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Research Article

Quinhydrone Chemical Passivation of a Silicon Surface for Minority Carrier Bulk-Lifetime Measurements

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For the measurement of the minority carrier bulk-lifetime the characterization method MW-PCD is used, where the result of measurement is the effective carrier lifetime, which is very dependent on the surface recombination velocity and therefore on the quality of a silicon surface passivation. This work deals with an examination of a different solution types for the chemical passivation of a silicon surface. Various solutions are tested on silicon wafers for their consequent comparison. The main purpose is to find optimal solution, which suits the requirements of a time stability and start-up velocity of passivation, reproducibility of the measurements and a possibility of a perfect cleaning of a passivating solution remains from a silicon surface, so that the parameters of a measured silicon wafer will not worsen and there will not be any contamination of the other wafers series in the production after a repetitive return of the measured wafer into the production process. The cleaning process itself is also a subject of a development.

1. Introduction

The main objective of this work is to propose a solution, which would meet a few key parameters. It has to exhibit an immediate startup of passivation properties as well as long-time stability (few hours for an appropriate high-resolution scan or degradation study). Last but not least the reproducibility of the lifetime measurement is very important, which means that a repeating of measurement-cleaning process will not lead to extreme lifetime degradation due to passivation solution residues on a silicon surface of the tested wafer. Therefore perfect cleaning of the wafer surface must be possible. If a contaminated wafer is returned back to the production process, the whole wafer series may be contaminated (mainly during the high-temperature processes). The carrier lifetime is measured by the WT-2000 machine using the MW PCD method [1]. Wafers with a resistivity of $20\,\Omega\cdot$cm and 4′′ in size used for the measurements went through saw damage removal (etching in 60% KOH at a temperature of 80–90°C for 1–5 min + washing 3×2 min in demineralized water). Some wafers were textured by an anisotropic texturing process in 3% NaOH + IPA. Excellent passivation properties of a solution are needed to gain the maximum average lifetime values. This means that there is nearly no surface recombination, which is the main objective of chemical passivation for experimental purposes [2].

2. Chemical Passivation in Iodine/Ethanol Solution

Testing of the standard passivation solution of 1% iodine/ethanol (see Figure 1) exhibits quite remarkable time instability. On the other hand, the immediate startup of the passivating ability is the big advantage of this solution. The measured average lifetime values are at their maxima from the beginning, and then they decrease by about 25% per hour. This may influence the final results (measurement of high-quality wafers even with a resolution of 1 mm takes up to 30 minutes).

The disadvantage of this solution is the somewhat problematic reproducibility of measurement, as a significant decrease of the average lifetime (more than 10%) was recorded after each rinsing. The main reason is that there are residues

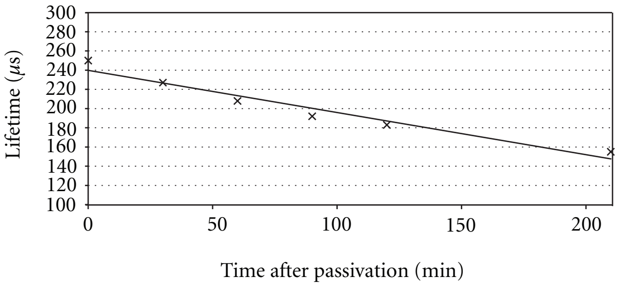

Figure 1: Time stability of iodine passivation.

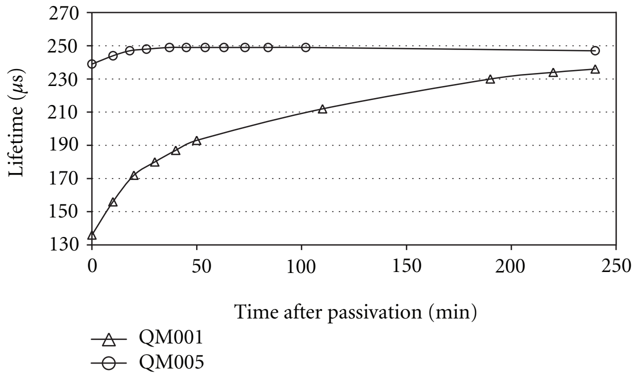

Figure 2: Comparison of the passivation startup between QM001 and QM005.

of the solution left on the surface thus degrading it, and therefore it is not possible to achieve equal or similar results. Next problem may be caused by ethanol, which can decrease surface tension and hinder the texture creating process after the postpassivation cleaning. There are areas without any texture on the surface after the alkaline texturing in 3% NaOH solution. For other solutions which contained methanol instead of ethanol, this phenomenon did not exist and the process of texturation was completed in the standard way.

3. Chemical Passivation in Quinhydrone/Methanol Solution

3.1. Comparison between QM001 and QM005. The quinhydrone/methanol solution shows a very good time stability [3, 4]. There is nearly no decrease in average lifetime values observed approximately after 2 hours after their stabilization at reached maxima, and even later the measured values decreased by only about 10% within 10 hours. The solution with the concentration of 0.01 mol/dm^3 marked QM001 (218 mg of quinhydrone in 100 mL of methanol) cannot be used for practical purposes, because the start-up of passivation abilities in this case is about 3 hours (see Figure 2).

This solution can be used to measure the efficiency of rinsing after the chemical passivation. Quinhydrone residues which remain on the surface increase the concentration of the solution near the surface and thus decrease the startup time of the passivating abilities. This can be recognized from a graph, and it can be estimated how much quinhydrone remains on the surface of the rinsed wafer.

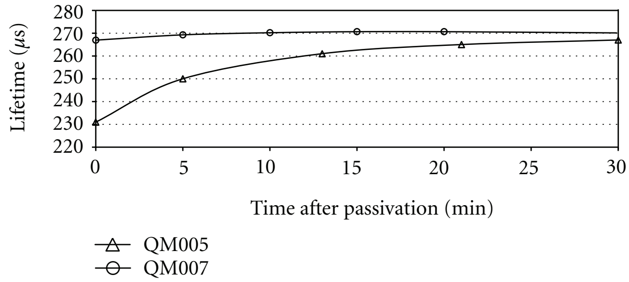

Figure 3: Comparison of the passivation startup between QM005, and QM007.

The solution marked as QM005 (the solution with concentration of 0.05 mol/dm^3) has a significantly lower passivation ability start-up time (20 minutes for polished wafers and 40 minutes for textured wafers). However, it is not yet sufficient enough for practical lifetime measurement for industrial use.

3.2. Quinhydrone/Methanol Solution QM007. It is possible to meet all the initial requirements with concentration of 0.07 mol/dm^3, marked QM007. The startup is nearly immediate (see Figure 3). This solution passivates immediately after the wafer diving for polished wafers and within 10 minutes for textured wafers. The solution also meets the time stability requirement (minimally 1 hour and then a decrease of 15% in 10 hours). This solution also exhibits a high reproducibility of the measurement with the possibility to texture Si wafers after effective rinsing.

3.3. Influence of Quinhydrone Concentration on the Temporal Stability of the Passivation Layer

Hypothesis H1. The increasing of quinhydrone concentration in the solution causes rapid degradation of the passivation layer. The reason for this hypothesis is to demonstrate zero impact on the temporal stability of passivation layer. The concentration has to be specified exactly, the high concentrated solutions do not have any importance.

Graphs for both concentrations are parallel (see Figure 4), which means that the velocity of decline is the same and therefore the time degradation of the passivation layer does not depend on the quinhydrone concentration in the solution, hypothesis H1 was rejected.

3.4. Quinhydrone/Methanol Solution with High Concentration for Textured Wafers

Hypothesis H2. The increasing of quinhydrone concentration in methanol will result in the an acceleration of start-up passivation ability for textured silicon wafers.

As the increasing quinhydrone concentration over 0.07 mol/dm^3 produces no effect for textured Si wafers, it is not desirable to increase the concentration (see Figure 5).

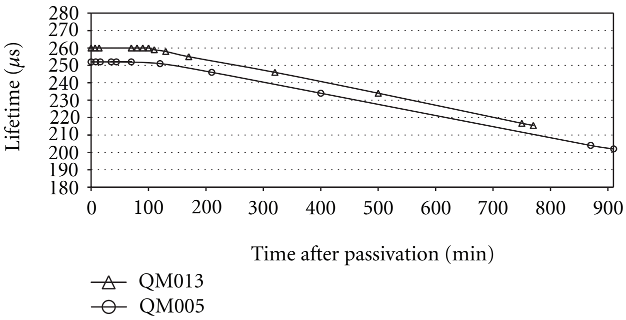

Figure 4: Comparison of the temporal stability of chemical passivation between QM005 and QM013.

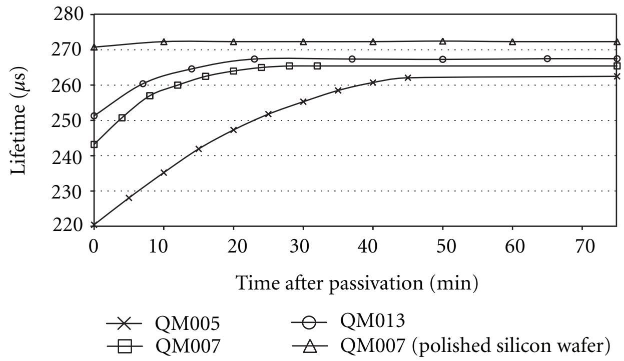

Figure 5: Comparison of the passivation startup between QM005, QM007, and QM013 for textured wafers.

With the concentration of 0.07 mol/dm^3, velocity saturation occurs for textured wafers and further concentration increasing has no effect on the startup of passivation. The solution with a concentration of 0.13 mol/dm^3 is useless for practical purposes, because there is a problem with dissolving of quinhydrone (the solution is "saturated") and quinhydrone crystallisation from the solution produces a large amount of quinhydrone waste. Another problem with the rinse is where the quinhydrone waste quickly pollutes methanol in the rinse cascade.

4. Postpassivation Cleaning

Postpassivation cleaning is important if the wafer should be returned back to the production process, and it is desirable that the silicon surface remains clean, without any remains of the passivation solution that could damage the final solar cell structure or even contaminate the whole series of wafers in next production operations (especially high-temperature operations). The cleaning in pure methanol (see Figure 6) requires an improved rinsing technique, because some surface degradation can be observed after multiple testing. The degradation of 3–5% after each testing is insignificant and caused by scratches and crystal-lattice defects during manipulation.

A possible modification of the cleaning process is based on adding another cleaning step—washing of the wafer in DEMI (demineralized) water with a temperature of 80°C

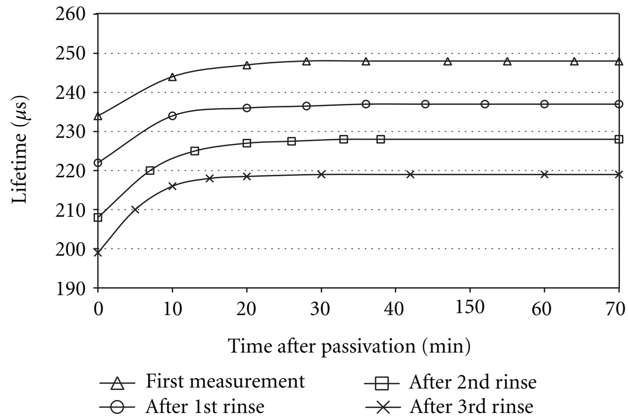

Figure 6: Three cycles of passivation-cleaning process (passivated in QM005).

after the cleaning in pure methanol. But since this rather time-consuming technique is not particularly efficient, the multiple-cleaning process in pure methanol seems to be more acceptable. As quinhydrone is more difficult to resolve and easy to catch at a silicon surface, a methanol cascade was designed. The cascade consists of three small baths filled with methanol. The cleaned wafer goes to the first bath, then it is rinsed by DEMI water (to get rid of most quinhydrone remains). After that comes the second and subsequently the third bath to ensure that the wafer is perfectly clean. After multiple tests the methanol in the last two baths is clean.

5. Conclusions

This work confirms the drawbacks of the commonly used iodine/ethanol passivation, where this solution shows the time instability of the passivation abilities, problems with the reproducibility of the measurement and mainly with cleaning of the solution residues from the surface after the passivation. As a consequence there is a problem in the texturing process after iodine passivation, which may be also caused by decreased surface tension (ethanol).

The quinhydrone/methanol solution, for which the ideal concentration of 0.07 mol/dm^3 was determined, has nearly ideal parameters of the silicon surface chemical passivation. This solution marked as QM007 exhibits a high time stability of the passivation abilities (at least 2 hours without average lifetime decrease and then only a slow decrease of about 10% in 10 hours), immediate startup of passivation abilities (for the polished wafers, and less than 10 minutes for the textured wafers: enlargement of the total surface and its different orientation, where the initial measured lifetime τ is 80% of the maximum), good reproducibility of the measurement (decrease of the average lifetime values by 3–5% after each cleaning, the degradation only due to scratches and crystal-lattice defects during manipulation), and possibility of perfect surface cleaning with the subsequent successful texturing process.

The influence of quinhydrone concentration on the degradation of passivation layer was verified. With increasing concentration, there was no degradation; therefore hypothesis H1 was rejected. When increasing quinhydrone concentration in methanol concentration over 0.07 mol/dm^3, a faster start-up passivation ability for textured wafers was not achieved and hypothesis H2 was rejected.

For practical use of chemical passivation of silicon surfaces for minority carrier bulk-lifetime measurements, the ideal solution is QM007 which overtops the commonly used chemical passivation in iodine/ethanol solution. Postpassivation cleaning in a methanol cascade is a sufficient rinsing technique.

Acknowledgments

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