EFFECT OF PRESSURE ON EMISSION OF HYDROGEN FROM SILICON Co - IMPLANTED WITH HYDROGEN AND HELIUM

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Introduction

Emission of hydrogen from silicon single crystals, co - implanted with hydrogen and helium and annealed under enhanced hydrostatic pressure (*HP*) of ambient, is unusual. The hydrogen out - diffusion rate at ≤ 923 K depends on the sequence of H – and He – enriched areas and can even increase with *HP* [1-3]. This last effect has been stated for Si:H,He [1,2] and Si:He,H [2,3], with the H - enriched layers placed, respectively, above and below of the He – enriched areas.

The effect of *HP* on hydrogen emission from Si:H-He, with the H and He concentration peaks at the 0.6 μm depth, is now reported.

Experimental

To produce Si:H-He, H_2^+ (energy, E = 135 keV and projected range, R_{pH2+} = 0.58 μm) and He^+ (E = 75 keV, R_{pHe+} = 0.65 μm) were co - implanted into (001) oriented Czochralski grown silicon, each to a dose $D = 2.5\times10^{16}$ cm^{-2}. Accounting for the spread of implanted ions (ΔR_p), the H- and He-enriched areas can be considered as overlapping. The reference Si:H samples were prepared by implantation of H_2^+ only, with the same E and D.

Si:H-He and Si:H were treated in Ar ambient for up to 10 h at 723 - 1070 K under *HP* up to 1.1 GPa. Photoluminescence (PL) and X - Ray methods were used to determine the microstructure of Si:H-He and Si:H; depth profiles of H and O were measured by Secondary Ion Mass Spectrometry (SIMS).

Results and discussion

Annealing of Si:H-He as well as of reference Si:H for 10 h at 723 K under 10^5 Pa results in a lowered hydrogen content (c_H) at R_{pH2+} (Figs 1,2). It is caused by hydrogen out - diffusion to ambient. However, contrary to the case of Si:H, where *HP* applied at 723 K results in distinctly higher c_H evidencing lower hydrogen out - diffusion (Fig. 2), the treatment of Si:H-He at 723 K under *HP* almost does not affect the c_H profile while markedly suppresses the oxygen accumulation within the implantation - disturbed area (Fig. 1).

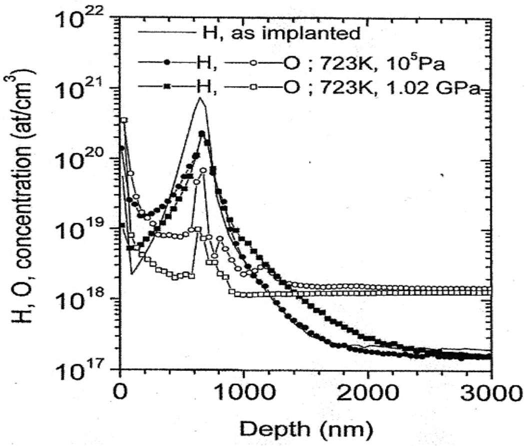

Fig. 1. SIMS depth profiles of hydrogen and oxygen in Si:H-He treated for 10 h at 723 K under 10^5 Pa and 1.02 GPa.

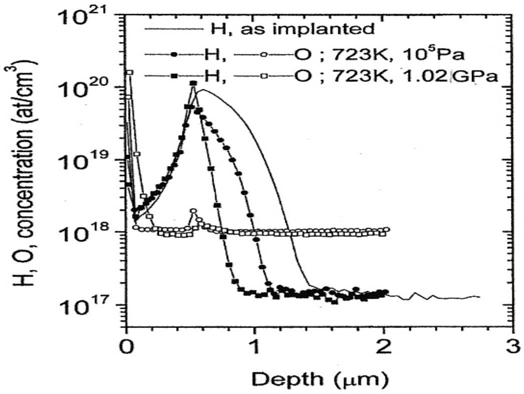

Fig. 2. SIMS depth profiles of hydrogen and oxygen in reference Si:H treated for 10 h at 723 K under 10^5 Pa and 1.02 GPa.

PL at 0.975 eV, detected for Si:H-He annealed at 723 K under 10^5 Pa, probably originates from divacancies (V_2) stabilized by He atoms. Decreased intensity of this PL line after the treatment under 1.1 GPa evidences a lowered V_2's concentration.

Annealing / treatment of Si:H-He at 923 K under 10^5 Pa / 1.06 GPa results in a creation of dislocations as evidenced by the dislocation – related D1 line at about 0.81 eV; its intensity increases with *HP* (Fig. 3). An absence of PL at 1.1 eV after the treatment under 1.06 GPa means that the treatment produces numerous centers for non - radiative recombination.

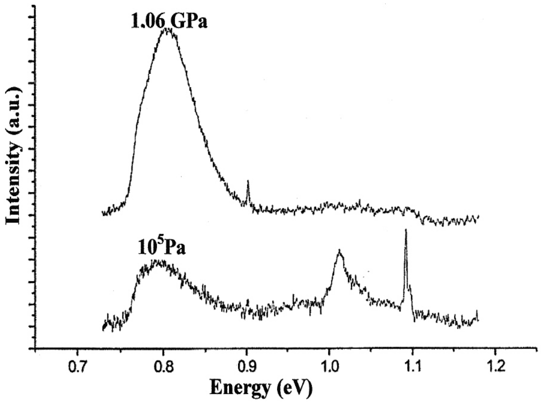

Fig. 3. PL spectra (at 6 K) of Si:H-He treated for 10 h at 923 K (excitation with λ = 488 nm).

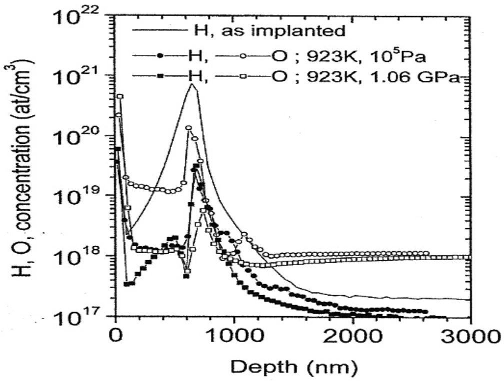

Fig. 4. SIMS depth profiles of hydrogen and oxygen in Si:H-He treated for 10 h at 923 K under 10^5 Pa and 1.06 GPa.

Annealing of Si:H-He at 923 K for 10 h results in markedly decreased c_H, to below 2 % of the respective value for the as implanted sample. Contrary to the case of Si:H, the c_H peak value for Si:H-He treated at 923 K is not dependent on *HP*. Oxygen accumulation (gettering by the implantation - induced defects as well as by the related defects produced at enhanced temperatures) near R_p is strongly suppressed in Si:H-He if treated under *HP* (Fig. 4).

Both H_2 and He are emitted from Si:H-He at enhanced temperatures. In the case of Si:H and Si:He treated under *HP* this emission is expected to be lower in comparison to that observed at annealing under 10^5 Pa. 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. In the case of prolonged annealing / treatment at high temperatures such cavities are finally collapsing creating extended defects, such as dislocations.

Annealing / treatment of Si:H-He at 1070 K results in almost full out - diffusion of hydrogen. Such processing produces numerous dislocations while no PL lines at about 1.1 eV are detected.

Contrary to the case of Si:H, hydrogen emission from Si:H-He is almost non - dependent on pressure. It is obvious that He atoms contained within the He - enriched layer in as prepared Si:(H,He) and out - diffusing towards the sample surface at annealing, are involved in the observed effect of *HP* on the emission of hydrogen.

It seems that different factors participate in the very specific behavior of Si:H-He in respect of the hydrogen emission under enhanced pressure. One of them is related to different dependencies of helium and hydrogen diffusivities on pressure [1,2]. Other factor involves the specific microstructure of Si:H-He created in effect of annealing / treatment. In particular, more widely spread and more numerous while smaller hydrogen – and helium filled cavities and other 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 the emission of hydrogen from silicon co - implanted with hydrogen and helium.

Conclusions

The emission of hydrogen at 723 K - 923 K from Si:H-He prepared by co - implantation of Cz-Si with H_2^+ and He^+, with the same values of R_{pH2+} and R_{pHe+} (equal to about 0.6 μm), is practically nondependent on hydrostatic pressure, at least up to 1.1 GPa.

Based also on earlier reported data [1-3], one can hope to produce the Si:(H,He) structures with the hydrogen emission decreasing (in Si:H), non-dependent (in Si:H-He) or even increasing (in Si:H,He and Si:He,H) with external pressure.

References

1. Misiuk A., Barcz A., Ratajczak J., Bak-Misiuk J. Effect of external stress at annealing on microstructure of silicon co-implanted with hydrogen and helium. Solid State Phen 2004; 95-95:313-318.

2. Misiuk A., Ratajczak B., Barcz A., Bak-Misiuk J., Shalimov A., Surma B., Wnuk A., Jagielski J., Antonova I.V. Effect of stress on accumulation of hydrogen and microstructure of silicon co-implanted with hydrogen and helium. In: Veziroglu T.N et al., editors. Hydrogen materials science and chemistry of carbon nanomaterials. Dordrecht/Boston/London: Kluver Academic Publishers, 2004. p. 579-592.

3. Misiuk A., Surma B., Ratajczak J., Katcki J., Wzorek M., Barcz A., Wnuk A., Jagielski J. Nanostructure formation by high temperature-pressure treatment of silicon implanted with hydrogen/helium. Superlattices and Microstructures 2004; 36:1-10.