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NANOSTRUCTURED LAYERS IN HIGH TEMPERATURE – PRESSURE TREATED SILICON IMPLANTED WITH HYDROGEN / HELIUM

A.Misiuk[1], J.Bak - Misiuk[2], M.Kaniewska[1], K.S.Zhuravlev[3], V.Raineri[4] and I.V.Antonova[3]

[1]Institute of Electron Technology, Al. Lotnikow 46, 02-668 Warsaw, Poland
[2]Institute of Physics, Polish Academy of Sciences, Al. Lotnikow 46, 02-668 Warsaw, Poland
[3]Institute of Semiconductor Physics, RAS, pr. Lavrentieva 13, Novosibirsk 630090, Russia
[4]CNR - IMETEM, Stradale Primosole 50, 95121 Catania, Italy

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Abstract. Structural, electrical and photoluminescence properties of single crystalline silicon implanted with hydrogen and helium, Si:H and Si:He (ion doses $\leq 5\cdot10^{16}$ cm^{-2}, energy, $E \leq 200$ keV) and subjected to annealing at up to 1470K under hydrostatic pressure up to 1.2 GPa were investigated. The temperature - pressure (HT - HP) treatment of Si:H and Si:He results in creation of nanostructured buried layers containing gas - filled cavities and numerous extended and point defects; the HT - HP treated Si:H structures are not splitted contrary to those annealed under atmospheric pressure. The HT - HP induced effects are related to creation of smaller, nanometer - sized structural defects and to retarded out - diffusion of hydrogen and helium at HP. The buried layers are active in respect of oxygen gettering. The Si:H and Si:He samples indicate visible photoluminescence after subjecting to specific HT - HP treatment.

1. INTRODUCTION

Hydrogen- and helium-implanted silicon (Si:H and Si:He) have become a topic of remarkable interest [1, 2], mostly because of potentials of implantation – induced bubbles and microcavities for creation of gettering – active areas [3] and for Si splitting. That latter application known as the Smart-Cut process [1], is widely applied in microelectronics to produce silicon-on-insulator (SOI) structures.

During annealing under atmospheric pressure the trapped hydrogen or helium atoms diffuse and segregate near the implanted ions range. Hydrogen-filled planar defects aligned parallel to the Si surface as well as small bubbles and point defect clusters are formed in the case of Si:H. The hydrogen atoms diffuse to the H-H platelets and agglomerate forming regions of highly pressurised H_2-filled microcavities, eventually even providing the force needed to generate a crack opening displacement. The calculated pressure in the H_2-filled microcavities is in Giga-Pascal (GPa) range [4]. At sufficiently high temperatures hydrogen can out-diffuse from Si completely.

Helium has also a high permeability in silicon. Being trapped in Si, He segregates in gas-vacancy complexes and forms bubbles just after implantation, depending on implantation parameters (first of all on ion dose, *D*, and energy, *E*). During annealing, especially at 1000K and above, the He-filled bubbles as well as voids and microcavities are created [5]. Besides creating platelets, voids or bubbles, typically of up to a few tens of nanometer dimension, numerous point and extended defects are formed in Si:H and Si:He at annealing.

Enhanced hydrostatic pressure of gas ambient at annealing (HT - HP treatment) of Si:H results in suppression of splitting, retarded hydrogen out-diffusion and in creation of cluster-like defects in the near - surface Si layer. The TEM images of the HT - HP treated Si:H samples resemble that of porous

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Corresponding author: A. Misiuk, e-mail: misiuk@ite.waw.pl

silicon (pSi), but, contrary to the case of pSi prepared by chemical etching, the pores are closed [6].

The HT - HP treatment exerts similarly strong effect on the Si:He structure, also because of slower out-diffusion of helium at HP [7].

Investigation of the HT - HP treatment influence on the properties of Si:H and Si:He in view of nanocrystalline character of the buried hydrogen- or helium containing layer created near the implanted ions range (R_p) is the main goal of present work.

2. EXPERIMENTAL

Czochralski or floating zone grown single crystalline silicon (Cz-Si or Fz-Si) wafers of 0.6 mm thickness (Cz-Si with interstitial oxygen concentration, $c_o \leq 9 \cdot 10^{17}$ cm^{-3}, boron doped) were implanted with H_2^+ or He^+ ions ($D \leq 5 \cdot 10^{16}$ cm^{-2}, E = 45 - 150 keV). The implantation energy, E, of the H_2^+ or He^+ ions was intentionally comparatively low to produce the samples with low R_p, and so with the buried layer placed close to the Si surface. The microstructure of such samples was easier for investigations by means of experimental methods applied in this work. For the same reason some Si wafers were oxidised prior the implantation (SiO_2 thickness up to about 200 nm, Table 1). That surface SiO_2 layer was etched away after the HT - HP treatment.

The samples of about 8x12 mm^2 dimension were cut from the Si:H and Si:He wafers and subjected to the HT - HP treatment in Ar gas [8] at up to 1470K – 1.2 GPa for up to 10 h.

The composition and structure of the HT - HP treated Si:H and Si:He samples were determined by means of Secondary Ions Mass Spectrometry (SIMS), Transmission Electron Microscopy (TEM) and X-ray Reciprocal Space Mapping (XRSM). Photoluminescence (PL) at infrared was measured at 10K (excitation by a Ar laser, λ = 488 nm) and that in the visible region was determined at 300K (excitation by a pulsed N_2 laser, λ = 337 nm or by a YAG laser, λ = 265 nm). To evaluate electrical properties, capacitance - voltage (CV) profiling was carried out.

3. RESULTS AND DISCUSSION

3.1. Effect of HT - HP on Si:H samples

Most of results presented below concern the samples implanted with $D = 4 - 6 \cdot 10^{16}$ cm^{-2} at E = 130 - 150 keV.

TEM images of the annealed and HT - HP treated Si:H4 samples (for sample characteristics see Table 1) are presented in Fig. 1. The sample annealed at 720K - 10^5 Pa indicates presence of platelets of about 50 nm size located near R_p, and oriented parallel to the (001) and (111) crystallographic planes (Fig. 1A).

The formation of a large density of microdefects of about 10 nm dimension in the near-surface layer of about 150 nm thickness was also detected. That sample was almost fully splitted at about 0.5 mm depth. The treatment at 720K - 1.2 GPa (Fig. 1B) resulted in an appearance of even smaller microdefects, while the splitting effect was much less pronounced.

The HT - HP treatment of Si:H at 920K resulted also in creation of microcavities over a more extended area (in comparison to that for Si:H annealed at 10^5 Pa), while the larger hydrogen-filled bubbles were less numerous and no splitting detected [6, 7].

The SiH:3 sample treated at 720K - 1.2 GPa for 10 h was strained at the top / buried layer interface (interference fringes detected) while intense diffuse scattering confirmed presence of numerous small defects (Fig. 2A). That strain and the concentration of small defects decreased with HT (compare Fig. 2A and B) and were practically non - detectable for the sample treated at 1470K - 1.5 GPa for 1 h (Fig. 2C). The HP - stimulated increase of the X-ray diffuse scattering intensity was detected also for the

Table 1. Designations of samples and implantation parameters *D, E* and projected ion range, R_p (in silicon).

Sample	$D \cdot 10^{16}$, cm^{-2}	E, keV	R_p, nm	Remarks
Si:H1	4	45	80	SiO_2 layer, 190 nm thick
Si:H2	4	130	600	SiO_2 layer, 50 nm thick
Si:H3	4	135	450	SiO_2 layer, 160 nm thick; pre-annealing at 720K-10^{5}Pa for 15 min.
Si:H4	6	135	650	–
Si:He5	5	150	880	–

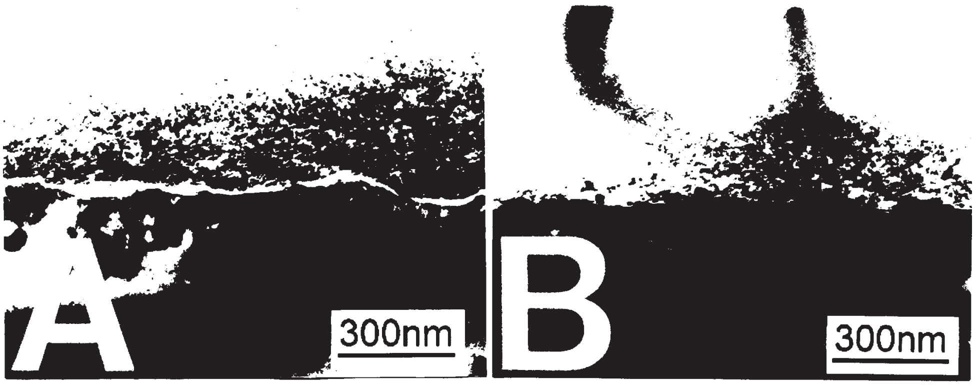

Fig. 1. Cross - sectional TEM micrographs of Fz-Si:H4 samples (111 oriented, oxygen concentration, c_o = 7.5·10^{17} cm^{-3}, implantation with H_2^+, D = 6·10^{16} cm^{-2}, E = 135 keV). A: annealing at 720K - 10^5 Pa for 10 h; B: HT - HP treatment at 720K - 1.2 GPa for 10 h.

Si:H samples implanted with higher hydrogen dose (D = 6·10^{16} cm^{-2}) and treated at 720K - 1.2 GPa [7].

Electrical properties of the Si:H samples are known to be strongly influenced by enhanced HP at annealing, especially at 720K [9]. On the basis of our results obtained by means of the electrical methods it is evident that the implantation at D = 4·10^{16} cm^{-2} (sample Si:H2) followed by annealing at 720K - 10^5 Pa is effective in producing deep as well shallow levels (SL's) in the Si energy gap (Fig. 3A). The defects show acceptor - like character. The deeper acceptor is a dominant defect that acts as a strong compensating centre in the n - type material. The presence of the shallow level acceptors (SLA's) results in forming a sub - surface layer with p - type conductivity. As revealed by C-V profiling at 80K, the layer is relatively thick (Fig. 3A).

The results of C-V measurements obtained with the Si:H2 sample treated 720K - 1.2 GPa (Fig. 3B) clearly show that the p - type layer is embedded in the n - type material. The latter is formed as a result of a conversion of the initially p - type material due to creation of shallow thermal donors (STD's) at 720K [9]. Both high – and low temperature C-V measurements provide useful information on spatial profiles of the defect concentration. A sharp rise in the carrier profiles measured at high temperatures (not presented in this paper) can be attributed to the deep level acceptor. This is in agreement with results reported by other authors in the case of a heavy damage caused by implantation [10].

The concentration of SLA's induced by hydrogen implantation was on a level of about 1·10^{15} cm^{-3}, as determined from C-V profiling at 80K (Fig.

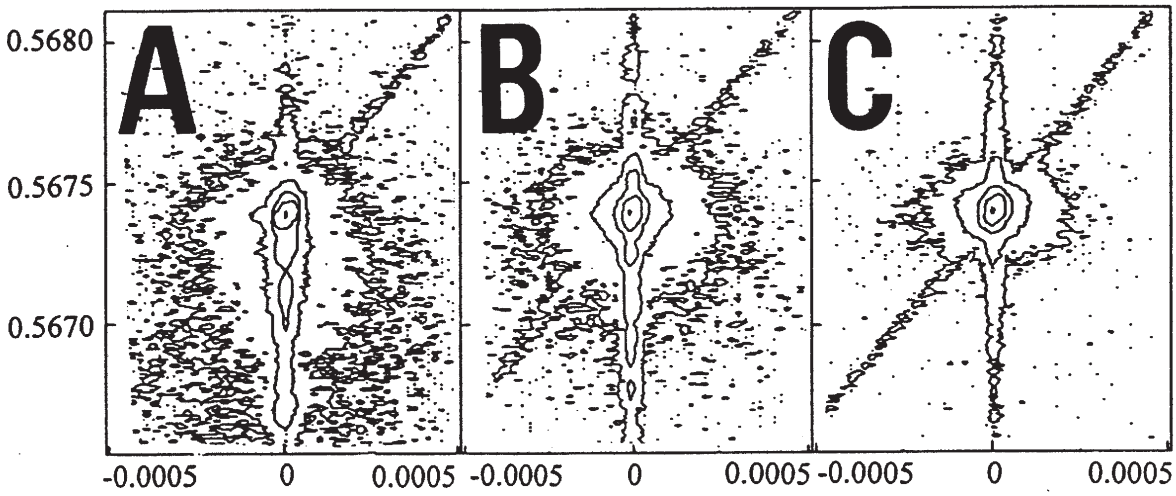

Fig. 2. XRSM recorded near the 004 reciprocal lattice point for (001) oriented Cz-Si:H3 samples (c_o = 8·10^{17} cm^{-3}, H_2^+ implantation through 160 nm thick SiO_2, D = 4·10^{16} cm^{-2}, E = 135 keV). Samples were pre-annealed at 720K - 10^5 Pa for 15 min. and HT - HP treated. A: at 720K - 1.2 GPa for 10 h; B: at 920K - 1.2 GPa for 10 h; C: at 1470K - 1.5 GPa for 1 h. Axes are marked in $\lambda/2d$ units (λ – wavelength; d – distance between crystallographic planes).

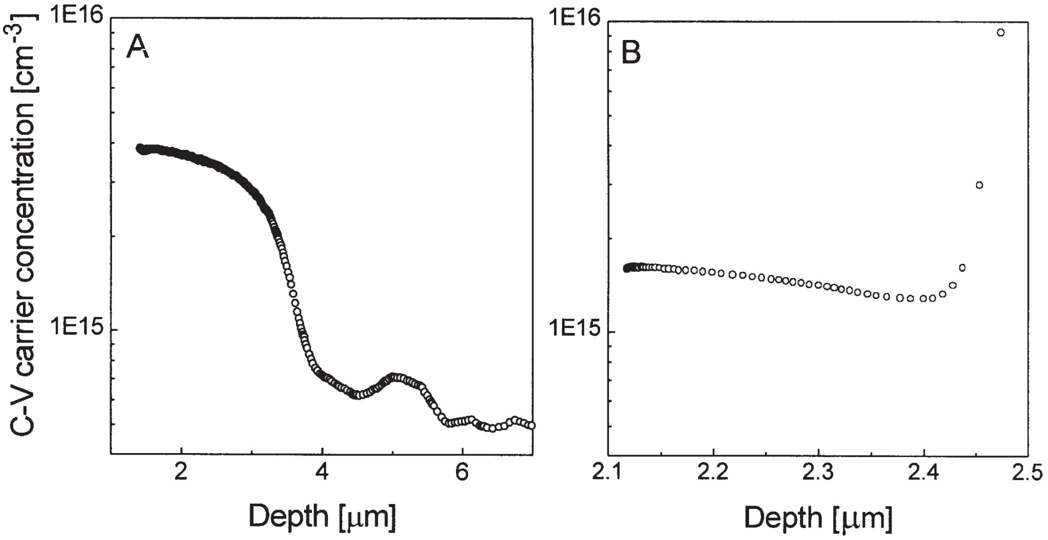

Fig. 3. Carrier concentration profiles at 80K for (001) oriented Cz-Si:H2 samples (c_o = 8·10^{17} cm^{-3}, H_2^+ implantation through 50 nm thick SiO_2, D = 4·10^{16} cm^{-2}, E = 130 keV). A: annealed at 720K - 10^5 Pa for 10 h; B: treated at 720K - 1.2 GPa for 10 h.

3B). The concentration is lower as compared to that of 4·10^{15} cm^{-3} obtained with the reference sample treated at 720K - 10^5 Pa (Fig. 3A).

Let us notice that the spatial profiles in Fig. 3 extend far beyond the range of the transport ions. Whereas the R_p value for the Si:H2 samples is about 0.6 μm, the C-V results give an evidence that the defects can migrate over a distance larger than 2.4 μm. The defects can move even deeper into the Si bulk, up to 3.8 μm, as determined in the sample treated at 720 K - 10^5 Pa (Fig. 3A). That difference in the distance from the source of the defect creation can be readily understood if one assumes that thermal donor (TD) formation is affected by the HP value. The effect of HP - stimulated generation of STD's has already been reported [6, 11].

It suggests that the treatment at 720K - HP leads to formation of numerous clusters containing oxygen, being responsible for the STD activity. As estimated, STD's were present at the concentration of above 10^{16} cm^{-3}. The presence of STD's in the surplus concentration can explain a decrease in the apparent width of the p-type sub-surface nanostructured layer created in effect of implantation with the subsequent HT - HP treatment. If not populated with electrons at 80K, TD's are positively charged, that is why they can effectively compensate SLA's introduced by implantation.

Moreover, our results indicate that the thermal activation energy of TD's shows a substantial dependence on HP with clear trend to increase in the energy with the decrease in HP. Due to this reason, a freezing charge was observed to take place in TD's at 80K if they were created under atmospheric pressure. Owing to this effect, particular feature in the carrier profiles in the form of a wide plateau with sharply falling edge moving deeper into the sample is revealed. It is interesting to note that the latter may be a characteristic feature for species migrating over large distances and creating clusters away from the damage location [10].

PL spectra at infrared (IR) of the as-implanted and HT - HP treated Si:H1 samples indicate the peak at 0.79 eV of not known origin, possibly related, however, to specific point defects [6] or dislocations [12]. Their concentrations are the highest for the Si:H1 samples treated at 720K - HP for 10 h or at 870K - HP for 1 h. The broad band at about 0.94 - 1.01 eV can also be related to the presence of dislocations (superposed D3 and D4 dislocations - related lines) or to specific defects induced by the internal stresses around hydrogen - related defects (optical centre M') as well as to radiative recombination at the hydrogen - related defects [13]. In any case, that defects are produced in the highest concentration by the treatment at 720K / 870K - HP.

The PL line at about 1.1 eV, known as originating from bound exciton recombination at boron as a shallow doping impurity, was of the lowest intensity for the as-implanted sample and for that treated at 870K - 1.2 GPa for 10 h. It can be considered as a proof that numerous non-radiative (oxygen-containing ?) recombination centres are present just in that samples.

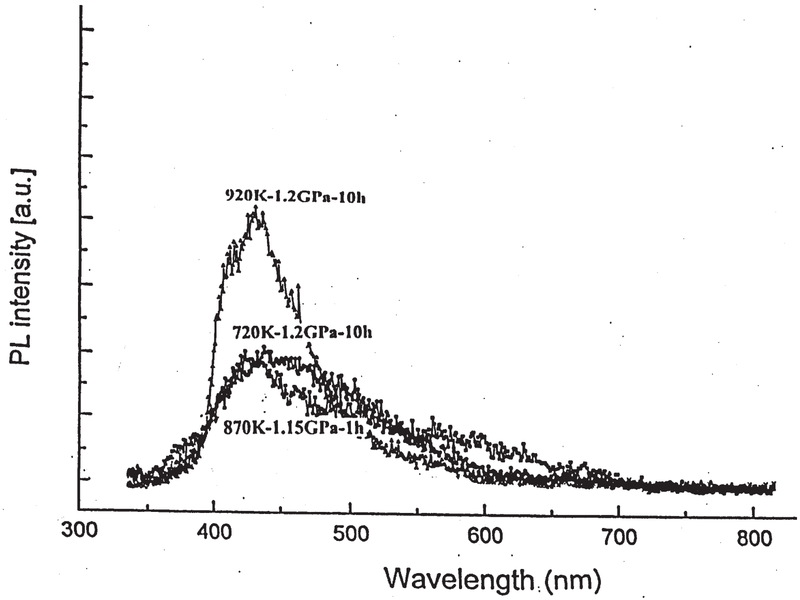

Fig. 4. PL of Si:H4 samples ($D = 4{\cdot}10^{16}$cm^{-2}, E = 135 keV), HT - HP treated (measurement at 300K, excitation by N_2 laser, λ = 337 nm). Treatment conditions are indicated.

The PL spectra at visible light region of the HT - HP treated Si:H3 are presented in Fig. 4. The samples indicated rather strong PL peaking at about 440 nm, of the highest intensity for the sample treated at 920K - 1.2 GPa for 10 h and of the much lower intensity for the samples treated at 720K - HP. Also SiH3 sample treated at 1470K - 1.5 GPa for 1 h indicated PL band in the same spectral region.

As it follows from SIMS data, oxygen atom (always present in Si, especially for Si grown by the Czochralski method) was gettered near R_p, especially in the case of the Si:H3 samples, subjected to pre-annealing at 720K - 10^5 Pa (Table 1, [14]), or of the Si:H samples with enhanced (> 420K) substrate temperature during implantation.

The nanostructured embedded layer is created near R_p in silicon implanted with hydrogen and subjected to subsequent annealing / HT - HP treatment. This buried layer contains numerous nanometer-sized hydrogen-filled bubbles, platelets and cavities as well as dislocations and point defects, subjected to evolution depending on temperature, pressure and time of the subsequent treatment. More numerous but smaller defects are created at 720 / 920K - HP (if compared with that produced by similar treatment but under 10^5 Pa).

Visible PL at about 440 nm can not be unambiguously associated, however, with the quantum confinement effect expected for Si nanocrystallites, because for all investigated HT - HP treated Si:H samples no meaningful shift of this PL band with the changing HT – HP treatment conditions was detected. So this PL seems to be related rather to some hydrogen and oxygen-related species (oxygen is gettered in the damaged layer) present in the buried damaged layer, similarly as suggested for mesoporous silica [15].

3.2. Effect of HT - HP on Si:He samples

TEM images of the HT - HP treated Si:He5 samples (for sample characteristics see Table 1; most below presented results concern just the Si:He5 sample) are presented in Fig 5.

The Si:He5 sample treated at 720K - 1.1 GPa for 10 h indicates presence of numerous very small voids (of about 5 nm dimension) within the wide helium-containing buried layer (Fig. 5A). The treatment at 870K - 1.1 GPa results also in creation of mentioned voids while the sample structure is even more disordered (Fig. 5B). No splitting was detected for the annealed as well as HT - HP treated Si:He5 samples.

The treatment of Cz-Si:He at > 870K - HP resulted in detectable oxygen accumulation at damaged buried layer, as confirmed by SIMS measurements [14].

Diffraction fringes were detected in XRSM of the as-implanted Si:He5 samples confirming presence of strain between the damaged He - containing bur-

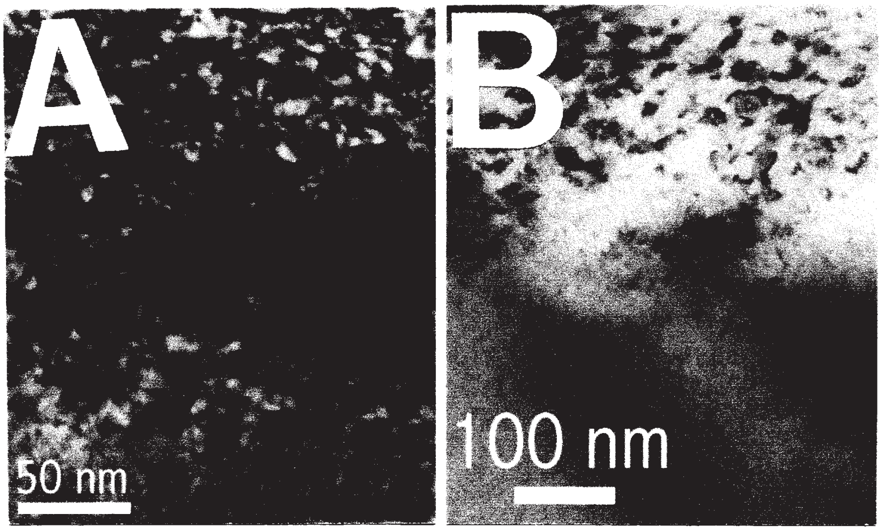

Fig. 5. Cross-sectional TEM micrographs of Si:He5 samples (001 oriented Cz-Si, implanted with He^+, $D = 5 \cdot 10^{16}$ cm^{-2}, $E = 150$ keV), treated for 10 h. A: at 720K - 1.1 GPa; B: at 870K - 1.1 GPa.

ied layer and the Si bulk. This strain was detected also for the Si:He5 samples, HT - HP treated at 720K - 1.1 GPa for 1 h and 10 h (Fig. 6). The more prolonged treatment resulted in decreased strain but in larger structural disturbances (compare Figs. 6A and B). The concentration of small defects responsible for more pronounced diffuse scattering has been reported to decrease with HP for the HT - HP treated samples (in comparison to those subjected to the same treatment but under 10^5 Pa) [7].

PL spectra at IR of the Fz-Si:He5 samples are presented in Fig. 7. All spectra indicate presence of the peaks at about 0.87 eV, 0.94 eV and 1.01eV, probably corresponding to the dislocation - related D2, D3 and D4 lines [16]. The PL line at about 0.94 nm (D3 dislocation - related line ?) was of the highest intensity for the Si:He5 sample treated at 870K - 1.15 GPa for 1 h. More prolonged (for 10 h) treatment of Si:He5 at the same conditions resulted in a marked decrease of the intensity of that line while

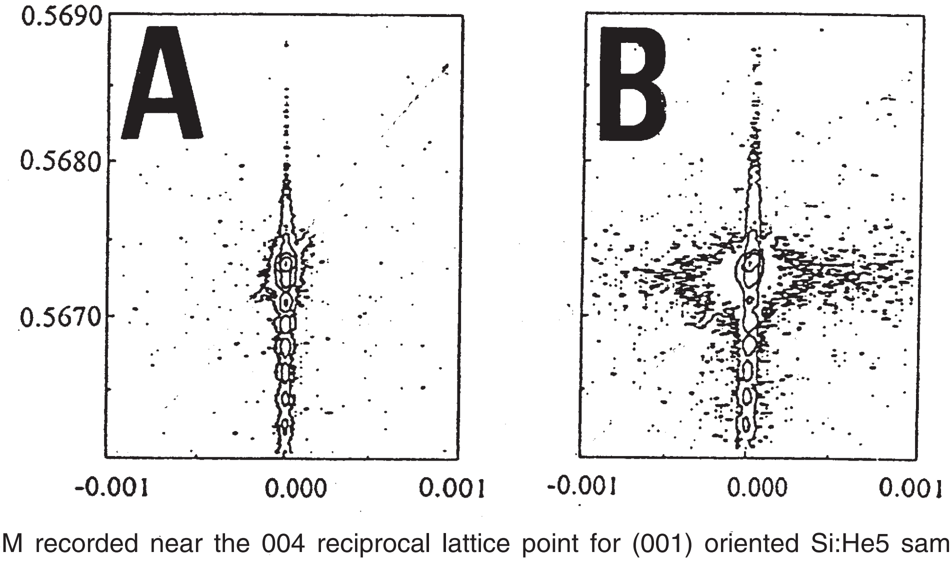

Fig. 6. XRSM recorded near the 004 reciprocal lattice point for (001) oriented Si:He5 samples (D = $5 \cdot 10^{16}$ cm^{-2}, E = 150 keV), HT - HP treated at 720K - 1.1 GPa. A - for 1 h; B- for 10 h. Axes are marked in $\lambda/2d$ units (λ – wavelength; d – distance between crystallographic planes).

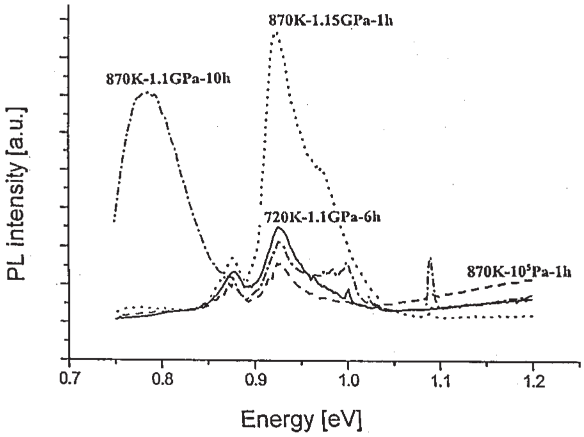

Fig. 7. Photoluminescence spectra at IR of Fz-Si:He5 samples ($D = 5{\cdot}10^{16}$ cm^{-2}, E = 150 keV), annealed / HT - HP treated at 720K and 870K. Treatment conditions are indicated. PL was determined at 10K (excitation by Ar laser, λ = 488 nm).

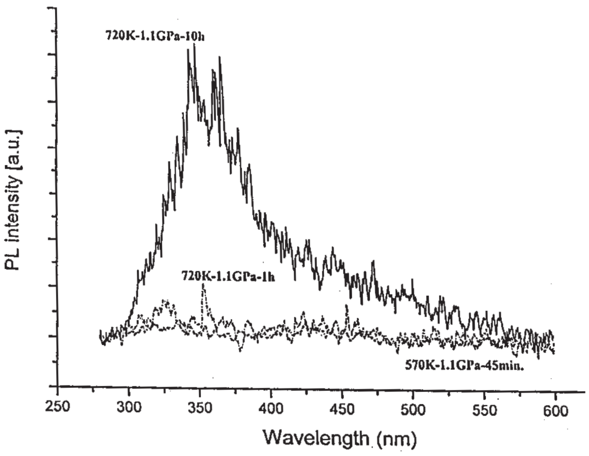

Fig. 8. Photoluminescence spectra at visible light region of HT - HP treated Cz-Si:He5 samples ($D = 5{\cdot}10^{16}$ cm^{-2}, E = 150 keV). Measurement at room temperature, excitation by YAG laser, λ = 265 nm. Treatment conditions are indicated.

the other PL line, at 0.79 eV, reached considerable intensity. It is reasonable to assume that the PL line at 0.79 eV is related to the presence of specific point defects, possibly tri- and tetra- self-interstitials defects I_3 and I_4 [15], created from Si interstitials produced during implantation. The same has been suggested for the case of Si:H treated at 920K - HP [6]. If so, the more prolonged treatment of Si:He at 870K - 1.1 GPa resulted in creation of that point - like defects in a high concentration. Still, similarly as in the case of earlier discussed effects of the HT - HP treatment on the Si:H samples, the origin of all detected PL lines at IR demands further clarification.

Ultraviolet PL peaking at about 360 nm is detected for the Si:He5 samples treated at 720K - 1.1 GPa for 10 h (Fig. 8); no PL was observed for the same samples but treated for 1 h or at lower temperatures (for PL excitation with λ = 265 nm, measurement at 295K). Similar PL band was observed also for the lower - dose ($2{\cdot}10^{16}$ cm^{-2}, 150 keV) helium - implanted oxygen - lean Fz-Si treated at 570 K - 1.1 GPa for 1 h. The origin of this band can be related rather with the presence of nanometer - sized Si crystallites in the disturbed buried layer produced in Si:He by implantation and subsequent HT - HP treatment. The hydrogen - and oxygen - related species (possibly responsible for visible PL in the HT - HP treated Si:H) could not be created in the disturbed buried layer (no hydrogen and oxygen present, in remarkable quantities, in Fz-Si:He). Still this question demands future clarification.

4. CONCLUSIONS

The temperature - pressure (HT - HP) treatment of Si:H and Si:He results in creation of nanostructured buried layers containing gas-filled bubbles, platelets, cavities as well as numerous extended and point defects; the HT - HP treated Si:H structures are not splitted contrary to the case of that annealed at 10^5 Pa.

The HT - HP induced effects in Si:H and Si:He are related to retarded out-diffusion of hydrogen and helium at HP.

The buried nanostructured layers in the HT - HP treated Si:H and Si:He are active in respect of oxygen gettering. Visible PL, resembling that of porous silicon, can be considered as an evidence of creation (owing to gettering effect) of optically active chemical bonds / species in Si:H and of nanometer - sized structural features in Si:He.

The HT - HP treatment of Si: H, He can be considered as an unique tool to produce optically active silicon structures with no use of chemical reagents (needed to produce porous silicon).

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