

INVESTIGATION OF HYDROGEN DIFFUSION, EFFUSION AND PASSIVATION IN SOLAR CELLS USING DIFFERENT MULTICRYSTALLINE SILICON BASE MATERIALS

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ABSTRACT: The diffusion of hydrogen into the bulk due to a microwave induced remote hydrogen plasma (MIRHP) process and the diffusion of hydrogen out of the bulk due to different annealing steps in N₂ at various temperatures were observed indirectly by spectral response and illuminated I-V measurements of solar cells made on different multicrystalline silicon base materials (BAYSIX (Bayer), EUROSIL (Eurosolare), SOLAREX (Solarex), EMC (Sumitomo Sitix), EFG (ASE), RGS (Bayer)). H-diffusion depths as a function of passivation times were obtained by fitting the internal quantum efficiency of not fully passivated cells under the assumption of different minority carrier diffusion lengths for the passivated and non-passivated regions. We observed that both processes - diffusion and effusion of hydrogen - are strongly dependent on the material. A fast/slow H-diffusion was observed in EFG/RGS with relative increases of the cell efficiency of up to 30%. In EFG the H-effusion from the bulk starts below 375°C, in EMC at 450°C and in Solarex material above 475°C. These observations suggest different diffusion channels and bonding states of hydrogen atoms in the investigated materials.

Keywords: Vienna Conference - 1: Multi-Crystalline - 2: Passivation - 3: Remote

INTRODUCTION

Due to the increasing importance of multicrystalline silicon (mc-Si) for photovoltaics, hydrogen defect passivation techniques such as microwave induced remote hydrogen plasma (MIRHP) passivation will become an important issue in solar cell technology. Besides the economical advantages of the MIRHP passivation process - fast passivation, low energy consumption, batch process compatible - this technique can also be used effectively to study H-diffusion processes in mc-Si.

The aim of this paper is threefold: 1) the optimum MIRHP process temperatures and times for different mc-Si materials are presented, 2) the H-diffusion depths in dependence of passivation times are obtained by fitting the internal quantum efficiency of not fully passivated cells and 3) the H-diffusion out of cells (H-effusion) during N₂-annealing steps at temperatures up to 475°C are investigated using I-V and spectral response (SR) measurements.

For this study selective emitter solar cells were processed using different ribbon silicon materials (EFG (ASE), RGS (Bayer)), conventionally cast multicrystalline silicon (BAYSIX (Bayer), EUROSIL (Eurosolare), SOLAREX (Solarex)) and electromagnetic cast multicrystalline silicon (EMC (Sumitomo Sitix)).

1. MIRHP PROCESS AND CELL PROCESSING

The MIRHP passivation technique used in this study is well described in literature [1-3]. By separating the generation of H atoms from the location of diffusion of H into the cell the MIRHP process does not seriously damage the surface of the cell like most of the other H-passivation techniques such as direct hydrogen plasma passivation [2] and hydrogen ion implantation [4]. Especially in experiments where H-diffusion parameters such as diffusion depth, diffusion coefficient, diffusion energy, etc. have to be determined as a function of the used mc-Si material, it is necessary to avoid surface damage which could enhance the H-diffusion [5] and therefore change the

result of the measurement. Furthermore the MIRHP process is the only known technique for the passivation of completely processed solar cells without damaging the front side - front grid, front surface passivation and emitter region. The sequence of the fabrication process of the used selective emitter solar cells are presented in Fig. 1. Solar cells with a selective emitter structure were needed to apply high temperature steps above 400°C which would cause a degradation in especially the fill factor and open circuit voltage of cells with a homogeneous emitter [6].

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

Fig. 1: Solar cell processing sequence of the selective emitter solar cells used in our study.

2. HYDROGEN PASSIVATION

In earlier publications we reported on the optimization of the MIRHP process on EMC silicon material with respect to plasma power, gas pressure, gas flow and passivation time [3, 6]. From these experiments it was concluded that there exists an optimum in the plasma power of 50 W, in the gas pressure of 0.1 mbar and in the gas flow of 4 ml/min. Especially no improvement was seen by the use of higher plasma powers and/or gas flows, whereas increasing the gas pressure above 1 mbar will result in a

slower passivation. Contrary to these process parameters which determine the concentration of atomic hydrogen at the place of the cells, the passivation time and temperature determine the dynamics of the H-diffusion in the bulk of the cell. Therefore in the present investigations only the passivation time and temperature were varied and the other process parameters were kept constant at the optimum values given above.

In literature it is generally supposed that the optimum temperature for diffusion of atomic hydrogen into a silicon substrate is somewhere between 350°C and 400°C [7]. At higher temperatures the hydrogen starts to diffuse out of the sample surface. However we found different optimum temperatures and passivation times (see Table I) depending on the crystallization process used for the production of the Si base material.

Table I: The influence of the mc-Si base material on the optimum passivation temperature and passivation time of the MIRHP process and the relative efficiency increases. The optimization was carried out using the following temperatures: 275, 350, 375, 400, 425 and 450°C.

	T _{opt} [°C]	t _{opt} [min]	Δη _{rel} [%]
EUROSIL	350	90	2-7
BAYSIX	350	120	5-8
SOLAREX	375	180	7-15
EMC	350	120-150	6-9
EFG	350	30	21-31
RGS	425	210	15-30

Conventionally cast mc-Si (EUROSIL, BAYSIX, SOLAREX) and electromagnetic cast mc-Si (EMC) differ only slightly in the optimum temperature, but strongly in the optimum passivation time between 90 and 180 min. This difference seems to be due to different dislocation densities [D], concentrations of interstitial oxygen [O_i] and other impurities in these materials. Values of [O_i] up to 2.4x10¹⁷ cm⁻³ [8] lead to a longer optimum passivation time and a slightly higher optimum temperature of the investigated SOLAREX material than for the other cast Si materials. The EMC material with high [D] of 10⁶ - 10⁸ cm⁻² but [O_i] below 7x10¹⁶ cm⁻³ [9] can be fully passivated in a shorter time. An astonishingly short passivation time of 30 min is sufficient to completely passivate cells based on EFG with an increase of the minority carrier diffusion length as determined by spectral response measurement from 16 - 20 μm to 77 - 112 μm due to the MIRHP passivation alone. Because of no increase was seen with forming gas annealing, the observed improvement is caused by the diffusion of atomic hydrogen at least 77-122 μm deep into the bulk during only 30 min. The diffusion coefficient D can be estimated using [10]:

$$D = x^2 / (4 \cdot t) \quad (1)$$

with x the diffusion depth and t the diffusion time. Using the values for EFG results in D = 0.8 - 1.7x10⁻⁸ cm²/s. This is to our knowledge the fastest diffusion of hydrogen at low temperature (=350°C) ever reported for mc-Si. The other ribbon silicon material investigated, RGS (Ribbon Growth on Substrate), behaves totally different as compared to the EFG material. Even at the relatively high optimum temperature of 425°C, the diffusion of hydrogen is slowed down by the considerably

higher concentrations of interstitial oxygen above 10¹⁸ cm⁻³ and the high dislocation density of up to 10⁸ cm⁻² [11] as compared to EFG with [O_i] below 5x10¹⁶ cm⁻³ [12] and with [D] of 10⁴ - 10⁸ cm⁻² [13]. For RGS the hydrogen diffusion length does not increase above 30 μm, which results together with a passivation time of 210 min in a diffusion coefficient of D = 1.8x10⁻¹⁰ cm²/s at 425 °C. Therefore even at the higher temperature - 425°C as compared to 350°C - the diffusion coefficient for RGS is a factor of 50 - 100 lower than for EFG.

Because of the large differences of the EFG and RGS materials in the MIRHP process and the H-diffusion, the results of the I-V measurements will be discussed in the next. For different MIRHP passivation temperatures and times the increases of the open circuit voltage ΔV_{OC} and the short circuit current density ΔJ_{SC} of solar cells based on these ribbon silicon materials are shown in Fig. 2a and b, respectively. EFG can be fully passivated at a process temperature of 275 °C within only 2h. For RGS at this temperature only a small increase in ΔJ_{SC} can be seen during 5h, whereas ΔJ_{SC} increases fast by using an additional MIRHP process step at 400°C for 2h. The open circuit voltage increases faster because it depends more on the surface and space charge region of the cell, which is more easily reached and passivated by the atomic hydrogen than the bulk of the cell.

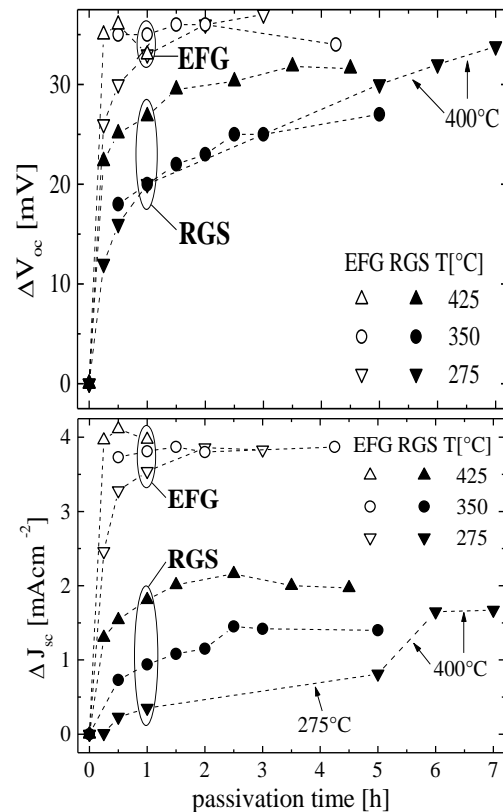


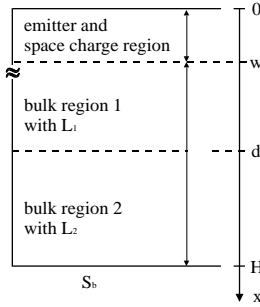
Fig. 2a,b: The influence of the temperature during the MIRHP process on the increase of the open circuit voltage ΔV_{OC} and the short circuit current density ΔJ_{SC} of solar cells based on RGS and EFG silicon.

3. HYDROGEN DIFFUSION

3.1 The IQE step model

The first calculations of the internal quantum efficiency (IQE) of solar cells date nearly back to the beginning of silicon solar cell processing. A detailed investigation is given in [14] where a formula for the IQE was developed which includes besides other aspects (electrostatic drift fields,...) the separation of the bulk of the cell into two regions with different minority carrier diffusion lengths. In Fig. 3 a schematic representation of the cell parameters is given.

Fig. 3: Sketch of a solar cell with two bulk regions 1,2 of different minority carrier diffusion lengths $L_{1,2}$. The other parameters are the junction depth w , the cell thickness H , the depth where regions 1 and 2 contact d and the back surface recombination velocity S_b .



However, the given formula can only be used to calculate the contribution of the emitter or base, but not the total IQE with the contribution of the space charge region included. Actually several equations or approximations for the IQE derived in literature deal only with the contribution of the bulk [15-18]. The authors have not found in literature any theoretical derivation that the generally used expression for the contribution of the bulk:

$$\frac{1}{\text{IQE}_{\text{bulk}}} = 1 + \frac{1}{\alpha \cdot L} \quad (2)$$

is also valid for the total IQE of a solar cell. This is also discussed in more detail in another publication of some of the authors [19].

Therefore we found it necessary to prove that with the general approximations used for deriving eq. 2 ($w \ll \alpha^{-1} \ll H$, $S_b \cdot L/D \gg 1$) and some approximations for the emitter given in [20] an analogous equation for the total IQE can be calculated [20]:

$$\text{IQE}_{\text{total}}(\alpha, L, w) = \left(1 + \frac{w}{L}\right) \cdot \frac{\alpha \cdot L}{\alpha \cdot L + 1} \quad (3)$$

For the total IQE of the cell with two bulk regions according to Fig. 3 the following approximation can be derived [20]:

$$\text{IQE}_{\text{total}}(\alpha \neq \frac{1}{L_{1,2}}, L_1, L_2, d - w) = \frac{\alpha_1}{\alpha_1^2 - 1} \cdot \left[\frac{1 + \frac{L_2}{L_1} \text{th}(dw) \text{th}(Hd) + \frac{(L_2^2 - L_1^2)}{L_1^2} [1 - \alpha_2 \text{th}(Hd)]}{\text{th}(dw) + \frac{L_2}{L_1} \text{th}(Hd)} e^{\alpha_1 dw} \right] \quad (4)$$

with $\text{th} = \tanh$, $\alpha_{1,2} = \alpha \cdot L_{1,2}$, $dw = (d-w)/L_1$, $Hd = (H-d)/L_2$ and the other parameters described in Fig. 3. For the

derivation of this formula the same approximations as for eq. 3 were used together with the approximation $w \ll L_1$.

3.2 Fit of the IQE step model

By assuming that the bulk of an incompletely H passivated cell can be described by a region 1 with high minority carrier diffusion length L_1 and region 2 with $L_2 < L_1$ eq. 4 can be used to extract a H-passivation depth d from IQE data. To show that this method works, the IQE of one cell made from SOLAREX mc-Si material has been measured before the MIRHP process and after several MIRHP process steps (see Fig. 4). L_2 of the unpassivated and L_1 of the fully passivated cell were obtained by a fit with eq. 3. For a more detailed view see Fig. 5, where the IQE is shown as a function of the mean penetration depth of the light, which is equal to the inverse of the absorption coefficient. It is clearly seen that with eq. 3 an excellent fit of measured IQEs can be obtained. Actually eq. 4 is also a good approximation for λ down to 600-700 nm and up to half of the cell thickness, which was for this cell 250 μm .

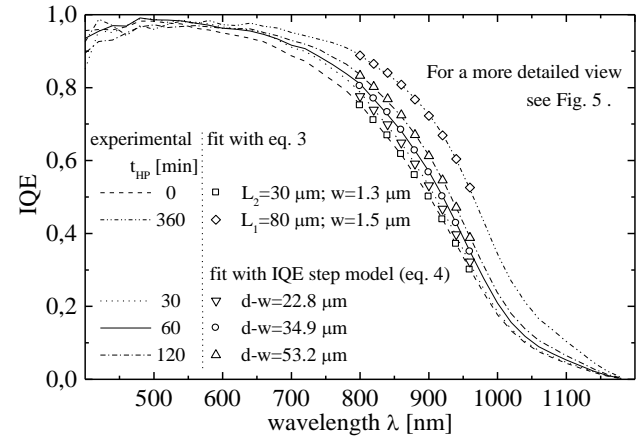


Fig. 4: IQE of one cell based on SOLAREX as a function of the wavelength before the MIRHP process and after several processing times. The MIRHP process temperature was 275°C during the first 120 min and 350°C during the following 180 min to ensure a complete passivation. Also shown are the simulated IQE curves calculated from eq. 4 and the obtained fit parameters.

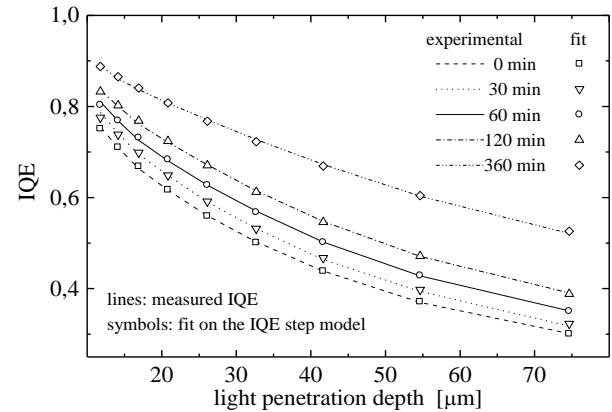


Fig. 5: Same as in Fig. 4 but the IQE is as a function of the mean light penetration depth. The shown range corresponds to wavelengths between 800 and 960 nm.

4. HYDROGEN EFFUSION

The diffusion of hydrogen out of the surface of the bulk of solar cells was studied by H-effusion experiments on fully passivated cells. The change of the IQE for wavelengths above 800 nm can be taken as a measure for the change of the hydrogen contributing to the passivation effect in the bulk. Fig. 6 shows the IQE for solar cells based on EFG, EMC and SOLAREX material due to the H-diffusion during a MIRHP process at 350°C into the bulk and due to the effusion of hydrogen during successive annealing steps (15 min) in N₂ at various temperatures. The H-diffusion out of the bulk starts for EFG below 375°C, for EMC at 450°C and for SOLAREX above 475°C. These differences in temperature correspond also to the different optimum passivation times of these materials (Table I), where it is shown that hydrogen diffuses fastest in EFG and slowest in SOLAREX material. For SOLAREX material the

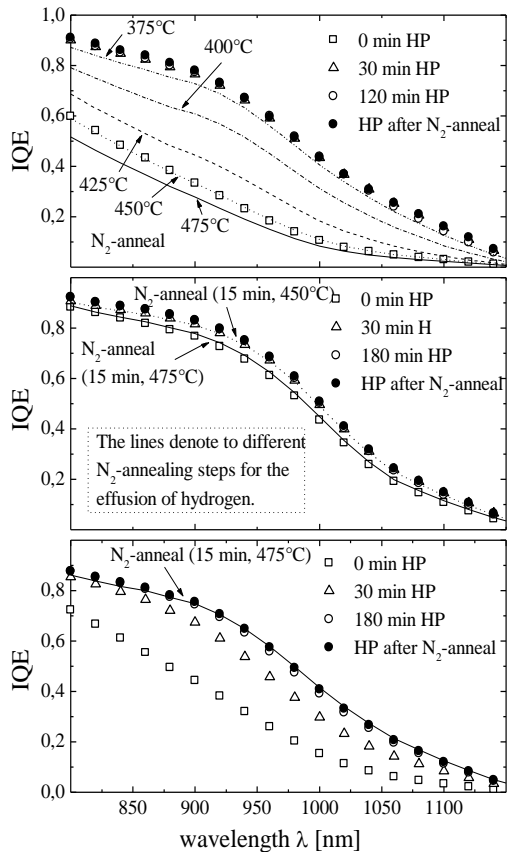


Fig. 6: The IQE for solar cells based on EFG, EMC and SOLAREX Si material measured before and after various H-diffusion (MIRHP at 350°C) and H-effusion (15 min N₂-annealing) process steps. The MIRHP processing time and the annealing temperatures are given in the figure.

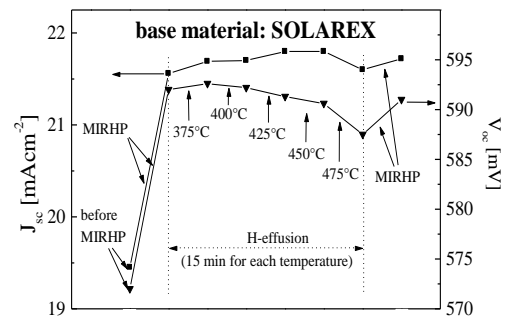


Fig. 7: The short circuit current density J_{SC} and the open circuit voltage V_{OC} as a function of different annealing processes for the same cell as in Fig. 6.

H-diffusion out of the bulk is negligible for temperatures below 475°C as can also be seen in Fig. 7, J_{SC} is nearly constant up to 475°C. The variation of 0.1 mAcm⁻² is within the measurement uncertainty. A measure for the H-diffusion out of the surface region is given by the V_{OC} which is more sensitive to the surface than J_{SC} . The effusion of hydrogen from the surface starts at a temperature between 400°C and 450°C.

CONCLUSIONS

The microwave induced remote hydrogen plasma (MIRHP) process was optimized according to process temperature and time using solar cells made from various mc-Si base materials. It was found that cast Si materials (EUROSIL, BAYER, EMC, SOLAREX) have nearly equal optimum process temperatures (350°C - 375°C) but different optimum passivation times (90 - 180 min). A different behavior is observed in the investigated ribbon mc-Si materials (EFG, RGS). A fast (slow) H-diffusion was observed in EFG (RGS) with optimum parameters of 350°C/30 min (425°C/210 min) and relative increases of the cell efficiency of up to 30%. In EFG, the H-effusion from the bulk starts below 375°C, in EMC at 450°C and in Solarex material above 475°C. H-diffusion depths were obtained using a step model for the internal quantum efficiency. It has been demonstrated by experiment that the derived approximation for the IQE results in excellent fits, therefore opening a door for further investigations of H-diffusion processes in solar cells.

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