

Microstructure of Czochralski silicon co-implanted with helium and hydrogen and treated at high temperature and pressure

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The effect of high temperature (HT) up to 1400 K and high pressure (HP) up to 1.1 GPa on Cz-Si co-implanted with He⁺ (energy, $E = 50$ KeV, dose, $D_{\text{He}} = 5 \times 10^{16} \text{ cm}^{-2}$) and H₂⁺ ($E = 135$ KeV, $D_{\text{H}} = 5 \times 10^{16} \text{ cm}^{-2}$), with almost overlapping implantation-disturbed layers, has been investigated. Numerous extended defects are created at HT and HP near the He and H concentration peaks, the overall structural perfection of annealed Si:He,H improves with HP. Oxygen gettering in the implantation-disturbed areas is much less pronounced under HP. The observed effects are related, among others, to decreased hydrogen out-diffusion and lowered dimensions of gas filled defects in Si:He,H treated under HP. Qualitative explanation of HP-mediated gettering of oxygen has been proposed.

Keywords: silicon, implantation, hydrogen, helium, high pressure, microstructure.

1. Introduction

Silicon co-implanted with helium and hydrogen (Si:He,H) is used in smart cut processing to produce the silicon-on-insulator (SOI) structures. Such co-implantation makes it possible to study the interaction of implanted gaseous species in respect of their role in out-splitting of the near surface layer in Si:H (Si:He,H) [1]. The smart cut takes place because of internal pressure of sufficiently high value (in the GPa range) created in Si:H (Si:He,H) at annealing within the buried layer containing H₂- or (H₂ + He)-filled bubbles and platelets.

It has been stated recently that, by changing of external (hydrostatic) pressure of ambient gas at annealing (HT and HP treatment) of the Si:H,He samples with the projected range of hydrogen R_{pH} below that of He and so with the H distribution maximum closer to the sample surface $R_{\text{pH}} < R_{\text{pHe}}$, it has been possible to tune some sample features [2,3]. In particular, the specific effect of He on out-diffusion of H₂ from the HT and HP treated Si:H,He samples has been reported [2].

The aim of present work is to determine the effect of annealing under HP exerted by inert gas atmosphere on Si:He,H with the reversed (in comparison to the earlier investigated case of Si:H,He [2]) sequence of the helium- and hydrogen-enriched layers $R_{\text{pHe}} < R_{\text{pH}}$.

2. Experimental

The Si:He,H samples were prepared by sequential implantation of H₂⁺ ($E = 135$ KeV, $R_{\text{pH}} = 0.58 \mu\text{m}$, hydrogen dose, $D_{\text{H}} = 5 \times 10^{16} \text{ cm}^{-2}$) and He⁺ ($E = 50$ KeV, $R_{\text{pHe}} = 0.42 \mu\text{m}$, $D_{\text{He}} = 5 \times 10^{16} \text{ cm}^{-2}$) into 001 oriented Czochralski grown silicon (Cz-Si) with oxygen interstitials concentration $\approx 6 \times 10^{17} \text{ cm}^{-3}$.

The Si:He,H samples were HT and HP treated at up to 1400 K under Ar hydrostatic pressure up to 1.2 GPa for up to 10 h in specially designed high temperature and pressure furnace [4].

The properties of HT and HP treated Si:He,H were investigated by secondary ion mass spectrometry (SIMS, using Cs⁺ for sample sputtering), photoluminescence (PL at 6 K, excitation with Ar laser, $\lambda = 488 \mu\text{m}$) and X-ray diffractometry (using CuK _{α} radiation to record X-ray reciprocal space maps, XRRSM's, and 004 rocking curves, RC's). All PL spectra presented in this paper were normalized to the intensity of transverse optical phonon assisted free exciton emission, FE(TO). Some samples were also examined by cross-sectional transmission electron microscopy (XTEM).

3. Results and discussion

The depth profile of hydrogen (He atoms cannot be detected by the applied SIMS method) in as prepared Si:He,H is presented in Fig. 1. The presence of the deeper placed

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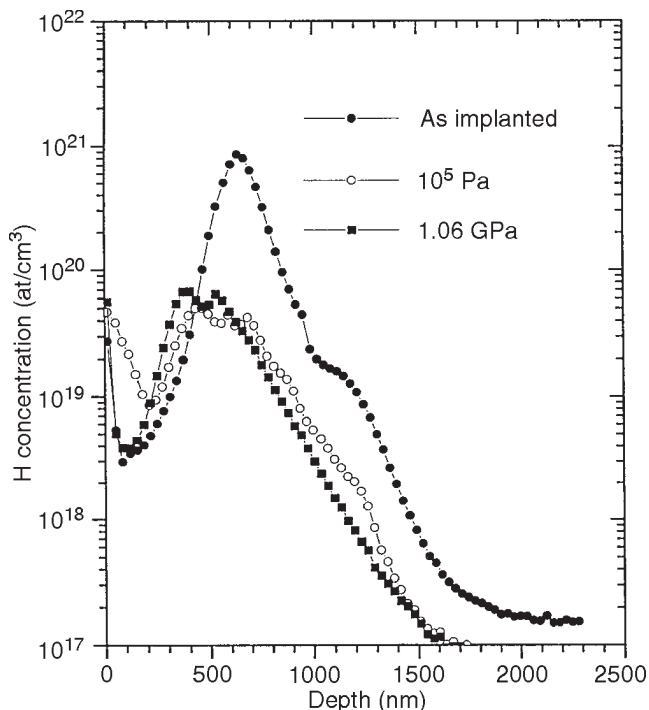


Fig. 1. SIMS depth profiles of hydrogen in Si:He,H: as implanted (●) and annealed or treated for 1 h at 920 K under 10^5 Pa (○) and 1.06 GPa (■).

hydrogen-enriched area (besides the main hydrogen peak near R_p of the implanted H_2^+) is related to about 10% fraction of H^+ in the implanting H_2^+ beam; H^+ ions are implanted deeper into the Si matrix as evidenced by the shoulder on the right side of the hydrogen concentration profile.

Co-implantation of Cz-Si with He^+ and H_2^+ (H^+) results in very strong structural disturbances as evidenced, e.g., by enhanced full width at half maximum (FWHM) of 004 RC's taken for as implanted Si:He,H (equal to 0.0050° , while $< 0.004^\circ$ for non-implanted Cz-Si).

At annealing/treatment hydrogen and helium migrate to the most implantation – disturbed sample areas, usually near R_{pHe} and R_{pH} , to form H_2 - and He- filled cavities, bubbles and platelets. Simultaneously, other implantation-induced defects (the point and extended ones) are subjected to transformation and out-annealing (healing), this process is dependent on numerous implantation- and treat-

ment- related parameters, among them HT, HP, and treatment time.

Typically, the FWHM values were lower for the samples treated under HP in comparison to these annealed under 10^5 Pa (for example, FWHM of 004 RC was equal to 0.0059° after annealing at 720 K and 10^5 Pa for 1 h while 0.0050° after the treatment at 720 K and 1.1 GPa). It is important to note that just lower FWHM evidences the improved sample structural perfection.

As evidenced by XTEM [Fig. 2(a)], Si:He,H subjected to the HT and HP treatment at up to 920 K indicates the presence of two near-touching buried disturbed areas with maximum concentration of cavities, bubbles, point and extended defects near R_{pHe} and R_{pH} . The layer closer to sample surface contains mostly He while the deeper one hydrogen.

The depth profiles of hydrogen in Si:He,H annealed/treated at 920 K are presented in Fig. 1. Important part of hydrogen (above 9%) was removed in effect of out-diffusion to environment (compare the profiles of the as implanted and of annealed/treated samples). The concentration of remaining hydrogen shifts towards the sample surface: important part of it (about 50%) is placed within the layer strongly disturbed by helium implantation. For this reason the hydrogen concentration profile indicates two maxima, corresponding approximately to R_{pHe} and R_{pH} . The hydrogen concentration in Si:He,H treated under HP is slightly above that detected for the sample annealed under 10^5 Pa evidencing HP- mediated out-diffusion of hydrogen. As it has been reported earlier [2,3], annealing at 720–920 K under atmospheric pressure of Si:He,H (and of Si:H,He) leads to very strong gettering of oxygen within the implantation-disturbed areas while, under HP, this effect is almost negligible.

The treatment of Si:He,H at 920 K and HP for 1–10 h results in PL at about 0.81 eV (the D1 dislocation – related line) evidencing the presence of extended defects; the PL line at 1.009 eV detected in Si:He,H annealed at 920 K and 10^5 Pa and presumably related to divacancies filled with He, disappears in the case of samples treated under 1.1 GPa.

Annealing of Si:He,H at 1070 K and 10^5 Pa results in a creation of strongly dislocated areas near R_{pHe} and R_{pH} [Fig. 2(b)] whereas more bubbles (gas filled) are seen after the treatment under 1.1 GPa [Fig. 2(c)]. It is so because some part of implanted gas species remain to be still contained in Si:He,H owing to earlier mentioned retarded out-diffusion of

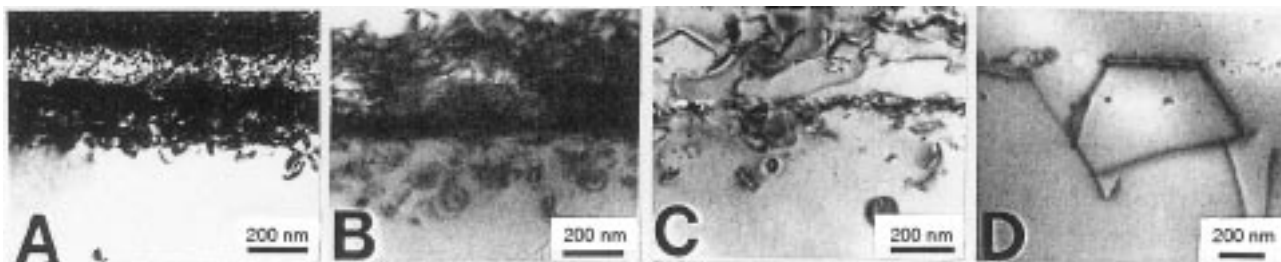


Fig. 2. XTEM images of Si:He,H samples annealed/treated for 1 h at 920 K and 1.1 GPa (a), and for 5 h at 1070 K and 10^5 Pa (b), 1070 K and 1.1 GPa (c) and at 1270 K and 1.1 GPa (d).

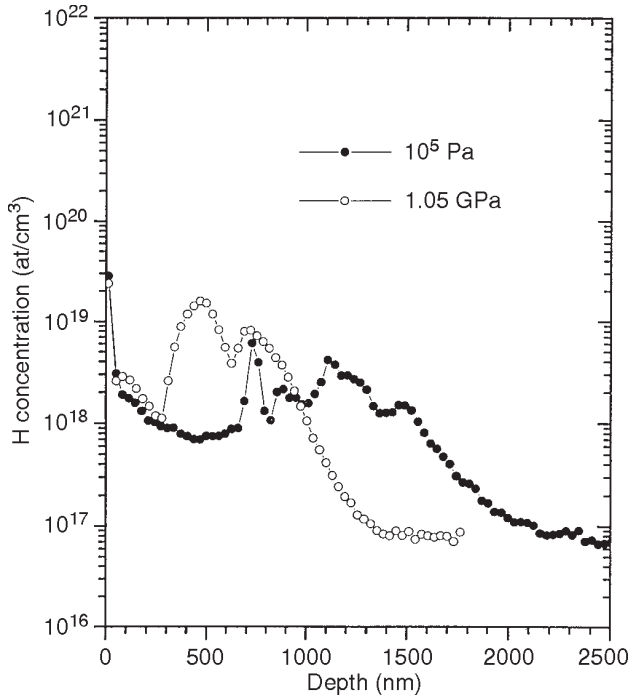


Fig. 3. SIMS depth profiles of hydrogen in Si:He,H annealed/treated for 5 h at 1070 K under 10⁵ Pa (●) and 1.05 GPa (○).

He and H₂ under HP (Fig. 3). It is interesting to note that, in the case of Si:He,H annealed at 1070 K under 10⁵ Pa, some part of hydrogen diffuses into sample depth (Fig. 3), this in-depth diffusion of hydrogen is, however, strongly quenched by HP, evidently because of strongly HP-suppressed hydrogen diffusivity even at so high temperature. Hydrogen distribution in the Si:He,H samples treated at 1070 K and 1.05 GPa is related to R_{pHe} and R_{pH} (Fig. 3) evidencing gettering of hydrogen at some sites (at the broken Si-Si bonds) within the implantation-disturbed areas, most probably hydrogen saturates the broken bonds and so is involved in a creation of H-Si bonds.

The FWHM values are also higher for the Si:He,H samples annealed under 10⁵ Pa in comparison to those treated under HP: FWHM of 004 RC is equal to 0.0047° after annealing at 1070 K and 10⁵ Pa for 5 h while to 0.0041° after the same treatment but under 1.1 GPa.

Annealing of Si:He, H at 1070 K under 10⁵ Pa leads to still marked gettering of oxygen, the oxygen distribution peak shifts to the deeper sample areas (to about 0.8 μm in depth, Fig. 4). Gettering of oxygen is strongly suppressed at 1.05 GPa, the oxygen concentration also peaks at 0.8-μm depth (below the areas with main implantation-induced disturbances, Fig. 2(c)). By comparing Figs. 4 and 2(b), 2(c) it can be concluded that gettering of oxygen takes place mostly within the areas with gas-filled bubbles and dislocations, acting probably as the active sites for oxygen gettering.

The creation of extended defects in Si:He,H annealed/HT and HP treated at 1070 K has been confirmed by PL measurements; just PL peaking at 0.81 eV (Fig. 5) is usually considered as a fingerprint [5] of the presence of dislocations. The broad asymmetric PL band peaking at

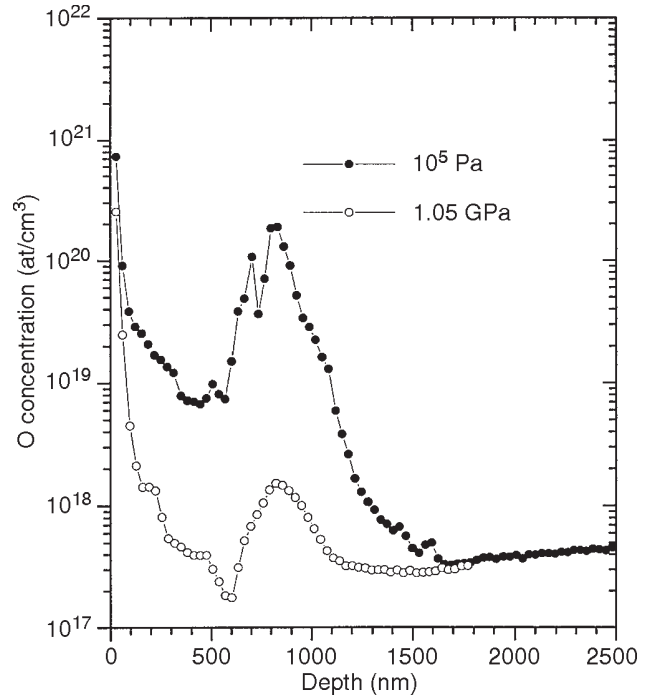


Fig. 4. SIMS depth profiles of oxygen in Si:He,H annealed/treated for 5 h at 1070 K under 10⁵ Pa (●) and 1.05 GPa (○).

0.809 eV detected for the Si:He,H sample annealed at 1070 K under atmospheric pressure suggests the presence of non-uniform stresses. The treatment at 1070 K under HP produces more dislocations while other extended defects (such as bubbles and cavities) are much less numerous [Fig. 2(c)]. The PL results correlate well with these obtained by XTEM (Fig. 2).

As it follows from the SIMS data, the annealing/HT and HP treatment of Si:He,H at 1270 K for 5 h results in practically complete out-diffusion of hydrogen to environment [2,3]. In effect of the treatment at 1270 K the Si:He,H sample structure is markedly healed [Fig. 2(c)]. Still, as it follows from the XRRSM data, enhanced HP affects the sam-

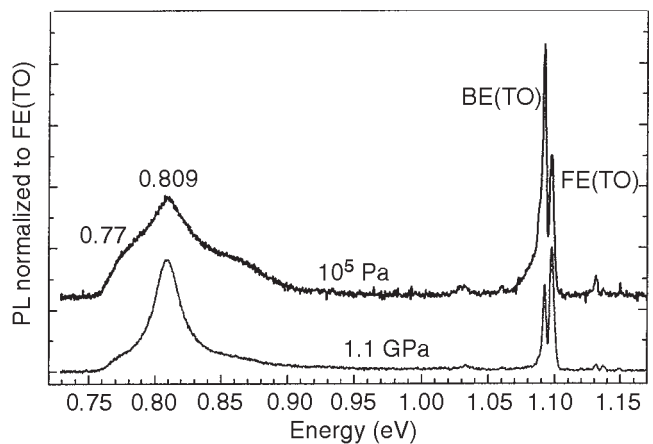


Fig. 5. PL spectra of Si:He,H, annealed / treated for 5 h at 1070 K under 10⁵ Pa and 1.1 GPa. BE(TO) and FE(TO) mean transverse optical phonon replicas of bound exciton and free exciton recombination, respectively.

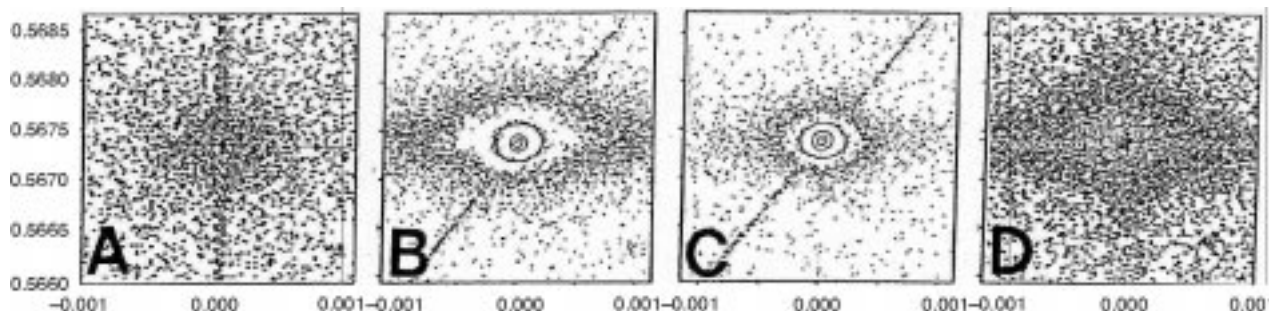


Fig. 6. XRRSM's recorded near 004 reciprocal lattice point for Si:He,H samples annealed/treated for 5 h at 1270 K and 10^5 Pa (a), 1270 K and 0.6 GPa (b), 1400 K and 10^5 Pa (c) and 1400 K and 1.1 GPa (d). Axes are marked in $\lambda/2d$ units (λ is the wavelength, d is the distance between crystallographic planes).

ple microstructure even at so high temperature, as evidenced by the lowered X-ray diffuse scattering intensity [Figs. 6(a,b)]. The FWHM value of 004 RC determined for Si:He,H treated at 1270 K is practically the same as that for non-implanted Cz-Si, for Si:He,H treated at 1270 K and 0.6 GPa for 5 h it equals to 0.0042° . This evidences the concentration of extended and point defects decrease with HT and, especially, HP.

This HP-dependent concentration of dislocations in Si:He,H treated at 1270 K has been confirmed by PL measurements: no dislocation related PL has been detected for Si:He,H treated for 5 h at 1270 K under 0.6 GPa and 1.1 GPa, contrary to the case of samples annealed at 1270 K under atmospheric pressure (Fig. 7). The EHD (electron-hole droplet) related recombination detected in these HP treated samples (the PL peak at about 1.08 eV) evidences their relatively high structural perfection.

Annealing/HT and HP treatment of Si:He,H at 1400 K for 5 h results in complete removal of hydrogen. The sample microstructure is restored to a considerable extent, only non-numerous dislocations remain to be detectable [Fig. 2(d)]. However, as it follows from XRRSM [Fig. 6(c,d)], enhanced HP applied at 1400 K effects in increased X-ray diffuse scattering intensity. Very wide PL band peaking at about 0.807 eV has been observed in Si:He,H annealed at

1400 K under atmospheric pressure while no transitions (except these near 1.1 eV) are detected after the same treatment but under 1.1 GPa. This can be interpreted as an evidence of out-annealing of most extended defects at 1400 K and HP while some other defects (small oxygen clusters ?) are created in Si:He,H treated under most severe conditions (1400 K and 1.1 GPa) applied in this study.

The implantation-disturbed areas in Si:He,H samples annealed/treated at ≤ 920 K are composed mostly of He- or H₂- filled cavities/bubbles, these ones near R_{pHe} are markedly smaller. There are evidences for partial sample splitting at upper part of the H₂- enriched buried layer. Part of hydrogen is shifted at HT and HP to the He-containing areas, as evidenced by shift of the hydrogen concentration profiles closer to the sample surface.

The HT and HP treatment at higher temperatures (> 920 K) produces extended defects (mostly dislocations) besides the cavities/bubbles, these last are relatively stable because of HP-tuned out-diffusion of implanted species. It is interesting to note that, contrary to the case of Si:H,He with the "reversed" sequence of H- and He-enriched areas [2], the rate of hydrogen out-diffusion from Si:He,H at HT is less sensitive to HP.

Prolonged (for 5 h) treatment of Si:He,H at HT ≥ 1070 K leads to almost complete out-diffusion of helium and, especially, of hydrogen so the microstructure of investigated samples becomes to be less sensitive to applied HP (it has been argued that just the more prolonged presence of implanted species in Si:H,He is responsible for the most hitherto stated HP-induced changes in silicon co-implanted with hydrogen and helium [2,3]).

Gettering of oxygen at the implantation-disturbed areas is almost negligible in the case of Si:He,H treated under HP while very strong in the case of samples annealed under atmospheric pressure. It seems that hydrogen contributes in the accumulation related effects as evidenced by oxygen gettinger mostly near R_{pH} . It is highly probably that just hydrogen-passivated broken bonds and hydrogen-assisted enhanced mobility of oxygen are responsible for discussed phenomenon.

Still important question remains to be answered: the origin of oxygen atoms agglomerated near R_{pH} . An explanation involving diffusion of oxygen from the deeper Cz-Si areas (compare Ref. 6) is not satisfying because has not

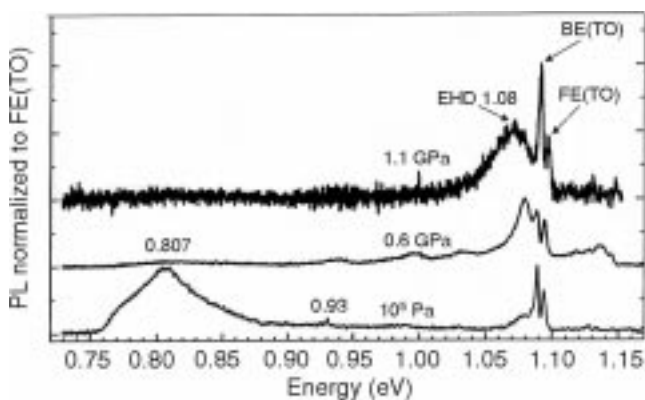


Fig. 7. PL spectra of Si:He,H, annealed/treated for 5 h at 1270 K under 10^5 Pa, 0.6 GPa, and 1.1 GPa. BE(TO) and FE(TO) mean transverse optical phonon replicas of bound exciton and free exciton recombination, respectively. EHD means recombination related to electron-hole droplets.

been supported fully by SIMS measurements, accounting for comparatively high oxygen concentration at the deeper tail of oxygen distribution (Fig. 4, see also Refs. 2 and 3). One needs to realise, however, that the dimensions of gas-filled bubbles and platelets are much bigger in the Si:He,H samples annealed under 10^5 Pa if compared to these treated under HP (Fig. 2). Some traces of blistering at the Si:He,H surface are detectable. Blistering has been reported for the similar hydrogen implanted samples (Si:H, Si:D) prepared by high dose hydrogen implantation, with $D \geq 5 \times 10^{16} \text{ cm}^{-2}$, if annealed under 10^5 Pa. Such blistering was not detectable, however, after the treatment of such samples under HP [7]. So one can suppose that thinned films and the bubble sides or even micro-channels, created at the near surface areas during sample annealing under 10^5 Pa allow for communication of the disturbed areas with gaseous atmosphere always containing some traces of oxygen. So, just these traces of oxygen from surrounding atmosphere are accumulated at the highly gettering active areas produced at implantation. Enhanced pressure at annealing results in a creation of much smaller cavities and bubbles, prevents blistering and thus communication of the gettering active areas with the surrounding atmosphere. This simple explanation demands further confirmation by dedicated experiments.

4. Conclusions

Both the presence of helium and parameters of the high temperature and pressure treatment exert pronounced effects on the microstructure of Czochralski silicon co-implanted with helium and hydrogen. Marked differences have been detected for the helium- and hydrogen- enriched areas in respect of their microstructure, accumulation of

hydrogen and oxygen properties. Qualitative explanation of some observed phenomena has been proposed. However, it is far from being complete and so additional investigations are needed to explain the effects observed in the high temperature and pressure treated silicon co-implanted with helium and hydrogen.

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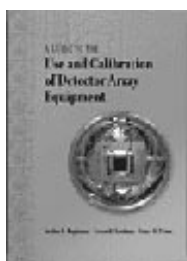
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