Oxide layer dissolution in Si/SiO\textsubscript{x}/Si wafer bonded structures

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The evolution of the interfaces of hydrophilic-bonded Si wafers and the corresponding low-angle twist boundary have been analysed in relation to thermal annealing and their relative crystallographic orientation. Two orientation relationships were investigated: Si<001>/Si<001> and Si<001>/Si<110>, where the interfaces are separated by thin native SiO\textsubscript{2} layers. The interfaces were analysed by TEM and STEM/EELS. It is found that the decomposition rate of the intermediate oxide layer and the formation of a Si–Si bonded interface depend very much on the lattice mismatch and on the twist angle. The velocity of the dissolution of the thin oxide layers and the formation of Si–Si bonds at the bonding interface depend on the orientation relations of the corresponding wafers. The processes of interface fusion and the dissolution of oxide layer are discussed.

Dedicated to Prof. Wolfgang Neumann on the occasion of his 65\textsuperscript{th} birthday

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1 Introduction

Tensile strain in silicon channels in CMOS devices results in enhanced mobility of both electrons and holes (see, e.g., [1]). Direct Wafer Bonding (WB) is a promising way to realize this effect in new types of electronic devices [2]. The formation of a perfect crystalline transition at the interface between wafers is a crucial problem in this technique [3-5]. Screw and edge dislocations as well as thin oxide layers and precipitates might be formed. There are two different bonding techniques: the hydrophobic technique and the hydrophilic one. In the latter case, which will be considered in this article, the as-bonded interface contains thin SiO\textsubscript{2} layers (native oxide on the surface of the two wafers, total thickness 2 to 3 nm) might hamper this fusion process [6]. For the formation of covalent Si-Si bonds across the interface an annealing at above 1000 °C is usually applied. How the native oxide layer is modified by such an annealing procedure depends on the specific parameters of both wafers (miscut, wafer twist and thickness of wafers).

In the case of bulk wafers (thickness about 0.5 mm), the oxide layer is locally transformed into precipitates. However, if the top wafer is thinned down to < 150 nm thickness before a subsequent bonding annealing, an out-diffusion of oxygen has to be taken into account. It is the aim of this paper to study some aspects of the latter case. Especially, the atomic structure and the composition of Si<001>/SiO\textsubscript{2}/Si<110>, Si<110>/SiO\textsubscript{2}/Si<001> and of Si<001>/SiO\textsubscript{2}/Si<001> hydrophilic bonded bulk/thinned wafers were studied. For convenience in this paper, the first orientation refers to the lower thick wafer, whereas the second orientation refers to the upper thinned wafer. The bonded interfaces were analysed by transmission electron microscopy (TEM) as well as by scanning transmission electron microscopy (STEM). Both techniques have been successfully applied in the past, for example, to study the stability of interfacial oxide in polycrystalline Si emitter bipolar transistors [7]. The behaviour of intermediate native oxide layers in WB-SOI structures during a high temperature annealing and the interfacial atomic structure are the main issues of this work.

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2 Experimental

Two sets of WB samples differing in the orientation relations of the Si<001>/Si<110> and Si<110>/Si<001> wafers were investigated. The samples were fabricated by a hydrophilic WB of 200 mm wafers, which had native oxide layers on their surfaces of about 2 nm thickness. In all experiments Czochralski Si material (Cz) was used. After the bonding, the upper wafers were thinned down to about 140 nm. Such a bonded structure is schematically represented in figure 1. It has the following configuration: (i) Si substrates of specific orientations, technologically referred as “handle wafer”, (ii) 4 nm thick SiO$_2$ layer, and (iii) a 140 nm thick Si layer (upper wafer).

![Fig. 1 Schematic view of the bonded structure. Thicknesses of the upper Si wafer and the SiO$_2$ layer amounts to 140 and 2 nm, respectively. In this specific case the wafer orientation is related to <001> (lower bulk wafer) and <110> (upper thinned wafer). Two more orientation relations were investigated within the experiments.](image1)

The above bonded stacks were subsequently thermally annealed in the temperature range of 1150 to 1200 °C in an argon atmosphere up to 2 h. In such samples we could observe decomposition of the SiO$_2$ interface layer and formation of a specific structure of the Si<001>/Si<110>, Si<110>/Si<001> and Si<001>/Si<001> interfaces, respectively. Concerning the investigated decomposition of the inner thin oxide layer, one has to keep in mind that the Cz wafer material contains a certain supersaturation of oxygen.

![Fig. 2 Cross-sectional TEM image of Si<001>/Si<110> bonded structure after an annealing at 1200 °C for 15 min. This lattice plane image show a thin oxide layer between the wafers with a thickness of 3 to 4 nm.](image2)

The morphology, the crystal structure and the chemical composition of the bonded structures were investigated by TEM, by high angle annular dark-field STEM (HAADF) and low-angle annular dark-field STEM (LAADF) using a JEM 4010 and a TITAN 80-300 electron microscope operating at 400 and 300 kV, respectively. The latter was equipped with a Cs-corrector illumination system, a gun monochromator and a GATAN energy-loss spectrometer (TRIDIEM) allowing the analysis of the composition with a spatial resolution and an energy resolutions of 0.1 nm and of 150 meV, respectively. Preliminary results were presented by Zakharov et al. [8].

3 Results and discussion

3.1 Si<001>/Si<110> bonding In this section the results related to the orientation relation Si<001>/Si<110> (lower bulk wafer/upper thinned wafer) are presented. Figure 2 shows a typical example of such hydrophilic-bonded Si wafers before thermal annealing. In this particular case the sample was heated just after pre-bonding at 1150 °C for 15 min. The interface is characterised by a uniform 2 nm thick oxide layer (SiO$_x$) between the Si substrate wafer and 140 nm thick Si layer. Beside the visible thin oxide layer, we also found regions where the crystal lattices of both wafers were in direct contact. Such a situation is presented in figure 3a. This indicates that the oxide layer was partly dissolved at this place (SiO$_x$ → Si + x O). The dissociated oxygen might probably diffuse out through the 140 nm Si layer. In the case of annealing at 1200 °C for 1 h, we observed extended regions where the crystal lattices at the interface seem to be directly bonded and
a rather large number of amorphous SiO$_x$ inclusions (see Fig. 3a and b). From plan-view images it follows that in this particular case the inclusions have a rod-like shape elongated in the <110> direction. This might be caused by the fact that in this direction both crystal lattices perfectly fit each other. Concerning their cross-section TEM micrographs as visible in figure 3b, these oxide inclusions have a pronounced curved expansion into the upper <110> oriented wafer with a height of about 5 nm.

![Figure 3](image_url)

**Fig. 3** TEM cross-section micrographs showing the evolution of the bonding interface after thermal annealing. The lattice plane images show the Si<110>/Si<001> interface after an annealing at 1200 °C for different durations: (a) 15 min, (b) 1 h and (c) 2 h. The SiO$_x$ inclusions visible in (b) are mainly extended in the upper <110> Si wafer layer. The volume of the SiO$_x$ inclusions decreases from (a) to (b) and triangular lattice features are generated as indicated by arrows in (c). Orientation relation: Si<001>/Si<110>. Growth of the Si–Si interface in (a) proceeds by the tangential movement of points A as shown by arrows.

![Figure 4](image_url)

**Fig. 4** (a) STEM micrograph taken under HAADF imaging conditions. Curves in (b) represent experimental EELS-profiles of the oxygen concentration (in %) relative to silicon in correspondence to the marked lines in (a). Oxygen concentration in profile 2-2 amounts to zero within the accuracy of EELS analysis.

![Figure 5](image_url)

**Fig. 5** Cross-section STEM micrograph taken at LAADF imaging conditions. Bright band indicates a strongly distorted area at the interface. Note that interface region A (SiO$_x$/Si <110>) is less distorted than interface B (<001> Si /SiO$_x$).

An annealing of the bonded structure at 1200 °C for 2 hours resulted in the formation of an interface almost free from oxygen inclusions as demonstrated by figure 3c. The lattice plane images suggest a direct contact of both crystals. The EELS analysis performed with a spatial resolution of 0.1 nm revealed a high oxygen concentration in these rod-like inclusions (Fig. 4). However, in the bonded interface regions in between characterized by direct contact of both lattices (see Fig. 4) no oxygen was detected within the resolution limit of the EELS measurement. The specific lattice structure of the interface shows periodic features marked by arrows in figure 3c. Due to the crystallographic orientation of both Si lattices, the interface has to be regarded more as a large-angle grain boundary than as an arrangement of misfit dislocations. Such periodic triangular lattice structures run along [110] with side facets of low index (111) and (11$ar{1}$) planes. These structures probably enable a reduction in the interface energy.

Figures 4a and 5 represent STEM images taken from a relatively thick TEM sample region (> 15 nm) under high-angle annular dark field conditions (HAADF) and low-angle annular dark field (LAADF) conditions,
respectively. The occurrence of a bright area in the LAADF image reveals the existence of highly strained regions. According to Zhieng et al. [9] this contrast feature is caused by a random strain field, i.e. a random shift of atoms away from their equilibrium positions. The resulting local de-channelling of electrons causes an intensive scattering at low angles. This effect causes the appearance of bright contrast features in LAADF images (e.g. see Fig. 5).

The interface energy of bonded structures depends in a straightforward way on the above type of lattice distortions. In the STEM micrograph (Fig. 5), one can see that the intensity of white contrast on the SiO$_x$/Si<001> interface (near B) is higher than that on the SiO$_x$/Si<110> (near A). This indicates that the SiO$_x$/Si<001> interface energy is higher than that of the SiO$_x$/Si<110> interface. We will use this qualitative finding later to explain the shape of the islands in bonded structures.

We observed a dissolution of the thin SiO$_x$ layers during annealing and formation of direct contact between the two Si lattices of both wafers. This is shown in figure 3a, where the direct lattice contact area A−A increased with annealing time. Furthermore, for longer annealing times also the number and the size of SiO$_x$ inclusions decreased (Fig. 3b) and they finally vanished (Fig. 3c). Concerning this process we assume that the SiO$_x$ decomposes as mentioned above. Here oxygen diffuses out through the 140 nm thick upper Si layer and self-interstitials diffuse from the surface to the interface, partially filling up the volume of the inclusion.

### 3.2 Si<110>/Si<100> bonding

To study the influence of crystal orientation on oxygen dissolution process, we carried out the same annealing experiments on bonded wafers but with inverted wafer orientations, i.e. that the substrate wafer and thinned upper wafer were oriented along the <110> and <100> directions, respectively. The corresponding pre-bonded wafers were annealed as in the above experiments at 1200 °C for different times up to 2 h (see Fig. 6). Also in this case, the continuous thin oxide layer was transformed into isolated SiO$_x$ inclusions. From the TEM plan-view investigations it follows that they have a rod-like shape elongated in the [110] as in the previous case (see Fig. 6b). This elongation takes place because both lattices fully coincide in this crystallographic direction. This is demonstrated in figure 6c by a plan-view electron diffraction pattern. The subscript ‘s’ refers to reflections from the bulk wafer, while the subscript ‘l’ refers to the thin layer. The reflection (022)$_s$ containing both subscripts correspond to common lattice planes.

![Fig. 6](image)

Fig. 6 (a) Cross-section TEM image of a Si<110>/Si<100> bonded sample. Some of the SiO$_x$ inclusions are marked by arrows. (b) Plan-view image of the bonded structure seen in <110> direction concerning the lower bulk wafer. Rod-like SiO$_x$ inclusions running along [011] concerning the bulk wafer are partly marked by arrows too. (c) Electron diffraction pattern from a Si<011>/Si<001> bonded structure. Subscripts ‘s’ and ‘l’ denote bulk wafer (s) and upper thinned wafer (l), respectively.

The cross-section images also show a pronounced expansion of the amorphous oxide into the <110> wafer (see figs. 7a and 7b), while a remarkable presence of oxide in the <001> material could not be observed. From the two sets of experiments, described in Subsecs 3.1 and 3.2, it follows that the SiO$_x$ inclusions preferably stay in the <110> oriented Si crystal. This can be explained by the anisotropy in the energies of the SiO$_x$/Si<001> and SiO$_x$/Si<110> interfaces, indicating that the interfacial energy of the latter is lower than that of the former. Qualitatively, this difference of the interface energy can be deduced from figure 5, where the micrograph was taken in STEM mode under LAADF imaging conditions. The interface band in the lower wafer (SiO$_x$/<001> interface) is brighter and wider than the upper interface, indicating a stronger distortion characterized by a higher interface energy.

### 3.3 Low twist angle Si<001>/Si<001> bonding

Here annealing experiments are described, where both the bulk wafer and the thinned wafer had the <001> orientation and the {001} bond interface. It should be mentioned that an exact orientation relation between the wafers was difficult to achieve and a small twist angle
(< 1°) has to be taken into account. Contrary to the previous examples, where the oxide layer disappeared after annealing at 1200 °C for about 1 h, in this case of low-angle twist boundaries the thickness of the oxide layer does not remarkably change during annealing. This situation is reflected by figure 8. A plan-view image of a bonded sample after 1.5 h annealing at 1200 °C is shown in figure 8a. Moiré fringes are the result of the double diffraction of electrons waves on the (220) atomic planes. The analysis of the fringe pattern revealed a twist angle φ of 0.18°, which serves in our case as a misfit parameter. This value is quite small; all previous investigations by other authors revealed much larger twist angles (for example, see [2, 3]). In our experiments surprisingly the oxide layer was retained and its thickness was reduced by about 0.8 nm (see Fig. 8c,d). This may be attributed to a reduction of SiOx decomposition rate which amounts to about 0.4 nm/h in this particular case.

![Fig. 7](image1.png)

**Fig. 7** (a) Cross-section image of SiOx inclusion in a Si<100>/Si<110> bonded sample. A larger part of the SiOx inclusion stays in upper <110> oriented layer. (b) Cross-section image of SiOx inclusion in Si<110>/Si<100> sample. Here the larger part of the inclusions stays below the interface in the substrate (lower wafer). The upper <100> layer is out of lattice plane contrast due to azimuthal misorientation (small rotation between the wafers).

![Fig. 8](image2.png)

**Fig. 8** TEM and HREM images of Si(001)/Si(001) bonded sample after annealing at 1200 °C for 1.5 h. (a) Plan-view image. Moiré fringes form square lattice. The regions of coherent coupling of crystal lattices are marked by A. An enlarged image of a coherent region is shown in upper right corner. (b) Cross-sectional image of coherent regions ‘A’. There are no structural defects at the place of bonding. (c) HRTEM cross-sectional image of the border A between SiOx and coherently bonded defect free region. (d) HREM cross-sectional image of the specimen Si(001)/Si(001) after annealing at 1050 °C for 15 min.

A large number of small rounded and square-shaped regions also appear in the interface corresponding to a direct bonding of the two lattices (see region A in figure 8a). Inside these regions the crystal lattice of the Si cap layer is counter-rotated elastically at an angle γ = −0.18° to fit the substrate (compensation of φ). The largest radius r of these coherently coupled regions never exceeded 120 nm. This gives the maximum value of the tangential elastic displacement on contour of this area τ = r tanφ = 0.38 nm. This value is equal to the Burgers vector |b| of a screw dislocation, which amounts in this case to |b| = 0.38 nm. This fact explains the absence of dislocations inside such areas, which can be nucleated only if τ > b. The formation of such coherently bonded regions results in the generation of three-dimensional elastic strain fields in the two-layer system. They are associated with an additional elastic energy proportional to the square of the misfit parameter equal i.e. ∝ nφ², where n relates to the number of such features per square area.
4 Summary and conclusions

Our experiments deal with the specific case of a bonded structure, where a thin Si wafer (thickness ≈ 140 nm) is bonded on a bulk one. This situation allows an interaction/diffusion of point defects with the adjacent specimen surface. All experiments started from hydrophilic-bonded wafers, separated by thin layer of native oxide. Subsequent annealing step should reduce the interfacial oxide to increase the bonding strength. The corresponding experiments have shown that the dissolution rate of these oxide layers strongly depends on crystallographic orientation of the two wafers. The reaction is faster in the case of Si<110>/Si<001> bonded wafers than in the case of Si<001>/Si<001> wafers. In this particular case, the formation of a Si–Si interface and the dissolution of SiO\(_x\) can proceed in two different ways: (i) perpendicular to the interface (normal dissolution), and (ii) in the interface plane (in-plane dissolution).

In the case of Si<110>/Si<001> bonded wafers, the decomposition rates for in-plane dissolution of the oxide and for a dissolution normal to the interface amount in our case to approximately 2 and 0.4 nm/h, respectively, at a temperature of 1200 °C. This process is represented by the reaction: SiO\(_2\) → Si + 2O. Oxygen is out-diffusing towards the surface of the thin wafer. The dissolution is simultaneously accompanied by the growth of a Si lattice. For this purpose the additionally needed Si atoms might be provided as self-interstitials from the surface of the thin wafer. The growing crystalline Si/Si interface (see A in Fig. 3a) is clearly faceted by the close-packed {111} planes. The shrinkage of the interfacial oxide layer is accompanied with the formation of a crystalline interface. This interface is characterized by a specific reconstruction which might be interpreted as a large-angle grain boundary containing a high density of misfit dislocations. Such grain boundaries as represented in figure 3c locally contain a huge lattice mismatch \(\varepsilon = 34\%\). Nevertheless, the formation of a interface reconstruction seems to be more favourable in comparison with the oxide containing interface.

In the case of low-angle twist-bonded wafers having a Si<001>/Si<001> orientation relation a different bonding mechanism was observed. The interfacial oxide is dissolved much slowly in this case (0.4 nm/h). We observed at first a homogeneous decrease in the thickness of this SiO\(_x\) layer with annealing time. This process is caused by an out-diffusion of oxygen towards the close surface. Such bonded interface regions are characterized in TEM images by a Moiré fringe system. With proceeding annealing time small areas in the interface are formed which are characterized by a direct lattice bonding. These small regions have diameters which are always below a critical size depending on the small azimuthal rotation of the two wafers. The maximum size of such coherent bonded regions cannot overcome the energy barrier necessary to nucleate a screw dislocation.

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