ABSTRACT: In this study the electronic quality of multicrystalline silicon material in the as grown state and after various POCl3 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 POCl3 diffusions on the Si materials under investigation.

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

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. 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.

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 than 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.

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 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.

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.
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 SiNₓ:H the temperatures for a-Si:H are considerably lower. For PECVD SiNₓ: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].

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.

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