

Carrier Bulk-Lifetime Measurement during Solar Cell Production

M. Solcansky¹, J. Vanek¹

¹Brno University of Technology, Faculty of Electrical Engineering and Communication
Technická 10, 616 00 Brno, Czech republic
E-mail : solcansky@phd.feec.vutbr.cz

Abstract:

The main material parameter of silicon is the minority carrier bulk lifetime and influences the effectiveness of photovoltaic cells. It may change in the technological process especially during high temperature operations. Monitoring of the carrier bulk-lifetime is necessary for modifying the whole technological process of production. 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 of this work 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.

INTRODUCTION

Crystalline silicon is still a dominant input material in photovoltaic technologies. There are two ways how to reduce costs for the electrical energy produced from silicon solar cells. The first way is to reduce the costs of production and the second way is to raise the conversion effectiveness of solar cells. The minority carrier bulk lifetime is the main material parameter that influences their effectiveness. The value of minority carrier bulk lifetime may change especially during the high temperature operations. Monitoring of the carrier lifetime is inevitable for debugging (modifying) the whole technological process of production.

Different characterisation methods for the detection of the minority carrier lifetime can be used. There are the most known methods - MW PCD (Microwave Photoconductivity Decay) and QSSPC (Quasi Steady State Photoconductivity). The result of a measurement using either of these methods is an effective carrier lifetime, which is extremely dependent on the surface recombination velocity and therefore on the quality of a silicon surface passivation.

The main goal of this work is to choose a solution, which will suit a few key parameters. It will show a long-time stability of a silicon surface passivation effect (few hours in a manufacturing process), immediate start-up of passivation properties is very important. Last but not least parameter is reproducibility of the measurement, which means that a repeating of measurement-cleaning process won't lead to extreme lifetime degradation due to passivating solution remains on a silicon surface of the tested wafer, thus there has to be a possibility of

perfect cleaning of the wafer surface, because the return of a contaminated wafer back to production process may lead to a whole wafer series contamination (mainly in high temperature operations). The carrier lifetime will be measured with WT-2000 machine using the MW PCD method. Wafers with the resistivity of $20 \Omega \cdot \text{cm}$ and the size of 4" used for the measurements went through MK1 process (etching in 60% KOH at a temperature of 80-110°C for 1 – 5 min. + washing 3x2 min. in DEMI water) and MK3 process (anisotropic texturing in 3% NaOH). Great passivation properties of a solution are needed to gain the maximum average lifetime values, that means there will be no surface recombination, which is the main objective of the chemical passivation for the experimental purposes.

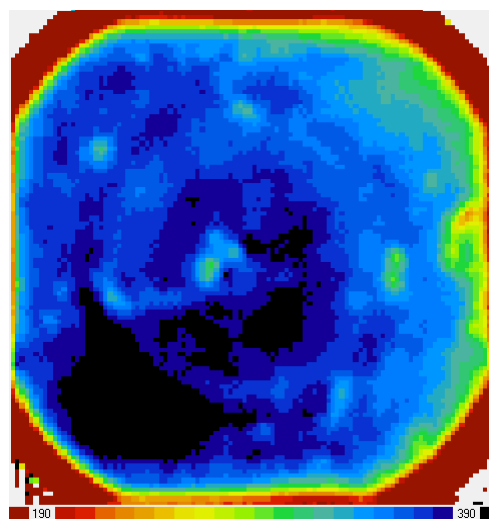


Fig. 1: Result after measurement of lifetime on silicon wafer by MW-PCD method.

CHEMICAL PASSIVATION IN IODINE/ETHANOL SOLUTION

Testing of the standard passivation solution of 1% iodine/ethanol (see Fig. 2) exhibits quite remarkable time instability. On the other hand, the immediate start-up 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).

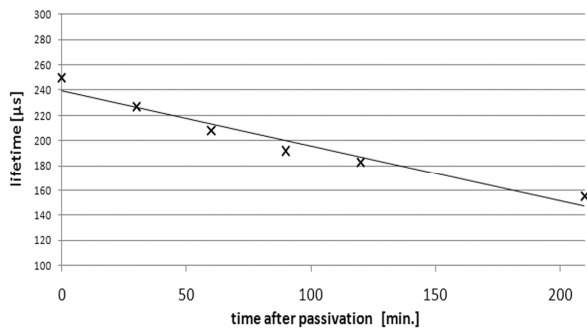


Fig. 2: Time stability of iodine passivation

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 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 post-passivation 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.

CHEMICAL PASSIVATION IN QUINHYDRONE/METHANOL SOLUTION

Comparison between QM001 and QM005

The quinhydrone/methanol solution shows a very good time stability. 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/dm³ 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 Fig. 3).

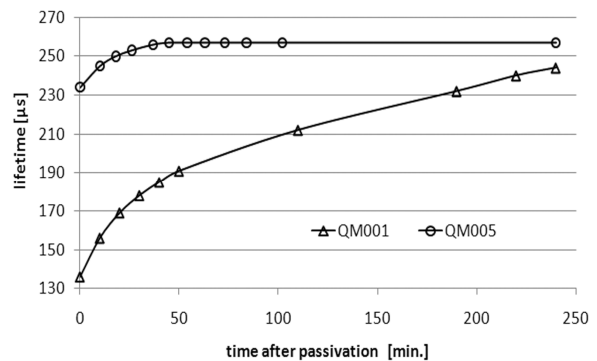


Fig. 3: Comparison of the passivation start-up between QM001 and QM005

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 start-up 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.

The solution marked as QM005 (the solution with concentration of 0,05 mol/dm³) 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.

Quinhydrone/methanol solution QM007

It is possible to meet all the initial requirements with concentration of 0,07 mol/dm³, marked QM007. The start-up is nearly immediate (see Fig. 4). 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.

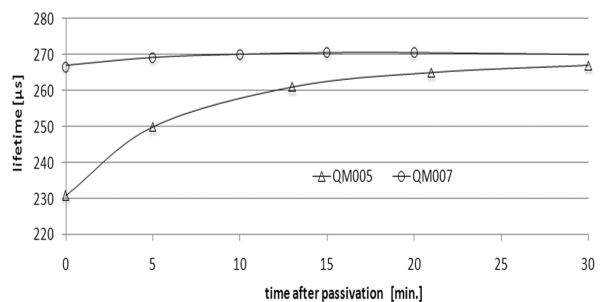


Fig. 4: Comparison of the passivation start-up between QM005 and QM007

Quinhydrone/methanol solution with high concentration for textured wafers

Hypothesis H1: The increasing of quinhydrone concentration in methanol will result in the an acceleration of start-up passivation ability for textured silicon wafers.

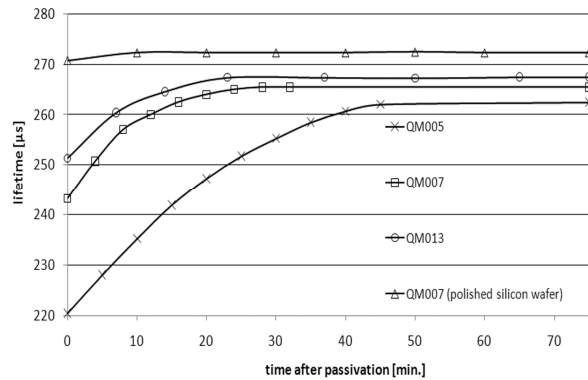


Fig. 5: Comparison of the passivation start-up between QM005, QM007 and QM013 for textured wafers

As the increasing quinhydrone concentration over 0.07 mol/dm^3 produces no effect for textured Si-wafers and, it is not desirable to increase the concentration (see Fig. 5). With the concentration of 0.07 mol/dm^3 velocity saturation occurs for textured wafers and further concentration increasing has no effect on the start-up 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, where the quinhydrone waste quickly pollutes the methanol in the rinse cascade.

POST-PASSIVATION CLEANING

Post-passivation 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 Fig. 6) requires an improved rinsing technique, because some surface degradation can be observed after multiple testing.

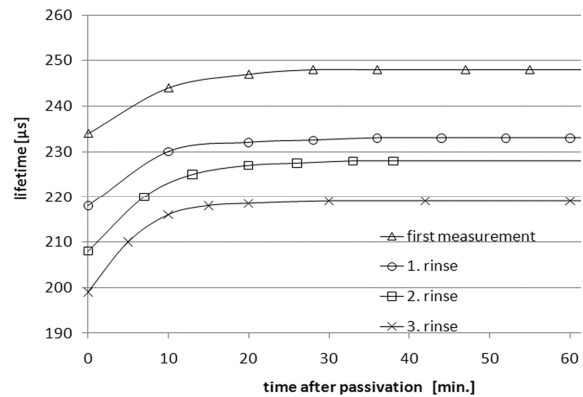


Fig. 6: Three cycles of passivation-cleaning process (passivated in QM005)

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 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's 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

DRY QUINHYDRONE PASSIVATION

In the first experiment the polished silicon wafer was dipped in the QM007 solution for 2 minutes, which should be long enough to create of a passivation layer according as it's in the case of the wet passivation (in bag with passivation solution). The average lifetime of this passivated wafer was measured when the methanol evaporated and the wafer remained dry. The value of the average lifetime was $360 \mu\text{s}$, which corresponds to the average lifetime values of standard measured wafers. But gradual process of creating quinhydrone crystals (see Fig. 7) damages continuous passivation layer, which is needed for perfect surface passivation, cause rapid decrease of the measured average lifetime.

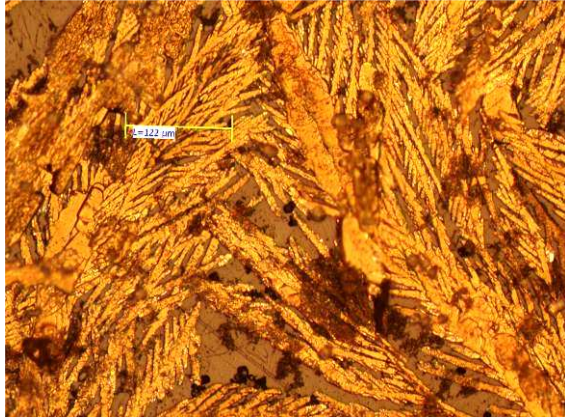


Fig. 7: Quinhydrone crystals created from the QM007 solution

In the second experiment only a very thin layer of the solution was laid on a next silicon wafer. The layer wasn't visible after the evaporation of methanol from the QM007 solution. The first measured average lifetime value after the wafer became dry was 380 μ s. The average lifetime remained constant for 20 minutes, which long enough for practical purposes. This passivation technique can be used for some special applications. This procedure was verified by more tests.

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/dm³ 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 start-up 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 “standard” cleaning – without decrease when using the methanol cascade), possibility of perfect surface cleaning with the subsequent successful texturing process.

The influence of quinhydrone concentration on the degradation of passivation layer was verified. 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. Post-passivation cleaning in a methanol cascade is a sufficient rinsing technique.

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