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BURIED NANO-LAYERS IN SILICON CO-IMPLANTED WITH H_2^+/He^+ AND ANNEALED UNDER HIGH HYDROSTATIC PRESSURE

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Abstract. Nano-structured layers were prepared in Czochralski silicon by co - implantation with H_2^+ (dose, D = 1.25 – 2.5·10^{16} cm^{-2}, energy, E = 135 keV) and He^+ (D = 2.5 - 5·10^{16} cm^{-2}, E = 50-150 keV) and subsequent high temperature (at up to 1070K) – high pressure (at up to 1.1 GPa) treatment in hydrostatic conditions. Depending on implantation and treatment parameters, the sponge – like buried layers composed of silicon nano – crystals and of amorphous silicon, with hydrogen/helium filled cavities and platelets / bubbles, are created. Such layers indicate specific microstructure and hydrogen emission, increasing with temperature and sometimes with pressure.

1. INTRODUCTION

Buried nano-structured layers with interesting properties are formed in hydrogen - or helium - implanted single crystalline silicon (Si:H or Si:He) subjected to annealing at $HT \leq$ 1070K, especially in the case of treatment under enhanced hydrostatic pressure (*HP*) [1]. Majority of implanted atoms in treated Si:H and Si:He are contained in over – pressurized gas filled cavities and bubbles, with hydrogen bonded to Si or / and in the form of molecules, H_2, and with He in the atomic form [2]. Enhanced *HP* at annealing (*HT* - *HP* treatment) of Czochralski grown silicon (Cz-Si, containing oxygen interstitials in a concentration up to 1.2·10^{18} cm^{-3}) co - implanted with H_2^+ and He^+ results in the specific *HP* - induced effects, dependent also on the sequence of the hydrogen – and helium – enriched areas [3-5]. The spatial position of these areas in Si:(H,He) depends on implantation energy (E) and dose (D) of H_2^+ and He^+ [3-5]. For example, the *HT* – *HP* treatment of Si:H,He, with the H-enriched layer placed shallower in respect to that He - enriched (i. e. for the case of E_{H2+} = 135 keV and E_{He+} = 150 keV), results in a creation of small cavities and bubbles, in strongly suppressed oxygen accumulation within the implantation – disturbed areas and in specific dependence of hydrogen out – diffusion on *HP* [3]. The hydrogen out - diffusion rate has been reported even to increase with *HP* for the case of some specific Si:(H,He) samples, *HT* – *HP* treated at 720 – 920K. This last effect has been stated for Si:H,He [3] and Si:He,H [4], with the H - enriched layers placed, respectively, above and below the He – enriched areas.

The effect of *HT* - *HP* on the formation of buried nano - structured layers in Cz-Si:(H,He) with different spatial positions of the H - and He - enriched areas is now reported.

2. EXPERIMENTAL

Three kinds of Si:(H,He) samples were prepared by sequential implantation of H_2^+ and He^+ into 001 oriented p type boron doped Cz-Si. While the spatial position of the H – enriched layer was the same in

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Corresponding author: A. Misiuk; e-mail: misiuk@ite.waw.pl all investigated samples (implanted hydrogen was placed mostly near the projected H_2^+ range, at R_{H2} = 580 nm), the He – enriched layer was located markedly deeper in Si:H,He, a little deeper (accounting for the spread of implanted ions, ΔR_p) - in Si:H-He, and a little shallower than that enriched in hydrogen (Table 1) – in Si:He,H. The total dose of implanted atoms in Si:H,He and Si:He,H was equal to $1 \cdot 10^{17}$ cm^{-2} while twice lower in Si:H-He.

Si:(H,He) samples were treated in argon for up to 10 h at 723-1070K under $HP \leq 1.1$ GPa [6]. Photoluminescence (PL), Transmission Electron Microscopy (TEM) and Secondary Ion Mass Spectrometry (SIMS) were used to determine the microstructure and related properties of as prepared, annealed (under 10^5 Pa) and *HT – HP* treated Si:H,He, Si:H-He and Si:He,H.

2. RESULTS AND DISCUSSION

Annealing and *HT – HP* treatment of Si:(H,He) result in a gradual recovery of the Si structure severely disturbed by implantation. Hydrogen and helium out – diffuse to environment; the diffusion rate increases with *HT*. It has been suggested [3,4] that He atoms contained within the He - enriched layer in as prepared Si:(H,He) and out - diffusing towards the sample surface at annealing, also affect out - diffusion of hydrogen.

The Si:H,He as well as of Si:H-He and Si:He,H samples (Table 1), annealed / treated at 723 – 783K, form the buried sponge-like structures with numerous hydrogen- and helium- filled over – pressurized cavities and bubbles located near R_{H2} and R_{He} [3,4]. These extended defects are placed within the strongly implantation – damaged, partially amorphous Si areas (Figs. 1A,B).

Annealing / treatment of Si:H,He at 723 / 783K for 1 h results in a very broad PL band at 0.85 – 1.05 eV indicating some local maxima and in the sharp PL peaks at about 1.1 eV. These peaks are related to the interband transitions in boron doped silicon. PL at 0.85 – 1.05 eV seems to originate, at least in part, from the presence of divacancies (V_2) in the Si lattice, stabilized by hydrogen and helium atoms. If so, the increased intensity of this PL in Si:H,He treated under 1.1 GPa confirms the creation of H_2 / He – filled cavities in a concentration increasing with *HP*.

Important part of hydrogen and of helium out – diffuses to ambient at enhanced temperatures; this out – diffusion is dependent on *HT*, *HP* and treatment time (Table 2). In Si:H,He treated at 920K remaining hydrogen and helium atoms are still confined within enlarged cavities and bubbles. Some bubbles are of the platelet form, especially within the H – enriched part of Si:H,He (Fig. 1C). The hydrogen – and helium – enriched areas in Si:H,He remain to be separated while Cz-Si regains gradually, at higher *HT*, its original structural perfection. Also dislocations and other extended defects have been detected [3] in Si:H,He annealed / treated at 920K under 10^5 Pa and as well as under *HP* (Fig. 1C).

Annealing / treatment of Si:H,He for 5 h at 1070K under $10^5 – 10^7$ Pa results in a still lower concentration of hydrogen within the implanted areas; relative content of hydrogen decreases to about 2 at.% of the original quantity introduced by implantation [3]. The treatment of Si:H,He at 1070K under 10^7 Pa produces the tenths nanometer sized bubbles and other extended defects while almost no gas filled bubbles are detected in Si:H,He treated under 1.1 GPa. Dislocations are much less numerous in such samples if treated under *HP*. Still the detection of distinct PL lines at 0.81 eV (the D1 dislocation related line) in Si:H,He treated at 1070K under 10^7 Pa as well as under 1.1 GPa and lack of PL lines at about 1.1 eV related to interband transition, evi-

Table 1. Characteristics of Si:(H,He) samples: implanted ions, their energies (*E*), doses (*D*), projected range of implanted ions (R_p) and ΔR_p.

Sample	Ions	*E,* keV	*D,* cm^{-2}	R_p, nm	ΔR_p, nm
Si:H,He	H_2^+	135	$2.5 \cdot 10^{16}$	580	90
	He^+	150	$5 \cdot 10^{16}$	980	210
Si:H-He	H_2^+	135	$1.25 \cdot 10^{16}$	580	90
	He^+	75	$2.5 \cdot 10^{16}$	650	190
Si:He,H	H_2^+	135	$2.5 \cdot 10^{16}$	580	90
	He^+	50	$5 \cdot 10^{16}$	490	170

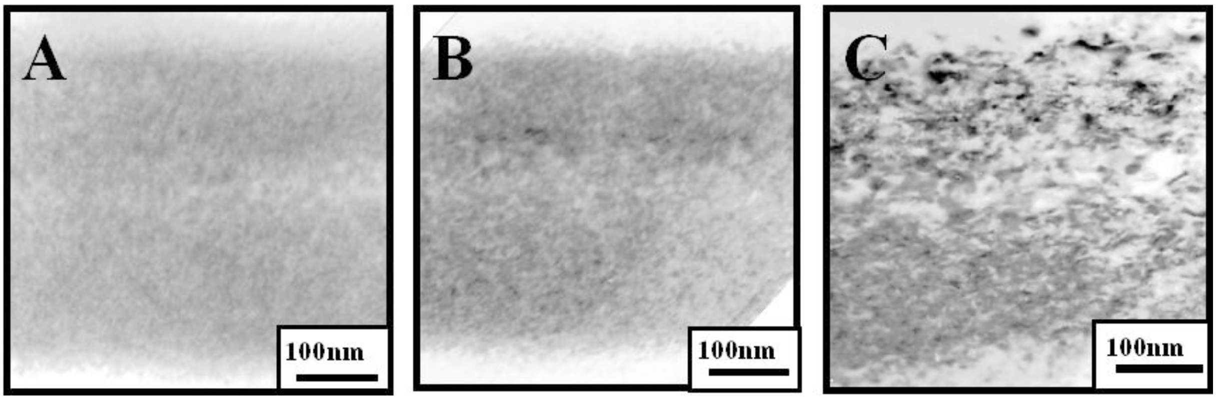

Fig. 1. Cross – sectional TEM micrographs of Si:H,He samples: A – annealed for 1 h at 783K under 10^5 Pa; B - treated for 1 h at 783K under 1.1 GPa; C - treated for 1 h at 920K under 1.1 GPa.

dences the presence of still non - healed damages within the implantation – disturbed areas.

Similarly as in the case of Si:H,He, annealing of Si:H-He for 1 – 10 h at 723K under 10^5 Pa results in a lowered content of hydrogen. However, if comparing with Si:H,He, hydrogen emission from Si:H-He treated for 10 h is a little less dependent on *HP* (Table 2).

Photoluminescence from Si:H-He annealed / treated at 723K for 1 h is almost the same as that detected for Si:H,He. Much sharper PL peaking at about 0.98 eV, detected for Si:H-He annealed for 10 h at 723K under 10^5 Pa, also most probably originates from divacancies (V_2) stabilized by the presence of hydrogen and helium atoms (as in the case of Si:H,He). The increased intensity of this PL line in Si:H-He treated under pressure suggests that the concentration of V_2's increases with *HP*.

Annealing / treatment of Si:H-He for 1 – 10 h at 920K under 10^5 Pa / 1 GPa results in the presence of wide PL band at 0.76 – 0.85 eV, corresponding to the dislocation – related D1 line at 0.81 eV broadened in effect of non - uniform strain. The intensity of this PL band increases with *HP* (Fig. 2).

The PL lines at about 1.1 eV were not detected in Si:H-He treated for 10 h at 920K under *HP* evidencing the creation of numerous non - radiative recombination centers.

Annealing / treatment of Si:H-He at 920K for 10 h results in lowered C_{Hrel}, decreasing to about 4% of the respective value for the as implanted sample. In this case C_{Hrel} almost does not depend on *HP* (Table 2). Oxygen accumulation (caused by gettering by implantation - induced defects as well as by other defects formed at *HT* near R_p) under *HP* is strongly suppressed in Si:H-He as well in Si:H,He [3-5].

Annealing / treatment of Si:H-He at 1070K results in almost complete out - diffusion of hydrogen and helium. Such processing produced numerous dislocations while no PL lines at about 1.1 eV were detected (compare Fig. 2) confirming still existing defects within the Si lattice.

In the case of Si:He,H, co-implantation of Si with hydrogen and helium ions results in formation of two touching buried nano – structured areas (Table 1), with the highest concentrations of cavities, bubbles, point and other nano - defects detectable near R_{He} and R_{H2} [4,5]. The nano – structured layer placed closer to the sample surface contains mostly implanted helium while the deeper one – hydrogen. Still, some hydrogen and helium atoms are intermixed, also because of their high permeability.

Similarly as in the case of Si:H,He and Si:H-He, the implantation – damaged layers in Si:He,H annealed / treated at 723 – 920K contain numerous He – / H_2 – filled cavities / bubbles; the cavities formed near R_{He} are markedly smaller [5]. Also similarly as in Si:H,He and Si:H-He, annealing / treatment of Si:He,H results in the *HT* – and *HP* – dependent out – diffusion of hydrogen (Table 2).

The PL spectra of Si:He,H samples annealed / treated at 723K – *HP* for 1 h indicate, besides the PL peaks near 1.1 eV (related to the interband transitions), the presence of PL lines peaking at about 0.96 eV, 1.02 eV and 1.07 eV (Fig. 3), much sharper than the these ones detected in the similarly treated Si:H,He and Si:H-He. The PL line at 1.02 eV is probably related to the W type centres related to Si interstitials [5] while the origin of remaining lines is not fully understood; their relation to the vacancy – related defects can not be, however, excluded.

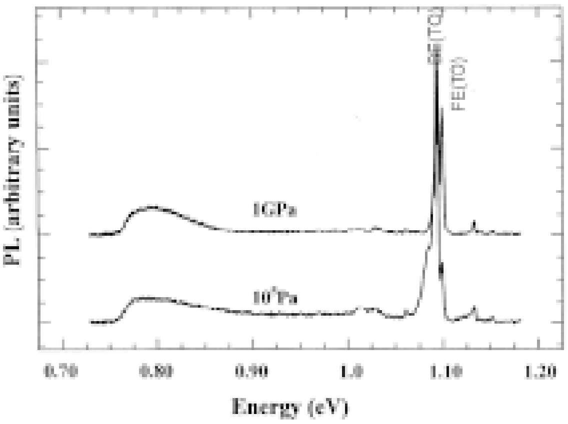

Fig. 2. PL spectra of Si:H-He samples annealed / treated for 1 h at 920K under 10^5 Pa and 1 GPa. BE (TO) and FE (TO) – emissions related to recombination of boron bound exciton and of transverse optical phonon replica of free exciton. PL has been recorded at 6K, excitation with Ar laser, λ = 488 nm.

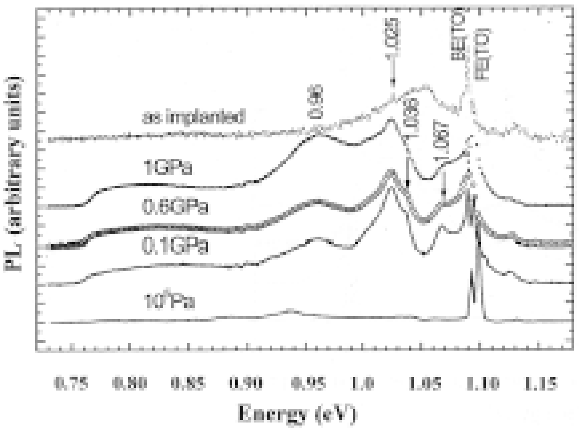

Fig. 3. PL spectra of Si:He,H samples, as implanted and annealed / treated for 1 h at 723K under 10^5 Pa, 0.1 GPa, 0.6 GPa and 1 GPa. BE (TO) and FE (TO) – emissions related to recombination of boron bound exciton and of transverse optical phonon replica of free exciton. PL has been recorded at 6K, excitation with Ar laser, λ = 488 nm.

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

Annealing of Si:He,H for 5 h at 1070K under 10^5 Pa results in formation of strongly dislocated areas near R_{He} and R_{H2} while the treatment for 5 h at 1070K under 1.1 GPa produces more numerous bubbles, evidencing the effect of *HP* on out - diffusion of He and of H_2.

As it follows from the SIMS data, gettering of impurities in Si:He,H takes place only near R_{H2}; this effect is practically absent in the case of Si:He,H samples treated under 1 GPa. Part of hydrogen has been shifted at *HP* from R_{H2} to the originally He – containing areas [5].

Different implantation (composition) – and treatment (annealing) - related factors are contributing in the resulting microstructure of Si:(H,He) samples. When discussing the effect of *HT – HP* on Si:(H,He) one needs to account that the samples under consideration are different in respect of the implanted ion doses as well of spatial position of the hydrogen – and helium – enriched layers. At enhanced temperatures H_2 and He inter - diffuse and out - diffuse from Si:(H,He).

Hydrogen emission under *HP* from Si:H is markedly lowered in comparison to that observed under 10^5 Pa [5]. The presence of He in Si:(H,He) affects the stability of H-Si bonds and so the kind, dimensions and concentration of H_2 - and He- filled cavities as well as of other defects [3-5]. In the case of prolonged annealing / treatment, especially at higher temperatures (e.g. at 1070K) such cavities are finally collapsing creating extended defects, such as dislocations. This results in gradual healing of implantation – disturbed layer exhibiting at lower temperatures the sponge – like structure.

The microstructure of Si:(H,He), *HT – HP* treated at 723 - 1070K, is dependent on the sequence of implanted layers, on *HT, HP* and treatment time.

The presence of He in Si:H,He leads to enhanced concentration of defects and to a more disturbed structure of the annealed / treated samples; the structural disturbances seem to increase with *HP*. The effects observed are most probably related to the influence of He on a creation of Si-H bonds; in the presence of pressurized He, the Si-H bonds in increased number are created at the interface between hydrogen - filled cavity and Si.

Both hydrogen and helium are removed gradually from Si:(H,He) at annealing. Under *HP* this removal is generally slower, more appreciably in the case of helium atoms (that last was not determined in the present study because the applied SIMS method was not sensitive in respect of He). The presence of He affects, in turn, the number of Si-H bonds and so the stability of He+H_2 filled cavities

Table 2. Relative peak concentration of hydrogen ($C_{Hrel.}$) in Si:(H,He) after annealing / treatment at 723K and 920K (C_H in as implanted Si:(H,He) equals to 100%).

Sample	*HT*, K	*HP,* Pa	Time, hour	$C_{Hrel.}$, %
Si:H,He	723	10^5	1	65
		10^9	1	25
		10^5	10	25
		10^9	10	17
	920	10^5	10	2.5
		10^9	10	3.5
Si:H-He	723	10^5	1	60
		10^9	1	25
		10^5	10	30
		10^9	10	28
	920	10^5	10	3.7
		10^9	10	4.2
Si:He,H	723	10^5	1	40
		10^9	1	35
		10^5	10	36
	920	10^9	10	23
		10^5	10	4
		10^9	10	6

and bubbles. After the *HT* – *HP* treatment it would result in the presence of more numerous but smaller internal cavities (vacancy clusters) filled with over – pressurized gazes, exerting internal stress on the surrounding matrix. Enhanced *HP* during the treatment can result even in relatively accelerated out - diffusion of hydrogen as it has been stated for Si:H,He with the specific sequences of the H- and He- enriched layers [3-5]. This means that the microstructure of *HT* – *HP* treated Si:(H,He) is a complex function of the parameters affecting hydrogen and helium diffusivities and, in turn, the number and strength of the Si-H bonds as well as the stability, dimension and number of H,He – filled cavities.

Ab initio calculations deliver useful information on the nature of the *HP* – induced effects and out – diffusion of hydrogen from Si:H and similar structures [7]. The formation energies for vacancy and divacancy in Si decrease by about 2 eV in the presence of hydrogen as follows from the density functional theory and ab initio pseudopotentials. The presence of He also reduces the divacancy formation energy but to a lesser extent: one He atom reduces it by 0.3 eV while two He atoms – by 0.4 eV. Thus, in general the presence of hydrogen and helium in silicon promotes the formation of vacancies and of their complexes.

Enhanced *HP* also results in a decrease of the formation energies of vacancy complexes. Leaving the silicon interstitial site for divacancy, H_2 molecule dissociates and passivates silicon dangling bonds with the energy gain of about 1.6 eV. The presence of one or two He atoms per divacancy reduces this energy gain by 0.1 eV. At low He concentration (with one He atom per divacancy), *HP* equal to about 5 GPa would result in additional decrease of this energy by 0.2 eV. This means that, under *HP*, the hydrogen bonding energy is lowered so hydrogen in Si becomes to be more mobile. In the case of high He concentration (two He atoms per divacancy) the same pressure would result in an increase of the H_2 bonding energy by 0.2 eV. Thus, He atoms in a high concentration reduce the hydrogen out – diffusion from silicon while in a low concentration – promote this out – diffusion.

Different factors participate in a very specific behavior of Si:(H,He) in respect of hydrogen emission under pressure affecting a creation of nano – structured layers. One of them is related to the effect of He on the energy of vacancy formation in hydrogen – containing silicon while other - to different dependencies of helium and hydrogen diffusivities on *HT* and *HP*. Still other factor involves the specific microstructure of Si:(H,He) created in effect of the treatment. More widespread and numerous while smaller H_2 - and He - filled defects are formed under *HP*. Also the sequence of H - and He - enriched layers as well as the energies and doses of implanted species are influencing a creation of buried nano - structured layers in silicon co - implanted with hydrogen and helium and subjected to the *HT* – *HP* treatment.

To summarize, the high temperature – high pressure treatment of silicon co – implanted with hydrogen and helium makes it possible to produce specific nano – layers buried in silicon and exhibiting interesting properties, especially in respect of hydrogen emission at annealing.

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