INVESTIGATIONS ON HYDROGEN IN SILICON BY MEANS OF LIFETIME MEASUREMENTS

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ABSTRACT

Various techniques (SIMS, Thermal Effusion, FTIR) have been suggested for the determination of the diffusion of hydrogen in multicrystalline silicon [1]. However these methods are either laborious or of a minor accuracy. Our work concentrates on the determination of hydrogen passivation depths in mc-Si by determining the minority carrier lifetime as a function of hydrogen passivation time. For the investigations EMC silicon and reference FZ silicon wafers have been used. From experimental data the passivation depth is obtained numerically using the simulation software PC1D and analytically using a simplified equation. For EMC passivation depths in regions of good and poor quality have been obtained indicating no significant influence on the passivation depth. Further experiments by polishing the wafer prior to lifetime measurements with a small angle have been performed for determination of the SRV.

INTRODUCTION

In many laboratories hydrogen passivation by means of a remote plasma is a well established method to improve the quality of mc-Si wafers [2-4]. Especially on low quality materials considerable improvements in the open circuit voltage Voc, the short circuit current Isc and the fill-factor FF have been reached. This leads to an increase in the efficiency of up to 2.3 % absolute or 38 % relative on commercially available mc-Si wafers [5]. The effectiveness of a hydrogen passivation step is well proven on the solar cell level, whereas some fundamental questions on the microscopic level are still open. A method for the determination of H-passivation depths in solar cells based on spectral response measurements is given in [6].

In this work the influence of atomic hydrogen on the passivation of crystal defects and therefore on the lifetime of minority charge carriers is investigated. From these results information on the penetration depth in different quality EMC material is obtained.

MINORITY CARRIER LIFETIME

By measuring the lifetime of the minority carriers, normally the effective lifetime $\tau_{eff}$ is determined, which is correlated with the bulk lifetime $\tau_b$ and the surface lifetime $\tau_s$ with the following equation:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{1}{\tau_s}.$$  \hspace{1cm} \text{eq. 1}

For a small surface recombination velocity (SRV) this can be approximated by [7]:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{2S}{H}.$$  \hspace{1cm} \text{eq. 2}

with H the thickness and S the surface recombination velocity of the wafer.

The surface recombination velocity can be obtained by determining $\tau_{eff}$ prior and after performing an etching step. Taking into account the measurement uncertainties the unknown values $\tau_b$ and $S$ can be extracted [8]. To reduce the statistical error we suggest the following wafer preparation method: Mechanical polishing of a wafer with a small angle, etching away the polish damage and measuring the lifetime at two or more different thicknesses by performing a lifetime line-scan over the polished surface. This method is also suggested for microscopic investigations of mc-Si material, e.g. determination of $\tau_b$ on single grains, or hydrogen diffusion depths by using the model presented in the following.

MODEL FOR HYDROGEN PASSIVATION

The penetration depth of hydrogen is determined by a simple 3 layer model for the description of the lifetime as shown in Fig. 1. In our experiments the outer regions have the same lifetime because using the MIRHP technique for the hydrogen passivation the hydrogen diffuses in from both sides of the wafer. The lifetime value of the unpassivated wafer corresponds to $\tau_1$, the one of the completely passivated wafer to $\tau_2$. 


HYDROGEN PASSIVATION BY A REMOTE PLASMA

Hydrogen does not diffuse into silicon from a molecular ambient, therefore it has to be dissociated. For the generation of atomic hydrogen the microwave induced remote hydrogen plasma (MIRHP) technique has been used. The atomic hydrogen is generated by a microwave plasma which is located separately from the wafers, ensuring that a damage of the wafer surface due to radicals and UV radiation of the plasma is avoided.

The MIRHP device consists mainly of a quartz tube with a diameter of 156 mm in a furnace with a heated length of 750 mm which may be heated up to 800°C. Perpendicular to this tube the inlet of the process gases are passed through a capacity. The latter is connected with a 2.45 GHz microwave generator. The gas mixture consisting of 10% H₂ and 90% He with a purity of 6N is dissociated when flowing through the cavity. Arriving in a large quartz tube the atomic hydrogen diffuses into the samples at typical temperatures of 275-450 °C, with an optimum passivation temperature for most mc-Si materials between 350 and 400°C. A total gas pressure of 0.4 mbar measured at the outlet of the gases was chosen.

For cell processes where at the end an annealing step is carried out the MIRHP process can replace the annealing, therefore avoiding an additional process step.
EXPERIMENTS

Neighboring p-type EMC wafers of thickness 330 µm were cut into 5x5 cm² pieces, as seen in Table 1. To confirm the comparability of the wafers no. 1 to 4 were measured without surface passivation. There was a slight increase in the mean value of the lifetime from 1.7 µs to 2.0 µs. Wafers 9 to 11 were cut into four 2x2 cm² pieces, wafers 1-8 were further processed with size 5x5 cm². All wafers are etched in NaOH to remove the saw damage with a following HCl cleaning and a HF-dip. Then one wafer is measured as a reference and the others are treated differently as seen in Table 1. The MIRHP process is carried out at a temperature of 400 °C and a pressure of 0.4 mbar. After loading the samples, the reactor is pumped down. When reaching a certain pressure the plasma is started. It takes approx. one minute until the plasma power, the gas pressure and gas flux are in a stable condition, therefore passivation times not below 5 min should be taken.

The smaller pieces of 4 cm² are treated the same way and are polished with a small angle (ca. 1°) afterwards. The polishing damage was etched away with NaOH and optional with CP4. Then the wafers were µ-PCD measured.

Table 1: Process sequence

<table>
<thead>
<tr>
<th>5x5 cm² samples</th>
<th>2x2 cm² samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>nr.: 1-8</td>
<td>nr.: 9-11</td>
</tr>
<tr>
<td>NaOH saw damage etching + HCl + HF-dip</td>
<td>Cleaning in H₂O₂/H₂SO₄</td>
</tr>
<tr>
<td>PCD-τ without surface passivation</td>
<td>MIRHP for 5, 10, 15, 30, 120 min</td>
</tr>
<tr>
<td>µ-PCD-τ</td>
<td>µ-PCD-τ</td>
</tr>
<tr>
<td>Polishing</td>
<td></td>
</tr>
<tr>
<td>at an angle of 1°</td>
<td></td>
</tr>
<tr>
<td>1 min. NaOH (+CP4, optional)</td>
<td></td>
</tr>
</tbody>
</table>

RESULTS

The strong effect of the hydrogen passivation for the minority carrier lifetime is shown in Fig. 1. The left one represents the untreated wafer and the right one is of wafer no. 4, which is passivated for 30 minutes. The scale is the same for both wafers. The peak of the lifetime distribution has moved from 2 µs to 6 µs and a third of the wafer is better than 15 µs after the passivation.

Fig. 1: Lifetime maps of wafer 1 (untreated) and wafer 2 (30 min MIRHP) with the same scale from 1 to 15 µs. Wafer 1 has a mean value of 3.9 µs, wafer 2 of 9.6 µs. The regions drawn in are used for Fig. 2. Upper rectangle = poor region, lower rectangle = good region.

After 5 to 10 min the lifetime saturation value is almost reached (See Fig. 2). The differences after 5 to 15 minutes of passivation are in the reproducibility of the measurements and the variation between the neighboring wafers.

![Influence of passivation time on the mean lifetime](image)

In Table 2 the results of the unpolished wafers are shown. The whole 5x5 cm² wafers were measured and also 2 regions with low and high lifetimes respectively were evaluated. The untreated wafer delivered τ₀ and the completely passivated wafer τ₁. Together with τ_{eff} of the partly passivated wafers the penetration depth is calculated. Already after 5 min of passivation only a layer with a thickness of (330-2x140) µm=50 µm remains unpassivated. This is consistent with the fact, that already the saturation level of the lifetime is reached.

![Influence of passivation time on the mean lifetime](image)
After 30 min. of passivation only 30 µm remain unpassivated. The values for the good and bad regions lead to comparable data, which means, that the diffusion of hydrogen is mostly independent of the quality and defect density in EMC silicon.

The results of the calculation were used in the PC1D simulation resulting in an excellent agreement of the measured and simulated $\tau_{\text{eff}}$ values.

Table 2: Results of the lifetime measurements of the unpolished wafers. The penetration depth is calculated with eq. 3 for the three layer model. The results are in very good agreement with the PC1D simulations.

<table>
<thead>
<tr>
<th></th>
<th>Whole wafer</th>
<th>Poor region</th>
<th>Good region</th>
</tr>
</thead>
<tbody>
<tr>
<td>None-passivated $\tau_2$</td>
<td>3.9 µs</td>
<td>2.5 µs</td>
<td>5.5 µs</td>
</tr>
<tr>
<td>Passivated $\tau_1$</td>
<td>10.4 µs</td>
<td>6.4 µs</td>
<td>14.2 µs</td>
</tr>
<tr>
<td>30 min. MIRHP: Calculated penetration depth $d_1$</td>
<td>151 µm</td>
<td>152 µm</td>
<td>154 µm</td>
</tr>
<tr>
<td>Measured $\tau_{\text{eff}}$</td>
<td>9.1 µs</td>
<td>5.7 µs</td>
<td>12.7 µs</td>
</tr>
<tr>
<td>PC1D $\tau_{\text{eff}}$</td>
<td>9.0 µs</td>
<td>5.7 µs</td>
<td>12.7 µs</td>
</tr>
</tbody>
</table>

In Fig. 3 is shown, that on the polished FZ wafer the lifetime decreases with decreasing thickness of the wafer. This is due to the bigger effect of the finite surface passivation quality with smaller thickness. Applying the method described in the chapter “minority carrier lifetime” values for SRV of about 200 cm/s are obtained. This value is not very good for a passivation with iodine-ethanol, but probably the damage of the polishing has not polished region seems even to be of better quality. We expected a lower effective lifetime for the thinner regions because of a lower bulk lifetime and a larger contribution of the SRV. This is not confirmed in this experiment. One reason is the very fast passivation of the wafer within 5 to 10 minutes. If the wafer is nearly totally passivated there is only a very thin layer none-passivated in the middle of the wafer. This region is therefore difficult to detect with a lifetime map over a polished surface. In further experiments mc-Si material which needs a longer passivation time to be saturated, such as oxygen rich mc-Si, will be chosen and the passivation time further reduced.

CONCLUSION

A simple 3 layer model for the determination of the penetration depth of hydrogen in mc-Si has been presented. The model takes into account the improvement of the minority carrier lifetime. Experiments were performed, using the $\mu$-PCD technique to determine the effective minority carrier lifetime. The experimental results are in excellent agreement with PC1D simulations. In addition a method has been presented based on angle polishing a FZ wafer for determining $\tau_s$ without knowing $\tau_b$. First experiments using this method to determine the H-passivation depth in mc-Si have not been successful. Further experiments changing the wafer cleaning procedure and using mc-Si material where hydrogen diffuses slower will be performed.

ACKNOWLEDGEMENTS

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REFERENCES