Fast New Method for Temporary Chemical Passivation

***Marek Solčanský*[1], *Jiři Vaněk* and *Aleš Poruba*[2]**

The main material parameter of silicon, that influences the effectiveness of photovoltaic cells, is the minority carrier bulk lifetime. 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. For the measurement of the minority carrier bulk-lifetime the characterization method MW PCD (Microwave Photoconductance Decay) 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 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. Another purpose of this work is to identify the parameters of other quinhydrone solutions with different concentrations as compared with the quinhydrone solution in methanol with a concentration of 0.07 mol/dm³ marked QM007 (referential solution).

The method of an effective chemical passivation with a quinhydrone in methanol solution was suggested. The solution with a concentration of 0.07 mol /dm³ fulfills all required criteria. The work also confirms the influence of increased concentration quinhydrone on the temporal stability of the passivation layer and the effect for textured silicon wafers. In conclusion, the influence of an illumination and the temperature on the properties of the passivating solution QM007 is discussed.

Key words: *chemical passivation, quinhydrone, carrier bulk- lifetime, Microwave Photoconductance Decay*

Introduction

A minority carrier bulk lifetime is the main material parameter of silicon that 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.

The main objective of this work is to propose a solution, which would meet a few key parameters. It has to exhibit an immediate start-up of passivation properties as well as long-time stability (few hours for an appropriate high resolution scan or degradation study). The carrier lifetime is measured by the WT-2000 machine using the MW PCD method. Wafers with a resistivity of 20 Ω.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 3x2 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.

This work deals with examination of quinhydrone/methanol solution for chemical passivation of silicon surfaces. The main objective of this work is to identify the parameters of other quinhydrone solutions with different concetrations as compared with a referential quinhydrone/methanol solution with a concentration of 0.07 mol/dm³, marked QM007. Silicon wafers passivated by the QM007 solution exhibit very good long-time stability, but relative slow startup of passivation abilities. For the textured Si wafers it takes about 10-15 minutes to eliminate this time dependence. We will show the influence of increased concentration of quinhydrone solution on startup abilities and temporal stability of the passivation layer. The last objective is to identify the influence of illumination and temperature on the properties of quinhydrone chemical passivation.

Chemical passivation in quinhydrone/methanol solution

The quinhydrone/methanol solution shows 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

[1] *Ing. Marek Solčanský, doc. Ing. Jiři Vaněk, PhD.,* Brno University of Technology, Faculty of Electrical Engineering and Communication, Technicka 10, 616 00 Brno, Czech republic, +420731925638, solcansky@phd.feec.vutbr.cz , vanekji@feec.vutbr.cz

[2] Aleš Poruba, Solartec s.r.o., Televizní 2618, 756 61 Rožnov pod Radhoštěm, Czech republic

be used for practical purposes, because the start-up of passivation abilities in this case is about 3 hours (Fig. 1).

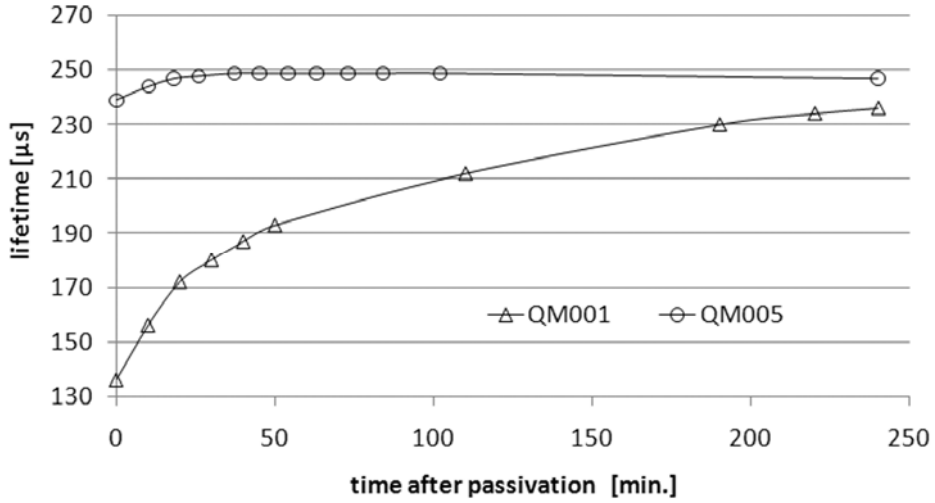

Fig. 1. Comparison of the passivation start-up between QM001 and QM005.

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.

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

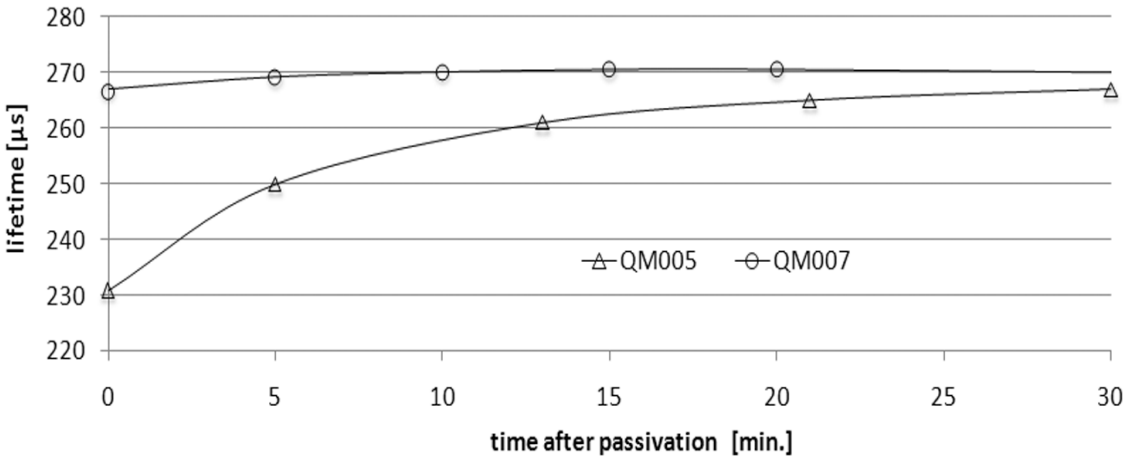

Fig. 2. Comparison of the passivation start-up between QM005 and QM007.

Influence of modified procedure of QM007-passivation

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.

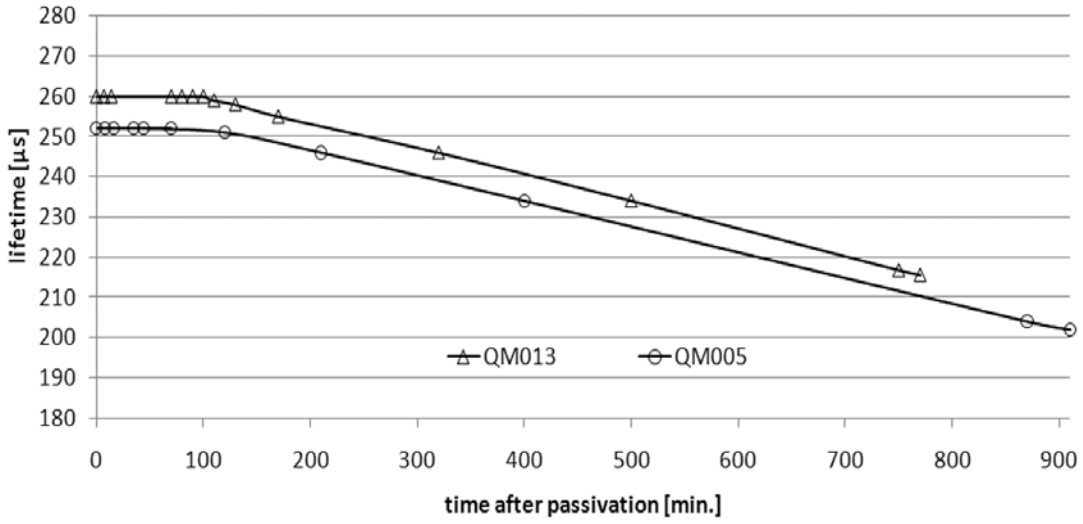

Fig. 3. Comparison of the temporal stability of chemical passivation between QM005 and QM013.

Graphs for both concentrations are parallel, 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.

Hypothesis H2: The increase of quinhydrone concentration in methanol will result in an acceleration of start-up passivation ability for textured silicon wafers. The main purpose of this experiment is to develop and improve chemical passivation for textured silicon wafer, where the solution QM007 is not enough sufficient.

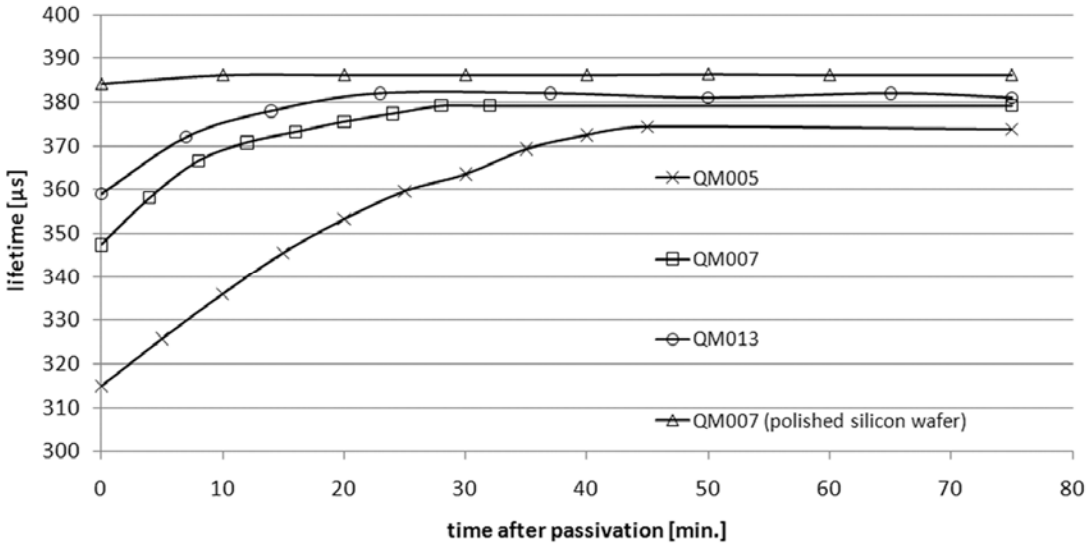

Fig. 4. Comparison of the passivation start-up between QM005, QM007 and QM013 for textured wafers.

The increase of quinhydrone concentration over 0.07 mol/dm³ produces no effect for textured Si-wafers and it is not desirable to increase the concentration. With the concentration of 0.07 mol/dm³ velocity saturation occurs for textured wafers and further increase of concetration has no effect on the start-up of passivation. The solution with a concentration of 0.13 mol/dm³ 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. There is another problem with the rinse, where the quinhydrone waste quickly pollutes the methanol in the rinse cascade.

Hypothesis H3: The illumination and temperature have positive effect on chemical passivation in solution QM007 and it can improve start-up of passivation layer for textured wafers.

For this experiment 2 kinds of illumination were used, halogen and neon source of illumination. First experiment was done for illumination with intensity 1000 W/m² during 60 seconds. Whole experiment with

halogen illumination met with problem with FeB (ferrum-boron) pairs, because high intensity of illumination broke FeB pairs therefore it caused to increase lifetime. Second problem was with time of illumination, time 60 seconds is sufficient for breakup of all FeB pairs. Third problem with halogen illumination was with higher temperature of source, which influences properties of chemical passivation.

For detection of illumination influence was necessary to use neon source, which has other spectrum of radiation (without infrared). First experiment was tested for time 30 seconds, but phenomenon with FeB was the same as for halogen illumination. The most successful test was for time 5 seconds of neon illumination, where one half of silicon wafer was illuminated. Lifetime in illuminated part was worse about 6 % than in unlighted part. The higher illumination has negative influence on chemical passivation. After neon illumination with intensity 1000 W/m² during 5 seconds was the lifetime decrease of about 5 %. Hypothesis was rejected, because illumination does not improve a quality and start-up of chemical passivation in QM007. The higher illumination has positive effect on value of measured lifetime, but the increase is caused by breakup of FeB pairs – breakup of recombination centers.

For better start-up of chemical passivation in QM007 is not possible to use higher illumination, finally it makes worse properties of chemical passivation. This phenomenon is not very significant and for practical usage of chemical passivation it is unnecessary. For common testing conditions it is not important to think about the influence of illumination. Hypothesis H3 was rejected.

Influence of a temperature is more significant for chemical passivation than influence of an illumination, there is substantial effect. This phenomenon can be caused higher activity of parasite processes on the surface of silicon, especially oxidation.

Lifetime τ of silicon wafer was measured with standard chemical passivation in QM007 at temperature of 20 ºC and lifetime was approx. 270 µs. Then there was done cleaning process in methanol cascade and silicon wafer was again put in QM007 and exposure to higher temperature with value 80 ºC during 60 second. This measurement shows than there is lifetime decrease of about 15 % - 20 %. Figure 5 also shows experiment with temperature of 50 ºC during 60 seconds.

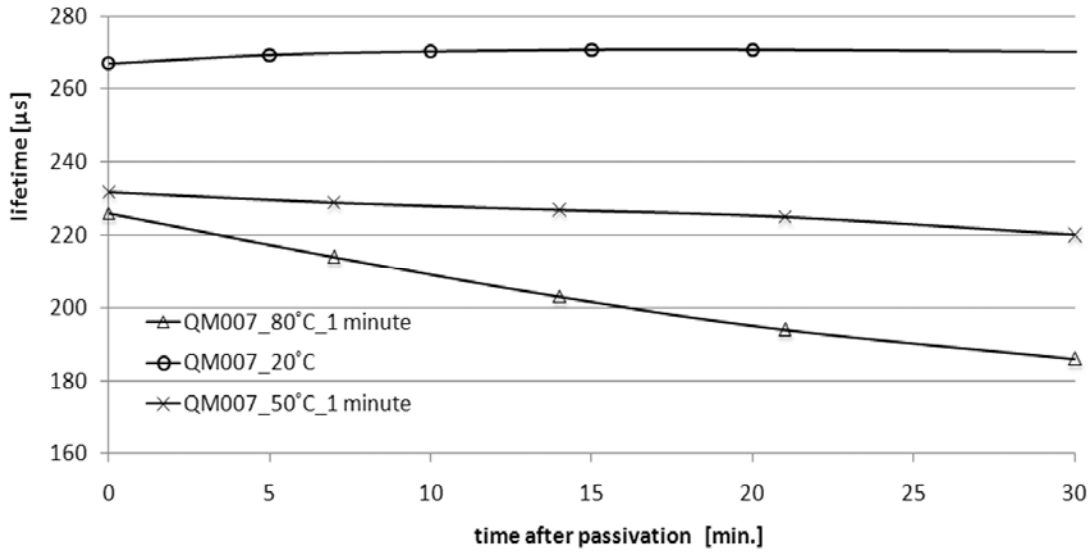

Fig. 5. Comparison of the passivation properties for various values of temperature, which influences on process of chemical passivation.

The reason of this experiment was a effort to find out if temperature improves start-up of chemical passivation, especially for textured wafer. (For textured wafers this phenomenon could be very useful, there is necessary time for start-up of passivating abilities)

Unfortunately, this hypothesis was rejected, temperature cannot improve properties of chemical passivation in QM007, it makes worse this chemical passivation. For practical usage and common testing conditions it is not important to think about this phenomenon.

Conclusion

The quinhydrone/methanol solution, for which was determined the concentration 0.07 mol/dm³, has nearly ideal parameters of the silicon surface chemical passivation. This solution marked as QM007 has a great 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, 15 minutes for the textured wafers – enlargement of the surface), good reproducibility of the measurement (decrease of the average lifetime values by 3-5 % after each "standard" cleaning – without decrease when using methanol cascade), possibility of a perfect surface cleaning with the subsequent successful texturation 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. If there is increase of quinhydrone concentration in methanol over 0,07 mol/dm³ so faster start-up passivation ability for textured wafers was not achieved and hypothesis H2 was rejected.

The higher illumination has negative impact on chemical passivation, this phenomenon is not very significant and for practical usage of chemical passivation it is unnecessary. For common testing conditions it is not important to think about the influence of illumination. After neon illumination with intensity 1000 W/m² during 5 seconds was the lifetime decrease of about 6 %. Hypothesis was rejected, because illumination does not improve a quality and start-up of chemical passivation in QM007.

Hypothesis about the increase of temperature was rejected, the higher temperature makes worse quality of chemical passivation in QM007. The reason, higher temperature accelerates activity of parasitic phenomena, especially oxidation of silicon surface.

By the help of modified procedure (temperature, illumination or extra concentration) it is not possible to improve a features of chemical passivation in QM007.

For practical usage of chemical passivation of silicon surfaces for minority carrier bulk-lifetime measurement 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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