

## MAPPING OF HYDROGEN BOND ENERGIES IN EFG SILICON SAMPLES BY ANALYSIS OF SPATIALLY RESOLVED MINORITY CHARGE CARRIER LIFETIMES AFTER ANNEALING STEPS

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**ABSTRACT:** Inspired by investigations on the *average* bond energies of hydrogen on various defect sites in silicon wafers a new method to determine these bond energies in a *spatially resolved* way was developed. This knowledge is useful for a better understanding of the hydrogenation process in defect-rich materials. Beyond that it serves to gain information about defect distributions especially in multicrystalline silicon material: as the bond energies of hydrogen depend on the defect type, mapping of the bond energies in principle permits to draw conclusions concerning the distribution of defects in multicrystalline silicon wafers.

The method is based on minority charge carrier lifetime measurements by  $\mu$ -PCD (microwave-detected PhotoConductance Decay). A hydrogen-passivated EFG (Edge-defined Film-fed Growth) silicon sample is heated in a RTP (Rapid Thermal Processing) oven for one second at a specific temperature. Afterwards the minority carrier lifetime is measured and the wafer is exposed to the next temperature step (again one second but at a higher temperature). This is repeated until all hydrogen has left the sample and no significant further decrease in lifetime can be detected. From the lifetime decrease after the different temperature steps the bond energies of hydrogen in EFG samples can be calculated with the same resolution as the lifetime measurements. Provided a direct correlation between extracted bond energy and defect type can be established the different bond energies can be attributed to the different defect types. With that a fast and cost effective method to examine defect distributions spatially resolved is available, particularly on large area wafers.

It could be shown that in EFG material regions with different hydrogen bond energies exist.

**KEYWORDS:** Hydrogen, Defects, Impurities

### 1 INTRODUCTION

This paper presents a new method to determine bond energies of hydrogen on defect sites in multicrystalline silicon in a *spatially resolved* way. From that knowledge one can learn more about the microscopic hydrogenation process. Based on the defect-typical bond energies of hydrogen conclusions can be drawn concerning possible defect distributions in multicrystalline silicon wafers.

### 2 THEORETICAL MODEL

The determination of the bond energies of hydrogen on defect sites in multicrystalline silicon is based upon the out-diffusion of hydrogen during several annealing steps in a RTP oven at specific - after each step increased - temperatures. The out-diffusion causes a decrease of minority charge carrier lifetime values after each temperature step that can be measured with  $\mu$ -PCD.

In literature [1-4], annealing-induced reactivation of defects is described by the equation

$$\ln \frac{N}{N_0} = t\nu \exp\left(-\frac{E_D}{k_B T}\right), \quad (1)$$

where  $N_0$  and  $N$  are the densities of passivated defects before and after an annealing step,  $t$  is the annealing time,  $\nu$  is the attempt frequency,  $E_D$  the bond energy and  $T$  the annealing temperature. In order to take advantage of the anti-proportionality between minority charge carrier lifetime values  $\tau$  and the density of unpassivated defects (valid for Shockley-Read-Hall defect species),  $N/N_0$  is expressed in dependence of the density of

unpassivated defects  $N_0'$  before and the density  $N'$  after an annealing step:

$$\frac{N}{N_0} = \frac{N_D - N'}{N_D - N_0'}. \quad (2)$$

$N_D$  is the density of all defects that possibly can be passivated by hydrogen. Assuming that  $\tau$  is inversely related to the active defect concentration and that all defects in the regarded area are the same, the fraction of passivated defects can be expressed by

$$\frac{N}{N_0} = \frac{1/\tau_r - 1/\tau_f}{1/\tau_r - 1/\tau_i}. \quad (3)$$

$\tau_i$  names the minority carrier lifetime before a temperature step,  $\tau_f$  afterwards.  $\tau_r$  is the lifetime value after reactivation of all initially passivated defects. In this experiment  $\tau_r$  is measured after a last temperature step at a temperature of 700°C for 60 s. The annealing time for all previous steps with lower temperatures is just 1 s.

From the combination of equations (1) and (3) the bond energies of hydrogen at defect sites can be determined:

$$E_D = -k_B T \ln \left[ \frac{1}{t\nu} \ln \frac{1/\tau_r - 1/\tau_f}{1/\tau_r - 1/\tau_i} \right]. \quad (4)$$

The frequency  $\nu$  lies in the range between  $10^{13}$  Hz and  $10^{14}$  Hz [1]. Another way to calculate the bond energy is given by fitting a double exponential function to the measured  $N/N_0(T)$  data points.

By measuring the minority carrier lifetime values spatially resolved with the  $\mu$ -PCD method, the bond energy can be determined for many points on a wafer. The resolution hereby equals the one of the lifetime measurement.

### 3 EXPERIMENT

Figure 1 shows the processing of the samples. In a first step EFG wafers were cut into 50 x 25 mm<sup>2</sup> samples. Afterwards all samples were treated with a Chemical Polishing etch called CP6 [5]. To prepare the samples for surface passivation by an iodine-ethanol solution (IE) [6] they were cleaned by a so called IMEC clean (Clean) [7] and a subsequent HF dip.

A part of the samples served as a reference, the other part was prepared with a gettering and a hydrogenation step. It is known that gettering improves the efficiency of hydrogenation [8]. For a first proof of the new method it was useful to have a very good hydrogenation and thus the samples obtained a phosphorous gettering step prior to hydrogenation.

In order to hydrogenate these samples a SiN<sub>x</sub>:H-coating layer was deposited on the samples' surface by PECVD (Plasma Enhanced Chemical Vapor Deposition) [9]. The hydrogenation was realized by firing these samples.

After etching off the SiN<sub>x</sub>:H coating of the hydrogenated samples, all samples were annealed in a first step in the RTP oven. The top temperature was held only for one second. Heating up and cooling down was done as fast as possible, at best nearly instantaneously. The deviation from the ideal case can be considered when determining the hydrogen bond energies with the model described above (figure 2, figure 3). The temperature was measured with a very fast reacting pyrometer. The pyrometer quality was controlled after all out-diffusion experiments by melting several metals with known melting points. Based on this verification the formerly measured temperatures were corrected.

To be able to measure the minority charge carrier lifetime in the bulk the samples were cleaned another time with an IMEC clean and passivated by iodine-ethanol. Before the next temperature step the iodine-ethanol residues at the surface were eliminated by a short CP6 etch. This was done to avoid in-diffusion of iodine or other impurities in the crystal during the annealing step.

The temperature treatments were performed at temperatures between 450°C and 700°C. The minimum interval between two temperatures was 25°C, but was chosen to be higher for very low and very high temperatures. In the last temperature step the annealing time was increased from 1 s to 60 s. Figure 2 and 3 show the influence of the shapes of the temperature profiles. According to the theoretical model the profiles should be shaped like the dashed red lines in figure 2 and 3. The solid lines show the temperature profiles we could realize in our RTP oven AST SHS 100. The black lines in the two graphs show the decrease of passivated defects due to out-diffusion of hydrogen for given bond energies. These calculations were carried out with differential small time intervals for each 1/10 000 s. All temperature profiles were analyzed for bond energies between 2 eV and 3 eV. The maximum deviation from the ideal case

was found for the temperature profile shown in figure 3 for a bond energy of 2.6 eV with less than 15 %.

After each annealing step the minority charge carrier lifetime was measured spatially resolved by  $\mu$ -PCD. With a resolution of 250  $\mu$ m the lifetime was measured at 20 000 points on the wafer. With the model described above the bond energies for each of these points could be determined from these lifetime maps. The challenge using this model was to match the different lifetime maps with each other. Therefore an image matching algorithm called *normalized cross correlation* was implemented in the analysis software. After this initial image registration the bond energies for each point on the sample were determined and the result is presented in a map in figure 5.

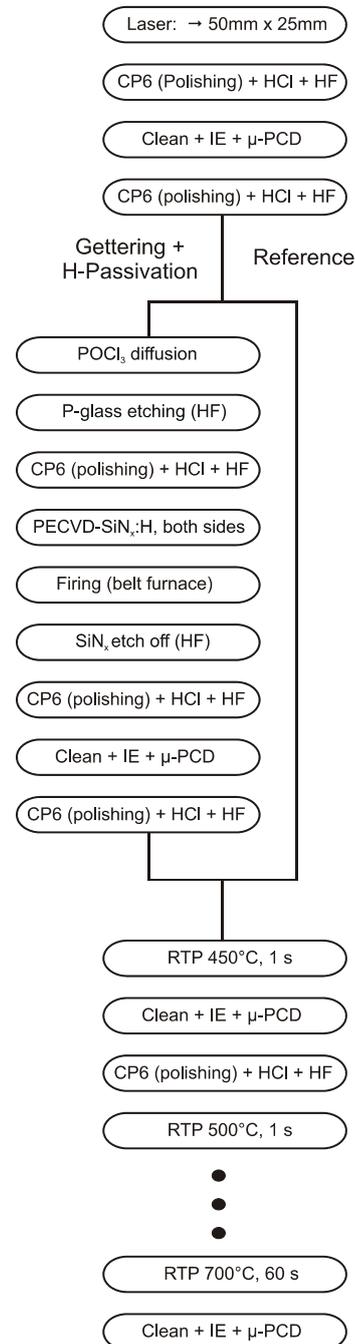
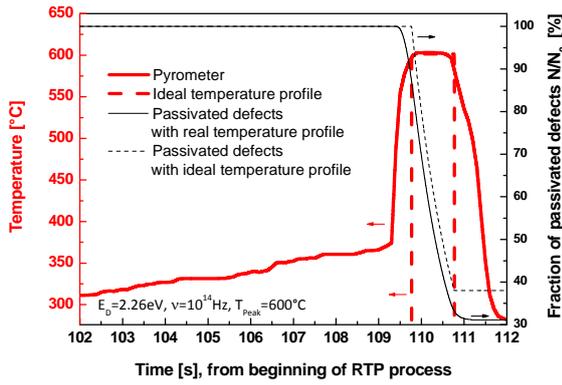
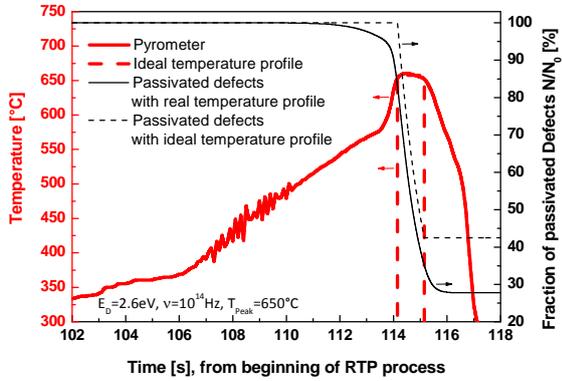


Figure 1: Processing of samples.



**Figure 2:** 600°C peak temperature profile and according theoretical hydrogen out-diffusion for ideal and real cases.  $N/N_0$  calculated for hydrogen-defect bond energy of 2.26 eV.



**Figure 3:** 650°C peak temperature profile and according theoretical hydrogen out-diffusion for ideal and real cases.  $N/N_0$  calculated for hydrogen-defect bond energy of 2.6 eV.

#### 4 RESULTS

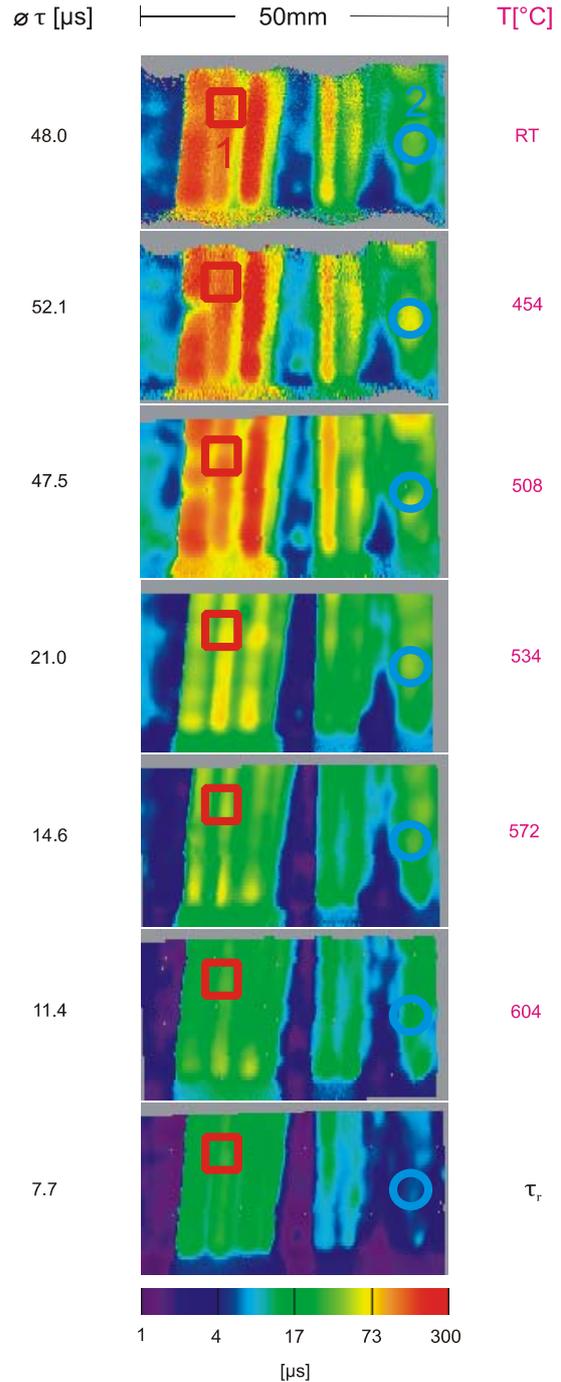
Figure 4 shows the correlated lifetime maps of a phosphorous-gettered and hydrogen-passivated EFG-sample after different annealing steps. The values were measured with a  $\mu$ -PCD setup without bias light and serve only to give proof of principle.

The analysis software allows different analysis methods and fitting routines. In this first run we focused on the analysis method described by equation (4). Figure 5 demonstrates a bond energy map of an EFG sample. The oscillation frequency  $\nu$  of the bond partners against each other (defect-hydrogen) was chosen to be  $10^{14}$  Hz because the values then were closer to the ones known from literature (Table I and [4]). Two areas with different bond energies are marked in figure 5. The corresponding areas in the lifetime maps are marked with the same symbols. Figure 6 shows the measured lifetime values in the center of the symbols. In figure 7 the determined values for the fraction of passivated defects  $N/N_0$  after the different annealing steps can be seen. The solid lines are fits through the data points according to the above described out-diffusion model. In both graphs one can see clearly that the hydrogen out-diffusion at position 1 started at lower temperatures compared to

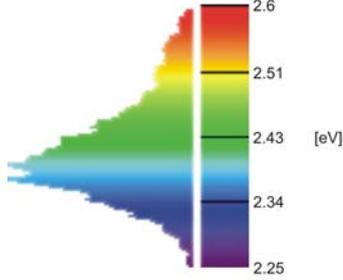
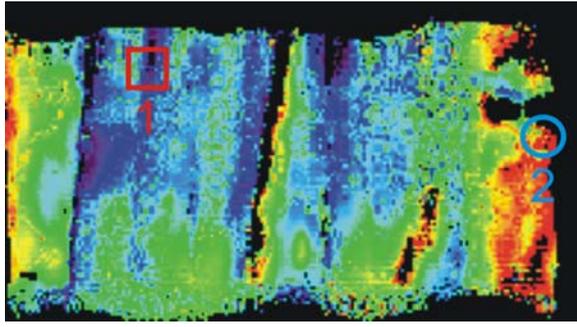
position 2, where it started at temperatures about 100 K higher.

These first results show that areas with different bond energies of hydrogen in EFG material can be detected and that the determined bond energy values lie in the range known from literature (Table I and [4]).

Further investigations will be carried out with a  $\mu$ -PCD setup including a bias light, so that the measured values will be more reliable due to the reduction of trapping effects.



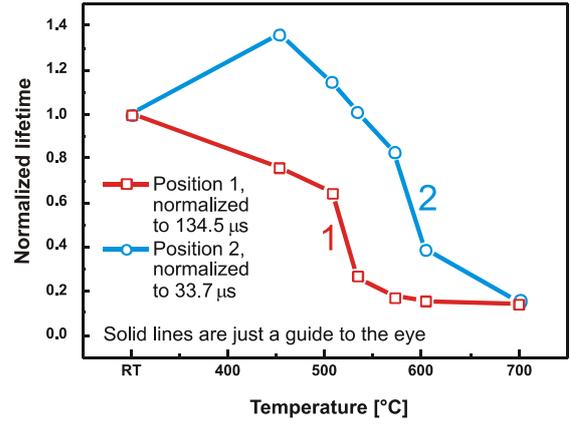
**Figure 4:** Correlated lifetime maps of a P-gettered and hydrogen-passivated EFG sample after different annealing steps.



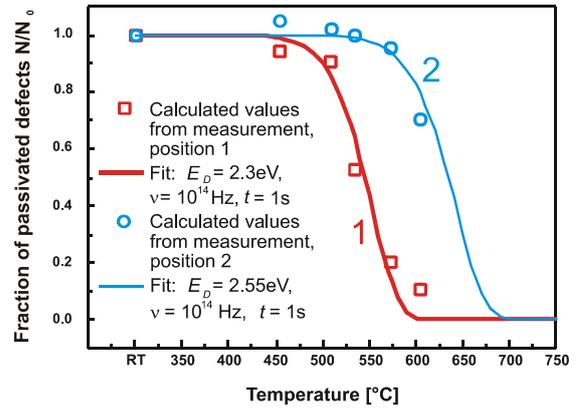
**Figure 5:** Map of bond energies of hydrogen on defect sites in an EFG sample determined according to equation (4) and assuming  $\nu = 10^{14}$  Hz. Corresponding minority charge carrier lifetime mappings are shown in figure 4. Hydrogen bond energy at position 1: 2.30 eV, at position 2: 2.55 eV.  $N/N_0$ -fits for these two positions are presented in figure 7.

**Table I:** Impurities or defects in silicon susceptible to hydrogenation including the corresponding energy levels (in brackets) and the corresponding hydrogen bond energy  $E_D$ . E and H refer to electron or hole trap, respectively [1, 2].

Impurity/Defect, Energy levels [eV]	$E_D$ [eV]
B	1.1
Fe, H(0.32, 0.39)	1.5
Ga	1.6
Al	1.9
V(Vacancy)-O, E(0.18)	1.9
Laser	1.9
In	2.1
S, Se, Te	2.1
Zn, E(0.54) H(0.32)	2.2
Ag, E(0.54) H(0.29)	2.2
Au, E(0.54) H(0.35)	2.3
Pt, E(0.28)	2.3
Pd, E(0.22) H(0.32)	2.4
Cu, H(0.20, 0.35, 0.53)	2.5
Ni, H(0.18, 0.21, 0.33)	2.5
Grain Boundary	2.5
Dislocation	3.1
Plastic Deformation	3.1



**Figure 6:** Decrease of minority charge carrier lifetime values after 1 s annealing steps at position 1 and 2, marked in figure 4 and 5. Figure 7 shows the corresponding values for the fraction of still passivated defects  $N/N_0$ .



**Figure 7:** Fraction of still passivated defects after 1 s annealing steps at position 1 and 2, marked in figure 4 and 5. Solid lines are fits through the data points. The values were calculated with the corresponding lifetime values from figure 6.

## 5 OUTLOOK

Further measurements are currently performed with a  $\mu$ -PCD equipment including a bias light. Iron- and copper-contaminated samples will be analyzed with the new method. Lifetime measurements directly after  $\text{POCl}_3$ -diffusion will be carried out in order to compare these mappings with the ones measured after all annealing steps to check for structural changes of defects during the annealing steps. The samples will be further examined by X-ray spectroscopy in order to link the bond energies of hydrogen with the defect types.

Table I shows hydrogen bond energy values from integral lifetime measurements. In the end such a table from measurements with a spatial resolution of hydrogen bond energies is the aim. This would open the door to a large area defect mapping of multicrystalline silicon wafers.

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