

INVESTIGATIONS ON HYDROGEN IN SILICON BY MEANS OF LIFETIME MEASUREMENTS

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ABSTRACT

Various techniques (SIMS, Thermal Effusion, FTIR) have been suggested for the determination of the diffusion of hydrogen in multicrystalline silicon [1]. However these methods are either laborious or of a minor accuracy. Our work concentrates on the determination of hydrogen passivation depths in mc-Si by determining the minority carrier lifetime as a function of hydrogen passivation time. For the investigations EMC silicon and reference FZ silicon wafers have been used. From experimental data the passivation depth is obtained numerically using the simulation software PC1D and analytically using a simplified equation. For EMC passivation depths in regions of good and poor quality have been obtained indicating no significant influence on the passivation depth. Further experiments by polishing the wafer prior to lifetime measurements with a small angle have been performed for determination of the SRV.

INTRODUCTION

In many laboratories hydrogen passivation by means of a remote plasma is a well established method to improve the quality of mc-Si wafers [2-4]. Especially on low quality materials considerable improvements in the open circuit voltage V_{oc} , the short circuit current I_{sc} and the fill-factor FF have been reached. This leads to an increase in the efficiency of up to 2.3 % absolute or 38 % relative on commercially available mc-Si wafers [5]. The effectiveness of a hydrogen passivation step is well proven on the solar cell level, whereas some fundamental questions on the microscopic level are still open. A method for the determination of H-passivation depths in solar cells based on spectral response measurements is given in [6].

In this work the influence of atomic hydrogen on the passivation of crystal defects and therefore on the lifetime of minority charge carriers is investigated. From these results information on the penetration depth in different quality EMC material is obtained.

MINORITY CARRIER LIFETIME

By measuring the lifetime of the minority carriers, normally the effective lifetime τ_{eff} is determined, which is

correlated with the bulk lifetime τ_b and the surface lifetime τ_s with the following equation:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{1}{\tau_s} \quad . \quad \text{eq. 1}$$

For a small surface recombination velocity (SRV) this can be approximated by [7]:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_b} + \frac{2S}{H} \quad \text{eq. 2}$$

with H the thickness and S the surface recombination velocity of the wafer.

The surface recombination velocity can be obtained by determining τ_{eff} prior and after performing an etching step. Taking into account the measurement uncertainties the unknown values τ_b and S can be extracted [8]. To reduce the statistical error we suggest the following wafer preparation method: Mechanical polishing of a wafer with a small angle, etching away the polish damage and measuring the lifetime at two or more different thicknesses by performing a lifetime line-scan over the polished surface. This method is also suggested for microscopic investigations of mc-Si material, e.g. determination of τ_b on single grains, or hydrogen diffusion depths by using the model presented in the following.

MODEL FOR HYDROGEN PASSIVATION

The penetration depth of hydrogen is determined by a simple 3 layer model for the description of the lifetime as shown in Fig. 1. In our experiments the outer regions have the same lifetime because using the MIRHP technique for the hydrogen passivation the hydrogen diffuses in from both sides of the wafer. The lifetime value of the unpassivated wafer corresponds to τ_1 , the one of the completely passivated wafer to τ_2 .

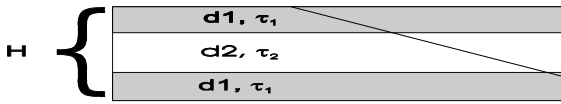


Figure 1: Diagram of a wafer, which is passivated in the outer regions (d_1, τ_1) and none passivated in the inner region (d_2, τ_2). The diagonal line represents the angle polish after the passivation, which is presented in the second part of the paper. Along this line the varying degree of passivation can be detected by lifetime measurements.

From Fig. 1 three methods to determine the thickness of the layers from the experimental data are suggested, whereas a small SRV has been assumed.

1. Analytical approach

For the evaluation the following equation is suggested:

$$\frac{1}{\tau_{eff}} = \frac{2d_1}{H} * \frac{1}{\tau_1} + \frac{H - 2d_1}{H} * \frac{1}{\tau_2} \quad \text{eq. 3}$$

In this model the effective lifetime of the whole wafer is the sum of the individual bulk lifetimes weighted by their thicknesses.

2. Numerical approach

The experimentally determined lifetimes are used for a simulation of the transient of the conductivity σ with PC1D. The same regions as above have been taken. For the simulation a short light pulse has been defined entering the wafer from one side. From the transient of the conductivity σ the effective lifetime of the whole wafer is determined, using the well known proportionality:

$$\frac{d \ln \sigma(t)}{dt} \sim -\frac{1}{\tau_{eff}} \quad \text{eq. 4}$$

Besides these evaluation methods also the following experimental procedure is suggested including a polished wafer. After the wafer is polished with a small angle the varying lifetime, depending on the degree of passivation in the different layers, is determined as indicated by the diagonal line in Fig. 1. This effect has an overlap with the increasing contribution of the surface passivation with decreasing wafer thickness, therefore either an excellent surface passivation is needed or with high accuracy known.

MICROWAVE PHOTOCONDUCTANCE DECAY

The microwave photoconductance decay technique (μ -PCD) measures the time dependent carrier concentration $\Delta n(t)$ after optical excitation which is directly related to the lifetime of the excess minority carriers. With the μ -PCD technique the carrier concentration is determined in a non-contact way by

measuring the microwave reflectivity P which is proportional to the conductivity of the semiconductor material. The excess carriers are generated by a pulsed laser beam with a wavelength of 904 nm. The measurements were carried out with a bias light of 3 suns due to problems with a filter wheel. In this investigation the lifetime in the bulk is of interest, therefore the SRV has to be reduced to a minimum. For the chemical surface passivation a preparation procedure incl. iodine ethanol passivation has been used. Prior to the iodine ethanol passivation, the wafers are cleaned in a solution of H_2O_2 and H_2SO_4 and are dipped in 5% HF. Between these steps the wafers are rinsed in DI water. With this procedure a SRV of less than 20 cm^2/s can be reached.

In first experiments with Baysix mc-Si wafers of very good quality it was shown that the surface passivation procedure using iodine ethanol can be applied several times resulting in reproducible measurements. Already measured samples were cleaned in a solution of H_2O_2/H_2SO_4 to remove the iodine ethanol. Afterwards they were passivated and measured again. This was repeated with several samples 4 times and the measurements were reproducible within an accuracy of 10 % at a value of 40 μs .

An effect, which has been found during these experiments is the improvement of the surface passivation due to repeated measurements of a wafer. The value for τ_{eff} increases during the first 5 to 10 measurements until it reaches a saturation value. This effect is not due to a change of the iodine ethanol passivation with time, but most probably due to an influence of the bias light on the surface passivation.

HYDROGEN PASSIVATION BY A REMOTE PLASMA

Hydrogen does not diffuse into silicon from a molecular ambient, therefore it has to be dissociated. For the generation of atomic hydrogen the microwave induced remote hydrogen plasma (MIRHP) technique has been used. The atomic hydrogen is generated by a microwave plasma which is located separately from the wafers, ensuring that a damage of the wafer surface due to radicals and UV radiation of the plasma is avoided.

The MIRHP device consists mainly of a quartz tube with a diameter of 156 mm in a furnace with a heated length of 750 mm which may be heated up to 800°C. Perpendicular to this tube the inlet of the process gases are passed through a capacity. The latter is connected with a 2.45 GHz microwave generator. The gas mixture consisting of 10% H_2 and 90% He with a purity of 6N is dissociated when flowing through the cavity. Arriving in a large quartz tube the atomic hydrogen diffuses into the samples at typical temperatures of 275-450 °C, with an optimum passivation temperature for most mc-Si materials between 350 and 400°C. A total gas pressure of 0.4 mbar measured at the outlet of the gases was chosen.

For cell processes where at the end an annealing step is carried out the MIRHP process can replace the annealing, therefore avoiding an additional process step.

EXPERIMENTS

Neighboring p-type EMC wafers of thickness 330 μm were cut into 5x5 cm^2 pieces, as seen in Table 1. To confirm the comparability of the wafers no. 1 to 4 were measured without surface passivation. There was a slight increase in the mean value of the lifetime from 1.7 μs to 2.0 μs . Wafers 9 to 11 were cut into four 2x2 cm^2 pieces, wafers 1-8 were further processed with size 5x5 cm^2 . All wafers are etched in NaOH to remove the saw damage with a following HCl cleaning and a HF-dip. Then one wafer is measured as a reference and the others are treated differently as seen in Table 1. The MIRHP process is carried out at a temperature of 400 $^{\circ}\text{C}$ and a pressure of 0.4 mbar. After loading the samples, the reactor is pumped down. When reaching a certain pressure the plasma is started. It takes approx. one minute until the plasma power is started, the gas pressure and gas flux are in a stable condition, therefore passivation times not below 5 min should be taken.

The smaller pieces of 4 cm^2 are treated the same way and are polished with a small angle (ca. 1 $^{\circ}$) afterwards. The polishing damage was etched away with NaOH and optional with CP4. Then the wafers were μ -PCD measured.

Table 1: Process sequence

5x5 cm^2 samples nr.: 1-8	2x2 cm^2 samples nr.: 9-11
NaOH saw damage etching + HCl + HF-dip	
PCD- τ without surface passivation	Cleaning in $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$
MIRHP for 5, 10, 15, 30, 120 min	
μ -PCD- τ	
	Polishing at an angle of 1 $^{\circ}$
	1 min. NaOH (+CP4, optional)
	μ -PCD- τ

RESULTS

The strong effect of the hydrogen passivation for the minority carrier lifetime is shown in Fig. 1. The left one represents the untreated wafer and the right one is of wafer no. 4, which is passivated for 30 minutes. The scale is the same for both wafers. The peak of the lifetime distribution has moved from 2 μs to 6 μs and a third of the wafer is better than 15 μs after the passivation.

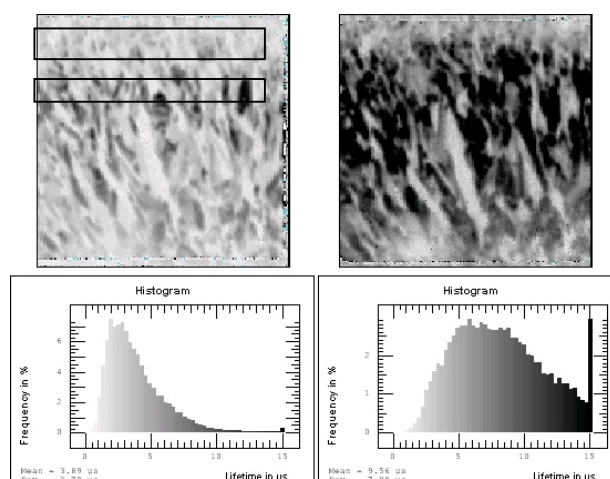


Fig. 1: Lifetime maps of wafer 1 (untreated) and wafer 2 (30 min MIRHP) with the same scale from 1 to 15 μs . Wafer 1 has a mean value of 3.9 μs , wafer 2 of 9.6 μs . The regions drawn in are used for Fig. 2. Upper rectangle = poor region, lower rectangle = good region.

After 5 to 10 min the lifetime saturation value is almost reached (See Fig. 2). The differences after 5 to 15 minutes of passivation are in the reproducibility of the measurements and the variation between the neighboring wafers.

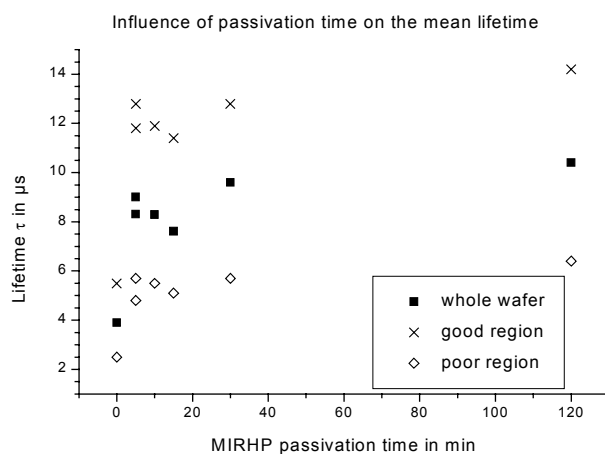


Fig. 2: Change of mean lifetime in dependence of the passivation time. Already after 5-10 min nearly the saturation value is reached for good and poor regions of the wafer. Good and poor region have an area of $\sim 2 \text{ cm}^2$.

In Table 2 the results of the unpolished wafers are shown. The whole 5x5 cm^2 wafers were measured and also 2 regions with low and high lifetimes respectively were evaluated. The untreated wafer delivered τ_2 and the completely passivated wafer τ_1 . Together with τ_{eff} of the partly passivated wafers the penetration depth is calculated. Already after 5 min of passivation only a layer with a thickness of $(330-2 \times 140) \mu\text{m} = 50 \mu\text{m}$ remains unpassivated. This is consistent with the fact, that already the saturation level of the lifetime is reached.

After 30 min. of passivation only 30 μm remain unpassivated. The values for the good and bad regions lead to comparable data, which means, that the diffusion of hydrogen is mostly independent of the quality and defect density in EMC silicon.

The results of the calculation were used in the PC1D simulation resulting in an excellent agreement of the measured and simulated τ_{eff} values.

Table2: Results of the lifetime measurements of the unpolished wafers. The penetration depth is calculated with eq. 3 for the three layer model. The results are in very good agreement with the PC1D simulations.

	Whole wafer	Poor region	Good region
None-passivated τ_2	3.9 μs	2.5 μs	5.5 μs
Passivated τ_1	10.4 μs	6.4 μs	14.2 μs
30 min. MIRHP:			
Calculated penetration depth d_1	151 μm	152 μm	154 μm
Measured τ_{eff}	9.1 μs	5.7 μs	12.7 μs
PC1D τ_{eff}	9.0 μs	5.7 μs	12.7 μs

In Fig. 3 is shown, that on the polished FZ wafer the lifetime decreases with decreasing thickness of the wafer. This is due to the bigger effect of the finite surface passivation quality with smaller thickness. Applying the method described in the chapter "minority carrier lifetime" values for SRV of about 200 cm/s are obtained. This value is not very good for a passivation with iodine-ethanol, but probably the damage of the polishing has not

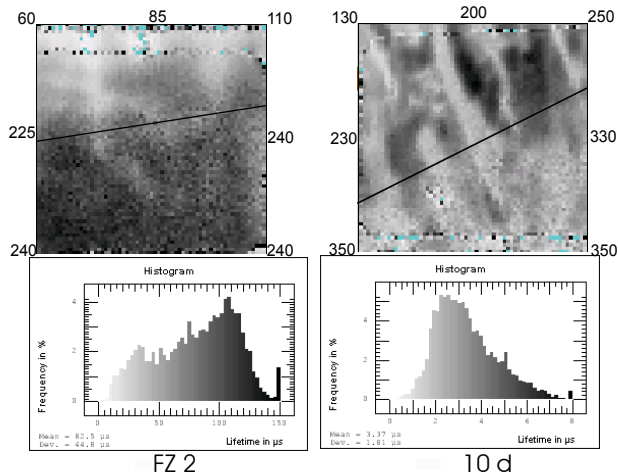


Fig. 3: Lifetime maps of wafer FZ 2 (scaled from 0 to 150 μs ; mean: 89 μs) and the EMC wafer 10 d (scaled from 0 to 8 μs ; mean: 3.5 μs). Both wafers are polished on the upper region in the graphs. The edge between polished and unpolished region and also the remaining thickness is drawn in. Wafer 10 d is MIRHP treated for 10 minutes. been etched away totally. In further experiments the last polishing step will be with a more fine-grained polishing wheel and the etching step will be extended.

It is also shown in Fig. 3, that on the polished EMC wafer no effect of the wafer thickness can be seen, the

polished region seems even to be of better quality. We expected a lower effective lifetime for the thinner regions because of a lower bulk lifetime and a larger contribution of the SRV. This is not confirmed in this experiment. One reason is the very fast passivation of the wafer within 5 to 10 minutes. If the wafer is nearly totally passivated there is only a very thin layer none-passivated in the middle of the wafer. This region is therefore difficult to detect with a lifetime map over a polished surface. In further experiments mc-Si material which needs a longer passivation time to be saturated, such as oxygen rich mc-Si, will be chosen and the passivation time further reduced.

CONCLUSION

A simple 3 layer model for the determination of the penetration depth of hydrogen in mc-Si has been presented. The model takes into account the improvement of the minority carrier lifetime. Experiments were performed, using the μ -PCD technique to determine the effective minority carrier lifetime. The experimental results are in excellent agreement with PC1D simulations. In addition a method has been presented based on angle polishing a FZ wafer for determining τ_s without knowing τ_b . First experiments using this method to determine die H-passivation depth in mc-Si have not been successful. Further experiments changing the wafer cleaning procedure and using mc-Si material where hydrogen diffuses slower will be performed.

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