HYDROGEN KINETICS IN CRYSTALLINE SILICON – PECVD SIN STUDIES IN MC AND CZ SILICON

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ABSTRACT: Trapping of hydrogen during diffusion in silicon due to impurities and/or other defects is a well known fact. Using SIMS we can demonstrate that high amounts of oxygen can significantly slow down diffusion of deuterium originating from PECVD SiN layers after a firing step (NH_3 exchanged by ND_3) in mc RGS Si. The slowed down diffusion results in unwanted longer passivation times and lower carrier lifetimes during solar cell processing. Experiments using Cz Si samples differing in oxygen content are presented as well. High temperature annealing steps generate O-precipitates of defined size and concentration, and more pronounced trapping of deuterium appears for higher oxygen concentration. Even more trapping can be detected when O-precipitates are generated, with the highest deuterium concentrations for large precipitates. An O-depleted region near the surface is mirrored by lower deuterium concentrations, proving the link between enhanced trapping when oxygen is present. The overall amount of D-atoms incorporated into the Si bulk after firing can be measured to about $1 \cdot 10^{14}$ cm^{-2}.
Keywords: Silicon-Nitride, Multi-Crystalline, Czochralski

1 INTRODUCTION

Defects in mc silicon wafers and solar cells can be passivated very effectively by in-diffusion of atomic hydrogen. Although hydrogenation has been applied to multicrystalline (mc) Si for a long time, there seems to be a difference in the kinetics of hydrogen in mc Si in comparison to almost defect free monocrystalline float zone Si (see e.g. [1] for a review for mc Si). We will show that the question, where hydrogen after in-diffusion from a PECVD (plasma-enhanced chemical vapour deposition) SiN layer is located and trapped, has a strong influence on the kinetics of hydrogenation. This is a key feature for the fabrication of efficient solar cells made from defect-rich but cost-effective materials allowing a reduction in W_p-costs, because trapping can significantly slow down the hydrogenation process.

Recent publications revealed that hydrogen kinetics are strongly influenced by the presence of oxygen in multicrystalline ribbon silicon wafer materials [2,3]. A close correlation between the amount of oxygen present and the concentration of hydrogen being measured by SIMS (secondary ion mass spectroscopy) could be detected. It was speculated that the amount of hydrogen (or in this case deuterium) being trapped is dependent on the surface area of oxygen precipitates formed inside the wafer during high temperatures. To test this assumption we will here present an additional study based on oxygen-rich Cz (Czochralski) silicon (first results already discussed in [4]). The big advantage of using mono Cz silicon is the fact that there are far less additional defects present as in the case of highly defected ribbon silicon materials used in [2,3]. In this way the influence of oxygen on hydrogen kinetics can be studied with more accuracy, provided that the hydrogen (here: deuterium) concentration is above the detection limit.

2 HYDROGENATION IN MC RIBBON SILICON

In [2] it could be shown that hydrogen kinetics in RGS (Ribbon Growth on Substrate) Si depend strongly on the overall oxygen concentration as well as on the thermal history of the samples. Deuterium profiles could

be measured deep in the Si bulk after a PECVD SiN deposition followed by a firing step provided the samples contained a high amount of oxygen (Fig. 1). For oxygen concentrations well below 10^{18} cm^{-3} like in the SR (String Ribbon) sample, the measured [D] is at or below the SIMS detection limit of $5 \cdot 10^{14}$ cm^{-3}. Furthermore, [D] seemed to be affected by the presence, concentration, and/or size of oxygen precipitates formed during high temperature steps in the RGS material [2]. Trapping of hydrogen in RGS was strongly reduced with decreasing [O], influencing the velocity of defect passivation and leading to higher minority carrier lifetimes and solar cell efficiencies [5,6].
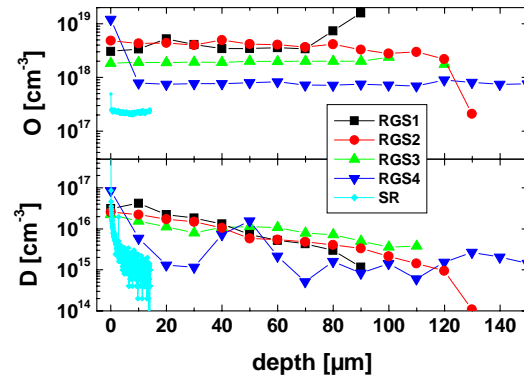
Figure 1: SIMS D-profiles in ribbon Si samples differing in O-concentration after a PECVD SiN deposition and firing. Higher oxygen concentrations lead to more trapping of D (see [2] for more details).

3 SETUP CZ EXPERIMENT

3.1 Selection of Cz material

The results for mc Si samples suffer from the fact that all kinds of defects could be present (dislocations, impurities, grain boundaries, precipitates), possibly obscuring the effect of oxygen on the H-kinetics during hydrogenation. Therefore we set up a second experiment, this time using monocrystalline Cz Si with oxygen being the only major contaminant. Two types of p-type Cz

materials (8-13 Ωcm, 350 µm thickness) high in [O] (1.0 and $1.7 \cdot 10^{18}$ cm^{-3} respectively) were selected and a mc SOLSIX sample was included as a reference.

The Cz samples underwent two different annealing sequences shown in Fig. 2 to generate O-precipitates. The procedure started with a 15 min homogenisation step at 1050°C for all Cz samples. Afterwards Anneal 1 produced a high concentration of small O-precipitates (24 h at 500°C followed by 48 h at 650°C) or Anneal 2 generates a lower amount of large O-precipitates (24 h at 1000°C). Note that all measured Cz samples underwent the initial short 1050°C homogenisation step, although samples without Anneal 1 or 2 will be called 'as grown'.
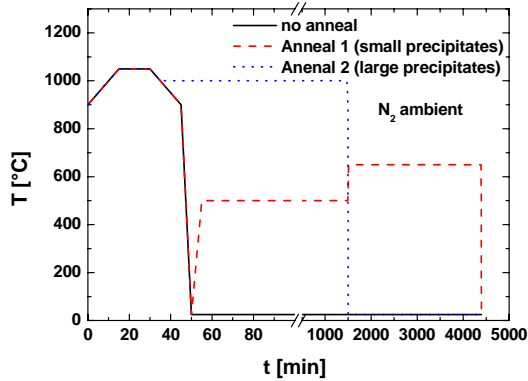
Figure 2: Annealing steps performed for the Cz material to produce O-precipitates. All Cz samples underwent the 1050°C homogenisation step (not the SOLSIX sample).

The effect of the annealing on O-precipitaion can be seen in Table I. Samples are characterised by FTIR (Fourier transformed infrared spectroscopy) and SIMS. For Cz1 both anneals lead to significant precipitation as can be judged by the difference in overall (SIMS) and interstitial oxygen concentration ([O$_i$] by FTIR). Precipitation is less pronounced for Cz2.

Material	[O$_i$] FTIR [10^{17} cm^{-3}]	[O] SIMS [10^{17} cm^{-3}]
Cz1 as grown	13.8	16.2
Cz1 Anneal 1	2.0	16.4
Cz1 Anneal 2	3.1	17.6
Cz2 as grown	7.2	~9
Cz2 Anneal 1	6.9	
Cz2 Anneal 2	6.0	9.9
mc SOLSIX as grown	~3	~4

Table I: [O$_i$] and [O] data determined by FTIR and SIMS for the samples investigated in this study after high temperature annealing steps. The effect of annealing on O-precipitation can clearly be seen.

3.2 Cz experiment

After annealing, the samples described in Table I were POCl$_3$ diffused (50 Ω/sq). PECVD SiN deposition was performed in a Roth & Rau remote plasma reactor using ND$_3$ instead of NH$_3$, resulting in a refractive index n of 2.1-2.2. The following firing step in a conventional belt furnace was the same as used for co-firing of screen-printed metal contacts in solar cell processing.
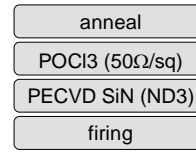
Figure 3: Applied processing steps.

Afterwards, samples have been analyzed by SIMS to measure D-profiles deep in the Si bulk. To save SIMS measurement time and increase accuracy, samples have been bevelled and profiles have been obtained in the way described in Fig. 4.

In addition, vacancy concentration [vac] has been determined according to the method described in [3].
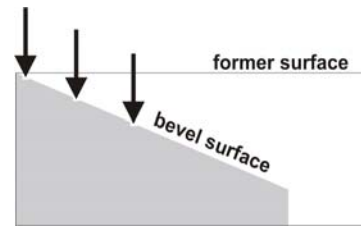
Figure 4: Beveled sample for deep SIMS profiling.

4   RESULTS HYDROGENATION IN CZ

4.1 D-profiles
SIMS data in Fig. 5 give [D] measured close to the SiN top and bottom side of the samples. Except for the SOLSIX reference, D is detectable for all samples with higher signals for Cz1 (higher [O]). Moreover, the more pronounced O-precipitation for both anneals in Cz1 leads to higher [D] as compared to the Cz1 as grown sample, proving that O-precipitates act as trapping centres for D.
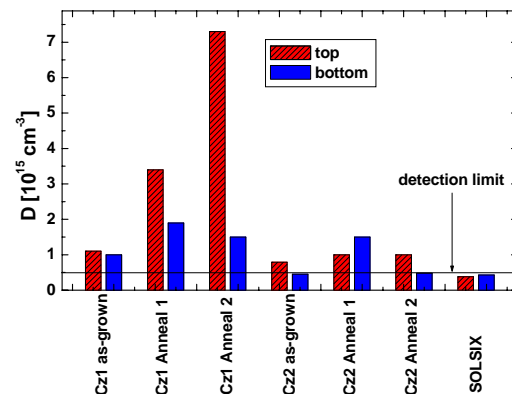
**Figure 5:** SIMS measurements on both sides of the samples after firing.

Results for the bevelled Cz1 samples are given in Fig. 6. [D] can be detected even deep in the Si bulk. Remarkable is the lower [D] close to the top surface (zero depth) for all Cz1 samples. To analyze this effect further, conventional SIMS profiles on unbevelled samples have been carried out, which are presented in Fig. 7.

Close to the surface an O-depleted zone of about 5 µm width can be detected. This can be explained by out-diffusion of O during the high temperature annealing
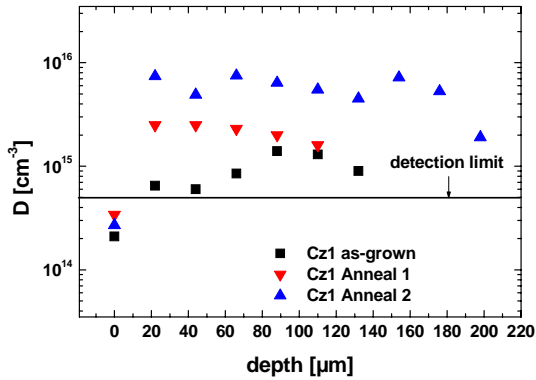
Figure 6: SIMS profiles in fired Cz1 samples (bevelled).

steps. As the depleted zone is visible as well for the as grown Cz1 sample, we have to conclude that even during the relatively short 1050°C homogenisation step for 15 min significant amounts of O diffuse out of the sample. Out-diffusion is more pronounced after Anneal 2, as the sample is kept at high temperature (1000°C) for a long time. The scattered signal for Cz1 Anneal 2 is due to the fact that only a limited amount of O-precipitates in the order of 10 (lower density compared to Anneal 1) is detected at a single measurement point, causing statistical fluctuations (see [4] for more details).
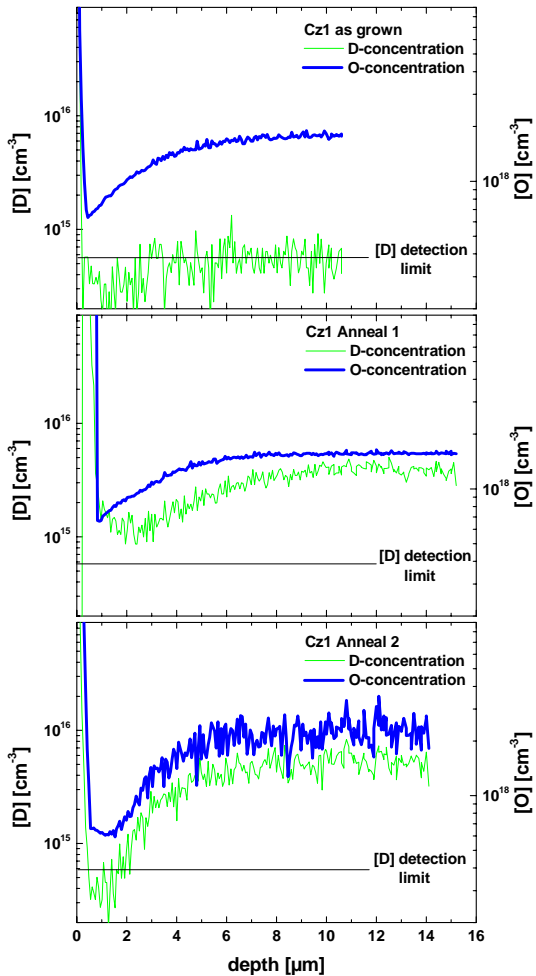
Figure 7: SIMS profiles for fired Cz1 samples showing an O-depleted zone at the surface.

The most striking feature visible in Fig. 7 is the fact that the [D] mirrors the shape of the [O], especially if precipitates are present (Cz1 Anneal 1 and 2). To a lesser degree this might hold true for Cz1 as grown, but [D] is too close to the detection limit for a proper analysis. This behaviour is the most direct prove that a) O causes trapping of D and b) O-precipitates can trap more D than O in interstitial form. Note that in-diffusion of D took place after out-diffusion of O. The microscopic location of trapping (surface of the precipitate, bulk of the precipitate, strain field or defects around the precipitate) is still unclear. The fact that Cz1 Anneal 2 with lower amount of large precipitates traps more D than Cz1 Anneal 1 with a high concentration of smaller precipitates (and therefore a higher surface to volume ratio) seems to contradict the assumption that the surface is the location of trapping as stated in [2].

4.2 Behaviour of [vac]

The concentration of vacancies [vac] might play a role in the diffusion kinetics of H (or D) in Si, as it is reported that vacancies can crack H_2-molecules [7] or H can diffuse as a H-vacancy complex [8]. We measured [vac] for samples in different states of processing according to the method already used in [3] and results are listed in Table II. Cz1 samples have been measured both directly after homogenization/annealing (labelled 'no POCl$_3$') as well as after POCl$_3$-diffusion, SiN deposition and firing (labelled 'POCl$_3$').

Sample	Anneal	POCl$_3$	[vac] $[10^{11} \text{ cm}^{-3}]$
Cz1	as grown	no	400
Cz1	as grown	yes	<3
Cz1	Anneal 1	no	50
Cz1	Anneal 1	yes	<3
Cz1	Anneal 2	no	2000
Cz1	Anneal 2	yes	20
Cz2	as grown	no	200
Cz2	Anneal 1	no	40
Cz2	Anneal 2	no	150

Table II: Concentration of vacancies [vac] after different processing steps for the Cz samples under investigation.

To understand the results, we have to consider the dynamics of O-precipitation in dependency on temperature. The formation of O-precipitates is combined with an increase in volume, normally causing the formation of Si self interstitials (Si$_i$) which can annihilate with vacancies. The overall [vac] at high temperatures is increased due to Fermi level effects [9] and there seems to be a mechanism present that prevents vacancies from being annihilated at 1000°C (e.g. by in-diffusion of nitrogen [10], causing trapping of vacancies [11]). At lower temperatures as used for Anneal 1 and POCl$_3$ diffusion, [vac] decreases most probably due to annihilation with Si$_i$.

With these considerations we can explain the behaviour of [vac] shown in Table II. Samples kept at higher T show a high [vac] without POCl$_3$ (Cz1 and Cz2 as grown and after Anneal 2), whereas O-precipitation at lower T for Anneal 1 results in a significant consumption of vacancies. Depending on the history of the samples [vac] can further decrease during the following high temperature step (POCl$_3$-diffusion) if a high [O$_i$] is still

present (Cz1 as grown), or if diffusion temperature is above the annealing temperature, causing dissolution of precipitates and re-precipitation during POCl$_3$-diffusion (Cz1 Anneal 1). In addition, Si$_i$ are injected during POCl$_3$ diffusion, further decreasing [vac]. Therefore a significant [vac] after POCl$_3$ diffusion can only be detected in the Cz1 Anneal 2 sample.

It should be noted that [vac] seems not to play the dominant role for D-kinetics if trapping is involved, as the concentration of $20 \cdot 10^{11}$ cm^{-3} for Cz1 Anneal 2 is in the same range as determined for sample RGS2 [2,3], which shows a much steeper D-profile (compare Fig. 1 and Fig. 6).

4.3 Amount of D released into the Si bulk

From the profiles shown in Fig. 1 and Fig. 6 it is easy to determine the amount of D atoms incorporated into the Si bulk after firing up to the depth where profiling stopped. Values are given in Table III with the indication of the depth up to which D-atoms were counted. This method would give the overall amount of D incorporated into the Si bulk, provided the D-profile drops down to zero. At least for RGS1-3 the concentration of the profiles drops down far enough to calculate that the overall amount of D incorporated into the Si is around $1 \cdot 10^{14}$ cm^{-2}. Assuming a 75 nm thick SiN layer with a H-content of 20 at% we would expect $1.5 \cdot 10^{17}$ H-atoms per cm^2 in the SiN (using data from [12]). The SIMS measurement only detects D originating from NH$_3$, so the overall amount of D plus H atoms released into the Si bulk might be larger, but it seems that only a fraction of about 0.1-1% of the H present in the SiN layer diffuses into the Si bulk during firing.

For the SR and Cz samples (except Cz1 Anneal 2) [D] is too low to add up all the D-atoms incorporated into the Si bulk within the profiled depth. We expect that profiles have to be extended to depths between 1 and 2 mm to observe the desired drop to zero [D], enabling the calculation of the overall incorporated amount of D. Experiments using 2 mm thick Cz samples with different SiN thicknesses are currently under way and it is expected that from these data the overall amount of D diffused into the Si in dependency of the SiN thickness can be determined with higher accuracy.

Sample	depth [µm]	D atoms [10^{14} cm^{-2}]
RGS1	90	1.32
RGS2	130	1.06
RGS3	110	1.05
RGS4	160	0.924
SR	14	0.101
Cz1 as grown	130	0.118
Cz1 Anneal 1	130	0.260
Cz1 Anneal 2	200	1.10

Table III: Amount of D-atoms per cm^2 incorporated into the Si bulk up to the depth determined by the length of the D-profiles shown in Fig. 1 and Fig. 6.

5   SUMMARY

We could show that diffusion kinetics of H (or here D) in mc Si samples is strongly affected by trapping. A higher [O] leads to steeper D-profiles after firing a H/D-rich PECVD SiN layer, resulting in slower D-penetration and passivation of the Si bulk.

Monocrystalline Cz samples differing in [O] have been used to study this effect further. Annealing steps have been applied to deliberately generate O-precipitates of different size and concentration. It could be shown that higher [O] leads to more trapping of D. For equal overall [O], samples with precipitates showed more trapping, with the sample containing large O-precipitates giving the highest [D]. Out-diffusion of O during high temperature annealing steps causing a lower [O] near the surface was mirrored by lower [D] in the same region, again proving that trapping of D is caused by the presence of O. It is yet unclear if the D is trapped inside the O-precipitate, at its surface, or in the strain field around it.

Monitoring of the vacancy concentration [vac] revealed that similar values in Cz and RGS material can be obtained, with totally different diffusion kinetics of D. Therefore [vac] does not seem to play the major role in D-diffusion kinetics if trapping in combination with O occurs.

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