*Transactions of the Materials Research Society of Japan* 33[3] 607-610 (2008)

# Similarity between Strain Fields Induced by the Xe/$NH_3$ Plasma Nitridation and the Kr/$O_2$ Plasma Oxidation Revealed by a Multi-Wave X-ray Diffraction Phenomenon

Wataru Yashiro, Yoshitaka Yoda*, Yuichiro Matsushita**, Takashi Aratani***, Akinobu Teramoto***, Takeo Hattori*** and Kazushi Miki****
Department of Advanced Materials Science, Graduate School of Frontier Sciences, the University of Tokyo, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8561, Japan
Fax: 81-4-7136-3997, e-mail: yashiro@mml.k.u-tokyo.ac.jp
*Japan Synchrotron Radiation Research Institute (JASRI), 1-1-1 Kouto, Sayo-gun, Sayo-cho, Hyogo 679-5198, Japan
**Department of Applied Physics, School of Engineering, the University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
***New Industry Creation Hatchery Center (NICHe), Tohoku University, 6-6-10, Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan
****Nanomaterials Laboratory (NML), National Research Institute of Materials Science (NIMS), 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan

Strain field under $Si_3N_4$/Si(001) interface formed by nitrogen-hydrogen (NH) radicals (the Xe/$NH_3$ plasma nitridation) was investigated by using a multiple-wave X-ray diffraction phenomenon, *i.e.*, interaction between Bragg reflection and crystal-truncation-rod (CTR) scattering. Information on distribution of strain field induced by $Si_3N_4$/Si(001) interface was qualitatively obtained, and compared with the results of $SiO_2$/Si(001) interfaces formed by the thermal oxidations (wet and dry oxidations) and the Kr/$O_2$ plasma oxidation; strain field induced the nitridation by NH radicals was similar to that by the Kr/$O_2$ plasma oxidation, but different from those by the thermal oxidations.
Key words: X-ray diffraction, Silicon, Silicon oxides, Oxidation, Strain

## 1. INTRODUCTION

Strain induced by an interface affects its electronic structure, but a full understanding of such strains is still lacking even in the case of the silicon dioxide-silicon interface, which has been applied to electronic devices since 1960s. In a previous paper [1-4], 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* [5-10], 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 the $SiO_2$/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 the strain field has been also obtained by the technique [2,3]. In the present paper the strain field under the $Si_3N_4$/Si(001) interface formed by high-density Xe/$NH_3$ plasma is investigated by the PSXD method. The $Si_3N_4$ film formed by the Xe/$NH_3$ plasma (NH radicals) attracts increasing attention as a high-$\kappa$ gate owing to its high relative dielectric constant and low interface state density not only in the case of Si(001) but in the cases of Si(111) and Si(110) [11]. Depth profile of strain field induced by the $Si_3N_4$/Si(001) interface is qualitatively obtained, and compared with the results of the $SiO_2$/Si(001) interfaces formed by the thermal oxidations (wet and dry oxidations) and the Kr/$O_2$ plasma oxidation[12,13].

## 2. EXPERIMENT

We investigated the strain fields under $Si_3N_4$/Si(001) interfaces by measuring modulation profiles of the CTR scattering on the 50 rod under the excitation of the 004 Bragg reflection (see Fig. 1) [1-4]. The PSXD technique allows us to determine the total displacement $\Delta \boldsymbol{D}_n$ (see Fig. 2) projected into the reciprocal lattice vector of the Bragg reflection $\boldsymbol{H}$. In addition the measurement becomes more sensitive to structures near the interface for a larger absolute value of $\Delta l$, 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). Thus depth profile of the strain field can be also determined; taking a lager $|\Delta l|$ allows us to measure strain field with a higher resolution in real space, which is represented by the inverse of $|\Delta l|$ [2-4,10]. We can change $\Delta l$ by changing the wavelength 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 [14]. 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 444 Bragg reflections from two Si(111) channel-cut crystals arranged in the (+ +) geometry. The wavelength of X-rays was fixed around 1.24 Å. The sample was put on a very flat plate on a high precision goniometer.

Glancing-angle ($\theta$) scan was performed around the Bragg 004 Bragg point, and at each angle the CTR scattering was analyzed by a Ge(111) crystal. The intensities measured by the NaI scintillation counter were integrated after subtraction of the backgrounds and then normalized by the counts of beam flux monitor placed in front of the sample.

As the sample n-type Si(001) substrates were prepared. First wet oxidation of these substrates was performed at 1100 °C to form oxide films. After etching the oxide films in HCl/HF mixture solution, nitridation of these substrates using NH radicals produced in a microwave-excited high-density Xe/NH$_3$ mixture plasma was performed at a pressure of 20 Pa and substrate temperature of 600 °C. The microwave frequency and power density were 2.45 GHz and 1.67 W/cm$^2$, respectively. The thickness of the Si$_3$N$_4$ film was estimated by spectroscopic ellipsometry to be 1.36 nm.

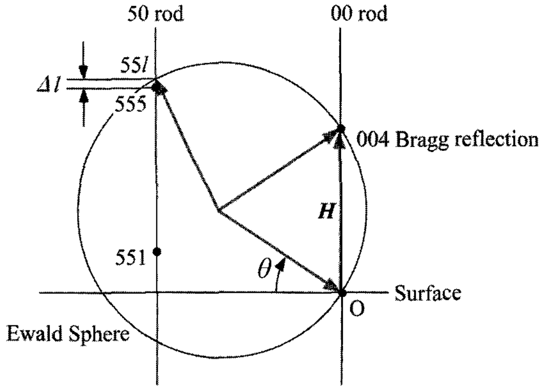


Fig. 1. Illustration of diffraction condition where intensity of CTR scattering is modulated by the excitation of the 004 Bragg reflection. The parameter $l$ is the momentum transfer perpendicular to the surface, and $\Delta l$ is the deviation of $l$ from the 555 Bragg point.

## 3. RESULT AND DISCUSSION

An Example of experimental results at two $\Delta l$'s are shown in Fig. 3. The abscissa is the deviation of the incidence angle from the center of the 004 Bragg reflection. Filled circles and crosses are experimentally obtained data. These were not explained by a perfect crystal. On the other hand experimentally obtained rocking curves of the 004 Bragg reflection were explained by a perfect crystal (broken lines). This fact supports that a very small and long-range strain field is induced by the NH radical nitridation, the depth of which is sufficiently small compared with the extinction depth of the 004 Bragg reflection [1]. Difference between the two experimental data of the CTR scattering intensity indicates that strain field under the Si$_3$N$_4$/Si(001) interface is not constant in the depth direction [4].

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 $\Delta \boldsymbol{D}_n{\cdot}\boldsymbol{H}$, while the 'visibility' does to static strain fluctuation in the lateral

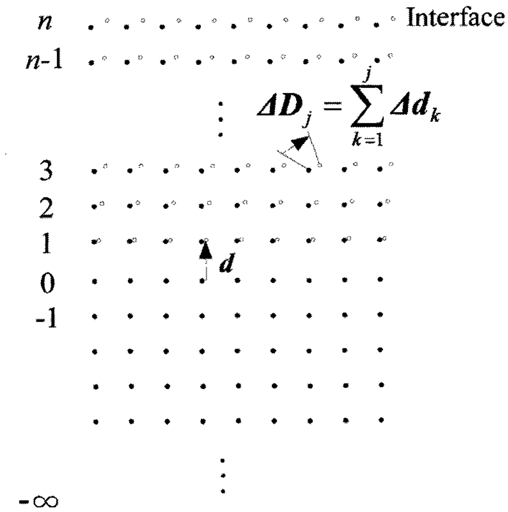


Fig. 2. Illustration of a model of mesoscopic-range strain field. A strained layer containing $n$ atomic planes is formed on an ideal semi-infinite perfect crystal. The filled circles represent to the positions of atoms or unit cells in bulk crystal, and the open circles represents those in the strained layer under the interface. The parameter $\Delta \boldsymbol{D}_j$ represents the sum of displacements under the $j$th atomic plane, and $\Delta \boldsymbol{d}_j$ does the deviation of the lattice spacing between the ($j$–1)th and $j$th atomic planes from the lattice spacing in bulk, $\boldsymbol{d}$.

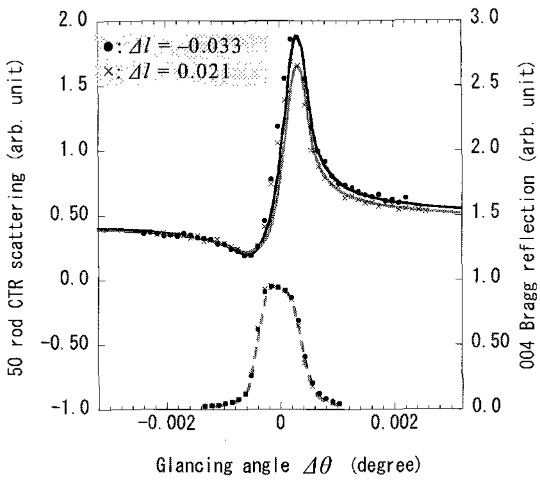


Fig. 3. An example of experimentally obtained modulation profiles. The abscissa is the deviation of the incidence angle from the center of the 004 Bragg reflection (denoted by $\Delta\theta$). Filled circles and crosses correspond to experimentally obtained data, and solid and broken lines does to the calculated curves fitted to the experimental data.

direction [1]. Solid lines in Fig. 3 are curves fitted to the experimental data. Black line corresponds to the curve of $\Delta \boldsymbol{D}_n{\cdot}\boldsymbol{H} = -10.0\%$, and gray line does to that of $\Delta \boldsymbol{D}_n{\cdot}\boldsymbol{H} = -11.1\%$, where $1/|\boldsymbol{H}| = d_{004}$ (the lattice spacing of

(004) plane). In Table I, $\Delta \boldsymbol{D}_n \cdot \boldsymbol{H}$'s determined by the least squares fittings are summarized. The results indicate that $\Delta \boldsymbol{D}_n \cdot \boldsymbol{H}$ becomes small with increasing $|\Delta l|$, the inverse of which represents spatial resolution, suggesting that $\partial \Delta \boldsymbol{D}(z)/\partial z$ increase with increasing $z$ near the interface [4]. The result presented here is similar to the case of $Kr/O_2$ plasma oxidation at 400 ℃, on which much attention is focused since it can realize lower leakage current not only in the case of Si(001) but Si(111). Figure 4 shows depth profile of strain field qualitatively obtained by the dependence of $\Delta \boldsymbol{D}_n \cdot \boldsymbol{H}$ on $|\Delta l|$, with other results reported in previous papers [2,3]. Gray solid and gray broken lines are strain fields in the cases of wet and dry oxidations at 900 ℃ [3], and black solid and black broken lines are those of the $Xe/NH_3$ plasma nitridation at 600 ℃ and the $Kr/O_2$ plasma oxidation at 400 ℃ [2]; strain fields under the interfaces formed by the $Xe/NH_3$ plasma and the $Kr/O_2$ plasma are characterized by $\partial^2 \Delta \boldsymbol{D}(z)/\partial z^2 > 0$ near the interface, while those under the $SiO_2$/Si(001) interfaces formed by thermal oxidations (wet and dry oxidations) are almost constant ($\partial^2 \Delta \boldsymbol{D}(z)/\partial z^2 \approx 0$) [4]. These results indicate the presence of characteristic local structures near the interfaces formed by the $Kr/O_2$ plasma oxidation and the $Xe/NH_3$ plasma nitridation. Although further experimental and theoretical studies are necessary, the results presented here should be related to formation mechanism of the interface with low interface state density.

Higuchi *et al.* performed the soft X-ray excited angle-resolved photoemission spectroscopy on the $Si_3N_4$ films formed on Si(100), Si(111), and Si(110) using the NH radicals [11]. They reported that the FWHM of Si 2*p* spectrum arising from Si substrate decreases with the approaching of the areal density of Si on the Si surface to that in $Si_3N_4$ layer. This should be attributed to the very small and long range strain field presented here. Our method is also applicable to Si(111) and Si(110) substrates and will provide much information on how the high quality interfaces are formed on not only on Si(100) but Si(111) and Si(110) substrates.

## 4. CONCLUSION

The phase-sensitive X-ray diffraction (PSXD) technique was applied to investigate dependence of strain field under $Si_3N_4$/Si(001) interface formed by NH radicals. The experimentally obtained modulation profiles of the intensity of the CTR scattering showed that there is a very small and long-range strain field under the $Si_3N_4$/Si(001) interface formed by the $Xe/NH_3$ plasma nitridation (NH radical nitridation). Depth profile of the strain field was also qualitatively obtained, and compared with results of thermal oxidation and the $Kr/O_2$ plasma oxidation. It was shown that, in the case of the $Xe/NH_3$ plasma nitridation, $\Delta \boldsymbol{D}_n \cdot \boldsymbol{H}$ becomes small with increasing $|\Delta l|$, the inverse of which represents spatial resolution. This suggests that $\partial \Delta \boldsymbol{D}(z)/\partial z$ increases with increasing $z$ near the interface, which is similar to the case of the $Kr/O_2$ plasma oxidation at 400 ℃, but different from the thermal oxidations (wet and dry oxidations). These results indicate the presence of characteristic local structures near the interface in the cases of the $Kr/O_2$ plasma oxidation and the $Xe/NH_3$ plasma nitridation.

Table I. The dependence of $\Delta D_n/d_{004}$ on $\Delta l$, where $\Delta D_n$ is the projection of $\Delta \boldsymbol{D}_n$ in the direction perpendicular to the surface and $d_{004}$ is the lattice spacing of the (004) plane.

| $\Delta l$ | −0.033 | −0.023 | 0.021 | 0.032 |
|---|---|---|---|---|
| $\Delta D_n/d_{004}$ (%) | −10.0 ±0.2 | −10.5 ±0.1 | −11.1 ±0.2 | −9.7 ±0.3 |

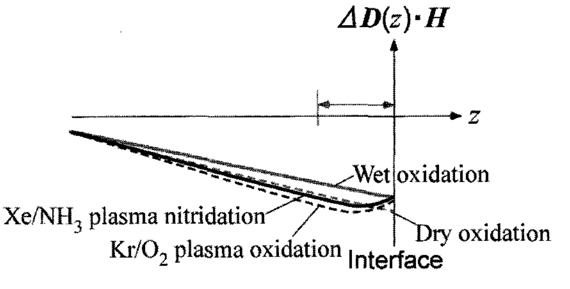


Fig. 4. Depth profiles of strain fields under the $Si_3N_4$/Si(001) interface (black solid line), where $z$ represents the depth and $\Delta \boldsymbol{D}(z)$ is the sum of displacements defined in Fig. 2. For comparison some results of other oxidation processes are shown: gray solid and gray broken lines are the displacements induced by the wet and dry oxidations at 900 ℃, and black broken line is that by the $Kr/O_2$ plasma oxidation at 400 ℃.

ACKNOWLEDGEMENT

The experiment was performed at SPring-8 (2007B1076). This research was partially supported by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid for Young Scientists (B), 19760020, 2007, and carried out under the Visiting Researcher's Program of the Institute for Solid State Physics, the University of Tokyo.

## REFERENCES

[1] W. Yashiro, K. Sumitani, T. Takahashi, Y. Yoda, and K. Miki, *Surf. Sci.* **550**, 93-105 (2004).

[2] W. Yashiro, K. Sumitani, T. Takahashi, Y. Yoda, K. Takahashi, T. Hattori, and K. Miki, *International Workshop on Dielectric Thin Films for Future ULSI Devices — Science and Technology (IWDTF2004)*, 109-110 (2004).

[3] W. Yashiro, S. Kusano, K. Miki, Y. Yoda, K. Takahashi, M. Yamamoto, and T. Hattori, Trans. *Mat. Res. Soc. Jpn.* **32**, 227-229 (2007).

[4] W. Yashiro, Y. Yoda, K. Takahashi, M. Yamamoto, T. Hattori, and K. Miki, *J. Phys: Conf. Ser.* **83**, 012009 (2007).

[5] T. Takahashi and S. Nakatani, *Surf. Sci.*, **326**, 347-360 (1995).

[6] V. M. Kaganer, M. Albrecht, A. Hirnet, M. Gierer, W. Moritz, B. Jenichen, and K. H. Ploog, *Phys. Rev.* B **61**, R16355-R16358 (2000).

[7] T. Takahashi, W. Yashiro, M. Takahasi, S. Kusano,

X.W. Zhang and M. Ando, *Phys. Rev.* B **62**, 3630-3638 (2000).
[8] W. Yashiro, K. Shimizu, K. Hirano, and T. Takahashi, *Jpn. J. Appl. Phys.*, **41**, L592-L594 (2002).
[9] W. Yashiro, K. Sumitani, Y. Yoda, and T. Takahashi, *Jpn. J. Appl. Phys.* **42**, 6658-6662 (2003).
[10] O. Litzman and Mikulik, *J. Phys.: Condens. Matter*, **11**, 5767-5779 (1999).
[11] M. Higuchi, S. Sugawa, E. Ikinaga, J. Ushio, H. Nohira, T. Maruizumi, A. Teramoto, T. Ohimi, and T. Hattori, *Appl. Phys. Lett.* **90**, 123114 (2007).
[12] Y. Saito, K. Sekine, N. Ueda, M. Hirayama, S.Sugawa, and T. Ohmi, *Tech. Dig. 2000 Symp. VLSI Tech., Hawaii*, 176 (2000).
[13] K. Takahashi, H. Nohira, T. Nakamura, T. Ohmi, and T. Hattori, *Jpn. J. Appl. Phys.*, **40**, L68-L70 (2001).
[14] Y. Yoda, M. Yabashi, K. Izumi, X.W. Zhang, S. Kishimoto, S. Kitao, M. Seto, T. Mitsui, T. Harami,Y. Imai, and S. Kikuta, *Nucl. Instrum. Meth.* A **467**, 715-718 (2001).

(Recieved December 10, 2007 ; Accepted February 26, 2008)