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PRESSURE-INDUCED TRANSFORMATIONS DURING ANNEALING OF SILICON IMPLANTED WITH OXYGEN

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Enhanced hydrostatic pressure (HP, up to 1.5 GPa) applied during annealing at up to 1570 K (HT) of silicon with oxygen introduced by implantation (Si:O), exerts pronounced effect on the transformation of oxygen admixture. In particular, HP affects the microstructure of Si:O and a creation of oxygen-enriched (for implanted oxygen dose, $D \leq 1 \cdot 10^{17}$ cm^{-2}) or continuous (for $D \geq 6 \cdot 10^{17}$ cm^{-2}) buried SiO_2 layers. Numerous treatment parameters contribute to the HP-induced phenomena in processed Si:O, among these are the HP-affected mobility and solubility of implanted oxygen as well as of silicon interstitials and of other implantation-induced defects and so the stability of oxygen clusters/precipitates; the misfit at the SiO_2/Si boundary is tuned by HP.

1. Introduction

Single crystalline silicon grown by the Czochralski method (Cz-Si) is the most important semiconductor used to produce integrated circuits (IC's). Cz-Si contains oxygen admixture in a concentration (c_O) up to above $1 \cdot 10^{18}$ cm^{-3}. This oxygen originates from SiO_2 crucibles in which Si melts at about 1685 K under 10^5 Pa. Oxygen is incorporated into Si mainly in the form of oxygen interstitials (O_i's). Part of oxygen is involved in a creation of complexes/clusters during growth or cooling the Cz-Si rods. Silicon interstitials (Si_i's) and vacancies (V's) are also involved in growth and transformations of oxygen-related defects in processed Cz-Si [1].

Other kinds of silicon single crystals, grown by the floating zone method (Fz-Si), with much lower oxygen content ($c_O < 1 \cdot 10^{17}$ cm^{-3}), are also used to produce IC's as well as another microelectronic devices.

During processing of Cz-Si under 10^5 Pa at enhanced temperature (*HT*), O_i's are subjected to transformations. At *HT*, when oxygen atoms become suffi-

ciently mobile, progressive clustering/precipitation of O_i's occurs, being dependent on c_O, temperature and time (t) of processing, on the sequence of annealing steps, etc.

Implantation of oxygen into Cz-Si or Fz-Si, to produce oxygen-implanted silicon (Si:O), is widely applied to produce silicon-on-insulator (SOI) structures by the SIMOX method. Transformations of oxygen admixture in Si:O at *HT* remind these in Cz-Si. However, important differences exist, among them are the following: a) in effect of O_2^+ implantation even with low dozes ($D \geq 10^{13}$ cm^{-2}) and low energies (E, in the tenths of keV range), the structural perfection of Si matrix becomes strongly worsened; partially or fully amorphized silicon (*a*-Si), is created, especially near the O_2^+ projected range (R_p), and b) local oxygen concentration near R_p can reach, depending on D and E, tenths of atomic percents.

Annealing of Si:O at sufficiently high temperature leads first of all to restoration of the structural perfection of the Si lattice [2] by solid phase epitaxial growth (SPEG). Depending mostly on D and annealing temperature, spatially resolved SiO_{2-x} precipitates or even buried continuous BOX (buried silicon dioxide) layers of dose-dependent composition and structural quality are created [3].

2. Fundamentals

Hydrostatic pressure (*HP*) up to about 1.5 GPa, applied in our research, is about eight times lower than that resulting in the phase transformations of Si (*HP* > 11 GPa) while it is of the same order as the stresses in the typical Si–O systems applied in microelectronics (e.g. at the SiO_{2-x} precipitate/Si matrix boundary). The temperature-induced oxygen clustering and precipitation are concomitant with stress [4,5], e.g. at the SiO_{2-x} precipitate/Si matrix boundary (chemical composition of silicon oxide forming precipitates is not stoichiometric, especially in the case of small clusters with hardly defined boundaries). This stress is related first of all to a larger volume of SiO_{2-x} (in comparison to that of the host Si atoms) formed by clustering oxygen. Other reason for internal stress is the difference in the thermal expansion coefficients of SiO_{2-x} [5] and of Si (*a*-Si in the case of Si:O).

This stress can be changed in the case of processing under enhanced *HP* of ambient or of annealing under *HP* (*HT–HP* treatment) [6,7]. In effect of the *HP–HT* treatment of Cz-Si with previously created oxygen precipitates, the misfit (ε) and so the shear stress at the SiO_{2-x}/Si boundary are changing; the same concerns processed Si:O.

The shear stress and so the misfit (ε) at the SiO_{2-x} precipitate/Si (or *a*-Si) matrix boundary are affected [7–9] by *HT* and *HP*, exerted by ambient, in accordance with

$$\varepsilon = \varepsilon_0 + \frac{3K_{SiO_{2-x}}}{K_{SiO_{2-x}} + 4G_{Si(a\text{-}Si)}} \times$$

$$\times \left[\Delta HT \left(\beta_{SiO_{2-x}} - \beta_{Si(a\text{-}Si)} \right) + HP \left(1/K_{Si(a\text{-}Si)} - 1/K_{SiO_{2-x}} \right) \right], \qquad (1)$$

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

It means that the shear stress at the SiO_{2-x}/Si (a-Si) boundary is changing (typically decreases) with HT and HP (for the case of Si–SiO_2, according to [4,9], at 295 K: $K_{Si} = 9.8\cdot10^{10}$ Pa; $K_{SiO_2} = 4\cdot10^{10}$ Pa; $\beta_{Si} \approx 1.3\cdot10^{-5}$ K^{-1}; $\beta_{SiO_2} \approx 0.16\cdot10^{-5}$ K^{-1}; $G_{Si} = 6.8\cdot10^{10}$ Pa). 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 $-2.4\cdot10^{-3}$ [10]. However, the values of K, G and β are dependent on the kind of material (e.g. Si or a-Si, stoichiometry of SiO_{2-x}, etc), on temperature and pressure. These dependencies are not well known, especially for high temperatures and pressures. Still, the critical misfit value (ε_{cr}) for a creation of extended defects (dislocations) at the SiO_2/Si boundary (for the SiO_2/Si system), can be estimated as close to $1\cdot10^{-3}$ [11]; this value is also dependent on the precipitate dimension. Enhanced hydrostatic pressure induces $\Delta\varepsilon$ just within this range and so affects generation of the misfit-induced defects (such as dislocations) at the oxygen precipitate/Si (a-Si) matrix boundary.

The HP-induced effect on the misfit value is quite strong if compared to the HT-induced changes. For the case of spherical SiO_2 precipitates embedded in the Si matrix, the equivalent (in respect of induced $\Delta\varepsilon$) magnitudes of HT and HP can be estimated [5] from:

$$\Delta HT \sim \Delta HP\left(1/K_{Si} - 1/K_{SiO_2}\right)\Big/\left(\beta_{SiO_2} - \beta_{Si}\right). \qquad (2)$$

In respect of the induced misfit and so of shear stress at the SiO_2/Si boundary, the effect of $\Delta HP \approx 1$ GPa is equivalent to ΔHT of about 1300 K.

«Additional» defects (for example, dislocations) at the SiO_{2-x}/Si boundary are created if the misfit at this boundary reaches the critical value for a creation of particular kind of defect. As follows from eq. (1), the ε value decreases with HT and HP for the Si matrix containing oxide clusters and precipitates (exerting compressive internal stress on the matrix at ambient conditions), so (under not too high HP) less numerous dislocations should be created in Cz-Si or in recrystallized Si in the case of Si:O treated under HT–HP.

As mentioned, creation of dislocations and of other defects at the SiO_{2-x}/Si boundary in Cz-Si or in Si:O during annealing or HT–HP treatment is dependent also on the dimension of SiO_{2-x} clusters/precipitates (less probable for small clusters [11]) and on their stoichiometry (more probable for precipitates composed of stoichiometric SiO_2, while less – for clusters of substoichiometric composition).

Enhanced HP during annealing affects also the kind and number of nucleation sites (NC's) for clustering/precipitation of O_i, the rate of diffusion (mobility) of O_i

as well as diffusivity and stability of Si$_i$'s and of vacancies created or involved into the transformations of oxygen admixture.

Dependence of the diffusion coefficient of oxygen in silicon, D, on activation energy, E_a, and on pre-exponential factor, D_0, is described by the well-known equation:

$$D = D_0 \exp(-E_a/kT). \tag{3}$$

Based on DLTS study of the dissolution of oxygen clusters/precipitates under *HP* at 1230–1550 K, it has been concluded [12] that D in single-crystalline Si decreases by a factor of two if *HP* increases from 0.01 to 1 GPa. This effect has been explained assuming that oxygen diffuses in the form of connected pairs of oxygen atom and of Si$_i$.

Oxygen atoms are not distributed uniformly in Si:O; even in as-grown Cz-Si they create cloud-like irregularities resembling small oxygen clusters. At *HT–HP* such irregularities can act as the nucleation centres for oxygen precipitation in Cz-Si or Si:O.

Pressure exerted upon the Si matrix affects the concentration of interstitials to a considerable extent [13]. While *HP* acts on bulk silicon, the formation enthalpy of interstitials increases by *HP* ΔV_I (where V_I is the value of the elastic volume expansion susceptible to the *HP* effect on Si$_i$). Therefore, under *HP*, the concentration of silicon interstitials, $C_{\mathrm{Si}_i(HP)}$, can be formulated as:

$$C_{\mathrm{Si}_i(HP)} = C_{\mathrm{Si}_i(HP=0)} \exp(-HP\Delta V_I / k_B HT), \tag{4}$$

where $C_{\mathrm{Si}_i(HP=0)}$ is the concentration of Si$_i$'s under 10^5 Pa (no external pressure applied). It means that the concentration of Si$_i$ decreases under *HP*.

The formation energy (E_V) for a vacancy in silicon equals ~ 3 eV under 10^5 Pa. E_V decreases almost linearly with pressure, by 1 eV for *HP* = 5 GPa [14]. Similar estimations were reported for a silicon divacancy (V_2). A pressure reduces the V_2 formation energy by about 1.2 eV, from 4.2 eV at 10^5 Pa to 3 eV at 5 GPa. It means that pressure exerts a relatively strong effect on vacancy formation in Si; this is consistent with the reported effect of compressive stress on the dopant-vacancy diffusion in silicon [15]. A decrease in the V and V_2 formation energies under *HP* can be attributed to reduced distances between Si atoms.

It is generally accepted that Si$_i$ in Si diffuses much faster than vacancy [16]. Diffusivity of dopant-interstitial pairs in a compressive medium decreases, while that of dopant-vacancy pairs increases.

The formation of clusters of few oxygen and silicon atoms represents the first stage of oxygen precipitation in crystalline or amorphous silicon [17]. Such clusters can either grow or dissolve depending on their dimension, oxygen concentration, temperature and so on. The most important parameter for nucleation of clusters is the temperature dependent degree of oxygen supersaturation defined as the ratio between the actual concentration of interstitial oxygen and its solubility limit (c_{Ol}) defined as:

$$c_{Ol} = F \exp(-\Delta H_s/kT), \tag{5}$$

where F is the constant equal to $9 \cdot 10^{22}$ cm^{-3} and $\Delta H_s = 1.52$ eV is the dissolution enthalpy.

Nucleation occurs in the regions where few O$_i$'s are close to each other (homogeneous nucleation) or at lattice defects (heterogeneous nucleation). Just homogeneous nucleation plays the most important role in the case of Cz-Si processed for microelectronic applications.

A very important parameter is the critical radius (r_c) of NC, i.e. the limiting value for sufficiently large NC to grow further upon annealing. Those NC's with $r < r_c$ will dissolve in the Si matrix while the larger ones grow further.

The r_c value increases rapidly with temperature, especially for $HT/HT_s^p > 0.7$ (HT_s^p means processing temperature at which all available oxygen will be fully dissolved in the matrix).

The critical radius of oxygen precipitates in Si depends on numerous parameters [13,18]:

$$r_c = 2\sigma \left\{ \left[(1 + \delta - \Phi)^3 x k_B HT / V_{HP} \right] \ln \left[c_O / c_O^* (c_V / c_V^*)^\beta \left(C_{Si_i}^* / C_{Si_i} \right)^\gamma \right] \right\}^{-1} , \quad (6)$$

where c_O, c_V, and C_{Si_i} are the concentrations of O$_i$'s, V's and of Si$_i$'s in the silicon crystal; the same symbols but with asterisk mean the equilibrium concentrations of O$_i$'s, V's and of Si$_i$'s, respectively; k_B means the Boltzmann constant; σ − the interfacial energy per unit area; δ − the linear misfit between the silicon lattice and SiO$_{2-x}$ precipitate; Φ − the constrained strain; V_{HP} − the volume of SiO$_{2-x}$ precipitate; x − the number of oxygen atoms in SiO$_{2-x}$ precipitate; β − the number of absorbed V's, and γ − the number of injected Si$_i$'s.

Based on eq. (6) one can conclude that decreased concentration of Si$_i$'s leads to the reduced value of r_c. This would mean that smaller oxygen clusters or precipitates are expected to be generated in Cz-Si/Si:O if treated under HP and that these clusters can be more stable under HT–HP [19].

While it is clear that HP influences a lot of Si (Si:O) parameters (such as c_{Ol}, c_O^*, $C_{Si_i}^*$ and c_V^*), affecting in turn the r_c value, no analytical expression explaining the dependence of r_c on HP has been proposed as so far (the quantitative data are difficult to be extracted from eq. (6) also because the knowledge concerning the values of numerous parameters in this equation and of their dependence on HP, HT is lacking).

In the case of comparatively large oxygen precipitates, the misfit at the defect/matrix boundary can reach the critical value for a creation of a defect of particular kind, so defects (dislocations, for example) are created at the SiO$_{2-x}$/Si boundary. The ε value decreases with HT and HP for Si (Si:O) containing oxide clusters exerting compressive internal stress on the matrix at ambient conditions, so less dislocations are usually created in Cz-Si treated at HT–HP.

3. Experimental details

To prepare Si:O, the 001 or 111 oriented Cz-Si or Fz-Si wafers were implanted with O_2^+ ($D \leq 2 \cdot 10^{18}$ cm^{-2}, $E \leq 200$ keV).

The Si:O samples were subjected to *HT–HP* treatments at up to 1570 K under *HP* up to 1.5 GPa in argon atmosphere, usually for up to 5 h in a specially designed high temperature–high pressure apparatus [20]. Sample cooling, from *HT* to about 500 K, lasted for about 10 min.

Distribution of implanted oxygen in processed Si:O was determined by secondary ions mass spectrometry (SIMS). Defects produced in Si:O at processing were revealed by transmission electron microscopy (TEM). Photoluminescence (PL) spectra were recorded at liquid helium temperatures using Ar laser excitation ($\lambda_{ex} = 488$ nm).

4. Results and discussion

The effects of *HT–HP* treatment on Si:O are of interest for microelectronics. This follows from the recently reported decreased formation of dislocations in Si:O annealed under *HP* within the specific *HT* ranges, in comparison to the case of annealing under 10^5 Pa [21]. Just dislocations exert most detrimental effect on the SOI structures, especially on SOI produced by oxygen implantation (the SIMOX structures).

In spite of considerable research effort [22–30], the understanding of the *HT–HP* induced effects in Si:O is still far from being complete.

Impact of the *HT–HP* treatment on Si:O is dependent on the numerous implantation − (mainly on *D* and *E*) and treatment-related parameters (*HT*, *HP* and *t*) [23–29]. Most important is, however, the dose of implanted oxygen atoms. Below presented results concern two most typical kinds of Si:O. The first one is represented by Si:O prepared by implantation with $D \leq 1 \cdot 10^{17}$ cm^{-2}, with spatially resolved SiO$_{2-x}$ precipitates formed in effect of post-implantation processing and the second one − by Si:O with semicontinuous or continuous SiO$_{2-x}$ layer created in effect of processing (the case of Si:O prepared by implantation with $D \geq 6 \cdot 10^{17}$ cm^{-2}). The effect of *HT–HP* processing on SOI with well defined BOX layers is also presented.

4.1. Effect of HT–HP treatment on Si:O prepared by low dose implantation

Individual SiO$_{2-x}$ precipitates embedded in the Si matrix are created at processing of Si:O prepared by oxygen implantation with comparatively low O_2^+ doses (for the case of $D \leq 1 \cdot 10^{17}$ cm^{-2}) [20,22,24,26,27,29–34].

Annealing of Si:O ($D \leq 1 \cdot 10^{17}$ cm^{-2}) at 1230–1400 K under 10^5 Pa leads to a creation of numerous extended defects (dislocations), originating from stress exerted by SiO$_{2-x}$ precipitates on the Si matrix. The presence of dislocations is evidenced by TEM observations (Fig. 1,*b*) and by detection of the dislocation related PL peaks, among them the D1 peak at about 0.81 eV for annealed/*HT–HP* treated Si:O (Fig. 2).
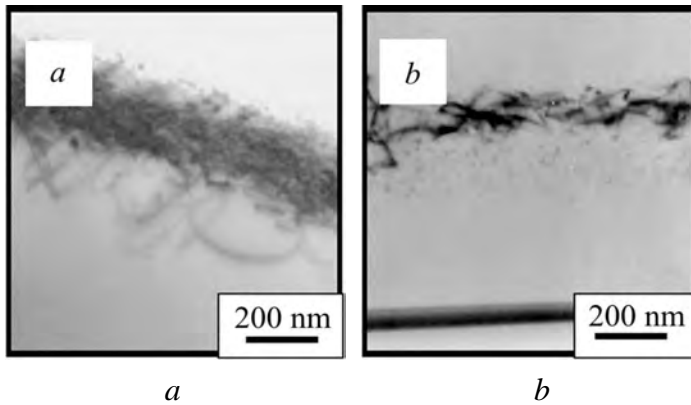
Fig. 1. TEM images of 001 oriented Cz-Si:O ($E =$ $= 200$ keV, $D = 1 \cdot 10^{16}$ cm^{-2}), annealed/treated for 5 h at 1230 K under 1.02 GPa (*a*) and for 10 h at 1400 K under 10^5 Pa (*b*)
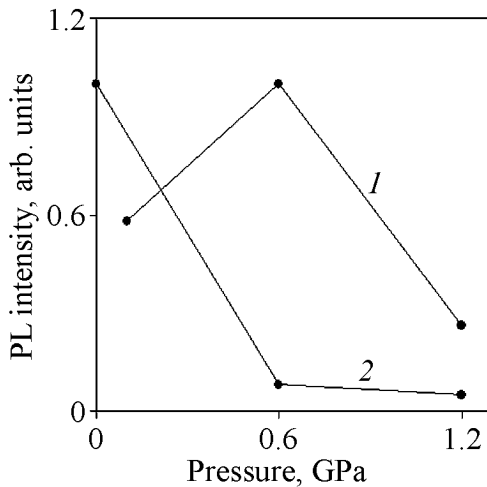
Fig. 2. Relative intensity of *D*1 dislocation-related PL line at 0.81 eV for 001 oriented Cz-Si:O ($E = 200$ keV, $D =$ $1 \cdot 10^{16}$ cm^{-2}), processed for 5 h at 1270 K (*1*) and 1400 K (*2*) under different *HP* up to 1.2 GPa

This means that the misfit at the SiO$_{2-x}$/Si boundary reaches the critical value for a creation of dislocations at SiO$_{2-x}$ precipitates with radii exceeding the critical r_c value (compare eqs (1) and (6)). While just this mechanism of a creation of dislocations seems to be the most important in the considered case, it is not the unique explanation of the effects observed. Other mechanism of a creation of extended defects (such as stacking faults, SF's) in Si:O at annealing/*HT–HP* treatment is related to the condensation of nonequilibrium silicon interstitials emitted during growth of SiO$_{2-x}$ into the Si bulk.

As follows from TEM images, the treatment under *HP* at about 1270 K of Si:O prepared by oxygen implantation with $D = 1 \cdot 10^{16}$ cm^{-2} also leads to a creation of dislocations (see Fig. 1,*a*). This is confirmed by the presence of *D*1 peaks at 0.81 eV of comparatively high intensity in the PL spectra of Si:O processed under *HP* (Fig. 2).

In the case of processing at 1400 K, the intensity of these dislocation-related PL lines definitely decreases with *HP* (Fig. 2). This means that the misfit at the SiO$_{2-x}$/Si boundary does not exceed the critical value for producing dislocations for the majority of oxygen precipitates, with the radii still not reaching the critical values.

The same results from TEM data: dislocations are much less numerous in Si:O processed for 5 h at 1400 K under *HP* (Fig. 3).

While about 250 nm thick near-surface zone in Si:O ($D = 1 \cdot 10^{16}$ cm^{-2}) annealed for 10 h at 1400 K under 10^5 Pa contains SiO$_{2-x}$ precipitates and dislocations (see Fig. 1,*b*) located at about 0.5 μm depth, much less or even no dislocations are detected in the case of treatment of these samples at 1400 K under 0.1 GPa and, especially, under 0.6 and 1.2 GPa (compare Fig. 3,*a* with Fig. 3,*b,c*).
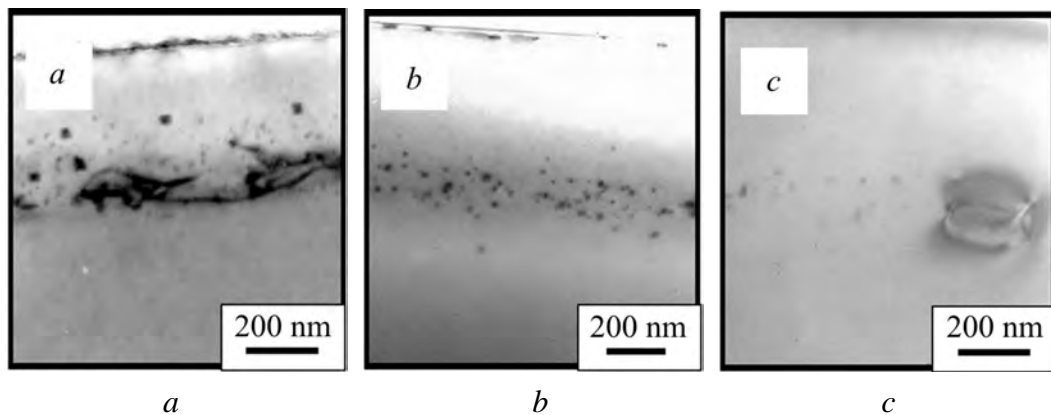
Fig. 3. TEM images of 001 oriented Cz-Si:O (E = 200 keV, D = $1 \cdot 10^{16}$ cm^{-2}), annealed/treated for 5 h at 1400 K under 0.1 GPa (*a*), 0.6 GPa (*b*) and 1.2 GPa (*c*)
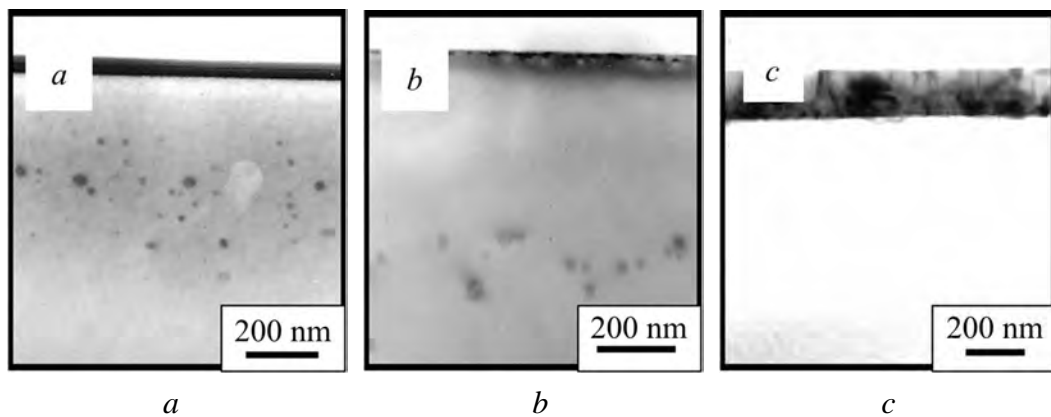
Fig. 4. TEM images of 001 oriented Cz-Si:O (E = 200 keV, D = $1 \cdot 10^{16}$ cm^{-2}), annealed/treated for 1 h at 1470 K under 1 GPa (*a*), under 1.5 GPa (*b*) and for 2 h at 1550 K under 1.5 GPa (*c*)
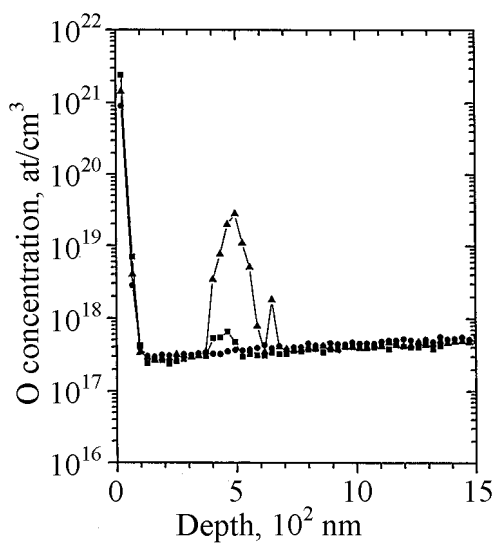
Fig. 5. SIMS depth profile of oxygen in 001 oriented Cz-Si:O (E = 200 keV, D = $1 \cdot 10^{16}$ cm^{-2}), processed for 5 h at 1570 K under 0.01 GPa (−●−), 0.6 GPa (−■−) and 1.2 GPa (−▲−)

Dislocations are practically absent also in the case of Si:O samples (D = $1 \cdot 10^{16}$ cm^{-2}) treated for 1 h at 1470 K under 1 and 1.5 GPa (Fig. 4,*a*,*b*). More prolonged processing produces, however, strongly disturbed area just at the sample surface (Fig. 4,*c*). This is probably related to a very rapid SPEG process at 1550 K producing badly oriented Si crystallites.

At 1400 K and at higher temperatures the implanted oxygen is subjected to partial dissolution in the Si matrix (Figs 3,*c*, 4,*c*), probably entering the interstitial positions (at these conditions the O–Si solid solution becomes undersaturated with oxygen).

As results from the SIMS depth profiles (Fig. 5), the concentration of oxygen near R_p after processing for 5 h at 1570 K is strongly dependent on *HP* [27], evidencing decreased solubility of oxygen in Si under *HP* or/and its decreased diffusivity rate under *HP*. This observation contradicts the conclusions drawn on the basis of theoretical calculations, suggesting rather a linear decrease of the diffusion barrier with *HP* [35].

TEM images of processed Si:O samples containing the 10 times higher amount of implanted oxygen ($D = 1 \cdot 10^{17}$ cm^{-2}) are presented in Fig. 6.

Processing at 1400 K both under 10^5 Pa and 1.2 GPa as well as short time processing at 1550 K under 1.5 GPa results in a presence of dislocations (Fig. 6,a–*c*). In the latter case the dislocation density is comparatively low (Fig. 6,*c*).

Dislocations were not created in the case of Si:O samples ($D = 1 \cdot 10^{17}$ cm^{-2}) treated for 5 h at 1570 K under 0.01 GPa (Fig. 6,*d*). Relatively large oxide precipitates, of up to 0.1 μm dimensions, are detected in Si:O treated at these conditions; numerous dislocation loops are seen in the same samples treated at 1570 K under 1.2 GPa (Fig. 6,*e*).
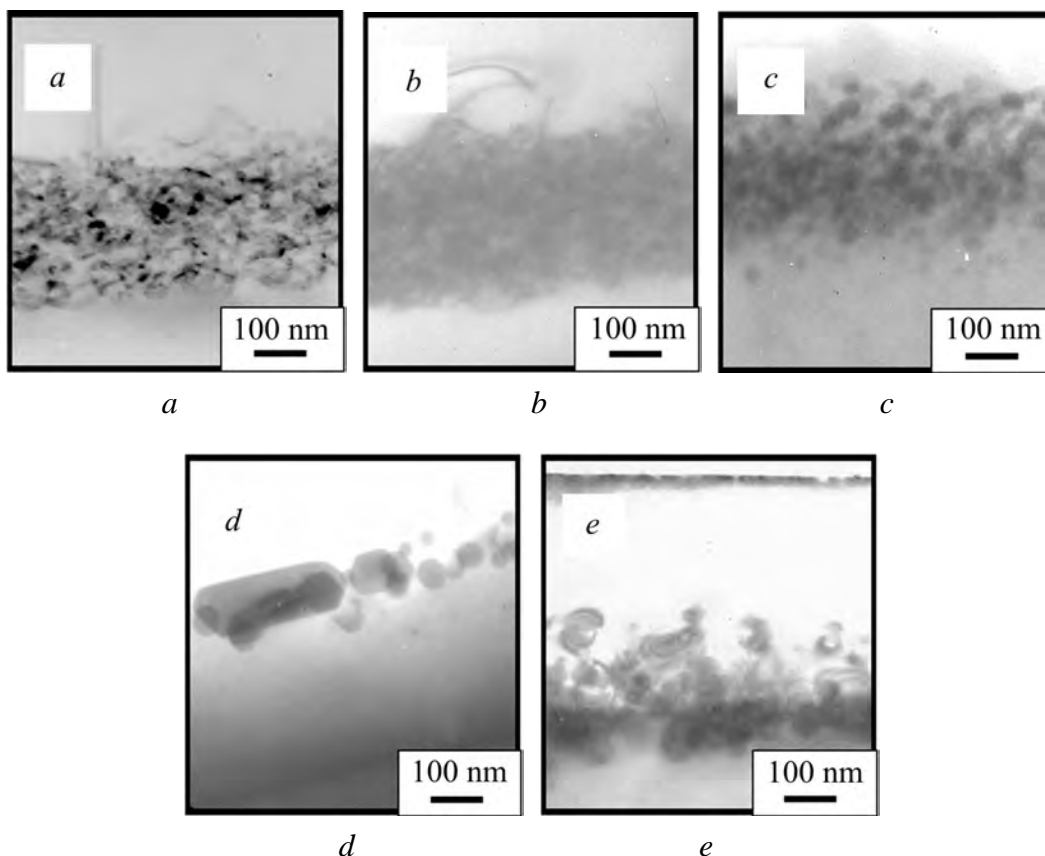
Fig. 6. TEM images of 001 oriented Cz-Si:O ($E = 200$ keV, $D = 1 \cdot 10^{17}$ cm^{-2}), annealed/treated for 5 h at 1400 K under 10^5 Pa (*a*), 1.2 GPa (*b*) and for 15 min at 1550 K under 1.5 GPa (*c*), for 5 h at 1570 K under 0.01 GPa (*d*) and 1.2 GPa (*e*)

The presence of dislocations in the Cz-Si:O sample treated at 1570 K under the highest pressure is most probably caused by the «overcompensation» of the «volume-related» misfit at the precipitate/matrix boundary (dependent on the difference of the relative volumes of Si and SiO_{2-x}) by the «*HP*-related» misfit of the opposite sign [29].

TEM observation concerning the *HP*-related decrease of dislocation density has been confirmed by PL measurements. In Si:O prepared by oxygen implantation with *D* over the $1\cdot10^{16}$–$1\cdot10^{17}$ cm^{-2} range and treated for 5 h at 1400–1470 K under sufficiently high *HP* the intensity of dislocation-related *D*1 peaks at 0.81 eV decreases with *HP* [23]. The treatments at $\leq$ 1400 K–*HP*, as well as at > 1400 K–*HP* but of short duration, result, however, in the presence of dislocations.

The treatment of Si:O at temperatures close to the melting point of silicon results generally in disappearance of dislocation related PL while the PL lines at about 1.1 eV, related to the interband transitions, become detectable. This confirms dissolution of oxygen clusters at so severe treatment conditions.

4.2. Effect of HT–HP treatment on Si:O prepared by high dose implantation

Semicontinuous or continuous SiO_2 layers (often containing Si inclusions) are formed in Si:O prepared by oxygen implantation with sufficiently high doses ($D \geq$ $\geq 2\cdot10^{17}$ cm^{-2}) and subjected to annealing at $\geq$ 1230 K (processing at $\geq$ 1550 K is usually recommended). Some data concerning the effects of *HT–HP* treatment on Si:O prepared by O_2^+ implantation ($D \geq 6\cdot10^{17}$ cm^{-2}) are presented below (see also [23–29,31,32,36–39]).
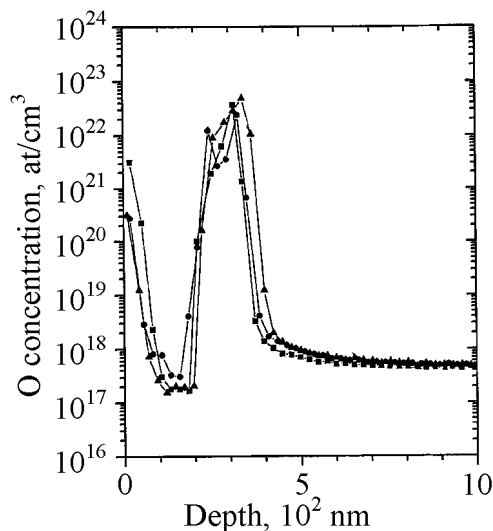

Fig. 7. SIMS depth profile of oxygen in 111 oriented Fz-Si:O (E = 170 keV, D = $= 6\cdot10^{17}$ cm^{-2}), processed for 5 h at 1570 K under 0.01 GPa (–●–), 0.6 GPa (–■–) and 1.2 GPa (–▲–)

The as-implanted Fz-Si:O samples ($D = 6\cdot10^{17} cm^{-2}$, E = 170 keV) indicated no PL peaks. Annealing of Fz-Si:O at 1230 K under 10^5 Pa results in weak dislocation-related PL at about 0.81 eV. The concentration of dislocations increases with pressure in the case of *HT–HP* treatment at 1230 K; this increase is not linear with respect to *HP* [26]. Numerous nonradiative recombination centers are created in heavily oxygen implanted Si:O annealed/treated at < 1230 K. Annealing at 1470 K under 10^5 Pa resulted in rather strong dislocation-related PL at about 0.81 eV; no dislocations were observed after the same treatment but under 1.2 GPa.

The SIMOX-like structure prepared by oxygen implantation into Fz-Si with D = $= 6\cdot10^{17}$ cm^{-2}, E = 170 keV and treated

for 5 h at 1570 K under 10^7 Pa–1.2 GPa, indicates the presence of well-defined buried SiO_2 layers (BOX); their widths are only slightly dependent on HP (Fig. 7).

The microstructure of the buried silicon dioxide layers in such samples remains, however, to be strongly dependent on *HT* and *HP* (Fig. 8).

a

b

c

d
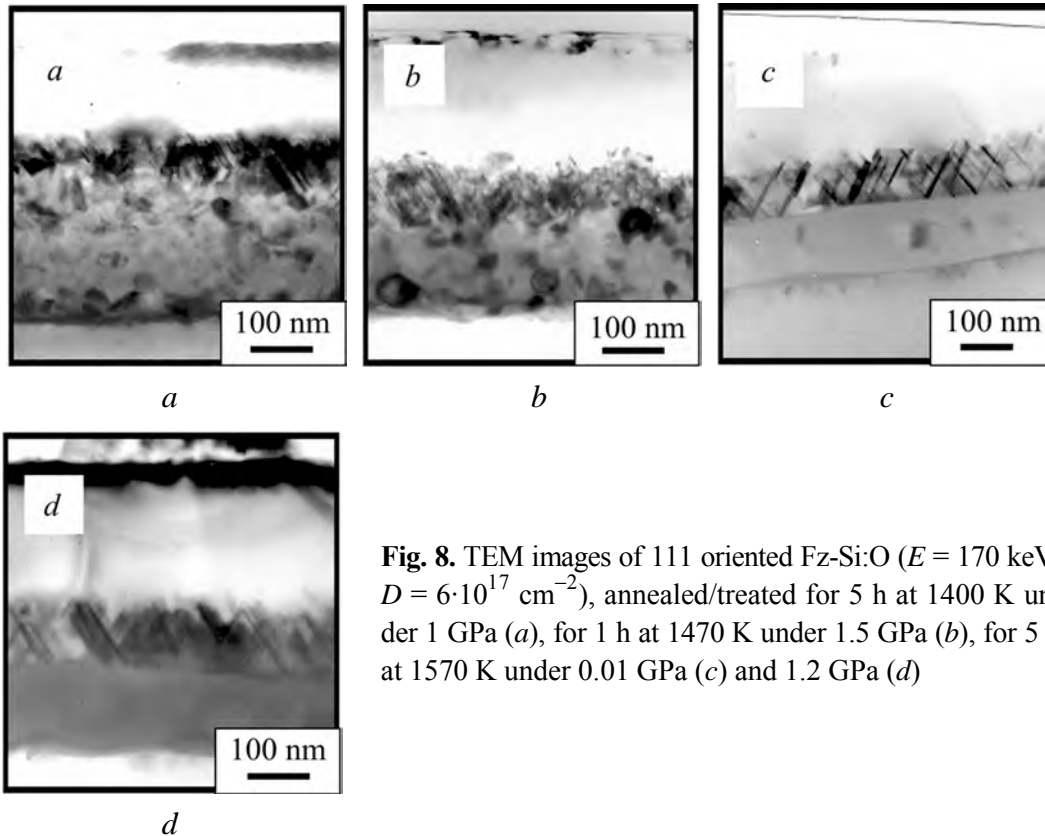
Fig. 8. TEM images of 111 oriented Fz-Si:O (E = 170 keV, D = $6 \cdot 10^{17}$ cm^{-2}), annealed/treated for 5 h at 1400 K under 1 GPa (*a*), for 1 h at 1470 K under 1.5 GPa (*b*), for 5 h at 1570 K under 0.01 GPa (*c*) and 1.2 GPa (*d*)

Processing of Si:O (D = $6 \cdot 10^{17}$ cm^{-2}, E = 170 keV) at 1400–1570 K results in a creation of about 130 nm thick buried SiO_2 layer (Fig. 8). Highly defected near-surface zone of about 100 nm thickness has been created just above the SiO_2/Si interface after processing at 1400–1470 K (Fig. 8,*a,b*). The non-symmetric distribution of defects on both sides of the BOX layers, is evidently related to the worsened, in effect of implantation, perfection of near-surface Si layer, shot through by implanted ions. The treatments at 1570 K but under 0.01 or 1.2 GPa produce the buried SiO_2 layer containing almost no inclusions. However, the 100 nm thick disturbed zone with numerous microtwins is formed near the sample surface (Fig. 8,*c,d*). The short time treatment at slightly different conditions produces the well-defined BOX layer but still with numerous Si inclusions and microtwins created near the surface [28,29].

The treatment at 1230/1400 K under 1.2 GPa of Si:O prepared by even higher dose oxygen implantation (D = $1–2 \cdot 10^{18}$ cm^{-2}, E = 50 keV) leads to a creation of well-defined continuous near-surface SiO_2 layer. Numerous dislocations are created in such samples; their density decreases with *HT*.

Processing of Si:O prepared by oxygen implantation with $D = 1.1 \cdot 10^{18}$ cm^{-2} ($E = 50$ keV) for 5 h at 1400 K under 1.2 GPa produces numerous precipitates of about 20 nm diameter as well as dislocations just below a BOX layer. The treatment of the same sample at 1570 K under 10^7 Pa resulted in a creation of the perfect BOX layer, while crystalline inclusions with propagating microtwins have been detected within the BOX layer in Si:O processed under 1.2 GPa [29].

The microstructure of Si:O prepared by implantation with the highest oxygen doses applied ($D = 2 \cdot 10^{18}$ cm^{-2}, $E = 50$ keV) is also strongly dependent on *HP* and *HT* applied during the treatments.

The treatment at 1230 K under 1.2 GPa produced dislocations propagating to about 0.5 μm depth.

The similar treatment but at 1400 K of the same Si:O ($D = 2 \cdot 10^{18}$ cm^{-2}, $E = 50$ keV) produced almost perfect BOX layer, with some irregularities (precipitates) being still detectable at its bottom surface.

It is interesting to note that the *HT–HP* processing of the SOI structure prepared by bonding (0.5 μm thick Si–0.4 μm thick SiO_2–bulk 001 oriented Si) does not affect the crystallographic perfection of such structure (Fig. 9).
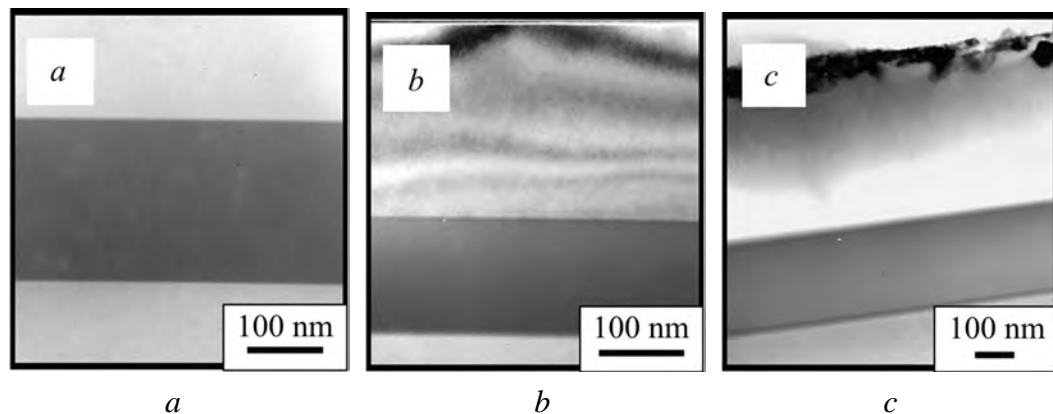
Fig. 9. TEM images of 001 oriented SOI structures, annealed/treated for 5 h at 1570 K under 0.01 GPa (*a*), 0.6 GPa (*b*) 1.2 GPa (*c*)

It follows that, in the case of SIMOX-like structures prepared by implantation, especially with $D \leq 1 \cdot 10^{17}$ cm^{-2}, enhanced *HP* applied at processing affects strongly the process of recrystallization of *a*-Si produced by oxygen implantation and so the creation of buried SiO_2 layer. Well-defined SiO_2 precipitates are created within the implantation-disturbed areas while much less dislocations and of other extended defects are formed at the first stage of the *HT–HP* treatment. Under the highest hydrostatic pressure, equal in our experiments up to about 1.5 GPa, these precipitates remain to be fully or partially isolated even after prolonged processing, so recrystallization of remaining *a*-Si can result in a creation of numerous extended defects (such as microtwins and silicon precipitates), also within the BOX layer.

It is interesting to note that the *HT–HP* treatment of Si:O prepared by oxygen implantation with $D \geq 1 \cdot 10^{18}$ cm^{-2} at low energy ($E \leq 50$ keV) results in PL also in the visible light region, related to the presence of defects, probably of oxygen deficient centers [40].

5. Conclusions

Processing of Si:O and related structures under enhanced hydrostatic pressure results in the specific structural transformations.

The near surface oxygen-enriched layer in Si:O is strongly disturbed just after implantation. The SiO_{2-x} agglomerates are formed at processing, serving subsequently as the nucleation centers for further growth of oxide and, in the case of sufficiently high doses of implanted oxygen, of the BOX-like SiO_2 layer. Dislocations at the SiO_2/Si boundary are created if the misfit at the defect/matrix boundary reaches the critical value for a creation of the particular defect kind. The misfit value decreases with *HT* and *HP* for bulk Si containing oxide clusters or precipitates (exerting compressive internal stress on the matrix at ambient conditions), so less dislocations are created in Si:O processed at *HT–HP*. The creation of dislocations and of other defects at the SiO_{2-x}/Si boundary during annealing or *HT–HP* treatment is dependent also on dimension of SiO_{2-x} precipitates (less probable for the smaller ones) and on their stoichiometry (more probable for stoichiometric SiO_2).

Numerous treatment parameters contribute to the *HP*-induced effects in *HT–HP* treated Si:O, among them:

− mobility and solubility of implanted oxygen as well as of silicon interstitials and of other implantation-induced defects (such as vacancies) are dependent on *HT* and *HP*;

− stability of oxygen agglomerates is dependent on *HP*;

− the misfit at the SiO_{2-x}/Si boundary is tuned by *HP*.

Some effects induced by the treatment of Si:O under enhanced hydrostatic pressure raise hopes for its practical application.

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