**Preprint 14th European Photovoltaic Solar Energy Conference, Barcelona**

# MICROWAVE INDUCED REMOTE HYDROGEN PLASMA (MIRHP) PASSIVATION OF SOLAR CELLS USING DIFFERENT SILICON BASE MATERIALS

M. Spiegel, S. Keller, P. Fath, G. Willeke and E. Bucher,
*University of Konstanz, Department of Physics, P.O.Box X916, D-78457 Konstanz, Germany*
*Tel.: 0049-7531-88-2082, Fax: 0049-7531-88-3895*
*email: markus.spiegel@uni-konstanz.de*

ABSTRACT: The increasing importance of multicrystalline silicon (mc-Si) for photovoltaics makes defect passivation techniques such as microwave induced remote hydrogen plasma (MIRHP) passivation an important issue in mc-Si solar cell technology. For the MIRHP-passivation selective emitter solar cells using different mc-Si base materials (Baysix SOPLIN (Bayer), EMC (Sumitomo Sitix), EUROSIL (Eurosolare), HEM (Crystal Systems), EFG (ASE)) were processed leading to efficiencies between 10.5% and 12.1% on 4cm$^2$ (without ARC). An optimization of the MIRHP-passivation processing conditions such as plasma power, gas pressure, gas flow and passivation time has been carried out on these materials. A clear separation of the impact of the MIRHP-process from passivation effects of a forming gas annealing step has been done. Special emphasis was focused on an observed degradation of solar cells with lowly doped homogeneous emitters.

The characterization of the solar cells was carried out by illuminated IV, spectral response and reflection measurements. Bulk diffusion lengths before and after MIRHP-passivation were determined according to the Basore extended spectral analysis.

**Keywords:** Passivation - 1: Multi-Crystalline - 2: Silicon - 3

## 1 INTRODUCTION

The increasing importance of multicrystalline silicon (mc-Si) for photovoltaics makes defect passivation techniques such as microwave induced remote hydrogen plasma (MIRHP) passivation [1,2] an important issue in mc-Si solar cell technology. Because of the separation of the generation of H-atoms by a microwave plasma from the place of the diffusion of the H-atoms into the sample it is believed that the microwave induced remote hydrogen plasma (MIRHP) process does not seriously damage the surface of the cell. For an optimization of the MIRHP-passivation it is advantageous to apply this process after the cell metallization. On the other hand it has been observed by the present authors that applying MIRHP after the metallization of solar cells with lowly doped homogeneous emitters can lead to a serious degradation in the fill factor [2]. To exclude this degradation in this work a selective emitter process has been used. An increase in all illuminated IV parameters for selective emitter solar cells based on different mc-Si materials (Baysix SOPLIN (Bayer), EMC (Sumitomo Sitix), EUROSIL (Eurosolare), HEM (Crystal Systems), EFG (ASE)) have been found within this work. Additional emphasis has been focused on the observed degradation of solar cells with lowly doped homogeneous emitters.

## 2 THE MIRHP PLASMA REACTOR

For H-passivation of multicrystalline silicon wafers and solar cells a MIRHP-device similar to the one described in the literature [2] has been used (shown schematically in Fig. 1). Molecular hydrogen is separated into atomic hydrogen by a microwave plasma. In order to prevent atomic hydrogen from recombining on the way to the sample, a $H_2$/He (10%$H_2$, 90%He, purity 6N) mixture was used. The temperature was measured inside the tube during the passivation treatment. The following process parameters can be varied: sample temperature, gas pressure, gas flow, microwave power and processing time.

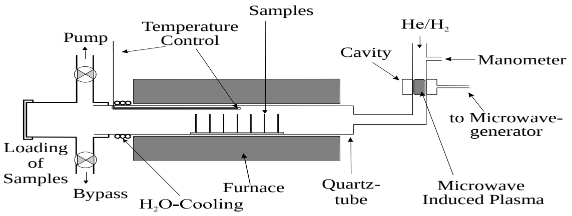


**Figure 1***: Schematic diagram of the microwave induced remote hydrogen plasma (MIRHP) device for passivation of silicon wafers and solar cells. To dissociate molecular hydrogen, microwave power is coupled through a cavity into a gas mixture consisting of 10%$H_2$ and 90%He. The atomic hydrogen, kept from recombining by the presence of the helium atoms, diffuses into the heated samples.*

## 3 HOMOGENEOUS EMITTERS

### 3.1 Experiment

In order to investigate the influence of a homogeneous emitter on the efficiency of the MIRHP-process solar cells using different mc-Si base materials (EUROSIL, EMC, HEM, EFG) were processed. In Fig. 2 the open circuit voltage $V_{OC}$, the short circuit current density $J_{SC}$ and the fill factor FF of solar cells with a homogeneous emitter with a sheet resistance $R_{SH}$ of 90 Ω/sqr are shown. For all materials a serious degradation of the FF correlated with a decrease in $V_{OC}$ are seen, whereas $J_{SC}$ increases rapidly within the first 30min. From these curves it appears that large reductions in $V_{OC}$ and FF are likely to be related to high densities of crystal defects and high oxygen concentrations as it is the case for EFG. On EUROSIL with a low defect density and a high oxygen concentration and on EMC with a low oxygen concentration and a high defect density much smaller degradations are observed. On the HEM material which we have used in our solar cell process, a serious degradation during the MIRHP was observed, which is probably also due to high defect densities. The excellent quality of HEM leading to the world record on 1cm$^2$ mc-Si solar cells [3] could not be confirmed in this work (see Fig. 7) which is probably due to quality variations of the HEM material.

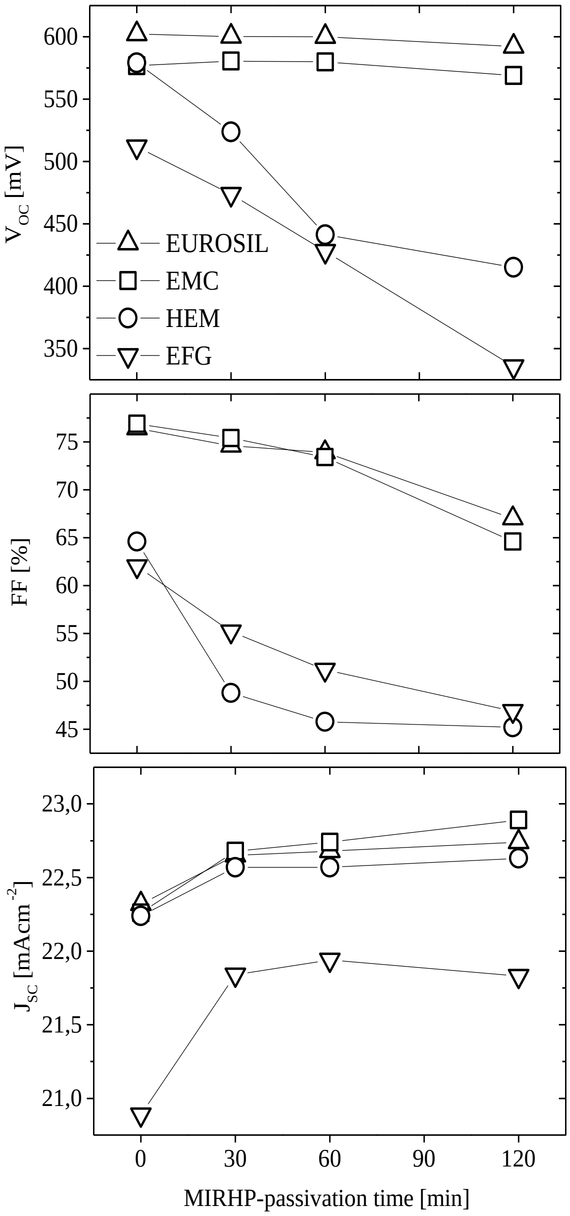
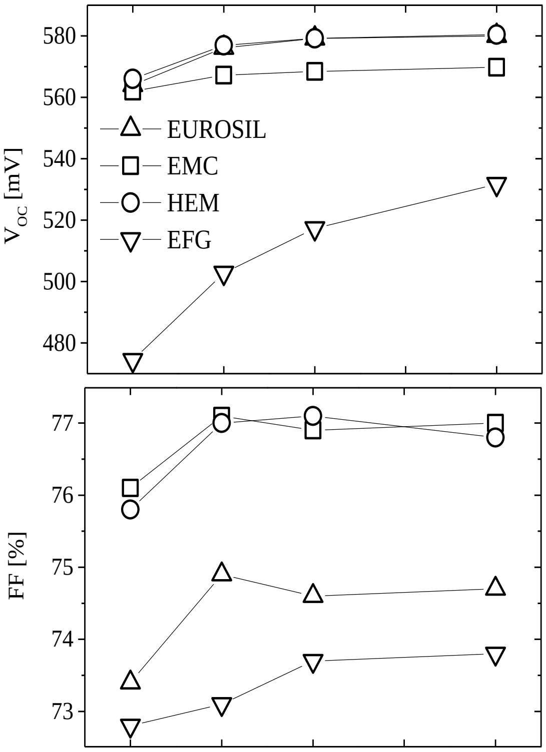


**Figure 2**: *Influence of the MIRHP-passivation time on $V_{OC}$, $J_{SC}$ and FF of solar cells with a homogeneous emitter with a sheet resistance $R_{SH}$ of 90Ω/sqr. For all materials a serious degradation of the FF correlated with a decrease in $V_{OC}$ are seen, whereas $J_{SC}$ increases rapidly within the first 30min. The process parameters are a sample temperature of 350°C, a gas flow of 12ml/min, a gas pressure of 1mbar, a microwave power of 150W.*

By using a more highly doped emitter of $R_{SH}$=26Ω/sqr the degradation effect can be avoided and this is shown in Fig. 3. For all investigated materials increases of all illuminated IV-parameters were obtained by the MIRHP-process. Also seen in Fig.3 is the slower increase on $J_{SC}$ of solar cells with a 26Ω/sqr emitter as compared to those with a 90Ω/sqr emitter. This is due to a reduced diffusion of hydrogen in highly doped silicon, which is intensively



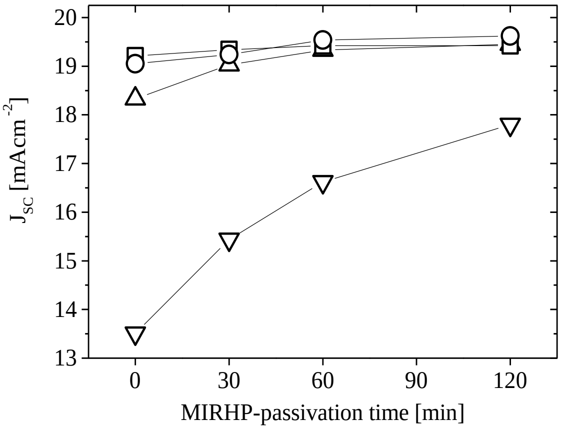


**Figure 3**: *Influence of the MIRHP-passivation time on* $V_{OC}$, $J_{SC}$ *and FF of solar cells with a homogeneous emitter with sheet resistance* $R_{SH}$ *of 26Ω/sqr. For all materials increases of* $V_{OC}$, $J_{SC}$ *and FF were obtained. The slower increase of* $J_{SC}$ *as compared to Fig.2 is discussed in the text. The process parameters are a sample temperature of 350°C, a gas flow of 12ml/min, a gas pressure of 1mbar, a microwave power of 150W.*

studied in the literature [4]. The high phosphorus concentration of $3*10^{20}cm^{-3}$ and the deep junction depth of 600nm of the 26Ω/sqr emitter as compared to $4*10^{19}cm^{-3}$ and 300nm of the 90Ω/sqr emitter retard the diffusion of hydrogen into the bulk of the solar cell and therefore increase the optimal time for the passivation.

### 3.2 Discussion of the degradation effect

The cause of the observed degradation of $V_{OC}$ and FF is not yet fully understood. No degradation on any of the solar cells of Fig. 2 and Fig. 3 was observed during a forming gas annealing (FGA) over one hour at 350°C before the MIRHP-process was applied and on other reference solar cells during an FGA over several hours. Also no degradation is observed when the MIRHP is applied before the cell metallization [2]. From these observations the degradation of $V_{OC}$ and FF might be caused by the interaction of several factors: high dislocation densities, high oxygen concentrations comparable to those of cast mc-Si materials, highly energetic H- or He-atoms and the presence of metallic atoms (in our case titanium) at the solar cell surface. An enhanced diffusion of titanium along grain boundaries supported by highly energetic H- or He-atoms of the MIRHP-process gas might explain the different behaviours of the mc-Si materials. High recombination rates in oxygen rich Si-materials [5] could explain the differences between the EMC and EFG-material, both with high defect densities but EMC with a much lower oxygen concentration.

## 4. SELECTIVE EMITTERS

### 4.1 Influence of the MIRHP-parameters

In order to investigate the influence of the process parameters on the efficiency of the MIRHP-passivation, selective emitter solar cells based on four different mc-Si materials (EUROSIL, EMC, HEM, EFG) were processed (Fig. 4).

1. surface defect etching
2. phosphorus diffusion of N++: 15-20Ω/sqr.
3. SiN-masking on front side
4. photolithography for NaOH emitter etching
5. NaOH emitter etching
6. phosphorus diffusion of N+: 90Ω/sqr.
7. dry thermal oxidation
8. E-gun Al evaporation / Al sintering at 800°C
9. photolithography for front contact definition
10. E-gun evaporation of Ti/Pd/Ag
11. lift-off
12. E-gun Al evaporation at backside
13. forming gas annealing
14. cell separation
15. cell characterization
16. MIRHP passivation
17. cell characterization

**Figure 4**: *Solar cell processing sequence of the selective emitter solar cell.*

Four different MIRHP-processing conditions (see Table I) were applied to solar cells prepared from the materials studied. For each material only solar cells with the same crystal structure were compared. The optimum temperature of 350°C was taken from literature [2,6]. The passivation time for each solar cell was successively increased from 30min up to 2h.

| process | pressure[mbar] | Power[W] | gas flow[ml/min] |
|---|---|---|---|
| H1 | 1 | 50 | 4 |
| H2 | 1 | 150 | 12 |
| H3 | 0.1 | 50 | 4 |
| H4 | 10 | 50 | 4 |

**Table I**: *MIRHP processing conditions used in this study. The optimum temperature of 350°C was taken from literature [2,6]. The passivation time for each solar cell was successively increased from 30min up to 2h.*

The influence of the different MIRHP-process conditions on $V_{OC}$ and $J_{SC}$ of selective emitter solar cells using EMC as base Si-material can be seen in Fig. 5. The process H3 with the lowest gas pressure is clearly the best which appears to fully passivate EMC solar cells within 1-2h. Whereas within the first 30min $V_{OC}$ increases rapidly for all processing conditions, a saturation of $J_{SC}$ is reached faster for the process H3 than for the other processes. This is due to the higher amount of H-atoms at the sample as mentioned by the authors in an earlier publication [2]. In agreement with this argumentation, the condition H4 with the highest pressure leads to the slowest increase in $J_{SC}$. By comparing the results of the H1 process with the H2

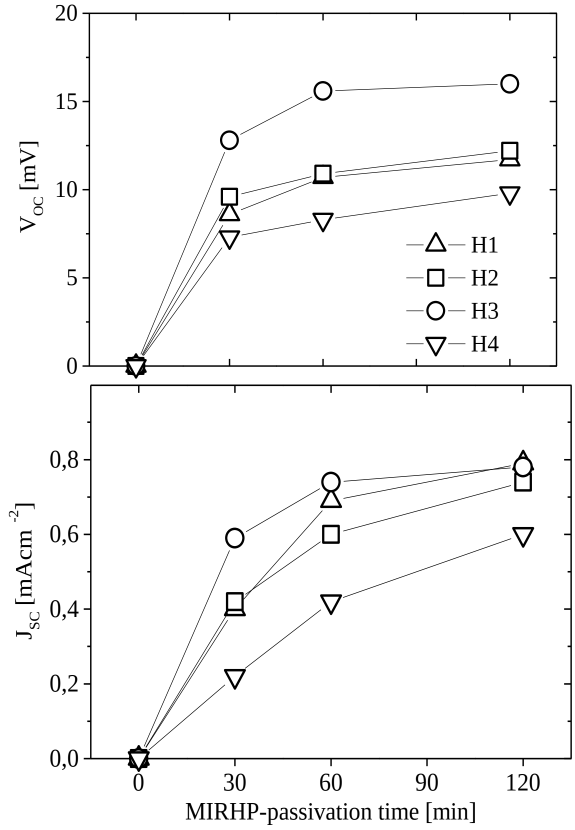


**Figure 5***: Influence of the MIRHP-process conditions on* $V_{OC}$, $J_{SC}$ *and FF of selective emitter solar cells using EMC as base Si-material.*

conditions it can be seen that higher microwave powers and higher gas flows do not lead to a faster passivation. Additionally there is no degradation of the illuminated IV characteristics with the use of the H2 process, which shows that the degradation of lowly doped homogeneous emitter solar cells cannot be explained by the MIRHP process conditions alone. The H3 process was also the best one for the other materials.

### 4.2 Influence of the Si-base material

Fig. 6 shows the absolute increase in the illuminated IV parameters due to MIRHP-processing of solar cells prepared from different multicrystalline silicon materials. A strong dependence of the efficiency of the MIRHP-passivation on the base material is clearly seen. Baysix SOPLIN (Bayer) and EUROSIL (Eurosolare), both high quality multicrystalline silicon materials with large grains and low dislocation densities, are only slightly improved by the MIRHP-process. Using the same process parameters (350°C, 0.1mbar, 50W, 4ml/min, 2h) for the solar cells based on the other materials EFG (ASE) with high defect densities showed the best improvements, whereas EMC (Sumitomo Sitix) and HEM (Crystal Systems) improved with a lesser extent. The illuminated IV parameters of the best $4cm^2$ solar cells with selective emitters after MIRHP and without ARC can be seen in Fig. 7. The figures in brackets denote the calculated $J_{SC}$ and $\eta$ values using an estimated average reflection of 5% of an ideal double layer antireflection coating.

Minority carrier bulk diffusion lengths $L_b$ before and after the MIRHP-passivation (see Table II) were determined by a linear fit of $L_{eff}$ to the inverse internal quantum efficiency according to the Basore extended spectral analysis [7]. The change in $L_b$ is in good agreement with the increases $\Delta J_{SC}$ of the short circuit current density.

| Material | $\Delta V_{OC}$ [mV] | $\Delta J_{SC}$ [$mAcm^{-2}$] | $\Delta FF$ [%] | $\Delta\eta$ [%] |
|---|---|---|---|---|
| SOPLIN | 3 | 0.3 | 0.2 | +0.2 |
| EUROSIL | 5 | 0.5 | 0.4 | +0.3 |
| EMC | 10 | 0.8 | 0.6 | +0.7 |
| HEM | 7 | 0.7 | 0.8 | +0.6 |
| EFG | 17 | 2.6 | 2.1 | +1.7 |

**Figure 6**: *Absolute increase in the illuminated IV parameters due to MIRHP averaged over four $4cm^2$ solar cells (without ARC).*

| Material | $V_{OC}$ [mV] | $J_{SC}$ [$mAcm^{-2}$] | FF [%] | $\eta$ [%] |
|---|---|---|---|---|
| SOPLIN* | 615 | 23.4 (34.0) | 77.2 | 11.1 (16.1) |
| EUROSIL | 623 | 25.6 (34.7) | 76.3 | 12.1 (16.4) |
| EMC | 589 | 25.2 (33.5) | 77.4 | 11.5 (15.3) |
| HEM | 589 | 23.6 (32.1) | 75.2 | 10.5 (14.2) |
| EFG | 571 | 25.3 (34.9) | 74.2 | 10.7 (14.8) |

**Figure 7**: *Illuminated IV parameters of the best $4cm^2$ solar cells with selective emitter after MIRHP and without ARC. The figures in brackets denote the calculated $J_{SC}$ and $\eta$ values using an estimated average reflection of 5% of an ideal double layer antireflection coating. (* On Baysix SOPLIN only a homogeneous emitter has been taken as reference.)*

| Material | $L_b$ [µm] | $L_b$[µm] | $\Delta J_{SC}$[$mAcm^{-2}$] |
|---|---|---|---|
|  | before | after |  |
| EUROSIL | 108 | 163 | +1.0 |
| EMC | 110 | 133 | +0.7 |
| HEM | 99 | 130 | +0.9 |

**Table II**: *Bulk diffusion lengths $L_b$ before and after MIRHP-passivation of solar cells based on some of the investigated materials. The change in $L_b$ is in good agreement with the increases in $J_{SC}$. $L_b$ was determined by the Basore fit of the internal quantum efficiency.*

## 5 CONCLUSIONS

Absolute increases in the cell efficiencies of between 0.2 and 1.7% (no ARC) were reached by applying the microwave induced remote hydrogen plasma (MIRHP) passivation on selective emitter solar cells based on different mc-Si materials. The dependence of the effectiveness of the MIRHP-process on the parameters gas pressure, gas flow, microwave power and processing time was investigated. The observed degradation of the open circuit voltage and the fill factor of solar cells with lowly doped homogeneous emitters during the MIRHP is proposed to be due to the diffusion of titanium – supported by highly energetic H- or He-atoms – into the emitter and space charge region of the solar cell. No degradation occurred by applying a forming gas annealing step. The strong dependence of this degradation on the quality of the mc-Si material suggests the diffusion of titanium along crystal defects.

## 6 REFERENCES

[1] H.E. Elgamel, A. Rohatgi, Z. Chen, C. Vinckier, J. Nijs, R. Mertens, Proc. 1. World Conference on Photovoltaic Energy Conversion, Hawaii, 1994, pp 1323

[2] M. Spiegel, G. Willeke, P. Fath, E. Bucher, Proc. 13th EC PV Solar Energy Conf., Nice, 1995, pp 421

[3] A. Rohatgi, S. Narasimha, S. Kamra, P. Doshi, C.P. Khattak, K. Emery, H. Field, 25th IEEE PVSEC, Washington, DC, 1996

[4] R. Rizk, P. de Mierry, D. Ballutaud, M. Aucouturier, Phys. Rev. B44, pp6141 (1991)

[5] K. Nauka at al., Appl. Phys. Lett. 43(3), 1983, pp241

[6] N.H. Nickel, N.M. Johnson, W.B. Jackson, Appl. Phys. Lett. 62(25), 1993, pp3285

[7] P.A. Basore, 23th IEEE PVSC, 1993, pp147

## ACKNOWLEDGMENTS

The authors would like to thank M. Keil for his technical support. This work was financially supported by the JOULE program of the European Commission under contract No. JOR3-CT 95-0030.