Transactions of the Materials Research Society of Japan 34[4] 597-600 (2009)

Quantitative Analysis of the Strain Field beneath the Si_3N_4/Si(001) Interface Formed by the Xe/NH_3 Plasma Nitridation using a Multiple-Wave X-ray Diffraction Phenomenon

Wataru Yashiro, Yoshitaka Yoda*, 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
**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

We show a quantitative analysis of the strain field beneath the Si_3N_4/Si(001) interface formed by nitrogen-hydrogen (NH) radicals (the Xe/NH_3 plasma nitridation). The strain field was investigated by using a multiple-wave X-ray diffraction phenomenon, *i.e.*, interaction between the Bragg reflection and crystal-truncation-rod (CTR) scattering. We present a master formula for the amplitude of CTR scattering from a crystal with strain. We constructed model functions for the strain field and determined several parameters using the least-squares fitting. The result suggests that inversion of the sign of the strain occurs near the interface.
Key words: X-ray diffraction, Silicon, Silicon nitrides, Nitridation, Strain

1. INTRODUCTION

Strain induced by an interface affects its electronic structure, but a full understanding of such strains is still lacking. This is true even in the case of the silicon dioxide-silicon interface, which has been applied to electronic devices since the 1960s. In previous papers [1-5], we have investigated strain fields beneath the SiO_2/Si interfaces using a multiple X-ray diffraction phenomenon, which is *modulation of the crystal-truncation-rod (CTR) scattering intensity under a Bragg reflection* [6-11]. Using this technique has revealed that there is a very small strain field beneath the SiO_2/Si interface whose depth extends up to several tens of nanometers and has a static fluctuation in the lateral direction. Information on the depth profile of the strain has been also qualitatively obtained using this technique [2,3,5]. In this paper we present a master formula for the CTR scattering from a crystal with strain, and attempt to quantitatively analyze the strain field beneath the Si_3N_4/Si(001) interface formed by the high-density Xe/NH_3 plasma using this technique. The Si_3N_4 film formed by the Xe/NH_3 plasma (NH radicals) is attracting increasing attention as a high-κ gate because of its high relative dielectric constant and low interface state density in the case of Si(001), Si(111), and Si(110) [12].

2. EXPERIMENT

We investigated the strain fields beneath the Si_3N_4/Si(001) interface by measuring the modulation profiles of the CTR scattering on the 50 rod under the 004 Bragg reflection (see Fig. 1) [1-4]. We define the surface unit cell vectors $\mathbf{a}_{s1}$, $\mathbf{a}_{s2}$, and $\mathbf{a}_{s3}$ by $\mathbf{a}_{s1} = \mathbf{a}_1/\sqrt{2} + \mathbf{a}_2/\sqrt{2}$, $-\mathbf{a}_1/\sqrt{2} + \mathbf{a}_2/\sqrt{2}$, and $\mathbf{a}_3$, where $\mathbf{a}_1$, $\mathbf{a}_2$, and $\mathbf{a}_3$ are the unit cell vectors of the diamond cubic structure of Si. From the modulation profile, we can determine the phase difference between two CTR scatterings: one is the CTR scattering from the incident X-rays and the other is that from the Bragg reflection. Here, we consider the strain field illustrated in Fig. 2, where $\Delta\mathbf{d}_j$ is the deviation of the lattice spacing between the (j-1)th and jth atomic planes from the lattice spacing in bulk $\mathbf{d}$ and $\Delta\mathbf{D}_j$ is the sum of displacements beneath the jth plane. The amplitude $A^{\mathrm{CTR}}(\mathbf{q})$ of the CTR scattering near a Bragg reflection can be related to the depth profile $\Delta\mathbf{D}(z)$ (defined as it satisfies $\Delta\mathbf{D}_j = \Delta\mathbf{D}(j\mathbf{d})$) as follows:

$$A^{\mathrm{CTR}}(\mathbf{q}) \approx \frac{F(\mathbf{q})\mathrm{e}^{2\pi i\mathbf{q}\cdot(n\mathbf{d})}\left[\mathrm{e}^{2\pi i\mathbf{q}\cdot\Delta\mathbf{D}_n} + \xi(\mathbf{q};\Delta q_z)\right]}{2\pi i\Delta q_z d} \quad , \tag{1}$$

where $\mathbf{q}$ is the scattering vector, $F(\mathbf{q})$ is the structure factor, Δq_z is the deviation of the z component of the scattering vector from the Bragg reflection (the z coordinate is defined perpendicular to the interface as shown in Fig. 2), and $\xi(\mathbf{q};\Delta q_z)$ is defined by

$$\xi(\mathbf{q};\Delta q_z) \equiv -\int_{-\infty}^{0} 2\pi i\mathrm{e}^{2\pi i\mathbf{q}\cdot\Delta\mathbf{D}(z)}\frac{d\left(\mathbf{q}\cdot\Delta\mathbf{D}(z+nd)\right)}{dz}\mathrm{e}^{2\pi i\Delta q_z z}dz \quad . \tag{2}$$

Note that $\mathbf{q}$ is almost constant around a Bragg point. $\xi(\mathbf{q};\Delta q_z)$ can then be regarded as the Fourier transform of $-2\pi i\mathrm{e}^{2\pi i\mathbf{q}\cdot\Delta\mathbf{D}}d(\mathbf{q}\cdot\Delta\mathbf{D})/dz$. Thus, we can obtain information about $\Delta\mathbf{D}(z)$ from the modulation profile.

Particularly when $|\mathbf{q}\cdot\Delta\mathbf{D}(z)|$ is sufficiently small and the band width of $\zeta(\mathbf{q};\Delta q_z)$ is much smaller than Δq_z, $\zeta(\mathbf{q};\Delta q_z)$ is negligible. We can then obtain $\mathbf{h}_B\cdot\Delta\mathbf{D}_n$ from the modulation profile, where $\mathbf{h}_B$ is the scattering vector of the Bragg reflection.

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 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 placed on a very flat plate on a high-precision goniometer. A glancing-angle (θ) scan was performed around the 004 Bragg point, and at each angle, the CTR scattering was analyzed using 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 the 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 in order to form oxide films. After etching the oxide films in an 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. Using spectroscopic ellipsometry, the thickness of the Si_3N_4 film was estimated to be 1.36 nm.

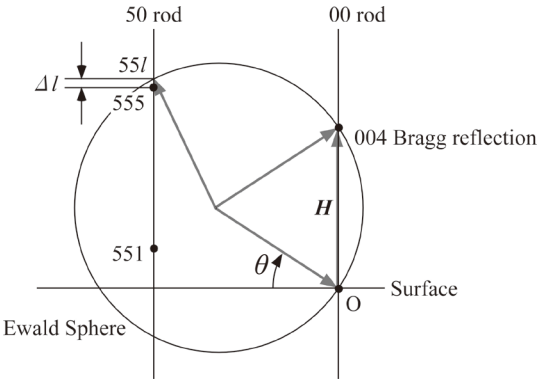

Fig. 1. Illustration of the diffraction condition where the intensity of CTR scattering is modulated by the 004 Bragg reflection. The parameter l is the momentum transfer perpendicular to the surface, and Δl is the deviation of l from the 555 Bragg point.

3. RESULT AND DISCUSSION

The experimental results of the phase difference are shown in Fig. 3. The abscissa of Fig. 3 is Δl, which is defined by $\Delta q_z d$ (see Fig. 1). The parameter Δl was changed by changing the wavelength of the X-rays, which moves the intersection point between the Ewald sphere and 50 rod.

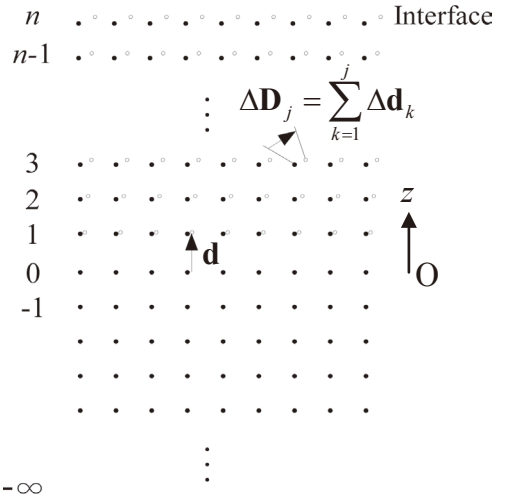

Fig. 2. Illustration of a strain field model beneath the Si_3N_4/Si(001) interface. A strained layer containing n atomic planes is formed on an ideal semi-infinite perfect crystal. The filled circles represent to the positions of atoms or unit cells in bulk crystal, and the open circles represents those in the strained layer beneath the interface. The parameter $\Delta\mathbf{D}_j$ is defined by the sum of displacements beneath the jth atomic plane, and $\Delta\mathbf{d}_j$ is the deviation of the lattice spacing between the (j–1)th and jth atomic planes from the lattice spacing in bulk, $\mathbf{d}$. The direction of the z axis is defined as perpendicular to the interface, and its origin is at the 0th layer.

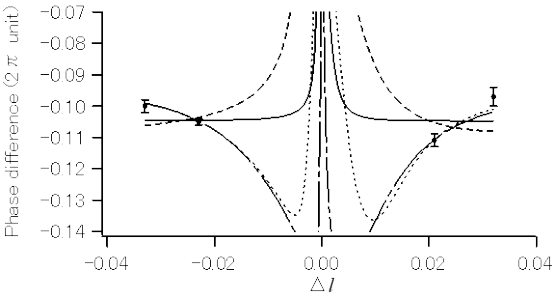

Fig. 3. The experimental results of the phase difference between the CTR scattering arising from the incident X-rays and that from the Bragg reflection (The experimental situation is presented in Fig. 1). The abscissa is Δl, which is defined by $\Delta q_z d$ (see also Fig. 1). The solid line corresponds to A = -0.108 and a = 0.001, while the broken line corresponds to A = -0.127 and a = 0.005 (model 1). The dotted line is the best-fitting curve when A = -0.134, a = 0.004, B = 0.130, and b = 0.012, and the dashed-dotted line is the curve when A = -0.099, B = 0.072, and b = 0.014 (model 2).

The phase differences were not zero, a fact that is not explained by a perfect crystal even when surface roughness is taken into account. Note that the rocking curves of the 004 Bragg reflection were explained by a perfect crystal. These facts support the idea 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 [2]. The phase difference's dependence on Δl suggests that the lattice spacing in the strain field is not constant.

First, we consider an exponentially decaying function model (model 1) for $\Delta\mathbf{D}(z)$ in order to explain the experimental result; that is, we assume that $\mathbf{h}_B \cdot \Delta\mathbf{D}(z+nd)$ is given by:

$$\mathbf{h}_B \cdot \Delta\mathbf{D}(z+nd) = A\mathrm{e}^{az} \quad . \tag{3}$$

Here, A corresponds to the total displacement of the atomic plane beneath the interface. The solid line in Fig. 3 is the calculated curve for A = -0.108 and a = 0.001. This case corresponds to $\xi \approx 0$ in Eq. (1), where the band width of ξ defined by Eq. (2) is sufficiently small. The broken line corresponds to A = -0.127 and a = 0.005. The inclinations of the curve on both sides become large as a increases, and their signs are contrary to the experimental data. This suggests that this model is not sufficient to describe the strain field.

Next, we consider a model function that is expressed by a sum of two exponential functions (model 2). That is, we assumed that

$$\mathbf{h}_B \cdot \Delta\mathbf{D}(z+nd) = A\mathrm{e}^{az} + B\mathrm{e}^{bz} \quad , \tag{4}$$

and performed the least-squares fitting. The dotted line in Fig. 3 is the best-fitting curve, where A = -0.134, a = 0.004, B = 0.130, and b = 0.012 (χ^2 = 1.93). It should be noted that, in this case, the number of data points is the same as the number of parameters; thus, the obtained parameters have large errors. In addition, parameter b and the signs of A and B obtained by the fitting were not sensitive to a; for example, when a is fixed at 0.0005, the fitting is also good (χ^2 = 2.89) when A = -0.099, B = 0.072, and b = 0.014 (dashed-dotted line in Fig. 3).

The depth profiles of the strain (ε_{zz}) obtained above are illustrated in Fig. 4. The solid and dashed lines are the depth profiles corresponding to the cases of a = 0.004 and 0.0005, respectively. The inversion of the sign of the strain is seen near the interface. This inversion is due to positive $d(\mathbf{h}_B \cdot \Delta\mathbf{D})/dz$ at the interface, which is given by $Aa + Bb$. We also performed the least-squares fitting under the condition of $Aa + Bb < 0$, but no good fit was obtained. Similar strain distribution has been reported under thick SiO_2 strips [14] fabricated on a Si substrate, although the strain field was deeper due to the thick strips and their edges. Although it is necessary to use more experimental data for a better fitting, the sign and order of B and b should be correctly given by the above fitting, which suggests that the inversion of sign actually occurs near the interface.

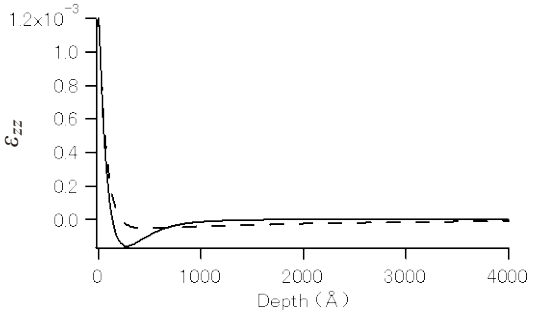

Fig. 4. Quantitatively obtained depth profiles of strain (ε_{zz}) beneath the Si_3N_4/Si(001) interface.

4. CONCLUSION

A multiple-wave X-ray diffraction technique was applied to quantitatively investigate the depth profile of the strain beneath the 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 beneath the Si_3N_4/Si(001) interface formed by the Xe/NH_3 plasma nitridation (NH radical nitridation). We constructed two models for the strain field, and performed the least-squares fitting to the experimentally obtained phase difference of CTR scattering amplitudes. The result suggested that inversion of the sign of the strain occurs near the interface.

ACKNOWLEDGEMENTS

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] W. Yashiro, Y. Yoda, Y. Matsushita, T. Aratani, A. Teramoto, T. Hattori, and K. Miki, *Trans. Mat. Res. Soc. Jpn*. **33**, 607-611 (2008).
[6] T. Takahashi and S. Nakatani, *Surf. Sci.*, **326**, 347-360 (1995).
[7] V. M. Kaganer, M. Albrecht, A. Hirnet, M. Gierer, W. Moritz, B. Jenichen, and K. H. Ploog, *Phys. Rev.* B

61, R16355-R16358 (2000).
[8] T. Takahashi, W. Yashiro, M. Takahasi, S. Kusano, X.W. Zhang and M. Ando, *Phys. Rev.* B **62**, 3630-3638 (2000).
[9] W. Yashiro, K. Shimizu, K. Hirano, and T. Takahashi, *Jpn. J. Appl. Phys.*, **41**, L592-L594 (2002).
[10] W. Yashiro, K. Sumitani, Y. Yoda, and T. Takahashi, *Jpn. J. Appl. Phys*., **42**, 6658-6662 (2003).
[11] O. Litzman and Mikulik, *J. Phys.: Condens. Matter*, **11**, 5767-5779 (1999).
[12] 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).
[13] 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).
[14] S. Di Fonzo, W. Jark, S. Lagomarsino, C. Giannini, L. De Caro, A. Cedola, and M. Müller, Nature, **403** 638-640 (2000).

(Received July 14, 2009;Accepted Septembe 17, 2009)