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# The microstructure and electrical properties of hydrogenated Czochralski silicon treated at high temperature–pressure

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## Abstract

Annealing at up to 1400 K of hydrogen plasma etched Czochralski silicon (Cz-Si:H) under enhanced hydrostatic pressure (HP) up to 1.1 GPa (HT–HP treatment) results in specific effects related both to the presence of hydrogen and to enhanced HP. The latter strongly affects the sample microstructure, precipitation of oxygen interstitials and creation of thermal donors (TDs).

The HT–HP induced effects in Cz-Si:H are related to the HP stimulated creation of nucleation sites for the creation of TDs and oxygen precipitation as well as to decreased hydrogen out-diffusion under HP.

## 1. Introduction

The incorporation of hydrogen by hydrogen plasma etching into oxygen-containing Czochralski grown single crystalline silicon (Cz-Si) has been reported to result in an enhanced formation rate of thermal donors (TDs, containing oxygen atoms) at around 670–720 K [1] and in a hydrogen-stimulated removal (precipitation) of oxygen atoms from the interstitial positions ( $O_i$ ) of the Si–O supersaturated solid solution at 770–970 K [2].

Enhanced hydrostatic pressure (HP) of ambient gas at annealing (HT–HP treatment) exerts quite similar effects on Cz-Si in respect of strongly HP-stimulated creation of TDs [3] and oxygen precipitation [4]. These HP-induced effects have been explained assuming the HP-induced activation of numerous nucleation sites for oxygen clustering in Cz-Si [3]; the enhancement of the oxygen diffusion rate at HP is also not excluded [5].

In view of the seemingly similar effects of hydrogen and of HP on the transformation of oxygen interstitials in Cz-Si at annealing, investigations of the effect of HT–HP treatment on hydrogenated Cz-Si are of considerable interest. It can be seen from the hitherto published,

rather preliminary data [6], that the HT–HP treatment of hydrogen plasma etched Cz–Si results in a markedly decreased hydrogen out-diffusion while the creation of TDs is even more promoted.

New results concerning the effect of HT–HP on microstructure ( $O_i$  precipitation) and electrical properties of hydrogenated (by hydrogen plasma etching) Cz–Si (Cz–Si:H) are reported in the present paper. In what follows we present mainly the results obtained for Cz–Si:H subjected to annealing/HT–HP treatment at 720–920 K. Hydrogen is still present in the Cz–Si:H samples annealed/HT–HP treated at that temperature region so just such treatments are most interesting in respect of the investigation of the presence of hydrogen and of the HT–HP treatment on the microstructure and other properties of hydrogenated Cz–Si.

## 2. Experimental details

A p-type (B doped) 001 oriented Cz–Si wafer (hole concentration,  $N_h = 1.34 \times 10^{15} \text{ cm}^{-3}$ ) of about 0.6 mm thickness, with  $O_i$  concentration ( $C_O$ ) equal to about  $9.5 \times 10^{17} \text{ cm}^{-3}$  (determined by Fourier transform infrared spectrometry, FTIR) was hydrogenated for 1 h at 533 K by hydrogen plasma etching ( $H_2$  flux of about 200 sccm) at 110 MHz frequency, power 50 W, under pressure of about 50 Pa (compare [7]).

The resulting Cz–Si:H as well as reference (non-hydrogenated) Cz–Si samples were subjected to the HT–HP treatments [8] at up to 1400 K under hydrostatic argon pressure HP up to 1.1 GPa for up to 10 h.

The as-prepared and HT–HP treated Cz–Si:H and reference Cz–Si samples were characterized by means of secondary ion mass spectrometry (SIMS), scanning electron microscopy (SEM), FTIR, capacitance–voltage ( $C-V$ ) and photoluminescence (PL, in the 0.75–1.15 eV range, measured at 6 K, excited with an Ar laser, 488 nm wavelength) methods. Most these methods (SIMS, SEM,  $C-V$ , PL) are sensitive to the features of the near-surface sample areas (of  $\leq 4 \mu\text{m}$  thickness) and so appropriate for characterization of the near-surface hydrogen-containing areas of Cz–Si:H.

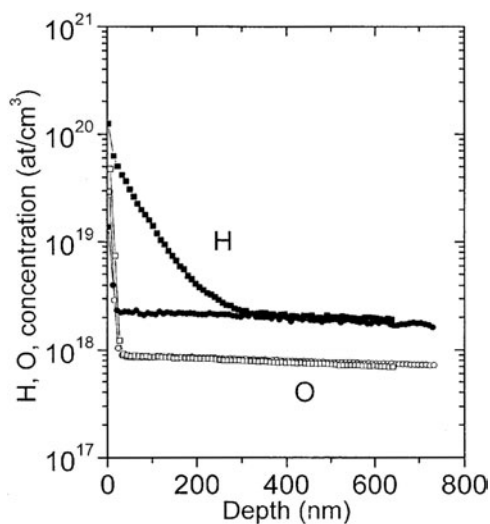
## 3. Results and discussion

Hydrogen plasma etching of Cz–Si resulted in the introduction of hydrogen into Cz–Si up to a depth of about 300 nm, with the maximum H concentration equal to about  $1 \times 10^{20} \text{ cm}^{-3}$  just below the sample surface (see figure 1). With an exception of the near-surface Cz–Si areas (where the native-like silicon oxide is also created), hydrogen plasma etching does not result in the detectable enrichment of Cz–Si:H in oxygen.

Contrary to the case of annealing under atmospheric pressure ( $10^5 \text{ Pa}$ ), hydrogen atoms remain to be detectable by SIMS in Cz–Si:H even after HT–HP treatment at 920 K for 2 h [6]. This means that enhanced HP at annealing of hydrogen-enriched silicon results in the marked hydrogen content in the HT–HP treated samples while hydrogen out-diffuses almost fully from the hydrogenated samples subjected to similar treatments but under low pressure [6].

The Cz–Si:H samples prepared by hydrogen plasma etching and treated at  $\geq 1070 \text{ K}$  under HP  $\leq 1.1 \text{ GPa}$  contained almost no hydrogen (its content does not exceed the detection limit of the applied SIMS technique, of about  $2 \times 10^{18} \text{ cm}^{-3}$ ).

It is worth mentioning that the highly hydrogen-enriched silicon samples prepared by hydrogen implantation into Cz–Si (H dose  $4 \times 10^{16}$ – $1.7 \times 10^{17} \text{ cm}^{-2}$ , energy 130 keV) retain some hydrogen at up to about 1070 K if treated under HP [9–11]. However, even such samples with a very high initial hydrogen content (above  $1 \times 10^{22} \text{ cm}^{-3}$ ) in the buried hydrogen-enriched



**Figure 1.** Depth profiles of hydrogen (H, full symbols) and of oxygen (O, open symbols) in as-hydrogenated (Cz-Si:H, squares) and reference (Cz-Si, circles) samples.

area at about  $0.5 \mu\text{m}$  depth indicated (SIMS data) only traces of hydrogen after subjecting them to the treatments at 1073–1400 K under 1.1–1.2 GPa for  $\geq 0.5$  h [9–11].

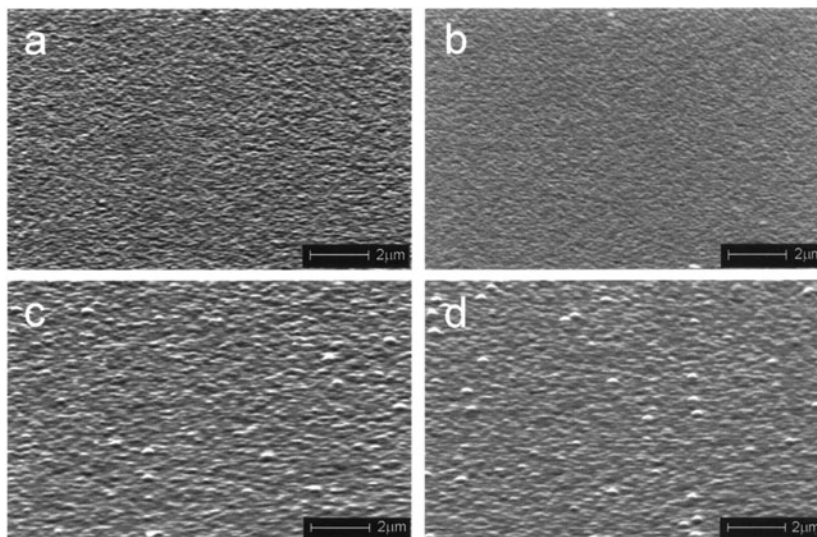
It has been stated that the surface of annealed and, especially, of HT-HP treated Cz-Si:H indicates enhanced chemical reactivity and that prolonged storage of Cz-Si:H in air results in its severe contamination by the components of environmental gases (by hydrogen and oxygen). For example, a Cz-Si:H sample treated at 1070 K– $10^7$  Pa for 5 h and stored for 1 year in air showed hydrogen and oxygen concentrations of about  $1 \times 10^{19}$  and  $5 \times 10^{20} \text{ cm}^{-3}$ , respectively, at the depth of 100 nm.

While the reference Cz-Si samples, also HT-HP treated (at up to 1070 K–1.1 GPa, for up to 10 h), indicated no distinguished (SEM detectable) surface features, the surface of as-hydrogenated Cz-Si:H was strongly structured (see figure 2(a)), down to about the 100 nm scale and below. Annealing of Cz-Si:H at 723 K– $10^5$  Pa for 10 h results in the much flatter sample surface (figure 2(b)), while the same treatment but under 1.1 GPa produces distinctly marked surface roughness (figure 2(c)). Almost the same surface roughness was detected for Cz-Si:H, HT-HP treated at 780 K but for 1 h only (figure 2(d)).

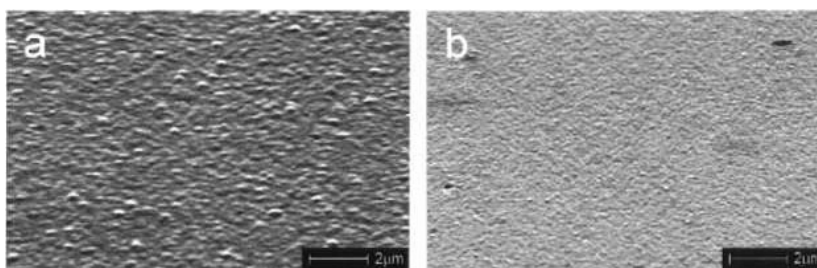
Contrary to the case of Cz-Si:H treated at 723/780 K, the treatments at 1070 K/1400 K–1.1 GPa result in much decreased dimensions of the surface features if compared to those after treatment under  $10^7$  Pa (see figures 3(a) and (b)).

As has been reported, based on TEM results, a pure hydrogen etching gas introduces a heavily damaged layer near the Si surface extending to a depth of about 20 nm; small amorphous-like regions have been reported to be detected while the Si surface becomes extremely rough [12]. Depending on the hydrogen etching conditions, microcracks and hydrogen-stabilized platelets appearing within  $0.1 \mu\text{m}$  of the exposed surface and oriented predominantly along the  $\{111\}$  crystallographic planes are created [13]. The different defect types have been also reported for the Cz-Si:H samples, among them stacking fault-like defects and dislocations [14].

High argon pressure during annealing of Cz-Si:H results in an enhanced concentration of hydrogen, especially for the treatments done at  $\leq 920$  K [6]. So one can speculate that the



**Figure 2.** SEM images of Cz-Si:H samples: as-prepared (a), annealed at 723 K– $10^5$  Pa for 10 h (b), HT-HP treated at 723 K–1.07 GPa for 10 h (c) and at 780 K–1.07 GPa for 1 h (d).

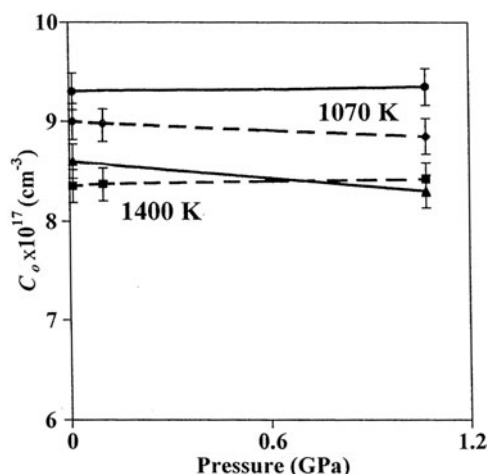


**Figure 3.** SEM images of Cz-Si:H samples: HT-HP treated for 5 h at 1070 K– $10^7$  Pa (a) and at 1070 K–1.07 GPa (b).

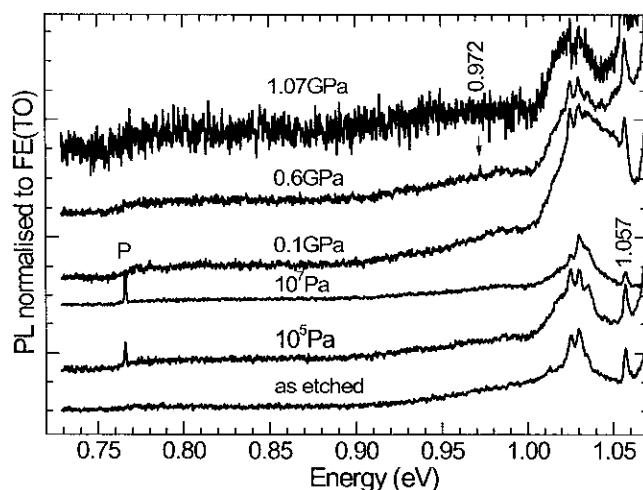
rather large structural features revealed by SEM on the surface of Cz-Si:H treated at 723/780 K–HP (figures 2(b), (c)) can be related to the presence of hydrogen-filled platelets created just below the sample surface. The samples HT-HP treated at  $\geq 1070$  K show a flatter surface (less developed structuring) if treated under 1.1 GPa. Most probably this means that much smaller H-filled platelets are created initially under HP and so the sample surface roughness is retained after the treatment when practically all hydrogen atoms out-diffuse from Cz-Si:H. This results from a very high mobility of hydrogen atoms at  $\geq 1070$  K and from the presence of more numerous HP-induced nucleation centres for the creation of hydrogen-filled platelets just at the first stage (beginning) of the treatment (compare [3]).

Annealing of the reference Cz-Si samples at  $10^5$  Pa results in a partial precipitation of  $O_i$ s (figure 4, compare [4]). At 1070 K this precipitation is minor, while it is clearly detectable for the samples annealed at 1400 K. No marked dependence of  $C_O$  on HP has been stated for the reference (non-hydrogenated) Cz-Si samples.

Enhanced HP during annealing/HT-HP treatment of Cz-Si:H at 1070 K resulted in even less pronounced oxygen precipitation, being non-dependent on HP.



**Figure 4.**  $O_i$  concentration ( $C_O$ ,  $\pm 0.5 \times 10^{17} \text{ cm}^{-3}$ ) versus HP for Cz-Si:H (solid lines) and for reference Cz-Si (dashed lines) annealed/HT-HP treated for 5 h at 1070 K (top lines) and at 1400 K (bottom lines).

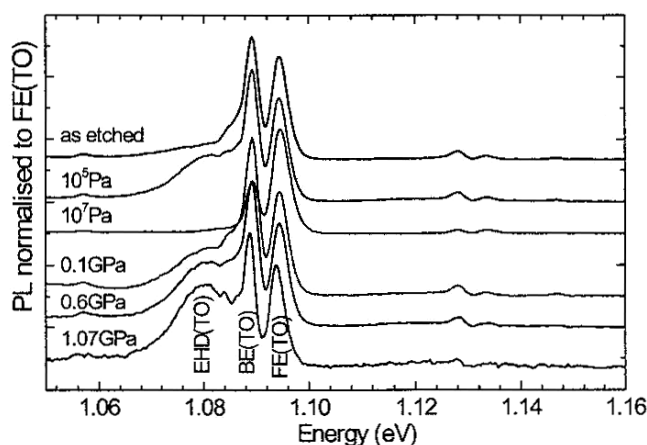


**Figure 5.** Normalised PL spectra (taken at 0.73–1.07 eV) of Cz-Si:H samples, as-etched and annealed/HT-HP treated for 10 h at 723 K–HP at different Ar pressures.

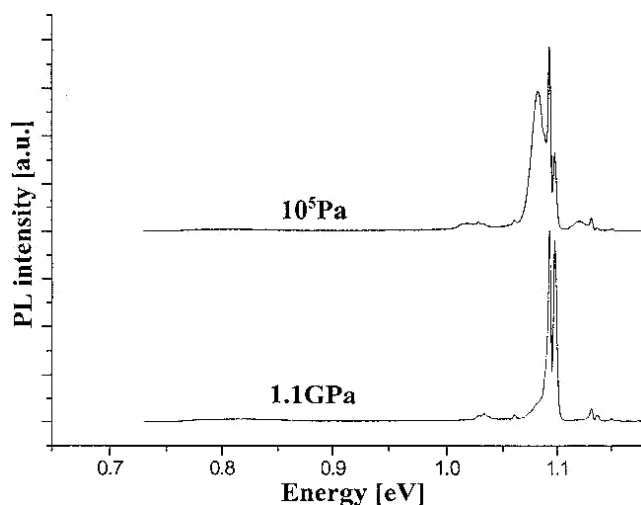
Annealing/HT-HP treatment of Cz-Si:H at 1400 K results in the pressure-dependent precipitation of oxygen (figure 4). The presence of hydrogen in Cz-Si:H (this hydrogen is rapidly removed at  $\geq 1070$  K) did not significantly affect the oxygen precipitation, also because most hydrogen atoms were initially incorporated only into the thin near-surface layers of the Cz-Si:H samples (figure 1) so their presence can be expected to affect strongly the oxygen precipitation in a rather minor fraction of the total Cz-Si:H sample volume.

PL spectra of Cz-Si:H samples, as-prepared and annealed/HT-HP treated at 723 and 920 K, are presented in figures 5–7.

The as-etched (hydrogenated) Cz-Si:H sample shows near-band-gap excitonic emission as well as the presence of PL lines at about 1.023, 1.03 and 1.057 eV (figures 5, 6). The PL



**Figure 6.** Normalised PL spectra (taken at 1.05–1.16 eV) of Cz-Si:H samples, as-etched and annealed/HT-HP treated for 10 h at 723 K-HP at different Ar pressures.



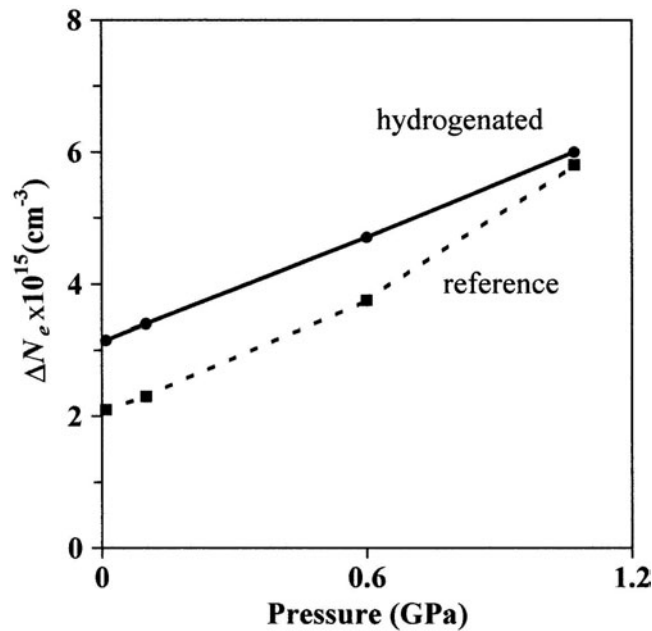
**Figure 7.** PL spectra of Cz-Si:H samples, annealed/HT-HP treated for 1 h at 920 K under  $10^5$  Pa and 1.1 GPa.

line at 1.03 eV can be related to platelet formation [13]; however, no other PL lines (at 0.95 and 0.98 eV) previously reported [13] for the as-hydrogenated samples were detected.

The PL line at about 1.02 eV resembles the so-called W line, attributed to a defect composed of silicon self-interstitials [15]. PL at about 1.057 eV was detected at 4.2 K for hydrogenated Si prepared by hydrogen implantation [16, 17]. Probably this line corresponds to an optical transition with the participation of momentum conserving phonons, TO + O, where TO denotes the transverse optical phonon and O—the zone centre phonon [17].

No typical dislocation related lines at 0.81 eV (D1), 0.87 eV (D2), 0.94 eV (D3) and 1.01 eV (D4) were detected for the Cz-Si:H samples, as-prepared, annealed and HT-HP treated at 723 and 920 K.

Annealing/treatment of Cz-Si:H and of reference Cz-Si at 723 K under  $10^5$  and  $10^7$  Pa results in a very weak PL line at 0.77 eV (the P line [18]); the P line disappears in the case of Cz-Si:H and Cz-Si treated under higher pressure.



**Figure 8.** The increase of electron carrier concentration ( $\Delta N_e$ ;  $\Delta N_e = |N_e - N_h|$ , where  $N_e$  is the concentration of electrons in HT–HP treated Cz-Si:H and  $N_h$  is the concentration of holes in non-treated reference Cz-Si) versus HP for Cz-Si:H (hydrogenated, solid line, circles) and for reference (dashed line, squares) Cz-Si after treatment at 723 K–HP for 10 h.

The PL at about 1.057 eV discussed above was also detected for the Cz-Si:H samples HT–HP treated at 723 K/920 K– $10^5$  Pa/HP (figures 5 and 7). The intensity of this line decreases slightly with HP for Cz-Si:H treated at 723 K– $10^5$  Pa/ $10^7$  Pa while it increases after treatments at 723 K– $10^7$  Pa/0.6 GPa and at 920 K–HP (figures 5, 7).

The excitonic emission (figures 6, 7) in the near-band-gap region was observed in all samples studied. This emission is dominated by recombination of the boron bound exciton ( $BE_{TO}$ ) at about 1.088 eV and of the longitudinal optical phonon replica of the free exciton ( $FE_{TO}$ ) at about 1.095 eV; the PL line at about 1.081 eV is related to the multiexciton complex recombination of the electron–hole droplet ( $EHD_{TO}$ ) [19]. The PL lines at 1.0254 and at 1.03 eV (figure 5) are most probably the phonon replicas of the BE and FE lines, respectively (their intensities are proportional to those of the  $BE_{TO}$  and  $FE_{TO}$  PL peaks). The intensities of the  $EHD_{TO}$  lines are much lower in the case of Cz-Si:H, if compared to those in the similarly treated reference Cz-Si samples. Moreover, the  $EHD_{TO}$  line intensity of the Cz-Si:H samples, HT–HP treated at 723 K, increases with HP (figure 6).

The as-hydrogenated Cz-Si:H samples were of p-type ( $N_h = 1.6 \times 10^{15} \text{ cm}^{-3}$ ). Annealing of these samples at 723 K for 10 h under atmospheric pressure converted them to the n conductivity type, with  $N_e = 1.7 \times 10^{15} \text{ cm}^{-3}$ . This change of the conductivity type is obviously related to creation of TDs [3].

The dependence of  $\Delta N_e$  on Ar HP applied during the treatment of Cz-Si:H and Cz-Si at 723 K–HP for 10 h is presented in figure 8. For the reference Cz-Si samples the  $\Delta N_e$  dependence on HP corresponds to that reported earlier for bulk oxygen containing Cz-Si [3, 5]. That dependence for the similarly treated Cz-Si:H samples remains in fact the same but shifted to the higher  $\Delta N_e$  values (figure 8). The  $\Delta N_e$  values for the Cz-Si:H and reference Cz-Si samples treated under the highest applied pressure, 1.1 GPa, were, however, practically the



same. This can be interpreted as a proof that for the case of Cz-Si:H treated at 720 K– $\leq 0.6$  GPa the influences of hydrogen and of HP on the creation of TDs are (at least to some extent) additive (acting almost independently) while, at the highest applied pressures (HP  $\geq 0.6$  GPa), just the effect of HP on the creation of TDs becomes dominating. This conclusion is confirmed by comparing the  $N_e$  values determined at the back side of Cz-Si:H (practically not enriched in hydrogen) with those for reference Cz-Si: after treatment at 723 K–0.6 GPa for 10 h they were almost the same,  $2.58 \times 10^{15}$  and  $2.44 \times 10^{15} \text{ cm}^{-3}$ , respectively.

The HT–HP treatment of Cz-Si:H at 920 K (typical temperature for creation of so-called new donors, NDs [3]) did not convert it to n-type. However, the  $N_h$  concentration decreased slightly with HP:  $N_h$  was equal to  $1.16 \times 10^{15} \text{ cm}^{-3}$  after annealing Cz-Si:H for 1 h at 920 K under  $10^5$  Pa while it decreased to  $9.7 \times 10^{14} \text{ cm}^{-3}$  after the same treatment but under 1.1 GPa. This means that part of the acceptors was compensated by electrons, originating from the oxygen-related TDs (in effect of the HP-stimulated creation of NDs).

Among others, the following HT–HP induced effects are detected in Cz-Si:H:

- its surface microstructure is clearly dependent on HP as well as on HT and treatment time;
- HP affects also the creation of point-like defects, as follows from the PL results;
- TD creation at 723 K depends strongly on HP; it seems that the effect of HP is even dominating over the effect related to the presence of hydrogen.

To a first approximation one can assume that the effects caused by the presence of hydrogen and by HP are additive. The real situation is, however, much more complicated. Cz-Si:H is gradually depleted in hydrogen admixture if annealed under atmospheric pressure. Enhanced HP of ambient gas at annealing results in markedly decreased hydrogen out-diffusion and even in its diffusion into the sample depth [6]. This means that the hydrogen- (and oxygen-) involving processes can last for a longer time under HP while some specific HP-induced effects (e.g. the creation of smaller but more stable H<sub>2</sub>-filled platelets) are highly probable, being, however, strongly dependent on the sample preparation and treatment conditions.

#### 4. Conclusions

High temperature–pressure treatment of hydrogenated Czochralski grown silicon exerts specific, pressure-dependent effects on its microstructure and electrical properties. While some of these effects are similar to those reported for HT–HP treated reference (non-hydrogenated) Cz-Si, others are obviously related to the effect of HP on hydrogen diffusivity and on the creation of hydrogen-related defects in hydrogenated silicon. Further investigations are needed to gain an understanding of the mechanisms involved.

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