

PROGRESS IN HYDROGENATION OF MULTICRYSTALLINE SILICON SOLAR CELLS

M. Kaes¹, G. Hahn¹, A. Metz²

¹University of Konstanz, Department of Physics, Jacob-Burckhardt-Str. 29, 78457 Konstanz, Germany

²SCHOTT Solar GmbH, Carl-Zeiss-Str. 4, 63755 Alzenau, Germany

Author for correspondence: Martin.Kaes@uni-konstanz.de, Tel.: +49 7531 88 2082, Fax.: +49 7531 88 3895

ABSTRACT: We focus on hydrogenation by firing a double sided PECVD SiN on EFG and block cast mc wafers. Compared to our standard high-efficiency process with a PECVD SiN on the front side and a full area Al-BSF on the rear side we replaced the full rear side Al-BSF by a SiO/SiN stack with a locally alloyed Al-BSF. In contrast to the local firing at the laser fired contacts approach, the whole wafer is heated to release hydrogen from the SiN into the bulk from both sides alloying the Al locally at the rear side. This double sided hydrogenation gives a better bulk passivation compared to the standard single sided hydrogenation. Especially areas of lower quality improve by the double sided hydrogenation, made visible by LBIC measurements.

With this contribution we try to give new insights to the wide field of hydrogenation.

Keywords: Hydrogen Passivation, Recombination, Multi-Crystalline

1 INTRODUCTION

Hydrogenation during processing of multicrystalline (mc) silicon wafers into solar cells is a key step to fabricate solar cells of high quality. In standard industrial processing the hydrogenation by firing hydrogen rich Plasma Enhanced Chemical Vapor Deposition (PECVD) silicon nitride is preferred. Hydrogenation by Microwave Induced Remote Hydrogen Plasma (MIRHP) is mainly used in research. Comparing these two methods, hydrogenation by SiN firing at high temperatures gives better results than the MIRHP hydrogenation at rather low temperatures. This holds for Edge-defined Film-fed Growth (EFG) and String Ribbon (SR) [1] silicon as well as for standard block cast mc [2]. In industrial application the PECVD SiN is deposited on the front side serving as emitter passivation, as antireflection coating and as hydrogen source during standard cofiring.

We think that one critical point for the single sided hydrogenation is the cooling down after the SiN firing in agreement to the results presented in [3]. During cooling down the SiN stops providing hydrogen but anyway the hydrogen already distributed in the bulk diffuses while the wafer temperature is still above 300-400°C. Hence the hydrogen can diffuse out at the rear side, lowering the overall hydrogen content in the bulk. Defects not already bonded to hydrogen in this temperature range can remain unpassivated after continuous cooling down due to lack of free available hydrogen atoms. With a fast cooling ramp as for a RTP anneal the hydrogenation can be improved by lowering the overall outdiffusion of the hydrogen. However, if a PECVD SiN is present on both sides of the wafer, these layers themselves work as a diffusion barrier for the hydrogen hindering the outdiffusion of the hydrogen. Thus the cooling down period after SiN firing should be less critical for a successful hydrogenation increasing the tolerance of firing conditions for contact formation. According to this theory standard block cast multicrystalline silicon as well as ribbons should benefit from a double sided PECVD SiN including a firing step.

2 HIGH EFFICIENCY SOLAR CELL PROCESS

2.1 Solar cell processes for mc materials

Al-BSF (A)	SiO/SiN (B)	Al-BSF + SiN (C)
cutting and etching	cutting and etching	cutting and etching
POCl ₃	POCl ₃	POCl ₃
Oxidation	Rear-side etching	Al Screenprint
PECVD SiN front side	Oxidation	Drying and Firing
Al Screenprint	PECVD SiN rear side	Al etching
Drying and Firing	PECVD SiN front side	PECVD SiN front side
Al etching	Al grid formation	PECVD SiN rear side
Photolithography	Drying and Firing	Firing
Ti/Pd/Ag evaporation	Photolithography	Rear side SiN etching
Al evaporation	Ti/Pd/Ag evaporation	Photolithography
Ag plating	Al evaporation	Ti/Pd/Ag evaporation
(contact sintering)	Ag plating	Al evaporation
MIRHP	MIRHP	Ag plating
SiN/MgF ₂ DARC	SiN/MgF ₂ DARC	MIRHP
		SiN/MgF ₂ DARC

Figure 1: Solar cell processes with single sided hydrogenation (A) and double sided hydrogenation (B+C).

Our standard high efficiency process for mc silicon material (process A) is able to reach efficiencies up to 18.5% on 0.8 Ωcm FZ material [4]. In this process the relatively high surface recombination velocity (SRV) of the Al BSF is limiting V_{oc} and lowering j_{sc} .

Using a local BSF structure together with a good surface passivation via a SiO/SiN stack (process B) the effective SRV can be significantly lower. After double sided POCl₃ diffusion the rear side emitter has to be etched off prior to the subsequent thin thermal oxidation. Alternatively, if gettering is not required, the POCl₃ diffusion can be carried out as a single sided diffusion with commonly used techniques. LPCVD SiN

could be applied to both wafer sides in a single process step, however, the hydrogenation capability of LPCVD SiN is poor compared to an optimized PECVD SiN which is deposited on both wafer sides in the next two steps after the oxidation. By means of photolithography and lift-off technique aluminum is evaporated as a grid on the rear side after opening the SiO/SiN stack. The firing now forms a local Al-BSF together with a double sided releasing of hydrogen from the SiN into the bulk. Except for omitting the contact sintering all further process steps are according to the single side SiN process.

Process C leads to the same solar cell design as for A if the oxidation in process A is omitted. However, the hydrogenation in process C is carried out in a second firing step. In the first firing step the rear side Al-BSF is formed. After etching the Al a PECVD SiN is deposited on both sides of the wafer. The second firing step gives a double sided hydrogenation comparable to the hydrogenation in process B but the solar cell design is comparable with process A. Before the subsequent formation of the contacts the rear side SiN is etched off.

2.2 Contact sintering via MIRHP

After the bulk hydrogenation every subsequent high temperature step is crucial for the effective bulk passivation in the processed solar cell. Here high temperatures mean temperatures at which significant out-diffusion of hydrogen and though depassivation occurs. On EFG these are temperatures above 300°C ascertained in earlier studies for depassivation after hydrogenation via microwave induced remote hydrogen plasma (MIRHP) [5]. After the SiN firing in the standard process a contact sintering under Ar/H₂ ambient for one hour at 380°C is applied. Thus it was investigated how the previous bulk passivation is affected by this anneal.

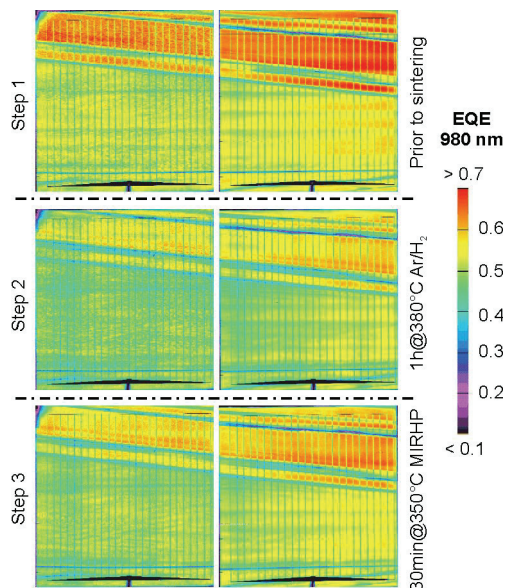


Figure 2: Depassivation of the bulk due to contact sintering. Subsequent MIRHP can only partly recover the bulk passivation. Illustrated are LBIC measurements of two adjacent EFG solar cells (left+right) after different process steps.

EFG wafers were processed to solar cells according to process A (without oxidation). After Ag plating four 2x2 cm² solar cells were isolated from a 5x5 cm² wafer by dicing and measured using Laser Beam Induced Current (LBIC). The LBIC results (figure 2, top) represent the condition after the hydrogenation with a good bulk passivation. A subsequent contact sintering in Ar/H₂ ambient for one hour at 380°C degrades most cell areas probably due to hydrogen out-diffusion (figure 2, middle). The following second hydrogenation by MIRHP for 30 minutes at 350°C enhances the bulk but cannot recover the good bulk passivation reached before contact sintering. A longer and hotter MIRHP treatment could help for better bulk passivation but leads to shunting by the Ti in the front contact.

An approach is to replace the contact sintering under Ar/H₂ ambient completely by the MIRHP to achieve a balance between out- and in-diffusion of hydrogen. It has to be tested if this kind of contact sintering is suitable to reach low contact resistances and if the quality of bulk passivation can be kept on the level after hydrogenation by SiN firing or even can be improved according to previous lifetime results.

Table I illustrates that the commonly used contact sintering under Ar/H₂ ambient can be successfully replaced by contact sintering using MIRHP. Fill factors above 80% could be reached. This is already in the range of the process limitations.

Table I: IV data of four 2x2 cm² FZ reference solar cells before and after contact sintering by MIRHP for 60 minutes at 350°C with a single layer antireflection coating.

	FF [%]	j _{sc} [mA/cm ²]	V _{oc} [mV]	η [%]
FZ prior MIRHP	55.8	33.8	633	12.0
FZ after MIRHP	80.1	34.0	635	17.3
FZ prior MIRHP	52.4	34.2	638	11.4
FZ after MIRHP	79.3	34.2	637	17.3
FZ prior MIRHP	51.5	33.9	636	11.1
FZ after MIRHP	80.0	34.1	636	17.4
FZ prior MIRHP	54.6	34.3	639	11.9
FZ after MIRHP	80.3	34.3	637	17.6

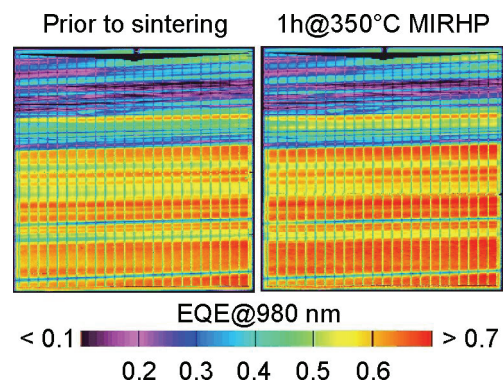


Figure 3: Contact sintering of a 2x2 cm² EFG solar cell with MIRHP. Compared to the Ar/H₂ contact sintering no depassivation is detected.

Figure 3 shows that the MIRHP step prevents the EFG solar cells from depassivation during the contact sintering in contrast to the depassivation occurring during contact sintering under Ar/H₂ ambient. Even a small improvement of the bulk is obtained. In comparison to earlier results of this 2-step hydrogenation (first SiN firing, second MIRHP) on lifetime basis, where significantly higher lifetimes could be measured after MIRHP, the improvement in the solar cell by the MIRHP is only marginal. However, the MIRHP hydrogenation for the lifetime analysis was carried out without the presence of the PECVD SiN at the front side of the silicon wafer leading to a double sided indiffusion of hydrogen from the plasma. In the EFG solar cells the front side PECVD SiN acts as a diffusion barrier for the hydrogen. Thus hydrogen diffuses into the solar cell only via the rear side through the evaporated aluminum, leading to a less effective distribution of hydrogen in the bulk.

It can be concluded that in both aspects of contact resistance and bulk passivation contact sintering by MIRHP is superior or at least equivalent to the conventional contact sintering under Ar/H₂ ambient. Obviously, the atomic hydrogen content in the remote plasma at the MIRHP is high enough to (over)compensate the out-diffusion of hydrogen from the bulk. By replacing the Ar/H₂ contact sintering with MIRHP in the solar cell processes A, B and C these processes are suitable to examine the different bulk passivation methods without a disturbing depassivation.

3 HYDROGENATION VIA A DOUBLE SIDED SiN

3.1 Al-BSF and SiO rear sides vs. a SiO/SiN rear side

Figure 4 illustrates three different rear sides on adjacent EFG wafers. The standard full rear-side Al-BSF (1,2 – process A), a local Al-BSF structure together with a thin thermal oxide (5,6 – process B without a rear side PECVD SiN) and a local Al-BSF structure together with a SiO/SiN stack (3,4,7,8 – process B with a rear side PECVD SiN). The double sided PECVD SiN leads to a homogeneous bulk passivation and mainly the regions of lower crystal quality benefit from that hydrogenation scheme compared to the single sided hydrogenation.

By lifetime measurements on symmetric samples using a SiO/SiN stack system on both sides of a p-doped floatzone wafer the surface recombination velocity (SRV) of this surface passivation is calculated to be much lower than 100 cm/s. This gives an excellent surface passivation compared to a full area Al-BSF using screen printing with commonly reported SRV values in the range of 1000 cm/s on 1 Ωcm wafers.

3.2 Al-BSF vs. Al-BSF + SiN

To prove the effectiveness of a double sided SiN hydrogenation the process A has been altered to process C, keeping the solar cell design but including the double sided SiN hydrogenation process step. Adjacent EFG wafers and neighboring block cast mc wafers were processed according to process A and C (without thermal oxidation).

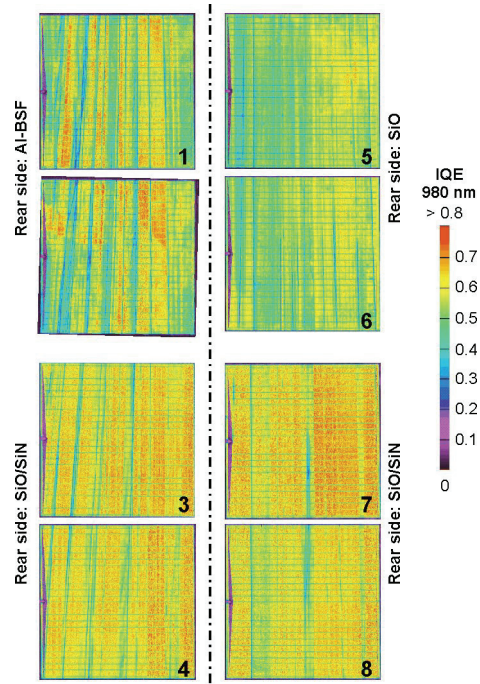


Figure 4: Comparison of single- and double-sided SiN hydrogenation. 1-4 and 5-8 are adjacent EFG solar cells, all with a SiO/SiN stack at the front side. 3,4,7,8 have an additional SiN at the rear side on top of a thin oxide.

As expected for the EFG wafers, grains of lower quality can be better passivated by the double sided hydrogenation compared to the standard process (see figure 5, left). This holds for block cast mc also. A lot of grain boundaries with higher recombination activity visible in the LBIC measurements on the mc solar cells processed according to process A vanish in the LBIC measurements of the solar cells processed according to process C. This means that the recombination activity of various defects can be dramatically decreased with the help of the double sided PECVD SiN hydrogenation.

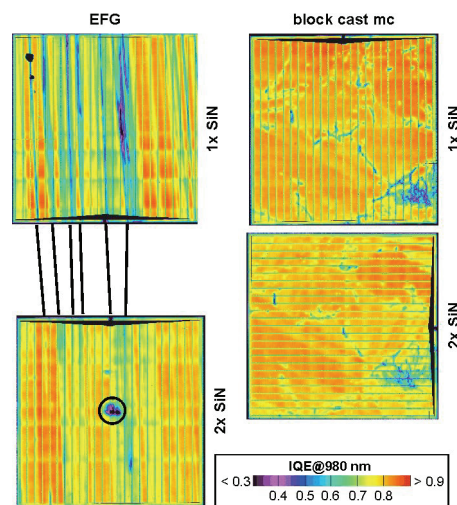


Figure 5: Comparison of single sided (top) with double sided (bottom) hydrogenation for adjacent 2x2 cm² EFG solar cells (left, approx. 1 cm spacing between both cells) and neighboring block cast mc wafers (right). The area marked indicates an emitter damage.

The LBIC measurements in figure 5 reveal the effectiveness of the hydrogenation especially for the areas of lower material quality. Whereas the areas with high IQE values are affected by the bulk lifetime and the rear surface passivation, the rear surface passivation plays a minor role for the area of lower IQE. The Al BSF seems to be partly passivated with hydrogen for process C, lowering the effectiveness of its rear side surface passivation. This is indicated by a slightly lower IQE signal for the best areas in the solar cells processed according to process C.

4 MODEL OF HYDROGENATION

We consider a single defect type (impurity, dislocation, precipitate,...) in the silicon wafer acting as a recombination centre called X with a concentration n_X which can be electrically passivated via a hydrogen bonding X-H with a certain bond energy E_{X-H} . During hydrogenation we assume a homogenous distribution of free hydrogen atoms in the wafer (neglecting transport mechanisms) with a concentration of n_H at a certain temperature T. The concentration of X-H bonds is n_{X-H} . In thermal equilibrium the ratio between free hydrogen atoms and passivated defects X should be $n_H/n_{X-H} = \exp(-E_{X-H}/kT)$ with k as Boltzmann constant. To get a perfect passivation for a given temperature we need a saturation of the X-H bonds $n_{X-H}=n_X$ with a demand for the free hydrogen density of $n_H > n_X \cdot \exp(-E_{X-H}/kT)$. If the free atomic hydrogen content falls below this critical value, a fast depassivation occurs especially for low bond energies to a dissociation frequency of ν in the order of 10^{13} - 10^{14} s⁻¹ [6]. This can be described by a decay

$$n_{X-H}(t) = n_{X-H}(0) \exp(-\nu \exp(-E_{X-H}/kT))$$

neglecting a presence of free atomic hydrogen [6]. For example, applying to the wafers 1h at 380°C for Ar/H₂ sintering, a defect with $E_{X-H}=2.5$ eV is only depassivated by a fraction of 0.2%. However a defect with $E_{X-H}=2$ eV is depassivated by a fraction of 20% after only 60 seconds (assuming a value ν of 10^{13} s⁻¹). Thus at high temperatures above 700°C for defects with moderate bond energies (~2-2.5 eV) a very fast depassivation occurs if the free hydrogen content falls below the concentration needed for saturation of the X-H bonds.

We assume a hydrogenation procedure as follows. We heat up the silicon wafer to a high temperature like 800°C. In a next step we flood the silicon wafer homogeneously with hydrogen with a very high concentration. Now we stop the hydrogen supply and start the cooling down ramp to room temperature. Hereby out-diffusion of hydrogen occurs, lowering the content of free hydrogen atoms in the wafer. This should be a rough simulation of the PECVD SiN firing hydrogenation.

If we consider a X-H bond with a high bond energy of 3.1 eV (e.g. dislocation [6]) only a very small surplus of free atomic hydrogen is needed for a successful defect passivation within the complete cool down cycle. Even if the free atomic hydrogen vanishes during cooling down the rate of depassivation of this defect is very low.

If we consider a X-H bond with a low bond energy of about 2 eV or lower, a significant depassivation occurs if the free atomic hydrogen content falls below a certain limit during cooling down.

Table II: Example values for the minimal free hydrogen density for defect saturation for certain bond energies and temperatures. No competitive reactions are considered.

n_H/n_X	1.5 eV	2 eV	2.5 eV	3 eV
25°C	$4.5 \cdot 10^{-26}$	$1.6 \cdot 10^{-34}$	$5.7 \cdot 10^{-43}$	$2.0 \cdot 10^{-51}$
350°C	$7.5 \cdot 10^{-13}$	$6.8 \cdot 10^{-17}$	$6.2 \cdot 10^{-21}$	$5.7 \cdot 10^{-25}$
600°C	$2.2 \cdot 10^{-09}$	$2.9 \cdot 10^{-12}$	$3.8 \cdot 10^{-15}$	$5.0 \cdot 10^{-18}$
700°C	$1.7 \cdot 10^{-08}$	$4.5 \cdot 10^{-11}$	$1.2 \cdot 10^{-13}$	$3.0 \cdot 10^{-16}$
800°C	$9.1 \cdot 10^{-08}$	$4.1 \cdot 10^{-10}$	$1.9 \cdot 10^{-12}$	$8.4 \cdot 10^{-15}$

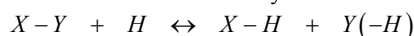
Thus the $n_H(T)$ -curve will determine the minimum bond energy with complete saturation of the X-H bond for the hydrogenation cycle. The $n_H(T)$ -curve itself is mainly affected by the initial free hydrogen content at the peak temperature, by the cooling ramp and the kinetics of the hydrogen. Thus a fast cooling ramp (RTP) as well as a double sided diffusion barrier for the hydrogen (figure 4 and 5) should improve the hydrogenation significantly.

Now we make a theoretical cut in the cooling down ramp at 350°C and compare the slope of $n_H(T)$ down to room temperature with a MIRHP hydrogenation carried out at 350°C. During hydrogenation with MIRHP $n_{H-MIRHP}(350^\circ\text{C})$ reaches an equilibrium with the surrounding hydrogen plasma if the hydrogenation is carried out for a long enough time. The hydrogen should be homogeneously distributed. Practically at the end of this hydrogenation, the plasma is turned off, the chamber is flooded with nitrogen and the samples are pulled out of the chamber and start to cool down. Thus the cooling down duration to room temperature after turning out the plasma is in the range of a minute. In contrast the cooling down from 350°C to room temperature for the SiN firing needs several seconds. If we assume an equal free hydrogen content for both methods at 350°C and if we regard the subsequent cooling down, the $n_H(T)$ -curve for the SiN hydrogenation should be higher or at least as good as the $n_H(T)$ -curve of MIRHP (with additional out-diffusion by the open front-side compared to SiN). Thus a subsequent MIRHP hydrogenation carried out after the SiN hydrogenation should not improve the bulk lifetimes in contrast to published results [7]. This is a hint that for hydrogenation by standard firing of a single sided PECVD-SiN the free hydrogen content during the cool-down ramp is not high enough to effectively passivate defects with small X-H bond energies if the previous estimations roughly explain the principle of hydrogenation.

With all these reflections hydrogenation by MIRHP should give the better bulk passivation compared to SiN hydrogenation if duration and temperature are high enough to distribute the free atomic hydrogen homogeneously throughout the wafer. However, it has been demonstrated that hydrogenation by SiN is favourable compared to hydrogenation by MIRHP [8]. Thus an important feature is missing in the previous model of hydrogenation. Additionally even for a X-H

bond energy of only 2 eV, and a high local defect density of $n_X=10^{18} \text{ cm}^{-3}$ a surplus of atomic hydrogen of only $0.4 \cdot 10^9 \text{ cm}^{-3}$ for 800°C down to 68 cm^{-3} for 350°C is needed for saturation of this defect. These values seem to be too low to explain the observed behaviour of the SiN hydrogenation.

Since now we assumed that the defect X is a ‘standalone’ defect, with no interaction with its environment, prepared to produce a bond with the hydrogen. In reality it could be already bonded to another defect called Y with a bond energy E_{XY} . If this bond energy is high enough (e.g. $> 2.5 \text{ eV}$) the dissolving of this pair X-Y at moderate MIRHP temperatures (350°C) is rather slow, making it unlikely to create X-H, Y-H bonds. (Annotation: A dissolving of the mentioned compound X-Y represents in general an activation energy for the hydrogen needed to create the bonding. However, for the conclusion of this model the cause of this activation energy is irrelevant.) If the temperature is high enough to break the X-Y bonds we have a reaction described by:



For a successful passivation of these defects this reaction has to be directed strongly to the right side. The equilibrium hereby is determined a) by the corresponding bond energies and b) by the concentrations of the reactants. Thus a multitude of the values given in Table II for n_H can be necessary for a satisfying hydrogenation. In many cases a complete passivation with hydrogen therefore cannot be expected, e.g. for precipitates.

Certainly the mechanics of hydrogenation is more complicated as the described scenario. Nevertheless, this simple model can qualitatively describe most observed phenomena about hydrogenation. If the corresponding parameters are known it could be a starting point for numerical simulations. Not every X-H pairing needs to be electrically inactive but this was accepted for a more simple description.

In conclusion, the ideal hydrogenation can be proposed. At least one silicon surface has to be deposited with a hydrogen rich layer (PECVD-SiN) that supplies enough hydrogen for passivation. All surfaces have to be covered with an excellent diffusion barrier for the hydrogen; this can be an appropriate PECVD-SiN which additionally supplies the hydrogen. The peak temperature during firing has to be high enough to brake up already established defect bonds very fast. This temperature could be higher than with the single sided PECVD SiN RTP approach. The subsequent cooling down should exceed a certain speed to compensate a lack of hydrogen due to out-diffusion. If necessary, the hydrogen diffusion barriers have to be etched off for a subsequent MIRHP hydrogenation.

5 ACKNOWLEDGEMENTS

The underlying project of parts of this report was supported with funding of the German BMU under contract number 0329846J and by the EC (SES6-CT-2003-502583). The content of this publication is the responsibility of the authors.

6 SUMMARY

To decrease silicon consumption silicon solar cells show the trend to become thinner and thinner. Thus the surface passivation of the rear side gets more and more important. A stack of a thin thermal oxide together with a PECVD silicon nitride on top of the oxide gives an excellent surface passivation with SRV values well below 100 cm/s. This stack system together with local rear contacts can be an option for future industrial application. We have showed that a rear side PECVD SiN together with the conventional already used PECVD SiN on the front side leads to a sophisticated bulk passivation. That means that an improvement of the rear side using a PECVD SiN can be reached together with an improvement of the bulk quality for multicrystalline silicon wafers. Most hydrogenation models only deal with the kinetic aspects. Based on reaction dynamic considerations we presented a simple model that is able to explain qualitatively the observed differences between hydrogenation by PECVD SiN firing, the hydrogenation using MIRHP, and the combination of both.

The implementation of MIRHP into standard industrial processing maybe supposed to be uneconomic. However, even in industrial environment the MIRHP can be useful as a tool to proof the effectiveness of the hydrogenation of industrially processed solar cells. After etching back metals and emitter, an initial lifetime mapping after solar cell processing could be done. A second lifetime mapping could be done after a MIRHP step between both lifetime mappings. If the MIRHP step would significantly improve the bulk lifetimes, this can be a hint that it is worth to optimize the hydrogenation during industrial processing.

7 REFERENCES

- [1] M. Kaes, G. Hahn, A. Metz, Proc. 31st IEEE PVSC, Lake Buena Vista 2005, p. 923
- [2] M. Rinio, M. Kaes, G. Hahn, D. Borchert: this conference
- [3] A. Rohatgi, D.S. Kim, V. Yelundur, K. Nakayashiki, A. Upadhyaya, M. Hilali, V. Meemongkolkiat: Bangkok, Thailand 2004, Technical Digest of the 14th PVSEC, Bangkok 2004 p. 635
- [4] M. Kaes, G. Hahn, K. Peter, E. Enebak: 4th WCPEC, Waikoloa 2006
- [5] T. Pernau, G. Hahn, M. Spiegel, G. Dietsche: 17th EUPVSEC, Munich 2001
- [6] J. Pearton, W. Corbett, M. Stavola: Hydrogen in crystalline semiconductors, Springer Verlag 1991, ISBN 3-540-53923-9
- [7] M. Kaes, G. Hahn, Th. Pernau, A. Metz, 20th EUPVSEC, Barcelona 2005, p. 1063
- [8] M. Kaes, G. Hahn, A. Metz, Proc. 31st IEEE PVSC, Lake Buena Vista 2005, p. 923