H-initiated extended defects from plasma treatment: Comparison between c-Si and mc-Si

Heidi Nordmark1,2, Alexander G. Ulyashin1, John C. Walmsley1,2 and Randi Holmestad1

1SINTEF Materials and Chemistry, NO-7465 Trondheim, Norway
2Department of Physics, NTNU, 7491 Trondheim, Norway
3SINTEF Materials and Chemistry, P.O. Box 124 Blindern NO-0314 Oslo, Norway

Heidi.Nordmark@sintef.no

Abstract. In this study n- and p-type polished Czochralski-grown Si (Cz-Si) and p-type polished and as-cut multi-crystalline (mc) Si wafers have been directly H plasma treated in a plasma enhanced chemical vapour system in order to study H subsurface defect formation. Raman spectroscopy, secondary ion mass spectroscopy, scanning electron microscopy and transmission electron microscopy have been used to characterise the samples. In polished Cz-Si wafers, H induced defects were only observed up to 1 µm below the surface [1,2], while in similarly treated mc samples H induced defects were observed on grain boundaries and dislocations up to several µm below the surface [3]. It is also established that the distribution of H in the subsurface regions of the Cz-Si substrates after hydrogenation as well as the formation of structural defects depend on the type of doping. Evolution of SiH bonds in hydrogenated Cz Si samples starts at 400 ºC, while evolution of H initiated structural defects starts at 600 ºC, when SiH bonds are mostly dissolved.

1. Introduction

Hydrogen plasma treatment is commonly used to passivate dangling bonds and impurities in Si to improve its carrier lifetime. However, the solubility of H in Si is very low [4], so the introduction of high H concentrations might lead to the formation of defects that act as “lifetime killers”. H defect formation is well studied and understood in mono-Si [1-17] but less is known about H segregation and interaction with extended defects like grain boundaries and dislocations in multicrystalline (mc) Si that is very widely used in solar cell fabrication.

Hydrogen plasma treatment can also be used to texture wafer surfaces on Cz Si as it etches and redeposits Si on the surface forming cones with {112}/{113}/{115} surfaces, depending on the hydrogenation temperature[5]. Surface texturing is also very dependent on the formation of {111} platelets in the wafers subsurface [6,7]. The surface morphology is found to differ for different grain orientation[8], surfaces being almost flat for {112} oriented grains and covered with large symmetrical cones for surfaces oriented close to {100}[3].

In this article several samples are studied, both Cz Si and mc Si, and different characterization techniques including scanning electron microscopy (SEM), transmission electron microscopy (TEM), secondary ion mass spectroscopy (SIMS) and Raman spectroscopy, are combined to get a deeper understanding of the H induced defects arising after heavily H plasma treatment.
In our prior work we have studied the temperature evolution of Cz Si samples [1,2] and as-cut and polished mc Si samples [3] in detail. In this article we have added two new samples, to study the influence of substrate temperature during H plasma treatment on H defect formation. Unpublished TEM and SEM images together with new Raman and SIMS results, from the samples studied in [1-3] are combined to try to get a better understanding of the H induced defects.

2. Experimental

n- and p-type polished Cz Si, p-type polished and as-cut mc Si wafers have been studied. Table 1 shows the sample processing details. Samples are denoted as A_d_x_y, where; A is the sample (column 1 in Table1), d the doping (column 2 in Table1), x and y are the post-annealing temperature and time respectively. Hydrogen plasma treatments of all wafers were performed in a Plasma Enhanced Chemical Vapor Deposition (PECVD) setup, as described in Table 1. Subsequent annealing was performed on ~ 1×1 cm samples at temperatures between 200 and 1000 °C for 1 and 10 hours in a furnace in air followed by a rapid cooling. U1 and U2 have not been described previously.

Table 1. Processing parameters and H⁺ treatment of the samples. The different samples are denoted as A_d_x_y, where; A is the sample (column 1 in Table1), d the doping (column 2 in Table1), x and y are the post-annealing temperature and time respectively. “None” means that the sample is not post annealed, denoted as 0_0 in the text.

| Sample | Doping | H⁺ plasma treatment | Post annealing | Ref. |
|--------|--------|---------------------|----------------|-----|
| U2     | p-type | 1 Ωcm               | 1h, 120 °C, 110 MHz | None | New |
| U1     | p-type | 1 Ωcm               | 1h, 180 °C, 110 MHz | None | New |
| S1     | n-type | 1.8-2.6 Ωcm         | 1h, 250 °C, 110 MHz | None, 1h at 200-1000 °C, 100 °C step, 10 h at 200-600 °C, 100 °C step, 20 h 400 °C | [1,2] |
| S2     | n-type | 0.005-0.018 Ωcm     | 1h, 250 °C, 110 MHz | None, 1h at 200-1000 °C, 100 °C step, 10 h at 200-600 °C, 100 °C step, 20 h 400 °C | [1,2] |
| S3     | n-type | 1.8-2.6 Ωcm         | 2 h, 250 °C, 13.56 MHz | None, 1h at 200-1000 °C, 100 °C step, 10 h at 200-600 °C, 100 °C step, 20 h 400 °C | [1,2] |
| S4     | p-type | 1-10 Ωcm            | 0.5 h, 250 °C, 110 MHz | None, 1h at 200-1000 °C, 100 °C step, 10 h at 200-600 °C, 100 °C step, 20 h 400 °C | [1,2] |
| 1.2/1.4| p-type | 10 Ωcm              | 1h, 250 °C, 110 MHz | None/2h 450 °C | [3] |
| S5     | p-type | 10-20 Ωcm           | 1h, 250 °C, 110 MHz | None, 1h at 200-1000 °C, 100 °C step, 10 h at 200-600 °C, 100 °C step, 20 h 400 °C | [1,2] |
| mc Si  | p-type | 10 Ωcm              | 1h, 250 °C, 110 MHz | 450 °C, 10h | [3] |
| as-cut | p-type | 10 Ωcm              | 1h, 250 °C, 110 MHz | 450 °C, 10h | [3] |

Cross-section samples were prepared for TEM study from every annealing condition by mechanical polishing down to a thickness of about 10 µm in the middle of the 3 mm disk and then thinned to electron transparency using a Gatan PIPS ion mill. The TEM-observations were performed using a
Phillips CM30 operating at 300 kV or a JEOL 2010F operating at 200 kV. The cross section plane used for observations was close to (110).

SEM measurements were performed using a secondary electron detector on a Hitachi s-3400se Field emission SEM (FESEM) operating at 5-20 kV and working distance 8 mm. The resolution of the instrument is 1.5 nm at 15kV.

Raman spectra were recorded with a multichannel spectrometer from Horiba (Jobin Yvon) model T 64000, employing a single monochromator with CCD detector at room temperature. The spectra were excited by a Milennia Pro diode-pumped (Nd:YVO4 crystal) laser from Spectra-Physics (Model J 40) adjusted to give approximately 100 mW of the 532 nm line on the sample. A slit of 200 µm was used and the resolution was ca. 2 cm$^{-1}$. All spectra were normalised to the maximum of the optical Si phonon line at ~520 cm$^{-1}$, and the background luminescence was subtracted from the data.

Secondary ion mass spectrometry (SIMS) was used for analysis of the hydrogen/deuterium distributions (CAMECA ims 7f instrument) in negative secondary ion mode with a 15 keV Cs$^+$ primary beam. The raw SIMS profiles are given as sputter time versus secondary ion intensity. The sputter time is related to depth and the conversion factor is determined by measuring the SIMS craters with a Dektak 8 surface stylus profilometer assuming a linear dependence.

3. Results and discussion

3.1 Hydrogenated Cz Si samples

![Figure 1](image)

Figure 1. Surface structure as observed with SEM on as plasma treated samples, (a) U2_p-1 Ωcm, (b) U1_p-1 Ωcm, (c) S4_p-1-10 Ωcm, (d) I.2_p-10 Ωcm
Figure 2. Microstructure as observed with TEM in the plasma treated Cz samples (a) U1_p-1-10 \( \Omega \) cm, (b) S4_p-1-10 \( \Omega \) cm, (c) I2_p-1-10 \( \Omega \) cm (d) S3_n-1.8-2.6 \( \Omega \) cm, (e) S1_n-1.8-2.6 \( \Omega \) cm, (f) S5_p-10-20 \( \Omega \) cm and (g) S2_n-0.005-0.018 \( \Omega \) cm.
Figure 2 (a)-(d) show TEM images of the Cz Si samples. No image is shown from sample U2_p-1 Ωcm, since no defects were observed in this sample. Due to the low hydrogenation temperature, 120°C, no platelets have formed. Since surface roughness depends on formation of \{111\} platelets [6,7], the surface is flat. In U1_p-1 Ωcm, plasma treated at 180°C, a high density of small defects, ~20 nm, was observed, formed up to about 1.2 µm below the surface. The formation temperature for platelets is somewhere between 120°C and 180°C. From the literature ~150°C is found to be the critical temperature for hydrogen platelet formation [7,9]. The microstructure is similar in samples S4_p-1-10 Ωcm and I.2_p-1 Ωcm plasma treated at 250 °C. Large platelets, 50-500 nm, are formed up to ~ 0.7 µm below surface. Lower substrate temperature during H plasma treatment gives a higher density of small platelets formed deeper into the bulk.

In Figure 2(d) from sample S3_p-1.8-2.6 Ωcm, very small platelets ~ 20 nm in diameter, can be observed up to 0.5 µm below the sample surface. The low plasma frequency used for 2 hours at 13.56 MHz, compared to 1 hour at 110 MHz for similar doped S1_1.8-2.6 Ωcm, Figure 2(e), led to less surface roughness and formation of smaller platelets [1,2]. Figure 2(e) and (f) show images from samples S1_1.8-2.6 and S5_p-10-20 Ωcm, respectively. In both of these samples H induced platelets were observed several µm below the substrate surface. In sample S1 a low density of large platelets, ~0.5 µm, are formed up to 6 µm below the surface [1,2], while in sample S5_p-10-20 Ωcm, a very low density of large platelets were formed up to ~3 µm below the surface. In the high n doped sample S2_n-1.8-2.6 Ωcm, very large platelets, 1-2 µm in diameter, has been observed, formed up to ~ 2 µm below the surface of the sample [1,2]. In low doped samples, platelets are formed deep into the samples. Note the flat cones in the sample H plasma treated at 180 °C make an angle of ~ 16 ° with the surface, Figure 2(a), compared to the other samples H plasma treated at 250 °C make an angle of ~35° with the surface, Figure 2(c). This fits well with the literature [5] and the cones form directions \{115\}/{112\} with the (001) surface respectively.

**Figure 3.** (a) S2_n-0.005-0.018 Ωcm_500°C_4h S4_p-1-10 Ωcm_600°C_1h, (b) S4_p-1-10 Ωcm_600°C_1h, (c) S5_p-10-20 Ωcm_600°C_1h, (d) S1_n-1.8-2.6 Ωcm_300°C_10h (d) S1_n-1.8-2.6 Ωcm_400°C_20h (f) dissolved platelets in S1_n-1.8-2.6 Ωcm_600°C_1h.
After annealing at 400 °C not much happened to the microstructure in the samples, except for S3 where the density of platelets is much lower. At the very top defect layer, the defect density decreases and the small defects start to dissolve [1,2]. Larger defects in the subsurface and defects formed deep into the sample are still stable [1,2]. Figure 3(a) shows the same platelets in S2_n-0.005-0.018 Ωcm as in Figure 2(g), after 500 °C annealing for 4 hours in the TEM. The small defects in the cones have dissolved and the large truncated plate in the upper right corner is also partly dissolved.

After 600 °C annealing for 1 hour also platelets formed deep into the samples start to dissolve in n type and low doped p type samples [1,2]. This is seen in Figure 3(b) and (c) where the microstructure after 1 h annealing at 600 °C is shown for sample S4_p-1-10 Ωcm and S5_p-10-20 Ωcm respectively. Dissolution of H induced platelets in n type samples at 600 °C is not shown. While the H induced platelets in S4 are almost unchanged, the platelets in the lower doped S5_p-10-20 Ωcm have started to dissolve. H induced platelets are well known to contain hydrogen bubbles after heavy hydrogenation [8,10,18,19]. Figure 3(c) and (d) show complete H induced platelets formed deep below the surface of sample S1, annealed at T < 600 °C. Figure 3 (d) shows a platelet with bubbles filled with H₂ gas, Figure 3(e) a H induced platelet with central H₂ gas filled cavity and granular contrast. Both types of platelets exist simultaneously in the samples. Figure 3(f) shows partly dissolved H induced platelets annealed for 1 hour at 600 °C. Only dislocations loops and small empty voids are left [1,2]. For annealing at higher temperatures the empty voids will grow in size due to Ostwald ripening [10].

It is important to note that the above-mentioned peculiarities of the H initiated defect formation in Cz-Si samples treated by hydrogen plasma are in a good agreement with those observed in [18-22].

3.2 Polished and as-cut mc Si

In the mc samples the surface is also etched by the H plasma as shown in Figure 4(a) and (b). Figure 4 (a) shows the surface of H plasma treated polished mc Si. The surface roughness and cone shape vary due to different grain orientation [3]. In some orientations the surface is almost flat while in others tilted cones are visible on the surface. The density and size of the cones also varies for the different grain orientations. Due to height differences between the grains, edge peculiarities can be observed at the interface of the grains in the image. Figure 4(b) shows another grain boundary at larger magnification. Fine structures can be observed on the almost flat surface on the right grain.

![Figure 4](image)

**Figure 4.** Surface structure as observed with SEM, (a) Triple grain boundary in polished mc Si_p-10 Ωcm, (b) Grain boundary in polished mc Si_p-10 Ωcm.

The microstructure of a grain with surface normal ≠ {100} is shown in Figure 5. H induced defects in this sample are similar to the H induced defects formed in (100) oriented substrates. The platelet defects still form on {111} and cones still form on the surface, although they are not symmetrical and
are more sparsely distributed. Prior investigations have showed that the cones formed in grain orientations other than (100) also have lateral surfaces of {112}, explaining their tilted appearance on the surface [3]. The density of defects in the subsurface and the platelet formation depth of the grain in Figure 5 are similar to the similarly treated Cz sample in Figure 2(c). Grains oriented close to {112} were found to have almost flat surfaces while grains oriented in {100} directions were found to have high density of symmetrical cones on their surfaces [3]. Some of the platelets in Figure 5 have started to dissolve due to post annealing for 10 h at 450 °C.

Figure 5. Microstructure as observed with TEM in polished mc Si p-10 Ω cm 450°_10 h.

Figure 6 (a) and (b) show the defect formation in as-cut mc Si samples. A high density of H induced defects can be observed in the subsurface, but also deeper into the sample on defects from sawing and in structural defects like grain boundaries and dislocations [3]. Structural defects act as effective H traps by lowering the platelet formation energy. In similar H plasma treated Cz-Si, Figure 2(c), H induced defect were only observed in the upper 1 μm subsurface of the substrate [3].

3 SIMS and Raman measurements

Figure 7 (a)-(d), show SIMS hydrogen depth profiles from selected Cz-Si samples. The hydrogen detection limit is ~10^{18} cm^{-3}. From Figure 7(a) it is observed that, after hydrogenation, S1_n-1.8-2.6 Ω cm (green curve) and S5_p-10-20 Ω cm (red curve) show similar H concentration profile with a second peak about 3-4 μm into the bulk, and that hydrogen is detected up to about 12-15 μm depth. In I2_p-1 Ω cm _0_0 (black curve), however, the hydrogen concentration drops rapidly below the detection limit at about 0.7 μm depth. Figure 7(b) shows details of the same profiles as 7(a) of the samples in the near-surface area. After 1 hour hydrogenation at 250 °C the samples contain about 1%, or 5x10^{20} cm^{-3}, hydrogen in the top layer, decreasing rapidly down to 0.1% at about 0.2-0.5 μm depth, depending on sample doping and type. The hydrogen concentration drops faster in S1_n-1.8-2.6 Ω cm(green curve) and S5_p-10-20 Ω cm (red curve) than in I2_p-1 Ω cm (black curve).

Hydrogen profiles after post annealing are shown for sample S1_n-1.8-2.6 Ω cm and S4_p-1-10 Ω cm in Figure 7(c) and (d), respectively. After annealing at 500 °C for 10 hours in air, hydrogen is still present in the n-type Si sample S1_n-1.8-2.6 Ω cm _0_0, Figure 7(c) (red curve), but the second peak is found closer to the surface, at about 1μm, and the hydrogen level drops below the detection limit at ~10 μm. After 10 hours annealing at 600 °C, almost no hydrogen is detected in S1_n-1.8-2.6 Ω cm (green curve), while in S4_p-1-10 Ω cm a second peak at about 0.2 μm depth can be observed in Figure 7(d) (red curve). In Figure 7(d), Sample S4_p-1-10 Ω cm is similar to I2_p-10 Ω cm, except from shorter hydrogenation duration, 0.5 h compared to 1h. While the H concentration peak in sample I2_p-10 Ω cm is very close to the surface of the sample, there is a second H peak in S4_p-1-10 Ω cm
at 0.25µm after 600 °C annealing, suggesting that some H close to the surface has diffused out of the sample.

The difference in hydrogen profile for p-doped samples I.2_p-10 Ωcm /S4_p-1-10 Ωcm and S5_p-1-10 Ωcm is most likely due to the difference in doping level. Boron is known to trap hydrogen effectively by forming B^−-H^+ complexes [11,12] which are stable up to ~ 250 °C. As a result, hydrogen diffuses deeper into the bulk in a low doped sample such as S5. Phosphorus can also trap hydrogen by forming P^−-H^+ complexes, but this is less probable and these complexes are less stable.

An early SIMS study of deuterium [12] showed the connection between doping and diffusion. In most cases the H concentration of n and p type silicon samples was found to decay exponentially with depth, while p type samples, with resistivity 0.1 and 1 Ωcm showed trap dependent diffusivity [12]. The substrate temperature also changed the profile [12]. Because of the very low solubility of hydrogen [4], high concentrations of in-diffused hydrogen result in hydrogen induced defect formation in the subsurface. Comparing the H concentration profiles of sample S1_n-1.8-2.6 Ωcm, I.2_p-10 Ωcm, S4_p-1-10 Ωcm and S5_p-10-20 Ωcm with the TEM observations in Figure 2 and 3, there is a strong correlation between the hydrogen concentration peaks and the hydrogen platelet formation. In sample S4/I.2, the platelets are formed up to ~ 0.7 µm depth, while in sample S1 and S5, a low density of large platelets is observed several µm below the sample surface[1,2]. The density of platelets formed deep into the sample is higher in S1 than in S5, in accordance with the higher concentration of H observed in S1 than in S5 in this region.

**Figure 6.** Microstructure observed with TEM in as cut mc Si_p-10 Ωcm. H induced defects form in the subsurface, on sawing defects and stacking faults (a) and on dislocations (b).
Figure 7. Hydrogen concentrations in hydrogen plasma treated samples measured by SIMS, (a) selected n and p type samples, S1_n-1.8-2.6 Ωcm, S4_p-1-10 Ωcm, S5_p-10-20 Ωcm, before annealing, (b) near-subsurface area, (c) S1_n-1.8-2.6 Ωcm after post annealing (d) I.2_p-10 Ωcm and S4_p-1-10 Ωcm after post annealing

Figure 8 shows Raman spectra from the Cz Si samples. The spectrum from U2_p-1 Ωcm is not shown since no hydrogen was detected, which can be explained by the low-concentration (below the sensitivity limit of the Raman measurements) of hydrogen, incorporated into the Si subsurface at 120 °C. At higher plasma treatment temperatures the Si-H bonds were detected by Raman. The spectra consist of several peaks, as shown by the green lines found by a Lorentzian fit (red) of the curves (black). The different lines are due to different Si-Hₙ complexes, where n varies from 1-4, and are shifted relatively due to different internal stresses in the supersaturated subsurfaces [8]. The dominant peak in all samples after H plasma treatment is ~ 2095 cm⁻¹. The p type samples, S4_p-1-10 Ωcm_0_0 and S5_p-10-20 Ωcm_0_0 show the highest signal of Si-Hₙ bonds in Figure 8(d) and (e) respectively.

After 1 hour post annealing at 300°C the Si-Hₙ peaks lower slightly, but the shape is similar, indicating that the silicon-hydrogen bonds are stable at this temperature. However, after 1 h post annealing at 400 °C, only ~2095 cm⁻¹ bonds in S4_p-1-10 Ωcm are found to be stable, as shown in Figure 9(c). In the other samples, S1_n-1.8-2.6 Ωcm, S2_n-0.005-0.018 Ωcm and S5_p-10-20 Ωcm shown in Figure 9(a), (b) and (d) respectively, the 2095 cm⁻¹ bond still dominates but is very weak. No hydrogen related bonds were observed by Raman measurements in S3 under the measurement conditions applied. U1 (and U2) were not post annealed at this temperature. After 20 hours post annealing of S4 at 400 °C, the peak at 2095 cm⁻¹ is strongly reduced and the peak at 2106 cm⁻¹ dominates, Figure 10(a). After 1 hour annealing at 600°C, SiHₙ bonds with peak at ~2106 cm⁻¹ are still detected in this sample, as shown in Figure 10(b).
Figure 8. Raman spectra after hydrogenation for the 6 plasma treated samples, (a) S1_0-1.8-2.6 Ω cm_0_0, (b) S2_ n-0.005-0.018 Ω cm_0_0, (c) S3_ n-1.8-2.6 Ω cm_0_0, (d) S4_p-1-10 Ω cm_0_0, (e) S5_p-1-10 Ω cm_0_0 and (f) U1_p-1-10 Ω cm_0_0.

Doping type and level influence the Si-H_x bonds being formed as has also been shown earlier [8,13-17]. Samples plasma treated with a frequency of 13.56 MHz have been found to contain the same amount of Si-H bonds as samples plasma treated with a frequency of 110 MHz [16]. This is not the case in this study, where hardly any Si-H bonds were observed in the low frequency treated sample S3_n-1.8-2.6 Ω cm. In this study several Si-H_x bond peaks were observed as indicated in the Raman spectra. Some of the peaks were very weak and some might be a combination of two or more overlapping peaks that were not resolved. It is hard to draw conclusions about the origin of all the peaks from these room temperature Raman measurements. Low-temperature Raman measurements are required to clarify this question. However, earlier studies of temperature evolution of the different Si-H_x bonds on beveled samples have assigned them to hydrogen induced platelets at different stages of
their evolution [16,17,23]. Si-H bonds, with a vibration frequency of about 2095 cm$^{-1}$, are assigned to the direct plasma damage layer at the top 200 nm of the substrate. Such bonds were found to be stable up to $\sim$350 °C [13,17]. The peak at $\sim$2105cm$^{-1}$ has been assigned to Si-H$_2$ bonds at the platelets inner surface at a final stage, and was found to be the most stable bond above 450 °C [17,24].

**Figure 9.** Hydrogen bonds studied by Raman in H plasma treated samples after 1 hour post annealing at 400°C, (a) S1_n-1.8-2.6 $\Omega$cm $400 \, ^\circ C \_1h$, (b) S2_n-0.005-0.018 $\Omega$cm $400 \, ^\circ C \_1h$, (c) S4_p-1-10 $\Omega$cm $400 \, ^\circ C \_1h$, (a) S5_p-10-20 $\Omega$cm $400 \, ^\circ C \_1h$

**Figure 10.** Hydrogen bonds detected by Raman in sample S4_p-1-10 $\Omega$cm after post annealing (a) 20 hours at 400°C and (b) 1 hour at 600°C.
The hydrogen profile observed fits well to the microstructure observed with SEM/TEM. The upper 0.2 µm of the samples consisting of surface cones and numerous defects caused by the plasma is found to be hydrogen rich, both from SIMS and Raman. After annealing at 400 °C for 1 hour, the small defects at the surface are almost annealed out in all samples (observed both in TEM images [1,2] and by the strong reduction of the 2095 cm⁻¹ peak in Figure 9), except from S4_p-1-10 Ωcm where no change is observed [1,2]. S4_p-1-10 Ωcm is also the only sample where the hydrogen bonds are stable after this annealing. However, after 20 hours annealing at 400 °C the 2095 cm⁻¹ peak is strongly reduced, and the peak at ~ 2106 cm⁻¹ dominates also in this sample, Figure 10(a). This peak is also the dominating peak in S4_p-1-10 Ωcm after 1 hour annealing at 600 °C, Figure 10(b). S4_p-1-10 Ωcm, the only sample where the platelets in the subsurface are stable after annealing at 600 °C, still contains a large amount of hydrogen in the subsurface, Figure 7(d), while the hydrogen content is below detection limit in the similar doped n type sample S1_n-1.8-2.6 Ωcm, Figure 7(c). It can be concluded that Si-H bonds exhibit a general trend to be dissolved at 600 °C. This result supports similar earlier observations, which were attributed to hydrogen out-diffusion upon annealing at 600 °C [25,26].

4. Conclusions

Our experimental results can be summarised as follows:

- Both surface roughness and defect formation in the sample subsurface after direct H plasma treatment are very dependent on the processing and sample parameters. Lower substrate temperature during H plasma treatment gives a different cone shape and higher density of small platelets formed deeper into the Cz Si bulk than higher substrate temperature.
- In Cz Si samples, H platelet defects form mainly on {111}.
- In mc Si, the density of H induced defects is independent of grain orientation. Some grains with different orientations are more etched than others leading to uneven etching of mc substrates.
- Defects from sawing and structural defects like dislocations and stacking faults in mc Si were found to effectively trap H.
- SIMS and Raman spectroscopy showed that the distribution of H in the subsurface regions of the Cz Si substrate after hydrogenation as well as the formation of structural defects were dependent on the type of doping of this material.
- H induced defects were found to be more stable in p-type samples than in n-type samples with temperature.
- In spite of an evolution of SiHₓ bonds at temperatures around 400 °C (Raman), very little evolution of structural defects (TEM) or morphology of the H textured surface (SEM) was observed.
- Evolution of structural defects initiated by hydrogen in the subsurface region of plasma treated Cz-Si samples starts at temperatures 600 °C and above.
- Care has to be taken when exposing both mc and Cz-Si to high concentrations of H during the passivation process used by the Si industry to avoid detrimental H induced defect formation.

References

[1] Nordmark H, Ulyashin A, Walmsley JC, Tøtdal B and Holmestad R 2006 *Nucl. Instrum. Meth. Phys. Res. B* **253** 176
[2] Nordmark H, Ulyashin A, Walmsley JC, Holt A and Holmestad R 2008 *Sol. Stat. Phen.* **131-133** 315
[3] Nordmark H, Ulyashin A, Walmsley JC, and Holmestad R 2009 *J. Appl. Phys.* **105** 033506
[4] Van Wieringen A, and Warmoltz N 1956 *Physica* **22** 849
[5] Ishii M, Nakashima K, Tajima I and Yamamoto M 1992 *Jpn. J. Appl. Phys* **31** 4422
[6] Hwang K-H, Yoon E, Whang K-W and Lee JY 1997 *J. Electrochem. Soc.* **144** 335-339
[7] Hwang K-H, Yoon E, Whang K-W and Lee JY 1995 *Appl. Phys. Lett.* **67** 3590
[8] Ulyashin AG, Job R, Fahrner WR, Richard O, Bender H, Clayes C, Simoen E and Grambole D 2002 J. Phys.: Condens. Matter. 14 13037
[9] Johnson NM, Ponce FA, Street RA and Nemanich RJ 1987 Phys. Rev. B. 35 4166
[10] Grisolia J, Ben Assayag G, Claverie A, Aspar B, Lagahe C and Laanab L 2000 Appl. Phys. Lett. 76 852
[11] Pearton SJ, Corbett JW and Shi TS 1987 Appl. Phys. A 43 153
[12] Corbett JW, Lindstrøm JL, Pearton SJ and Tavendale AJ 1988 Solar cells 241 27
[13] Ma Y, Job R, Huang YL, Fahrner WR, Beufort MF and Barbot JF 2004 J. Electrochem. Soc. 151 G627
[14] Düngen W, Job R, Ma Y, Huang YL, Mueller T, Fahrner WR, Keller LO, Horstmann JT and Fiedler H 2006 J. Appl. Phys. 100 034911
[15] Düngen W, Job R, Mueller T, Ma Y, Fahrner WR, Keller LO, Horstmann JT and Fiedler H 2006 J. Appl. Phys. 100 124906
[16] Ma Y, Huang YL, Düngen W, Job R and Fahrner WR 2005 Phys. Rev. B 72 085321
[17] Ma Y, Huang YL, Job R and Fahrner WR 2005 Phys. Rev. B 72 085321
[18] Ghica C, Nistor LC, Bender H, Richard O, Van Tendeloo G and Ulyashin A 2006 Philosophical Magazine 86 5137
[19] Ghica C, Nistor LC, Bender H, Richard O, Van Tendeloo G and Ulyashin A 2007 J. Phys.D: Applied Physics 40 395
[20] Job R, Ma Y and Ulyashin A 2004 Continuous-nanophase and Nanostructured Materials, MRS Symp. 788 571
[21] Job R, Ulyashin AG, Fahrner WR, Beaufort MF and Barbot JF 2002, Defect and Impurity Engineering Semiconductors and Devices III, MRS Symp. Proc. 719 217
[22] Fahrner WR, Job R and Ulyashin AG 2001 Proc. 2001 I"th IEEE Conference on Nanotechnology (IEEE-NANO 2001) 282-287.
[23] Job R, Ma Y, Huang YL, Ulyashin AG, Fahrner WR, Beaufort MF and Barbot JF 2004 Solid State Phenom. 95-96 141
[24] Job R, Ulyashin AG, Fahrner WR, Beaufort MF and Barbot JF 2003 Europ. J. Phys. 23 25
[25] Ulyashin AG, Job R, Fahrner WR, Grambole D and Herrmann F 2002 Solid State Phenom. 82-84 315
[26] Job R, Ulyashin AG and Fahrner WR 2001 Mater. Sci. Semicond. Proces. 4 257