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Effect of uniform stress on SiO_2/Si interface in oxygen-implanted Si and SIMOX structures

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The effect of high temperature–hydrostatic pressure (HT–HP) treatment on SiO_2/Si interface in oxygen-implanted (oxygen doses up to 2×10^{18} cm^{-2}) silicon (Si:O) and reference silicon-on -insulator (SOI) samples has been investigated by the transmission electron microscopy (TEM) and the photoluminescence (PL) methods. The Si:O and SOI samples have been HT–HP treated at 1230–1570 K under argon pressure up to 1.23 GPa for 5 h. Depending on the dose of implanted oxygen and other implantation and HT–HP treatment conditions, the dispersed SiO_{2-x} precipitates or buried SiO_2 layer are created in the Si bulk. The HT–HP treatment affects the creation of dislocations and other defects at the SiO_2/Si interface; this effect is related in part to a decreased misfit at the SiO_2/Si boundary at HT–HP.

1. Introduction

Oxygen-implanted single crystalline silicon (Si:O) is widely used for the fabrication of the Si wafers with buried insulating SiO_2 layer (the separation by implanted oxygen, SIMOX, technology). Depending on the dose of implanted oxygen D, after annealing under atmospheric pressure, the dispersed SiO_2 precipitates (sometimes of sub -stoichiometric composition SiO_{2-x}) or continuous buried SiO_2 layer (typically for $D \geqslant 2\times10^{17}$ cm^{-2}) are formed in Si:O.

Formation of SiO_{2-x} precipitates or of continuous SiO_2 layer is concomitant with stress, both at the implantation stage and at annealing (volume of SiO_2 is more than twice that of Si, thermal expansion of SiO_2 and of Si differs considerably). That stress can be tuned by an application of enhanced HP of ambient gas at annealing (HT–HP treatment) [1].

The HT–HP treatment can affect markedly the Si:O structure. The result of the treatment is dependent on implantation conditions (*e.g.*, on oxygen dose and energy

E), as well as on high temperature, high pressure, *etc.* [2]–[4]. The HT–HP treatment results, among others, in significantly decreased concentration of dislocations [5] and in the varied composition and structure of precipitated SiO_{2-x} [6].

The purpose of this work has been to perform a systematic investigation of the HT–HP treatment influence on the defect formation at/or near the SiO_2/Si interface in Si:O prepared by oxygen implantation with $D = 1\times10^{16}$–2×10^{18} cm^{-2}. The PL measurement just makes it possible to obtain valuable information on the features of such systems [5], [6].

The Si:O samples were annealed under atmospheric pressure or treated at 1230–1570 K under HP (just annealing at about 1570 K under atmospheric pressure is typically used to prepare the commercial SIMOX structures). For reference, the SOI structures with continuous buried SiO_2 layer were HT–HP treated and investigated.

2. Experimental

Czhochralski (Cz) Si with interstitial oxygen content (c_0) of about 7.5×10^{17} cm^{-3} or practically oxygen free floating zone Fz-Si wafers ($c_0 \leqslant 2\times10^{16}$ cm^{-2}) of 0.4–0.6 mm thickness were implanted with different doses of oxygen ($D = 1\times10^{16}$–2×10^{18} cm^{-2}); for sample designations and other details see the Table. The reference SOI samples (0.5 μm thick, (111) oriented Fz-Si/0.4 μm thick SiO_2/(001) oriented Cz-Si) were prepared by bonding the oxidised Si wafer to the bare one followed by the removal of excessive Si with the aid of the smart cut method [7].

Table. Characteristics of (001) oriented Si:O samples: method of Si growth, oxygen dose *D*, energy *E*, temperature of a substrate during implantation *T*, and oxygen ion projected range R_p.

Sample	Growth method	D [cm^{-2}]	E [keV]	T [K]	R_p [μm]
A	Cz	1×10^{15}	200	360	0.4
B	Cz	1×10^{16}	200	360	0.4
C	Cz	1×10^{17}	200	360	0.4
D	Fz	6×10^{17}	170	650	0.35
E	Cz	2×10^{18}	50	650	0.1

The Si:O and SOI samples were annealed under atmospheric pressure or HT–HP treated in Ar atmosphere at 1230 K, 1270 K, 1400 K and 1570 K under HP up to 1.23 GPa, typically for 5 h. Perfection of the samples was determined by TEM and PL measurements, at latter done at 10 K with Ar laser excitation ($\lambda = 488$ nm).

3. Results and discussion

Almost all currently investigated Si:O samples were prepared from Cz-Si (see the Table). The earlier published results (especially on PL) concerned mostly HT–HP treated oxygen-implanted Fz-Si [2]–[4], [6], [8], [9].

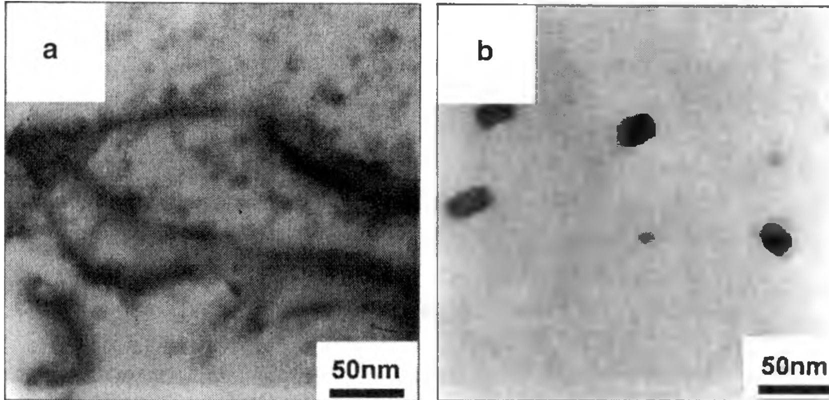

Fig. 1. TEM images of oxygen implanted Cz-Si ($D = 1\times10^{16}$ cm^{-2}, sample B in the Table), annealed -treated at 1400 K for 5 h: under 10^5 Pa (**a**), under 1.2 GPa (**b**).

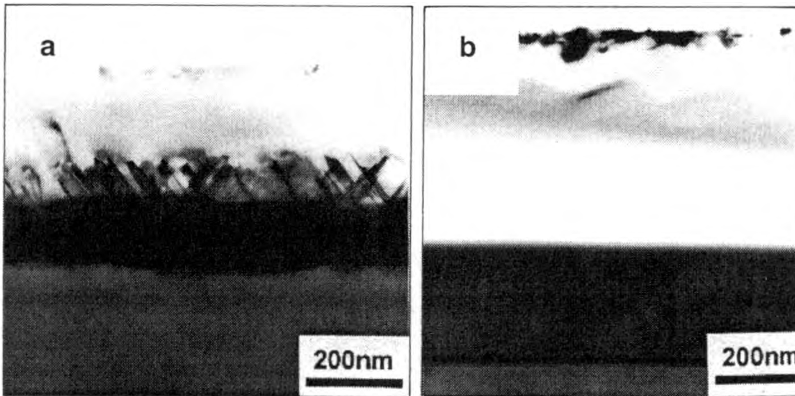

Fig. 2. TEM images of samples treated at 1570 K under 1.23 GPa for 5 h: oxygen implanted Fz-Si, $D = 6\times10^{17}$ cm^{-2} (sample D in the Table) (**a**), SOI structure (**b**).

The effect of the HT–HP treatment on the Si:O samples is dependent first of all on the implanted oxygen dose: dispersed oxide precipitates (Fig. 1) were created in Si:O prepared by implantation with $D = 1\times10^{15}$–1×10^{17} cm^{-2} (samples A, B and C in the the Table), while semi-continuous or continuous buried SiO_2 layer (Fig. 2) was formed in the HT–HP treated Si:O produced by oxygen implantation with $D = 6\times10^{17}$ cm^{-2} and 2×10^{18} cm^{-2} (samples D and E in the Table).

For that reason the results for the above specified Si:O sample groups will be presented and discussed in two different sections. However, to make the comparison of the HT–HP treatment effect on those samples easier, the PL results (dependent strongly also on the temperature, HT, of the treatment) are sometimes presented jointly (*e.g.*, in Fig. 3, see also the Table) for both, above-mentioned groups of samples.

The PL spectra of the Si:O samples annealed at 10^5 Pa or HT–HP treated for 5 h at different HT and HP are presented in Figs. 3–6. When discussing PL results, the

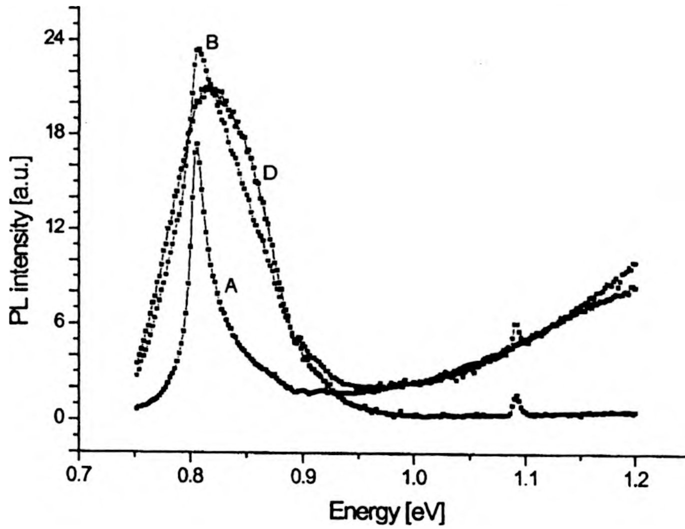

Fig. 3. PL spectra of oxygen-implanted Cz-Si and Fz-Si (samples A, B and D, the Table) treated at 1230 K under 1.01 GPa for 5 h.

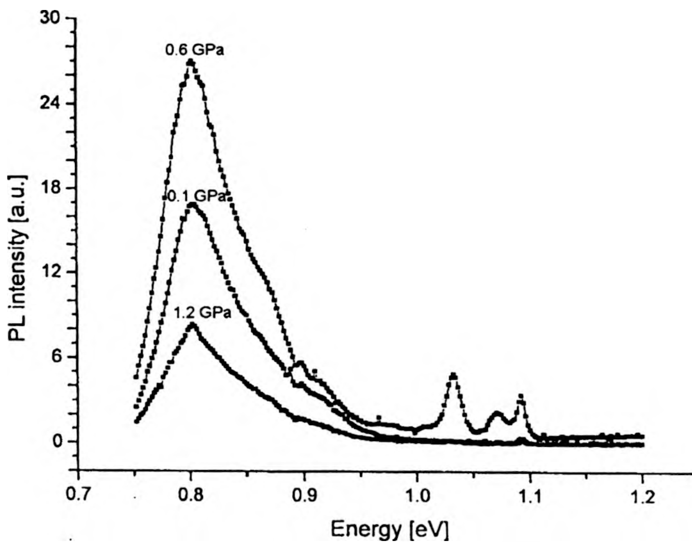

Fig. 4. PL spectra of sample B (see the Table) treated at 1270 K under 0.1 GPa, 0.6 GPa and 1.2 GPa for 5 h.

joint effect of PL-active species (defects) in the annealed/treated Si:O and of non -radiative recombination centres (*e.g.*, of small oxygen clusters) also created due to the HT–HP treatment, ought to be taken into account. In other words, the presence of PL peak at some specific energy can be considered as a proof of the existence of some specific PL-active defects, while the PL intensity is strongly influenced by the mentioned non-radiative recombination centres. It needs to be also stressed that, in the

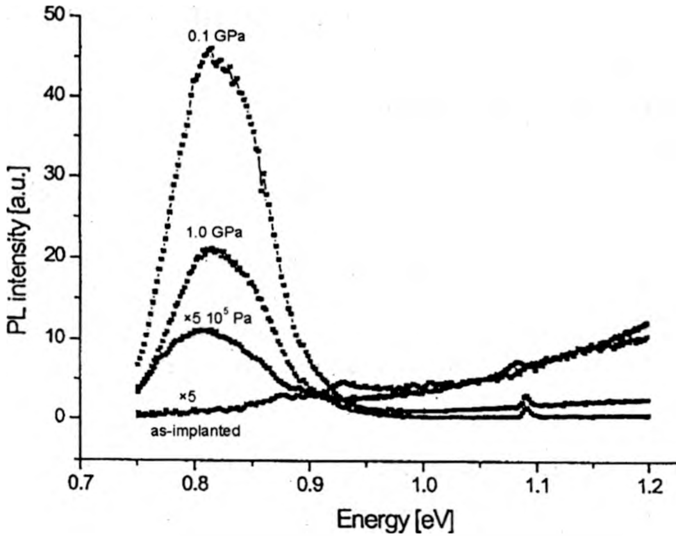

Fig. 5. PL spectra of sample D (see the Table), as-implanted and annealed/treated at 1230 K under 10^5 Pa, 0.1 GPa and 1 GPa for 5 h.

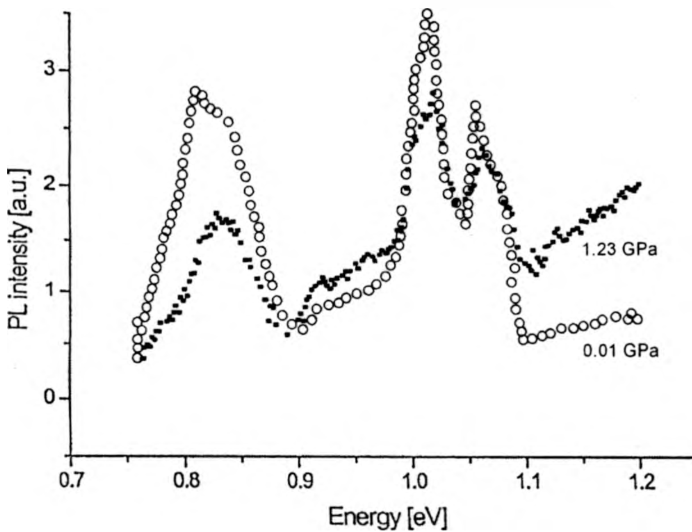

Fig. 6. PL spectra of sample B (see the Table) treated at 1570 K under 0.01 GPa and 1.23 GPa for 5 h.

case of bulk Cz-Si (Cz-Si always contains some oxygen admixture), the HT–HP induced formation of silicon oxide precipitates has been reported to occur in the whole sample volume [10]. Those clusters and precipitates can be also PL-active. Still, because of rather low interstitial oxygen content in the Cz-Si-containing samples ($\leqslant 7.5\times10^{17}$ cm^{-3}) used in this work to prepare Si:O, the formation of bigger precipitates within the Si matrix, with extended SiO_2/Si interface, was less

probable. The smaller oxygen-containing clusters, formed at HT–HP and exhibiting the non-radiative recombination activity, were present in all sample volume.

3.1. Effect of HT–HP on Si:O prepared by oxygen implantation with $D = 1\times10^{15} - 1\times10^{17}$ cm^{-2}

Typical TEM images of the annealed and of HT–HP treated Si:O samples ($D = 1\times10^{16}$ cm^{-2}) are presented in Fig. 1.

Annealing at 1230–1400 K of the Cz-Si:O samples, prepared by implantation with D within the range $1\times10^{15} - 1\times10^{17}$ cm^{-2}, under 10^5 Pa for 5 h, resulted in the creation of small, cluster-like SiO_{2-x} precipitates. Numerous dislocations detected by TEM (Fig. 1**a**) are nucleated at the badly defined Si/oxide precipitate interface (see also [4], [5]).

The treatment of the sample B (see the Table) at 1400 K under 1.2 GPa for 5 h resulted in the creation of pillow-like SiO_{2-x} precipitates of almost equal, of about 10 nm, dimensions while no dislocations were detected (Fig. 1**b**). It means that the misfit between the precipitate and matrix materials was not big enough to result in the formation of dislocations at HT–HP. The same effect was reported for Si:O ($D = 1\times10^{16}$ cm^{-2}) treated at 1470 K and 1550 K under 1.5 GPa for 1 h [4], [5] but not for that treated at 1230 K under 1 GPa for 5 h [8].

The annealing and HT–HP treatment of the Si:O samples prepared by oxygen implantation with the higher oxygen dose ($D = 1\times10^{17}$ cm^{-2}) also cause creation of dispersed oxide precipitates, while the formation of dislocations was partially suppressed as a result of the treatment at 1400 K-HP [5].

All investigated Si:O samples, prepared by implantation with $D \leqslant 1\times10^{17}$ cm^{-2}, show the presence of distinct PL peak at about 0.81 eV (Fig. 3) after the treatment at 1230 K under 1 GPa for 5 h. For the Si:O samples A and B, prepared by the relatively low-dose oxygen implantation, the PL peak shows the presence of dislocations (D1 dislocation-related peak at 0.81 eV [3]). This peak was shifted to a higher energy for the similarly treated sample D; its intensity decreased with increasing HP.

It follows that dislocations were present near the SiO_2/Si interface of the Si:O samples annealed/HT–HP treated at 1230 K (see also [8]). The concentration of dislocations increased with D for the low-dose oxygen implanted samples (samples A–C), with Si oxide platelets randomly distributed in the Si matrix near oxygen ion range R_p (Fig. 1, the Table).

The effect of HP on PL from the sample B treated at 1270 K under HP for 5 h is presented in Fig. 4. Intensity of dislocation-related PL at 0.81 eV was the lowest for Si:O, HT–HP treated under 1.2 GPa. The PL peak at 1.09 eV was absent, contrary to the case of sample B treated under 0.6 GPa.

The treatment at 1400 K under 1.2 GPa for 5 h also resulted in a strongly decreased intensity or even in an absence of PL at 0.81 eV. That last peak was recognizable for the samples A–C annealed at 1400 K at atmospheric pressure (10^5 Pa) or at 0.1 GPa (compare [2], [3]). The PL peak at 1.09 eV was almost unrecognizable for the Si:O samples implanted with low D (samples A–C) confirming high concentration of

non-radiative recombination centres present in those samples. Their presence can just explain the absence of the PL peak at about 1.09 eV, related to the band-to-band transition.

The wide but very weak PL band detected at 0.75–0.88 eV for the samples B and C treated at 1400 K under 1.2 GPa resembles the one reported for the SIMOX structures annealed at 1570 K under 10^5 Pa [11]. Supposedly it is related to some point-like defects [12] induced by the implantation followed by annealing under HP.

The HT–HP treatment of the samples C at 1570 K for 5 h resulted in the presence of the D1 dislocation-related lines superposed with the D5 lines at 0.826 eV [13]; the intensities of the D1 lines decrease with HP (Fig. 6). Those samples show also the presence of PL lines at 1.02 eV and 1.07 eV. The line at 1.02 eV can be related to the presence of small interstitial clusters (W band [14]), while the origin of the PL line at about 1.07 eV is not yet known.

More numerous, but smaller SiO_{2-x} agglomerates are created in the HT–HP treated Si:O samples prepared by implantation with $D \leqslant 1\times10^{17}$ cm^{-2}. The reason was a larger number of nucleation centres for the precipitate growth, while oxygen diffusivity decreased with HP. The HT–HP treated Si:O samples showed the presence of oxide precipitates, while the creation of other extended defects (dislocations, stacking faults) was suppressed because of HP-induced decrease of misfit at the SiO_{2-x}/Si interface.

3.2. Effect of HT–HP on Si:O prepared by oxygen implantation with $D = 6\times10^{17}$ and 2×10^{18} cm^{-2} (SIMOX-like structures) and on reference SOI samples

Typical TEM images of the HT–HP treated Si:O ($D = 6\times10^{17}$ cm^{-2}) and SOI samples are presented in Fig. 2.

The HT–HP treatment of such (higher oxygen dose) Si:O samples (sample E, the Table) at 1400 K under 1.2 GPa for 5 h resulted in the formation of a continuous buried partially amorphous SiO_2 layer containing numerous silicon inclusions, while small dislocation loops were detected at the bottom of SiO_2/Si interface [9]. No threading dislocations were observed at the top, near-surface Si layer.

The SiO_2/Si interface of the sample D (Fig. 2**a**), prepared by oxygen implantation with $D = 6\times10^{17}$ cm^{-2} (the Table) and treated at 1570 K under 1.23 GPa, was waved. Below the bottom interface a brighter area was separated by a darker one. No defects were present in this area. The brighter contrast below the oxide layer could be considered as an evidence of changed stoichiometry in this area, similarly to that in the diffused areas. Strongly defected layer, approximately 100 nm thick, was visible above the 150 nm thick SiO_2 layer. This layer consisted of dislocation half-loops starting from the top of the SiO_2/Si interface. These dislocations glided on the interface due to stress in the Si layer above the SiO_2/Si interface. The expansion of dislocation half-loops resulted in released stresses; no dislocations were detected above the defected sub-surface buried layer.

Both the top and bottom interfaces of SiO_2 layer in the SOI structure treated at 1570 K under 1.23 GPa for 5 h remained to be flat (Fig. 2**b**). No lattice defects were observed both at and near the top and bottom SiO_2/Si interfaces.

The SIMOX-like structure prepared by the treatment of the sample E at 1230 K under 1.01 GPa for 5 h showed the presence of the weak, wide PL peak at 0.80–0.86 eV, while strong band-to-band transition at about 1.09 eV was also detected, confirming structural perfection of that sample. That last peak at 1.09 eV, but of much decreased intensity, was detected also for the samples B and D but not for the sample A (Fig. 3). The concentration of dislocations decreased with *D* for the SIMOX-like samples D and E, with continuous buried oxide layer (Fig. 2). The area of the SiO_2/Si interface in such samples was comparatively low because no dispersed precipitates with extended SiO_2/Si interface were created.

No PL peaks at 0.81 eV were detected for the reference SOI samples (with the smallest relative areas of SiO_2/Si interface) if treated at the same HT–HP conditions.

The effect of HP on the PL peak intensity of the sample D with a semi-continuous (SIMOX-like) buried oxide layer (Fig. 2**a**) is presented in Fig. 5. The as-implanted sample showed no marked PL peaks, while that annealed at 1230 K under atmospheric pressure disclosed a very weak wide PL at about 0.81 eV. One can suppose that both those samples contained the non-radiative recombination centres in a high concentration, introduced as a results of implantation. Their presence results in quenching of PL at 1.09 eV. The treatment at 1230 K under 0.1 GPa resulted, however, in strong dislocation-related PL; it was of the lower intensity for that sample HT–HP treated under 1.01 GPa.

The treatment at 1400 K under 1.2 GPa for 5 h also resulted in a strongly decreased intensity or even in an absence of PL at 0.81 eV. That last peak was recognizable for the D samples annealed at 1400 K at atmospheric pressure (10^5 Pa) or at 0.1 GPa (compare [2], [3]). The presence of the weak PL peak at about 1.02 eV was also detected in the case of D samples treated at 1400 K under 0.1 and 0.6 GPa. The relative intensity of the PL peak at 1.09 eV increased with HP for the D samples.

The treatment at 1400 K under HP of the samples E and SOI (the last one with well-defined buried oxide layer) resulted in PL at about 1.09 eV confirming their high structural perfection.

The samples E treated at 1570 K under 1.23 GPa showed the presence of superposed D1 and D5 dislocation-related PL lines; no PL at 1.09 eV was detected [9]. An absence of the PL peak at about 1.09 eV, as well as of other PL peaks, was stated for the SOI reference samples treated at 1570 K under 0.01–1.23 GPa for 5 h.

It is known that annealing and the HT–HP treatment of the oxygen-implanted Si samples at about 1570 K results in out-diffusion of oxygen atoms to the sample surface, as well as in their diffusion into deeper sample area [8]. At cooling those oxygen atoms precipitate and create small oxygen clusters. Some of them act as the non-radiative recombination centres responsible for quenching the photoluminescence at 1.09 eV. Therefore, the presence of PL lines at 1.02 eV and 1.07 eV in the low oxygen dose implanted Si:O samples (*e.g.*, samples C, the Table) can be considered as an evidence of the formation of such defects.

The as-implanted Si:O sample consists of the bulk of perfect crystallinity, thin disturbed layer containing most implanted oxygen atoms and of the top Si layer with

implantation-induced damages. An increase in D is related to an increased energy introduced by the implanted oxygen atoms into the Si host lattice and so to more pronounced structural disturbances.

In the samples D and E, implanted with $D = 6\times10^{17}$ cm^{-2} and $D = 2\times10^{18}$ cm^{-2}, the semi-continuous or continuous oxide layer was created even at comparatively low temperature (1230 K). As it follows from PL measurements, the structural perfection of the SiO_2/Si interface in such samples was improving with HT and HP, also because of the HT–HP induced changes (decrease) of the misfit at the SiO_2/Si interface. Similarly as in the case of Si:O prepared by low dose implantation, the mentioned misfit was tuned at HT–HP to the values below the critical one for the creation of the misfit dislocations.

Enhanced solubility of oxygen in Si at $\geqslant$ 1400 K seems to exert a marked effect on the Si:O samples prepared by oxygen implantation with $D \geqslant 6\times10^{17}$ cm^{-2} (samples D and E), as well on the reference SOI samples. The treatment at 1570 K under HP resulted in out-diffusion of implanted oxygen atoms from the areas near R_p and/or in dissolution of the silicon oxide clusters/precipitates formed at the initial stages of the HT–HP treatment. Numerous oxygen-containing defects acting as non-radiative recombination centres were created in such samples at cooling because oxygen solubility in Si decreases with decreasing temperature, so the "excessive" oxygen atoms, introduced into the Si lattice at HT–HP, create just such oxygen clusters and precipitates at releasing HT and HP to ambient conditions.

4. Summary and conclusions

Two different groups of the HT–HP treated Si:O samples were investigated: those with $D = 1\times10^{17}$ cm^{-2} (samples A, B and C in the Table) and those with $D \geqslant 6\times10^{17}$ cm^{-2} (samples D, E and reference SOI). While, at the HT–HP conditions, the "individual" silicon dioxide agglomerates were created in the Si:O samples belonging to the first group, the continuous (sample E) or semi-continuous (sample D) buried SiO_2 layer was created in the samples belonging to the second group or it existed from the very beginning in the reference SOI samples.

Some effects related to enhanced HP during the sample treatment were, however, common for the both mentioned groups. This observation suggests the similar mechanism of the sample structure changes induced by the treatment under HP. In particular, no or less dislocations were detected in the samples treated at 1400 K under very high HP or their presence was limited to the oxygen precipitate/buried layer interfaces with the Si matrix.

The below mentioned factors seem to be responsible for the HT–HP induced effects in Si:O and SIMOX structures:

– The oxygen-containing layer was highly disturbed just after implantation. During annealing at atmospheric pressure or the HT–HP treatment, the oxygen-containing agglomerates, in fact of the sub-stoichiometric, SiO_{2-x} composition, are created, mostly within the volume of implantation-disturbed layer. It is known that, at HT–HP,

numerous structural irregularities are active as the nucleation centres for further growth of larger amorphous silicon oxide agglomerates [15].

– The oxygen diffusion rate seems to decrease with HP [16]; still, at the highest temperatures used (1570 K), oxygen out-diffuses to the sample surface and to the sample depth.

– The misfit at the SiO_{2-x}/Si interface decreases with HP [1], [16].

The role of the above mentioned factors is also dependent on the initial sample features (implantation conditions) as well as on the HT–HP treatment conditions.

A detailed explanation of all observations demands future studies, so at present only qualitative explanation of some HT–HP induced effects in the Si:O and related (SOI) structures has been given.

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