 nm) for VIS and UV was obtained, revealing for the first time a direct absorption in the SiN_{x} by using a VIS picosecond laser. The layer is removed in a partial lift-off process based on breaking off the heat-affected dielectric layer volume induced by mechanical stress generated by the melting of the underlying silicon. For IR the layer is removed in a lift-off caused by stress inside the layer due to increasing vapor pressure of melting silicon. For all used wavelengths the crystalline silicon structure is influenced due to recrystallization and amorphization. Only for UV in a broad fluence range a removal of SiN_{x} without affecting the V_{oc} is possible using a picosecond laser. Thus, a first step towards selective laser ablation is done. However, further investigations using even shorter laser pulse durations are necessary due to the increasing possibilities of non-linear absorption effects.

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References