## SURFACE PASSIVATION STUDY ON GETTERED MULTICRYSTALLINE SILICON

Sarah Gindner, Bernhard Herzog, Giso Hahn
University of Konstanz
Department of Physics, P.O. Box X916, 78457 Konstanz, Germany
Author for correspondence: Sarah.Gindner@uni-konstanz.de, Tel.: +49 7531 88 2132, Fax: +49 7531 88 3895

ABSTRACT: In this study the electronic quality of multicrystalline silicon material in the as grown state and after various $POCl_3$ diffusion steps is analyzed. For this purpose two different surface passivations (quinhydrone-methanol and a-Si:H) are tested and also their reproducibility is checked. It is found that the chemical passivation using quinhydrone-methanol is more complicated to apply for detecting small differences on a relatively high lifetime level which can be reached by the applied $POCl_3$ diffusions on the Si materials under investigation.

Keywords: Minority carrier lifetime, surface passivation, phosphorus gettering, multicrystalline material

### 1 INTRODUCTION

Phosphorus gettering can tremendously improve the electronic quality of multicrystalline (mc) silicon. Since P-diffusion (e.g. using $POCl_3$) is an essential step in solar cell processing on p-type crystalline silicon, the gettering effect is not only of scientific interest, but also of high industrial relevance. Understanding the effect in more detail can help finding optimized parameters of the respective processing step and subsequently reaching better cell performance.

Measurements of minority charge carrier bulk lifetime are performed on wafers that have to be surface passivated. First a chemical passivation called quinhydrone-methanol is tested [1]. It is found that the results on gettered material are sometimes difficult to reproduce using this type of surface passivation. This may be explained on the one hand by the high electronic material quality after gettering, which makes the material more sensitive to surface passivation. On the other hand the surface treatment (cleaning and passivation procedure) has to be carried out very carefully to show good passivation results and allows no room for small variations in handling. To avoid these difficulties for detection of small differences on higher bulk lifetime level, other surface passivation mechanisms based on dielectric passivation layers can be tested. But it has to be considered that all of these other schemes involve hydrogen containing layers and at least slightly elevated temperatures, which could cause a rearrangement of defects in the mc-Si bulk or diffusion of hydrogen and possibly hydrogenation effects to occur. But it is expected that a more robust and stable passivation scheme using e.g. a-Si with low annealing temperature for activation [2] is better suited for detecting fine differences between varying gettering diffusion steps. Therefore, a-Si:H, is applied in this study for comparison. Lifetime measurements with this passivation are checked for reproducibility and stability over time [3].

### 2 EXPERIMENT

$5 \times 5$ $cm^2$ lifetime samples are cut out of a $15.6 \times 15.6$ $cm^2$ boron doped (~1 $\Omega$cm) p-type mc-Si wafer (thickness ~150 µm) as shown in Fig. 1. The shown PL image of the wafer reveals that the edges to the right and to the bottom are close to the crucible wall with impurities diffusing in from these walls, reducing the wafer quality. The mc material originates from different blocks, block heights (bottom, center and top) and wafer positions (C, D, F and I shown in Fig. 1). Samples are cleaned by a polishing etch consisting of HF, $HNO_3$ and $CH_3COOH$. An 80 Ohm/sq $POCl_3$ emitter is applied at a diffusion temperature above 800°C. After emitter removal, surface piranha cleaning containing $H_2O_2/H_2SO_4$ followed by HF dip and surface passivation QSSPC (Quasi Steady State PhotoConductance) and PL (PhotoLuminescence) measurements are performed. The described process flow for gettered material is depicted in Fig. 2.
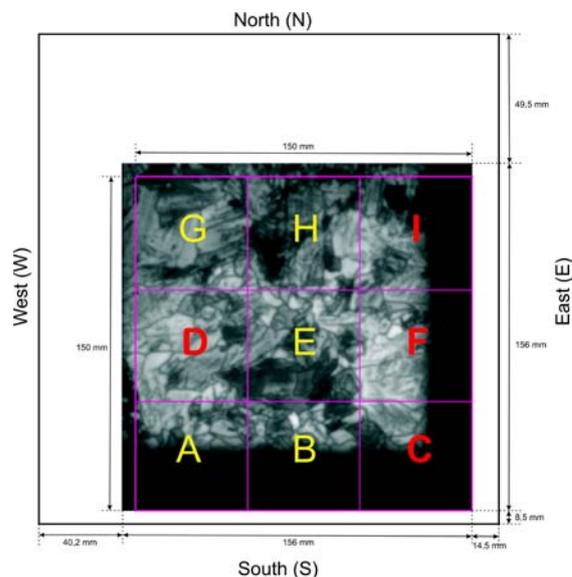


**Figure 1:** Cutting sketch of a $15.6 \times 15.6$ $cm^2$ wafer. Positions C, D, F and I marked in red are analyzed in this study. The as grown PL image is shown.

In case of measurements with quinhydrone-methanol (QM) the surfaces must be etched again between experiments in the above described polishing etch removing ~0.5 µm of silicon and then again piranha cleaned. Therefore, the surface passivation is renewed on each measuring day since it is known that it is not stable over long time scales [4]. It should be mentioned that special care is taken in order to reduce possible sources of error. The samples are measured in the same time sequence after HF dip and putting them into plastic bags filled with 0.07-M quinhydrone solution. Also the wafers

are measured with same orientation with respect to the QSSPC measuring coil. This is considered as well for the measurements with a-Si:H passivation.
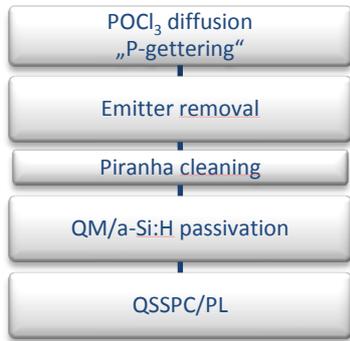
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┌─────────────────────────────┐
│      POCl₃ diffusion        │
│       „P-gettering"         │
└─────────────────────────────┘
              │
┌─────────────────────────────┐
│       Emitter removal       │
└─────────────────────────────┘
              │
┌─────────────────────────────┐
│       Piranha cleaning      │
└─────────────────────────────┘
              │
┌─────────────────────────────┐
│     QM/a-Si:H passivation   │
└─────────────────────────────┘
              │
┌─────────────────────────────┐
│          QSSPC/PL           │
└─────────────────────────────┘
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**Figure 2:** Process flow of gettered material.

The a-Si:H samples are passivated in a PECVD (Plasma Enhanced Chemical Vapour Deposition) system from Oxford Instruments. The deposition temperature is 225°C and the passivation activating annealing step is performed for 12 min at 250°C, respectively. In between repeated measurements all samples are kept with the same passivation layer in the dark [3].

## 3 RESULTS

Fig. 3 shows fluctuations of QSSPC lifetime with QM passivation on different measuring days, measuring exactly the same spot in the same orientation of the sample to exclude effects caused by the inhomogeneous distribution of bulk lifetime in mc-Si wafers. Again it should be mentioned here that the wet chemical passivation layer is renewed on each measuring day. Three positions I, F and C of wafer SQ3_center (block SQ3 central height) after POCl₃ diffusion gettering are presented. It is clearly seen that lifetime of one wafer position varies with measuring day, but for each position not in the same way. This means, for example, that for position I highest lifetime is measured on day 62. On the same day the lowest lifetime is determined for position F. This excludes the possibility that the observed results can be explained by etch effects, as all samples have been prepared in the same etch and cleaning step one day before each measuring day.

Fig. 4 represents the QSSPC lifetimes of the same gettered sample but with a-Si:H passivation before and after the passivation activating annealing step on day 1, 5, 22 and 34. For better comparison to Fig. 3 the QM measurement on day 62 is included. As can be seen here the lifetime directly after a-Si:H deposition is lower than the included lifetime curve measured with QM passivation. Due to the passivation activating annealing the lifetime is more than tripled (activation of the a-Si:H surface passivation). An increase from 106 µs (blue curve) up to 354 µs (red curve) at an injection level of $10^{15}$ cm$^{-3}$ is reported for the sample SQ3_center_C. After four days lifetime is stable within measurement error (grey curve). The subsequent two measurements, each after two weeks without further processing and storage in the dark, exhibit a clear drop in lifetime. This drop is also observed in PL maps shown in Fig. 5.
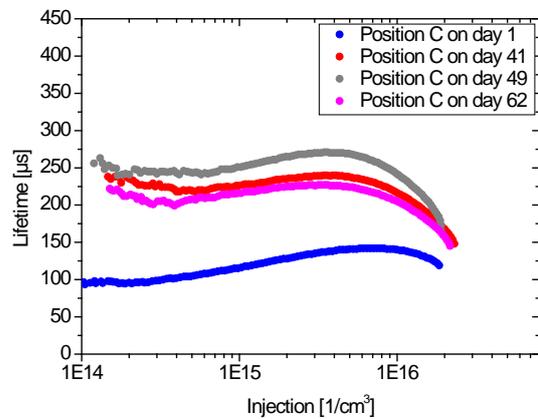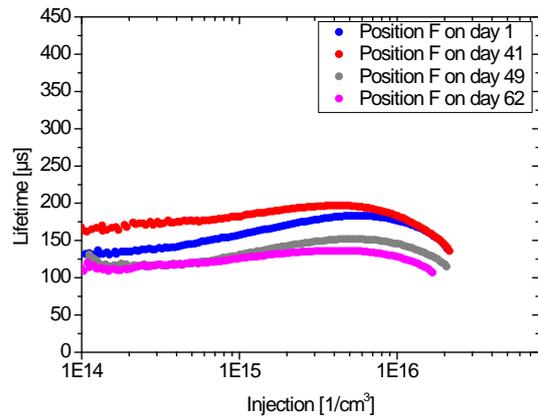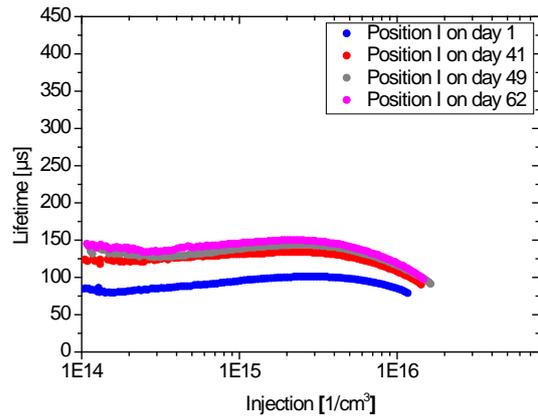


**Figure 3:** QSSPC lifetime measured with renewed QM passivation on different days. Three positions I, F and C of wafer SQ3_center are shown.

The PL intensities in Fig. 6 represent an as grown wafer at position D from the top region of the SQ3 block passivated with QM. Since as grown material is of lower quality compared to gettered material, it is less sensitive to surface passivation inhomogeneities. Even for this material a clear difference between QM passivation on day 1 and on day 5 is observed. Whereas mean values of intensity do not vary strongly, local intensity distributions obviously change. Fig. 7 shows the same wafer passivated with a-Si:H and measured on day 1 (after activation of a-Si passivation) and 5 after keeping in the dark in between measurements. Within experimental error no difference between these two maps can be identified in neither the arithmetic means, nor the local intensity distributions. It can be noticed that good regions

with QM passivation seem to be of better quality then the ones with a-Si.H passivation. This is probably explained by the lower reflectance of the sample in the plastic bag containing QM solution compared to the sample with an a-Si:H layer with higher reflectance. That way more light can be absorbed inside the Si wafer with QM solution at the same irradiated light intensity.
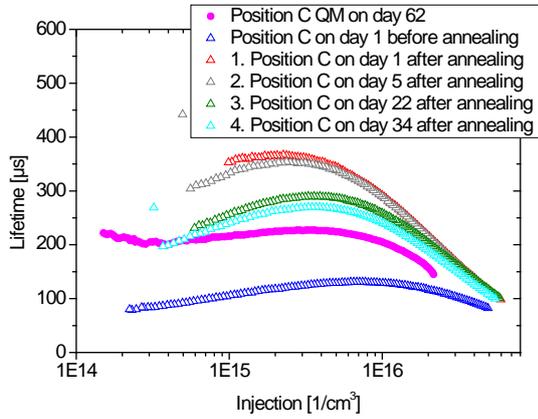


**Figure 4:** QSSPC lifetime of sample SQ3_center_C with a-Si:H passivation before and after the passivation activating annealing step, measured on four different days. The QM passivated measurement on day 62 from Fig. 2 is included as well.
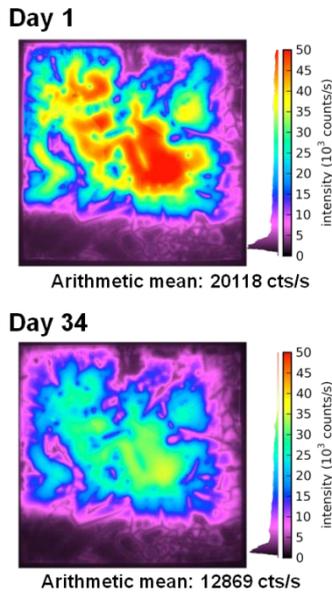


**Figure 5:** PL intensities at ~0.35 suns of SQ3_center_C with the same a-Si passivation layer on different days (day 1 after activation and day 34) after storage in the dark.

The repeated QSSPC lifetime measurements belonging to the PL maps in Fig. 6 and with the additional one on day 4 are presented in Fig. 8. The mean percentage deviation of the measurements with QM passivation (including a few more as grown samples not shown here) is 25%.

It can be concluded from these measurements that samples with a-Si passivation in contrast to QM

passivated ones exhibit reproducible QSSPC lifetimes and PL intensities, respectively, as long as they are measured within a few days.
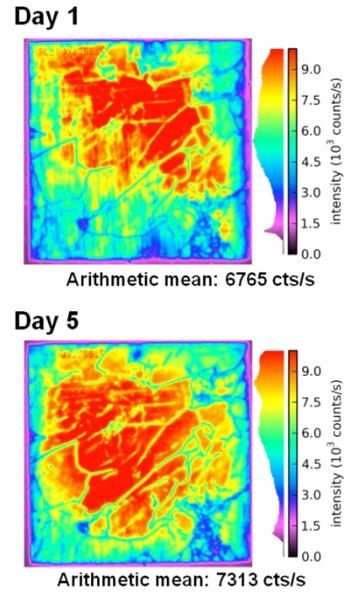


**Figure 6:** PL intensities at ~1 sun of SQ3_top_D with QM passivation on different days (day 1 after activation and day 5) after storage in the dark.
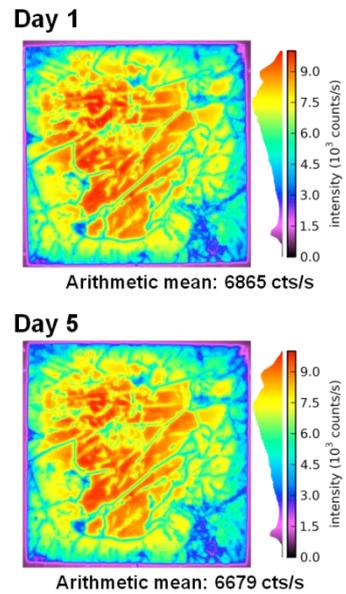


**Figure 7:** PL intensities at ~1 sun of SQ3_top_D with the same a-Si passivation layer on different days (day 1 after activation and day 5) after storage in the dark.
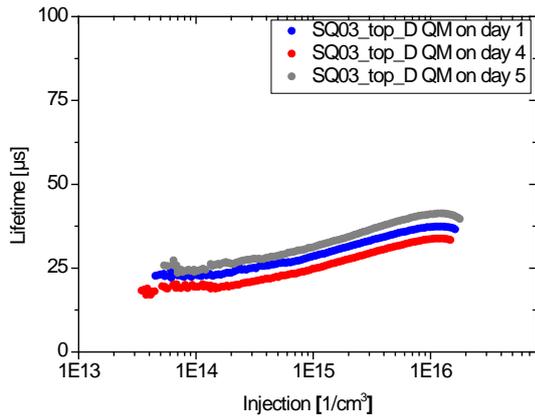
**Figure 8:** QSSPC lifetime of sample SQ3_top_D with QM passivation measured on three different days.

## DISCUSSION

The presented measurements lead to the conclusion that a-Si:H is a suitable passivation type for the mc material under investigation as long as wafers that are compared are measured within a few days and not after weeks using the same passivation layer. On the contrary, both QM measurements on day 41 (red) and 49 (grey) in Fig. 3 exhibit a significant deviation in lifetime at least for positions F and C.

The reason for the strong deviation of the repeated QM measurements is still not exactly clear. Since it was taken care of the exact time sequence between passivation and measuring, this should not lead to such high errors of about 25%. Another possible reason is the orientation of a sample onto the measuring coil of the QSSPC set up which was also tried to keep constant for all measurements. Both possible sources of error are checked. In Fig. 9 one gettered sample SQ03_center_F is measured with QM passivation after different time steps. As expected from earlier investigations lifetime continuously rises with time after the wet chemical passivation is applied [4]. The percentage deviation after 8 min is 8%. This shall give a maximal value for the error that is expected from measuring not at the exact same time after sample passivation. A time inaccuracy of 2 min is more plausible. For Fig. 10 the sample is shifted towards all four directions up to about 1 cm, so that it still covers the QSSPC coil. This shifting experiment gives a maximal error of 17% which can originate from wrong sample orientation. In the actual measurement samples are oriented in a centered position with an accuracy of about ±1 mm.

These measurements cannot explain an error of 25%, but it is possible that a combination of both lead to a higher error. But then the shifting problem should also emerge in the a-Si:H measurements, which is not the case here.

Concerning the a-Si:H passivation there are two major problems which were already mentioned above. First is the application of higher temperatures around 200°C and the second is the hydrogen content of the passivation layer. Compared to other surface passivation methods like e.g. PECVD $SiN_x$:H the temperatures for a-Si:H are considerably lower. For PECVD $SiN_x$:H the standard deposition temperatures are 400-450°C and a

typical firing temperature for passivation activation and bulk hydrogenation is even higher: 800-900°C. During these thermal treatments the Si bulk is changed and also hydrogen can diffuse into the Si [5, 6]. At temperatures of only up to 250°C, which are applied in the presented experiment, hydrogen effusion out of the a-Si:H layer into the Si matrix is not likely to appear according to previous measurements by Einsele [7].
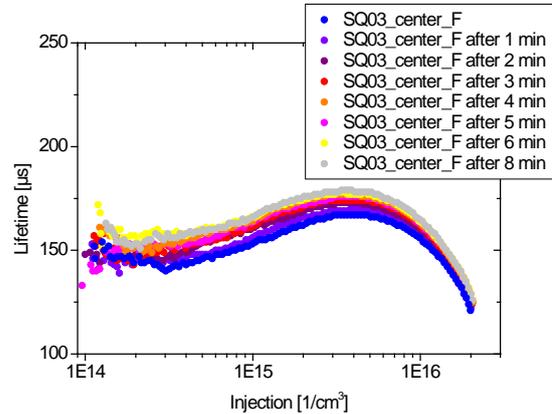


**Figure 9:** Gettered sample SQ03_center_F with QM passivation after different time steps. An error of 8% is reported after 8 min.
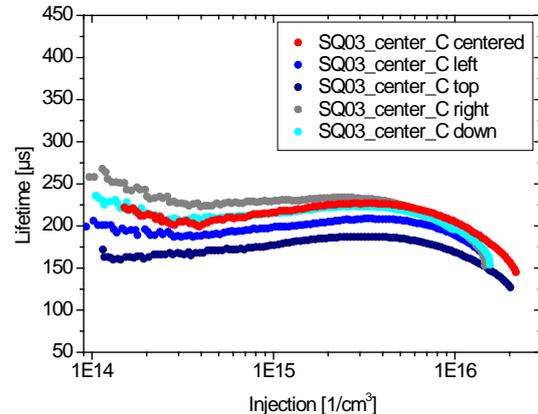


**Figure 10:** Gettered sample SQ03_center_C after shifting towards all four different positions on the QSSPC coil. Percentage deviation from centered orientation is 17%.

## SUMMARY

A detailed analysis of QM passivation on gettered mc-Si is given in this paper. QSS lifetimes are strongly not reproducible for three different 5x5°cm² wafer positions of one 15.6x15.6 cm² wafer. On the same measuring day one position shows the highest lifetime while another position exhibits its lowest value. Also as grown material from the same mc block originating from another position and ingot height is checked for reproducibility. This type of material is of lower quality and hence less sensitive to surface passivation inhomogeneities. Even for this material an error of 25% between different measurements is reported. Two experiments with QM passivation are added in order to

find a possible explanation for such high errors. Firstly, lifetime in one minute time steps was determined. An error of 8% is reported. Secondly, shifting the mc sample within the sensitive region of the QSSPC measuring coil is tested. Here an error of 17% is found. Since both results give an upper limit for the experimental error they cannot explain an error of 25%.

In contrast to these findings a-Si:H passivation leads to highly reproducible QSS lifetimes and PL maps. The only aspect which has to be considered is that samples should be measured within a few days after the activation annealing step of the passivation layer.

## ACKNOWLEDGEMENTS

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