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Hydrogen gettering in annealed oxygen-implanted silicon

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Abstract. Hydrogen gettering by buried layers formed in oxygen-implanted silicon (Si:O prepared by O_2^+ implantation at the energy 200 keV and doses 10^{14} and 10^{17} cm^{-2}) was investigated after annealing of Si:O at temperatures up to 1570 K, including also processing under enhanced hydrostatic pressure, up to 1.2 GPa. Depending on processing conditions, buried layers containing SiO_{2-x} clusters and/or precipitates were formed. To produce hydrogen-rich Si:O,H structures, Si:O samples were subsequently treated in RF hydrogen plasma. As determined using secondary ion mass spectrometry, hydrogen was accumulated in sub-surface region as well as within implantation-disturbed areas. It has been found that hydrogen was still present in Si:O,H structures formed by oxygen implantation with the dose $D = 10^7$ cm^{-2} even after post-implantation annealing up to 873 K. It is concluded that hydrogen accumulation within the disturbed areas in Si:O as well as in SOI structures can be used for recognition of defects.

Keywords: Cz-Si, implantation, oxygen, hydrogen, high temperature, high pressure, gettering, defects.

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1. Introduction

Silicon-on-insulator structures (SOI) can be produced by O_2^+ implantation into Czochralski grown silicon (Cz-Si) at doses $D \geq 2 \cdot 10^{17}\,\mathrm{cm}^{-2}$ and subsequent annealing of resulting Si:O at high temperatures (HT) approximately up to 1600 K [1]. Microstructure of the SOI samples depends, among other factors, on the implanted oxygen ion energy E, on D, HT and on processing time t. An enhanced hydrostatic pressure (HP) applied upon processing of the Si:O samples results in formation of specific structures with an improved quality of the SiO_x/Si interface [1, 2].

In the case of self-implanted silicon (Si:Si), buried defect layers can getter hydrogen embedded into Si from hydrogen plasma [3]. This effect is now investigated for the SOI-like structures produced from Si:O prepared by oxygen implantation into Cz-Si with the doses of $D \leq 1 \cdot 10^{17}\,\mathrm{cm}^{-2}$ and processed under HT-HP [1, 2, 4]. Such structures are interesting in view of possible application of the hydrogen decoration/gettering for the recognition of the structural defects in SOI-like structures.

2. Experimental

Cz-Si wafers of (001) orientation and the interstitial oxygen concentration $c_O \approx 1 \cdot 10^{18}$cm^{-3} were implanted with O_2^+ at room temperature. Sample labelling and implantation parameters are listed in Table.

Afterwards, the Si:O samples were annealed for up to 10 h in purified Ar atmosphere at HT ≤ 1570 K under HP ≤ 1.2 GPa.

To introduce hydrogen, the Si:O samples were subsequently treated for 2 h at 530 K in RF hydrogen plasma by using a plasma enhanced chemical vapour deposition (PECVD) reactor [3].

Table. Sample labelling, E, D (calculated for implanted oxygen atoms) and projected range of implanted ions, R_p.

Sample	E, keV	D, cm^{-2}	R_p, nm
A	200	$1 \cdot 10^{14}$	400
B	200	$1 \cdot 10^{17}$	400

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The depth profiles of hydrogen and oxygen in the as-prepared Si:O,H samples as well as in the samples subjected to subsequent annealing for 1 h at 723 K or 873 K were determined using secondary ion mass spectrometry (SIMS) with Cs^+ ions for sample sputtering. Transmission electron microscopy (TEM) was used for defect structure determination.

3. Results and discussion

Two types of Si:O samples were investigated (Table): samples A were prepared by low dose O_2^+ implantation. In what follows, they will be considered as the reference ones. The B samples were prepared by implantation with the oxygen dose only 2-3 times lower than that used in high dose SIMOX processing ($D \geq 2 \cdot 10^{17}\,\text{cm}^{-2}$). In both cases implantation resulted in the creation of an amorphous silicon (a-Si) layer in the projected range (R_p) area.

Upon annealing, this a-Si buried layer was subjected to solid phase epitaxial re-growth (SPER). Depending on the HT, HP and other processing conditions, buried SiO_{2-x} nanoclusters, precipitates and/or semi-continuous layers can be formed near R_p [6].

The treatment of the as-implanted reference sample A in hydrogen plasma resulted in a remarkable hydrogen enrichment of the sub-surface area, up to about 300-nm depth, while no hydrogen was observed near R_p (Fig. 1).

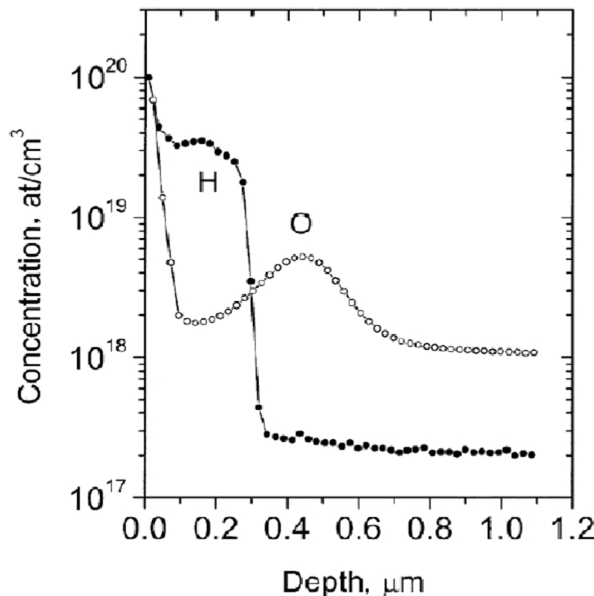

Fig. 1. SIMS depth profiles of oxygen and hydrogen in Si:O,H structure obtained for the as-implanted A Si:O sample.

Surface enrichment with hydrogen can be attributed to the in-diffusion of hydrogen towards the sub-surface defect area disturbed by hydrogen plasma treatment itself as well as to the presence of near-surface defects induced due to oxygen implantation.

No hydrogen gettering near R_p was detected in the reference samples A after the plasma treatment and processing at 923 K (Fig. 2) as well as at higher temperatures. The near-surface hydrogen-enriched layer was, however, much narrower (compare Figs 2 and 1). This means that most of implantation-induced defects formed by implantation of O_2^+ ions are healed at $T \geq 923$ K upon HT(HP) processing of low dose implanted samples. As a result, in-diffusion of hydrogen during the plasma treatment was limited to the depths below 100 nm (Fig. 2). The relatively small damages near R_p in the A Si:O samples were healed in effect of SPER, so they did not create the gettering sites for accumulation of hydrogen.

For the as-implanted B Si:O sample ($D = 1 \cdot 10^{17}\,\text{cm}^{-2}$), plasma treatment leads to the almost depth-independent accumulation of hydrogen within the sub-surface area up to about 200-nm depth, with $c_{\text{H}} = 1 \cdot 10^{20}\,\text{cm}^{-3}$. This treatment of the as-implanted B Si:O sample (prepared using the 10^3 higher dose of implanted oxygen comparing to that in the A Si:O sample, Table) also does not result in remarkable hydrogen content near R_p.

Contrary to the case of as-implanted Si:O,H sample B, the hydrogen content within the deeper areas of the B Si:O,H samples processed at 920-1570 K follows in general the profile of implanted oxygen and depends on HP applied upon processing (Figs 3, 4, 6, 7).

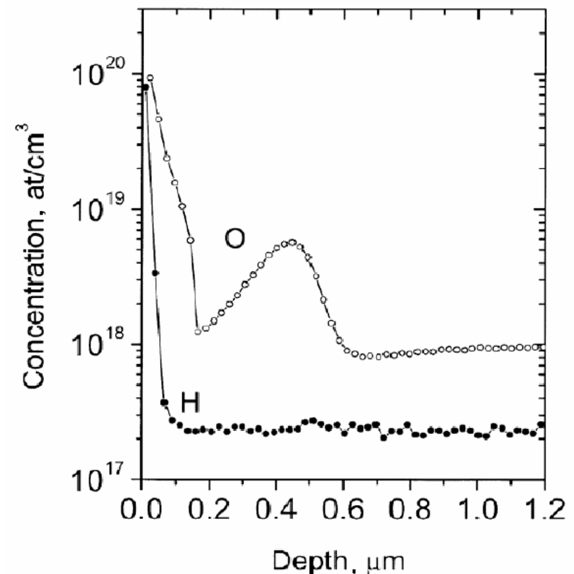

Fig. 2. SIMS depth profiles of oxygen and hydrogen in Si:O,H structure obtained for the A Si:O sample processed for 10 h at 923 K under 10^5 Pa.

Processing the B Si:O sample at 923 K results in a distinguished hydrogen gettering near R_p, with the hydrogen concentration c_{H} reaching $7 \cdot 10^{18}\,\text{cm}^{-3}$ (Fig. 3, compare to Fig. 2).

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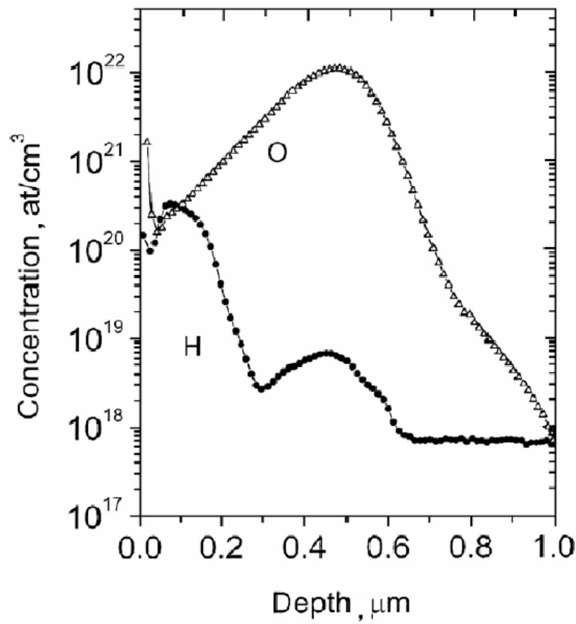


Fig. 3. SIMS depth profiles of oxygen and hydrogen in Si:O,H structure obtained for the B Si:O sample processed for 10 h at 923 K under 10^5 Pa.

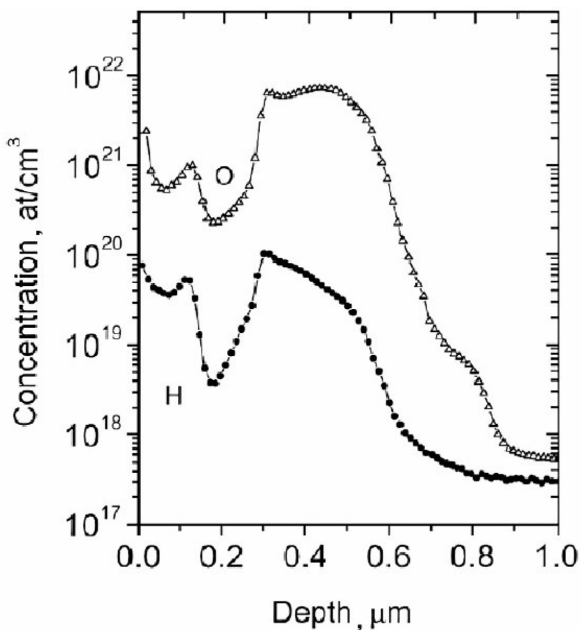
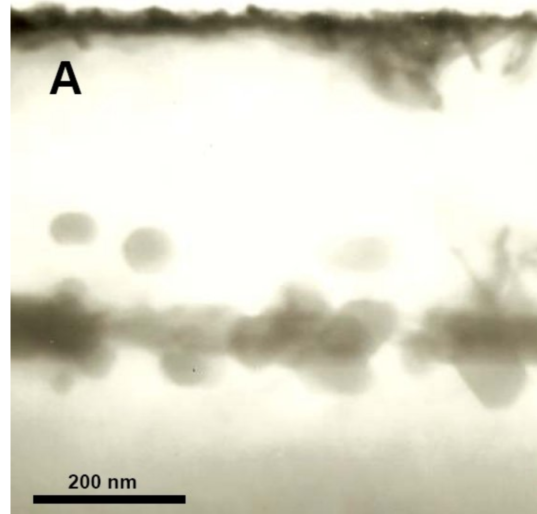
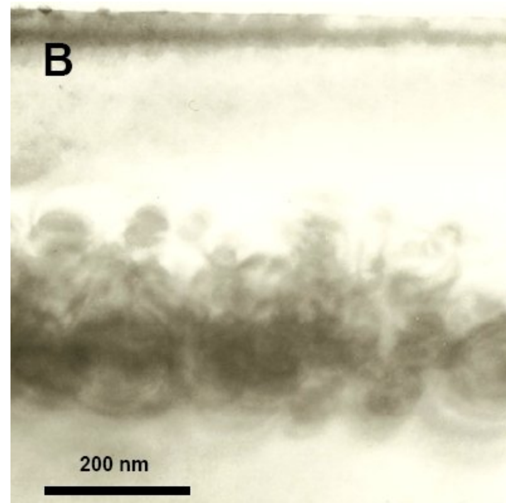


Fig. 4. SIMS depth profiles of oxygen and hydrogen in Si:O,H structure obtained for the B Si:O sample processed for 5 h at 1230 K under 10^8 Pa.



a



b

Fig. 5. TEM images of the B Si:O samples ($D = 10^{17}\,\mathrm{cm}^{-2}$) processed for 5 h at 1570 K under 10^7 Pa (a) and 1.2 GPa (b) (compare to [5]).

The peak concentration of hydrogen c_H accumulated near R_p is dependent crucially on the HT-HP processing conditions. In the case of B Si:O sample processed at 1230 K under 10^8 Pa, this concentration exceeds $1 \cdot 10^{20}\,\mathrm{cm}^{-3}$ (Fig. 4).

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The quasi-continuous SiO_{2-x} layers were formed near R_p (Fig. 5) in the case of B Si:O samples processed at 1570 K (temperature close to that used at SIMOX processing); the sample microstructure is strongly dependent on HP (compare Figs 5a and b). These samples indicate specific accumulation of hydrogen (Figs 6, 7).

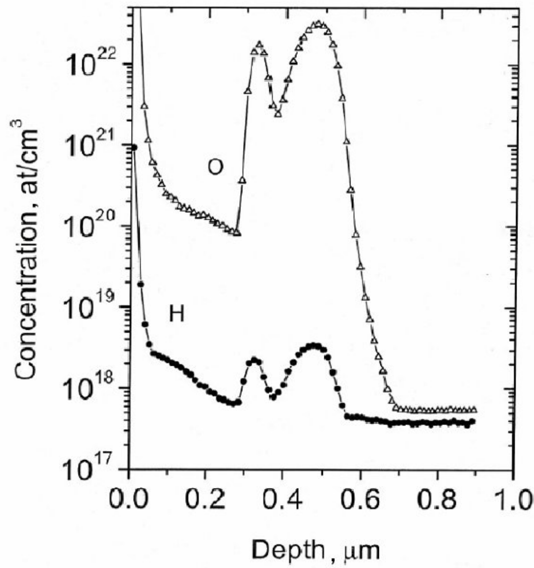

Fig. 6. SIMS depth profiles of oxygen and hydrogen in Si:O,H structure obtained for the B Si:O sample ($D = 10^{17}\,\mathrm{cm}^{-2}$) processed for 5 h at 1570 K under 10^7 Pa (compare to Fig. 5a).

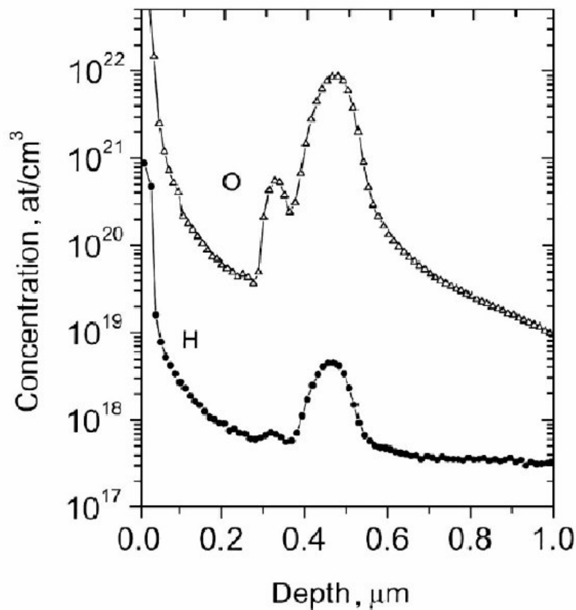

Fig. 7. SIMS depth profiles of oxygen and hydrogen in Si:O,H structure obtained for the B Si:O sample ($D = 10^{17}\,\mathrm{cm}^{-2}$) processed for 5 h at 1570 K under 0.6 GPa.

It is clearly seen that hydrogen content within the deeper areas of the B Si:O samples processed at 923-1570 K corresponds to the profile of implanted oxygen and depends on HP applied upon processing. The profiles of oxygen and those of gettered hydrogen depend on the microstructure and therefore on the presence of numerous, HT, HP-induced effects, among them [6]:

– mobility and solubility of implanted oxygen as well as of silicon interstitials and other implantation-induced defects (such as vacancies, V),

– stability of oxygen agglomerates,

– diffusivity of oxygen as well as of silicon interstitials, Si_i, and of vacancies,

– the misfit at the SiO_2/Si boundary.

Oxygen clustering and precipitation in Cz-Si produce shear stress at the SiO_{2-x}/Si boundary. This stress is attributed to the enlarged volume of SiO_{2-x} precipitates (in comparison to that of the host Si lattice). Other reason of the internal stress is the difference in thermal expansion of SiO_{2-x} and Si. The misfit and so the shear stress at the SiO_{2-x} precipitate/Si matrix boundary are affected by HT and HP in accordance [6] with Eq. (1):

$$\varepsilon = \varepsilon_0 + \frac{3K_{SiO_{2-x}}}{K_{SiO_{2-x}} + 4G_{Si}} \times \left[\Delta HT\left(\beta_{SiO_{2-x}} - \beta_{Si}\right) + HP\left(\frac{1}{K_{Si}} - \frac{1}{K_{SiO_{2-x}}}\right)\right], \quad (1)$$

where ε_0 is the misfit at the SiO_{2-x} precipitate/Si matrix boundary at 295 K under 10^5 Pa; β_{Si} and $\beta_{SiO_{2-x}}$ – coefficients of volume thermal expansion; K_{Si} and $K_{SiO_{2-x}}$ – bulk moduli; G_{Si} – shear modulus (the bottom indexes denote the respective material), and $\Delta HT = HT_{experiment} - 295$ K.

It means that the shear stress at the SiO_{2-x}/Si boundary changes (typically decreases) with HT and HP. For example, in the case of HP = 1.3 GPa applied at room temperature, the HP induced change of misfit at the SiO_2/Si boundary, $\Delta\varepsilon$ ($\Delta\varepsilon = \varepsilon - \varepsilon_0$) can be estimated as equal to about $-2.4\cdot10^{-3}$ [6]. The values of K, G and β are dependent on temperature and pressure; however, these dependences are not known, especially for high temperatures and pressures.

Accumulated hydrogen in the Si:O,H samples remains to be detectable even after subsequent annealing of the Si:O,H structures at temperatures up to 873 K (Figs 8, 9). This suggests chemical interaction of hydrogen with oxygen (probably in the form of sub-stoichiometric SiO_{2-x}), while some part of hydrogen may be bonded to defects (to Si dangling bonds, etc.)

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[4]. It is necessary to note that similar effects (accumulation of hydrogen at R_p and stability of the SiO,H structures at high temperatures) were reported earlier for the helium-implanted Si:He samples annealed in hydrogen-containing ambient [7-9].

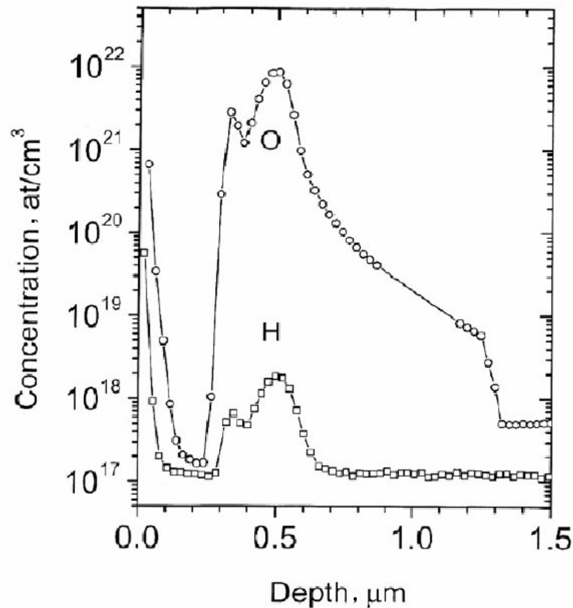

Fig. 8. SIMS depth profiles of oxygen and hydrogen in Si:O,H structure obtained for the B Si:O sample ($D = 10^{17}$ cm^{-2}) after processing for 5 h at 1570 K under 1.2 GPa (compare to Fig. 5b) and subjected for 1 h to desorption annealing at 723 K under 10^5 Pa.

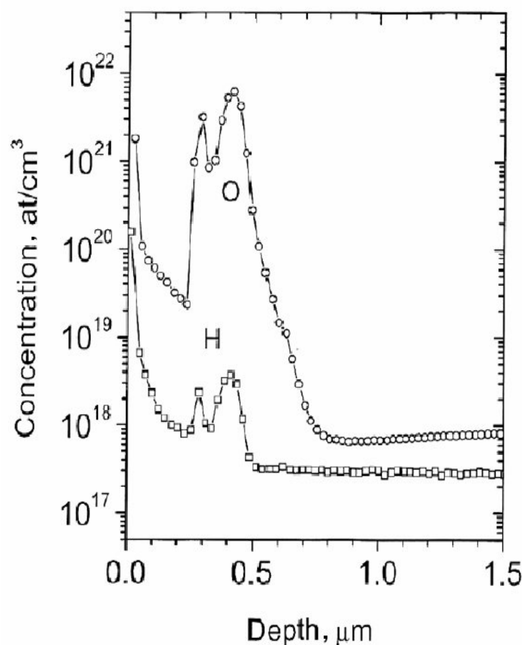

Fig. 9. SIMS depth profiles of oxygen and hydrogen in Si:O,H structure obtained for the B Si:O sample ($D = 10^{17}$ cm^{-2}) processed for 5 h at 1570 K under 10^7 Pa (compare to Figs 5a and 6) and subjected for 1 h to desorption annealing at 873 K under 1.1 GPa.

4. Conclusions

The specific character of hydrogen interaction with defects and oxygen in silicon has been stated for the processed SOI-like structures prepared by oxygen implantation into silicon. This suggests a possibility to use hydrogen plasma treatments for the detection of structural as well as oxygen-related defects in SOI and similar structures prepared by oxygen implantation into monocrystalline silicon.

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