Oxidation process dependence of strain field under the SiO₂/Si(001) interface revealed by X-ray multiple-wave diffraction

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Abstract. A multiple-wave X-ray diffraction phenomenon, i.e., interaction between Bragg reflection and crystal-truncation-rod (CTR) scattering, is applied to characterize strain field under SiO₂/Si(001) interface. Application of this phenomenon to strain characterization allows us to reveal that there is very small strain field extending over a mesoscopic-scale depth under the SiO₂/Si interface and having a static fluctuation in the lateral direction. It also allows us to obtain information on distribution of strain field. In this paper oxidation-process dependence of strain distribution is discussed: some recently obtained results of wet oxidations at 900°C and 1100°C are compared with those of dry oxidation and Kr/O₂ plasma oxidation.

1. Introduction
Strain near an interface affects its electronic structure, but a full understanding of such strains is still lacking even in the case of SiO₂/Si(001), which has been applied to electronic devices since 1960s. In a previous paper [1], we have proposed a new technique: the phase-sensitive x-ray diffraction (PSXD) technique. This technique is an application of a multiple X-ray diffraction phenomenon, modulation of the crystal-truncation-rod (CTR) scattering intensity under the excitation of a Bragg reflection [1-7], and allows us to characterize strain field in a crystal. Using the technique it has been revealed that there is very small strain field under SiO₂/Si interface, which extends over depth up to several tens of nanometer and has a static fluctuation in the lateral direction. Information on distribution of strain field has been also obtained by the technique [1]. In the present paper, some recently obtained results of wet oxidation at 900°C and 1100°C are compared with those of dry oxidation and Kr/O₂ plasma oxidation.
oxidations at 900°C and 1100°C are compared with those of dry oxidation at 900°C and Kr/O₂ plasma oxidation at 400°C [8,9].

2. Experiment

We investigated strain fields under SiO₂/Si(100) interfaces by measuring modulation profiles of the crystal-truncation-rod (CTR) scattering on the 50 rod under the excitation of the 004 Bragg reflection (see Fig. 1 (a)). The PSXD technique allows us to determine the total displacement ΔDₙ (see Fig. 1 (b)) projected into the reciprocal lattice vector of the Bragg reflection H. In addition the measurement becomes more sensitive to structures near the interface for a larger absolute value of Δl, which is the deviation of the momentum transfer perpendicular to the surface from a Bragg point (the 555 Bragg point in the case of Fig. 1 (a)). Thus depth profile of the strain field can be also determined; taking a larger |Δl| allows us to measure strain field with a higher resolution in real space, which is represented by the inverse of |Δl| [1]. We can change Δl by changing the wavelength λ of the incident X-rays.

The experiment was performed at BL09XU in SPring-8, where a high-brilliance horizontally polarized X-ray beam from the undulator is available [10]. The premonochromatized SR beam was shaped by slits into a size of 1 mm (vertical) × 1 mm (horizontal), and then highly monochromatized by using two 440 Bragg reflections from two Si(220) channel-cut crystals arranged in the (+ +) geometry. Then samples put on a highly-precision goniometer were irradiated by the beam. Each glancing-angle scan was carried out at a fixed wavelength around 1.24 Å. The wavelengths were determined by the difference between the 555 and 004 Bragg angles. The samples were prepared as
follows: they were first oxidized at 1000 °C in a dry oxygen atmosphere, so that thermal oxide layer about 500 nm was formed on it. Next the oxide layer was removed by HF solution, and oxidized again to form an oxide layer of about 1000 nm thickness. Then the oxide layer was removed again, and finally oxidized by wet oxidation process at 900 °C and 1100°C.

3. Results and Discussion

Results of wet oxidation at 900°C are shown in Fig. 2. A modulation profile is mainly characterized by two parameters, the ‘phase’ and ‘visibility’ of the profile: the ‘phase’, which corresponds to the peak or dip position of the modulation profile, reflects $\Delta D_n H$, while the ‘visibility’ does to static strain fluctuation in the lateral direction [1]. Squares, triangles, filled circles, crosses, open circles, and filled squares are experimentally obtained modulation profiles at $\Delta l = -0.030, -0.023, -0.016, 0.015, 0.027$, and 0.037, respectively. In Fig. 2 a result of dry oxidation at 900 °C ($\Delta l = -0.017$, gray crosses) is also shown as a reference [1]. The scale factors of these experimental data are adjusted for comparison among them. Difference between the two oxidation processes is clearly seen; it reflects difference in strain field under SiO$_2$/Si(001) interface. On the other hand there is no difference among rocking curves of Bragg reflections for the three samples; they were explained by a perfect crystal (broken line). This fact supports that the depths of the strain fields are sufficiently small compared with the extinction depth of the 004 Bragg reflection. The black and gray solid lines correspond to calculated curves for $\Delta D_n H$’s of $-9.5\%$ and $-12\%$, respectively. Here $\Delta D_n H = \Delta D_n n/d_{004}$, where $d_{004}$ is the lattice spacing of the (004) plane, and $n$ is the unit vector perpendicular to the surface. The former curve is in good agreement with the experimental results of the wet oxidations at 900°C, while the latter is with that of the dry oxidation at 900°C.

Fig. 2. Results of wet oxidation at 900°C. The abscissa is the glancing angle $\theta$, the origin of which is taken here near the center of the 004 Bragg reflection. Squares, triangles, filled circles, crosses, open circles, and filled squares are experimentally obtained modulation profiles at $\Delta l = -0.030, -0.023, -0.016, 0.015, 0.027$, and 0.037 ($\lambda (\text{Å}) = 1.24504, 1.24432, 1.24362, 1.24024, 1.23893$, and 1.23792), respectively. In the figure a result of dry oxidation at 900 °C ($\Delta l = -0.017$, gray crosses) is also shown.

Black and gray solid lines correspond to calculated curves for $\Delta D_n H$’s of $-9.5\%$ and $-12\%$, respectively, and broken line does to the theoretically calculated curves for the 004 Bragg reflection.
The fact that $\Delta D_nH$'s were almost constant (–9.5%) for different $\Delta l$'s (different resolutions in real space) along the rod in the case of the wet oxidation at 900°C indicates that the distribution of strain field is almost constant in the depth direction. This tendency was similar to that of the dry oxidation at 900°C. It should be noted that in the case of the dry oxidation $\Delta D_nH$ was somewhat larger (–12%) than that of the wet oxidation. This should be due to more dense oxide layer formed by the dry oxidation than that formed by the wet oxidation.

In Fig. 3 results of wet oxidation at 1100°C are shown with the result of the dry oxidation at 900°C. Triangles, filled circles, crosses, and open circles are experimentally obtained modulation profiles at $\Delta l = -0.021, -0.012, 0.009$, and 0.021 ($\lambda$(Å) = 1.24411, 1.24312, 1.24089, and 1.23963), respectively. In contrast to the wet oxidation at 900°C, the modulation profile depends on $\Delta l$; $|\Delta D_nH|$ seems to be smaller for a larger $|\Delta l|$ (a higher spatial resolution). This tendency was similar to that of the Kr/O$_2$ plasma oxidation at 400°C, suggesting that the strain field changes near the interface. In addition, there is asymmetry around $\Delta l = 0$; the modulation profile at $\Delta l = -0.021$ is different from that at $\Delta l = 0.021$. This makes contrast to the case of the Kr/O$_2$ plasma oxidation, where variation in modulation profile was almost symmetric around $\Delta l = 0$ [1].

The asymmetry may be attributed to strain field localized very near the interface. If strain field is very small and varies sufficiently slowly compared with $d/\Delta l$, the scattering amplitude $A_{\text{CTR}}$ from the strained crystal should be given by
\[
A^{\text{CTR}}(\mathbf{q}) = \left[ 1 - \frac{1}{\Delta q_z} \cdot \frac{d(\mathbf{q} \cdot \Delta \mathbf{D}(r))}{dz} \bigg|_{z=nd} \right] + \left( \frac{1}{\Delta q_z} \cdot \frac{d(\mathbf{q} \cdot \Delta \mathbf{D}(r))}{dz} \bigg|_{z=nd} \right)^2 \cdot \frac{i}{2\pi(\Delta q_z)^2} \cdot \frac{d^2(\mathbf{q} \cdot \Delta \mathbf{D}(r))}{dz^2} \bigg|_{z=nd} \right) \times F(\mathbf{q}) e^{2\pi i q (nd+\Delta q_z)} \left[ 1 - e^{-2\pi i q d} \right].
\]

Here \( \mathbf{q} \) is the scattering vector, \( \Delta q_z \) is the \( z \)-component of \( \Delta \mathbf{q} \), where \( \Delta \mathbf{q} \) is the deviation of \( \mathbf{q} \) from the nearest neighbor Bragg point and the \( z \)-direction is taken perpendicularly to the surface (\( \Delta q_z = \Delta l/d \)), \( \Delta \mathbf{D}(r) \) is defined as it satisfies \( \Delta \mathbf{D}_i \equiv \Delta \mathbf{D}(d) \), and \( F(\mathbf{q}) \) is the structure factor. The first derivative changes the intensity of the CTR scattering, while the second derivative changes only the phase of the amplitude of the CTR scattering and doesn’t change the intensity. In the case of Kr/O\(_2\) plasma oxidation the intensity of the 50 rod CTR scattering around the 555 Bragg point was almost same as that of a perfect crystal, and the phase changed almost symmetrically around the Bragg point. This should be due to a negligible first derivative in the above equation. In the case of the wet oxidation at 1100°C, change in the phase was asymmetric. This should be due to strain field existing within a depth smaller than \( d/\Delta l \). More detailed analysis will be presented elsewhere.

### 4. Conclusion

The phase-sensitive x-ray diffraction (PSXD) technique was applied to investigate dependence of strain field under \( \text{SiO}_2/\text{Si}(100) \) interface on oxidation method. Results of wet oxidations at 900°C and 1100°C were compared with results of dry oxidation at 900 °C and Kr/O\(_2\) plasma oxidation at 400 °C. In the case of the wet oxidation \( \Delta \mathbf{D}_z \mathbf{H}'s \) were almost constant for different \( \Delta l \)'s along the rod, which indicates that the distribution of strain field should be almost constant. This tendency was similar to that of dry oxidation except that \( \Delta \mathbf{D}_z \mathbf{H}'s \) were somewhat larger (–12%) than that of the wet oxidation at 900°C, and made contrast to the cases of the wet oxidation at 1100°C and Kr/O\(_2\) plasma oxidation at 400°C, which can be attributed to strain field localized very near the interface.

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