Strain at Native SiO_2/Si(111) Interface Characterized by Strain-Scanning Second-Harmonic Generation

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***Abstract*— A strain-scanning second-harmonic generation technique is proposed for high-sensitivity measurement of weak strain in film surfaces or interfaces. The basic idea is the sequential application of tensile and compressive strains to a strained film sample. From the strain-dependent second-harmonic generation (SHG) intensity, the type of the strain can be easily judged from whether the SHG is enhanced or weakened, and its magnitude can be precisely calibrated by an externally applied strain that is known. Thus, the built-in strain of a SiO_2/Si interface could be determined as tensile with a magnitude of 3.07×10^{-4}.**

***Index Terms*— Biaxial strain, femtosecond laser, native SiO_2/Si interface, second-harmonic generation.**

I. Introduction

THE Si surface and the SiO_2/Si interface have continuously attracted tremendous research attention because of their important roles in microelectronics, particularly when the linewidth of integrated circuits falls from hundreds of nanometers to tens of nanometers. Properties of micro-nano devices such as metal oxide semiconductors are sensitively affected by the intrinsic mechanical strain built at the SiO_2/Si interface. In fact, the intrinsic strain determines the displacement of atoms, subsurface layer symmetry modification, charge redistribution, dioxide-trap charging, and defect formation [1]–[3]. However, the strain in native SiO_2/Si interface has not been systematically studied because of the lack of appropriate characterization tools. Several experimental techniques have been employed to meet this end, including Raman scattering, piezoelectroreflectance, and X-ray diffraction [4]–[6]. Their sensitivity is good enough for thermal-oxidation SiO_2/Si interface, in which the strain is of the order 10^{-3}, but insufficient for intrinsic SiO_2/Si interface strain, which is generally one order smaller [1], [7], [8]. Moreover, the state of the strain tensor remains unknown. On the other hand, optical second-harmonic generation (SHG) as a high-sensitivity ($10^{-5}-10^{-4}$) nonlinear optical method has been implemented for characterizing the SiO_2/Si interface by resolving the tiny change of centrosymmetry of Si bulk materials [2], [9]. However, an open problem associated with technique is arriving at a reliable relationship between the measured second-harmonic (SH) intensity and the strain without any simplified theoretical assumptions [10]. In this paper, we have solved the problem using a strain-scanning second-harmonic generation (SS-SHG) approach. The fundamental idea is to continuously apply mechanical stress to induce strains from tensile to compressive or vice versa, until the built-in strain at the interface is completely compensated. As both the strain and SHG intensity are accurately measurable, a natural link between them is built for quantitative calibration of the strength and status of the strain between SiO_2/Si interfaces.

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II. Experiments

A single-side-polished naturally oxidized Si(111) wafer with a diameter of 50.8 mm and thickness of 0.5 mm was chosen. The thickness of the native oxide film formed due to substrate passivation in air is around 4 nm, as determined by ellipsometry. Its existence prevents further oxidation of the wafer. A strain-supplying device was designed to exert biaxial spherical strain, from which a spherical tensile strain [11, Fig. 1(a)] was induced by pushing a stainless steel ball (3 mm in diameter) along the [111] direction of the wafer, i.e., z-axis, from the center of its backside. On the other hand, the biaxial compressive strain [Fig. 1(b)] was achieved by pushing a stainless steel disc with a center hole, the latter for allowing light to pass from the oxidized surface to the front side. Both the ball and the ring were driven by a propeller micrometer for high-precision force imposition. There are two types of strains at the SiO_2/Si interface: a tensile strain is exerted by the SiO_2 ultrathin film, and the other, either tensile or compressive depending on the substrate bending direction, comes from the lower portion of the wafer. The strain distribution across the entire thickness of the silicon wafer is roughly divided by a zero-strain layer into two parts when an external force is applied as illustrated in the inset of Fig. 2. The upper part undergoes tensile strain while the lower part feels compressive strain if the wafer protrudes upward at the center. Considering the effects of the crystalline orientation, the strain distribution in the inner portion of the silicon wafer is quite complicated. However, what we are concerned with in this paper is the surface layer, solely about 100 nm in thickness, as determined

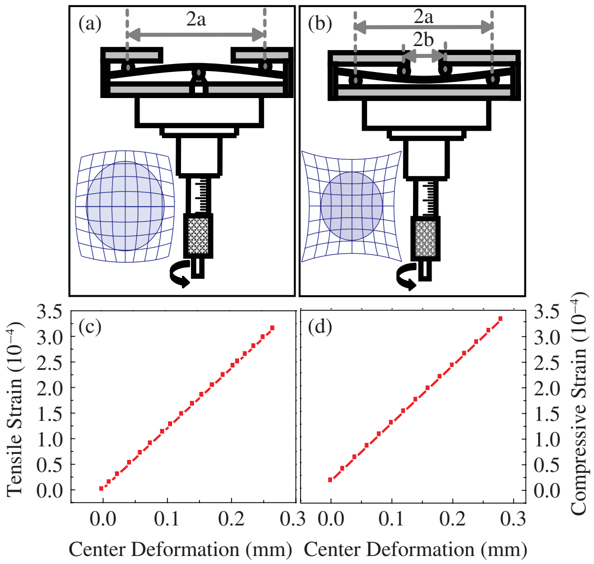

Fig. 1. (a) Right, the setup of biaxial tensile strain device using a center force to bend the Si wafer with 2a = 45.0 mm; Left, the scheme of deformed Si wafer after applying of the biaxial tensile strain. (b) Right, the setup of biaxial compressive strain device using a circular force to bend the Si wafer with 2a = 45.0 mm and 2b = 22.5 mm; Left, the scheme of Si wafer near the center after applying of the biaxial compressive strain. (c) Tensile strain as a function of the moving distance of the micrometer system and the data points are obtained by measuring the radius of curvature. (d) Compressive strain as a function of the moving distance of the micrometer system and the data points are obtained by measuring the radius of curvature.

by the penetration depth of the 400-nm wavelength of the SHG laser. This layer thickness is only 1/5000 of the wafer thickness. The strain distribution on the surface layer may therefore be reasonably considered as uniform.

When an external force is added, two orthogonal strain components in SiO_2/Si(111) surface were kept proportional to the displacement of the wafer center, where the maximum strains were expressed as $\varepsilon_{xx} = \varepsilon_{yy} = \varepsilon_0 = h/2R$ (ε_0 is the strain at the wafer center) [12]–[14], where h is the thickness of the Si wafer and R denotes the radius of bending curvature, which can be directly measured by the deflection of a monitoring laser beam [11]. In addition, the x- and y-axis were chosen as the $[1\bar{1}0]$ and $[11\bar{2}]$ directions, respectively. The strain as a function of the displacement of the center of the wafer as the wafer bends toward the two opposite directions is shown in Fig. 1. As the forces are locally exerted, the strain distribution should be inhomogeneous in the Si(111) surface but uniform along the [111] direction. Consequently, the inversion symmetry of a single-crystalline Si wafer would be destroyed in the volume near the wafer center, where SHG would arise [15], [16]. For the SHG experiment, a 120-fs, 82-MHz repetition rate Ti: sapphire femtosecond laser oscillator was used. The beam diameter was about 10 μm and the laser intensity was 140 mW. The s-polarized fundamental light of 800 nm was focused onto the sample at an incident angle of 45° with respect to the Si [111] direction. The reflected p-polarized SHG signal was selected using a polarization analyzer, filtered by a saturated $CuSO_4$ solution, and then detected by a photomultiplier tube and a lock-in amplifier. The experimental setup is shown in Fig. 2. The use of the 800-nm femtosecond laser is, on one hand, for minimizing thermal effect, which is the major source of drift of the SHG signal,

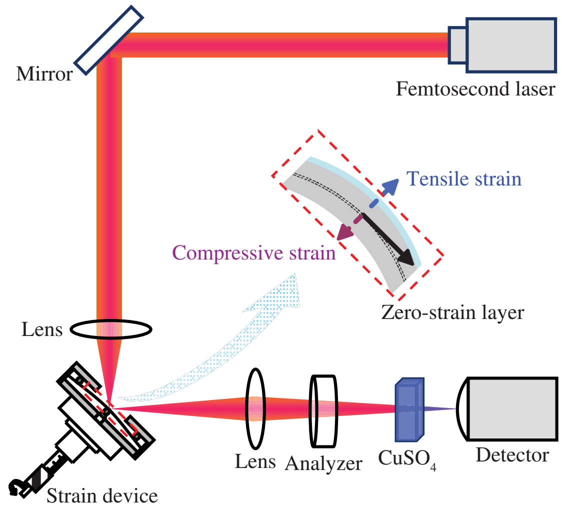

Fig. 2. SS-SHG experimental setup. The s-polarized fundamental light of 800 nm was focused onto the strained sample at an incident angle of 45° with respect to Si [111] direction. The reflected p-polarized SHG signal was selected using a polarimeter, filtered by the saturated $CuSO_4$ solution, and then detected by detector. Here, the detector includes a photomultiplier tube and a lock-in amplifier. The inset shows the strain distribution across the interface when the sample is convex.

and on the other hand for improving the longitudinal spatial resolution by its penetration depth around 100 nm. In order to further avoid thermal fluctuation, SHG signal measurement was performed 5s after the laser irradiation on to the silicon sample.

III. Results and Discussions

To clarify the strain type at the built-in native SiO_2/Si(111) interface, p-polarized SH signal reflected from the interface under s-polarized excitation with external mechanical forces was measured. The SH intensity, dependent on the azimuthal angle ϕ, under different strains is shown in Fig. 3(a), where ϕ starts from the $[1\bar{1}0]$ direction and around the wafer surface normal. The SH intensity as a function of the external tensile strain at $\phi = 60°$ is shown in Fig. 4. The SH intensity is enhanced when the Si sample is subjected to a biaxial tensile strain. The enhancement of SH signal could be attributed to the inhomogeneity of distribution of the strain, which resulted in the so-called strain-induced second-order nonlinear susceptibility $\chi^{(2)}_{\text{strain}}$ [4]. The SHG curves for both unstrained and strained SiO_2/Si(111) interfaces, shown in Fig. 3(a), possess a threefold symmetry for s-input/p-output. The distortion of the SHG intensity curve may arise from the 3° miscut [1] of the surface plane toward $[11\bar{2}]$ direction and it is exaggerated when forces are loaded. According to the phenomenological theory of surface SHG, the p-polarized SH generated from SiO_2/Si(111) interface with the s-polarized excitation can be written as [4], [16], [17]

$$\begin{aligned} I_{s\to p}(2\omega) &= \left|a_{sp} + c_{sp}\cos 3\phi\right|^2 \\ &= \left[\left|a_{sp}\right|^2 + \frac{\left|c_{sp}\right|^2}{2}\right] + \mathrm{Re}(a_{sp}c_{sp}^*)\left[e^{i3\phi} + e^{-i3\phi}\right] \\ &\quad + \frac{\left|c_{sp}\right|^2\left[e^{i6\phi} + e^{-i6\phi}\right]}{4} \end{aligned} \tag{1}$$

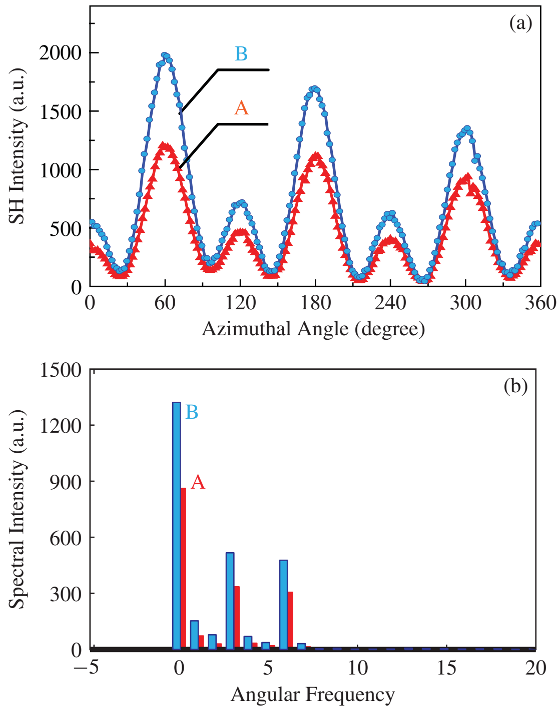

Fig. 3. (a) *s*-polarized input/*p*-polarized output SH intensity as a function of azimuthal angle of Si(111) sample. Curve A corresponds to the SHG from unstrained Si(111) wafer and curve B is measured when the tensile strain is equal to 2.41×10^{-4}. (b) Fourier transforms of SHG patterns of (a). Graph A is the Fourier transform corresponding to curve A of (a) and graph B is the Fourier transform corresponding to curve B of (a).

where the coefficients a_{sp} and c_{sp} represent the total SH contributions that result from the interface dipolar polarizations, bulk electric quadrupole, the contributions induced by dc electric field, and the built-in strain at the SiO_2/Si(111) interface for unstrained SiO_2/Si(111). With the external strain applied, a new term describing the external strain-induced second-order nonlinear polarization in a_{sp} and c_{sp} coefficients appears. The curves in Fig. 3(a) agree well with (1). Curves A and B are the SH signals reflected from the unstrained Si wafer and strained Si sample, respectively. The SH signal enhancement (curves A and B) with the increase in the external tensile strain indicates that the strain in the built-in native SiO_2/Si interface has the same sign as the externally applied one. In other words, the intrinsic strain is tensile. The underlying physics of the enhancement should be a result of the shift of the point group symmetry from O_h to C_{3v}. The strained Si has the same symmetry as the SiO_2/Si(111) interface and the nonvanishing independent components of the strain-induced $\chi^{(2)}_{strain}$ are $\chi^{(2)strain}_{zzz}$, $\chi^{(2)strain}_{zxx} = \chi^{(2)strain}_{zyy}$, $\chi^{(2)strain}_{yyy} = \chi^{(2)strain}_{xxy}$ [4]. In addition, the *p*-polarized SH electric field reflected from the strained Si with an *s*-polarized field is found to be proportional to [4], [16], [17]

$$E_{s\to p}(2\omega) \propto i\chi^{(2),strain}_{zyy} + K_{2z}(2\omega)\zeta \tag{2}$$

where K_{2z} is the component of effective spring constant in the direction that is perpendicular to SiO_2/Si interface and ζ is the bulk quadrupole contribution which is independent of the external strain. $\chi^{(2),strain}_{zyy}$ is the component of strain-induced second-order nonlinear susceptibility, which is proportional to

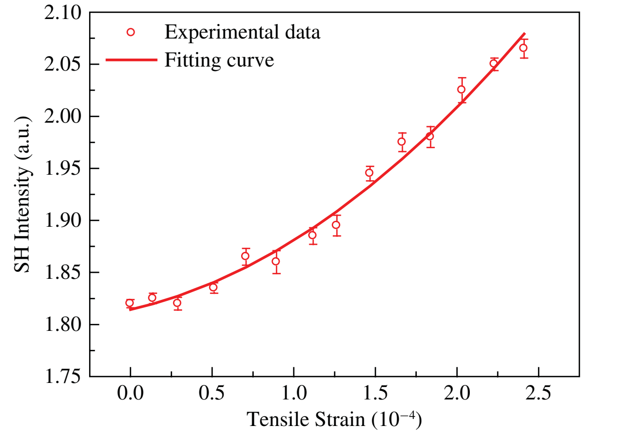

Fig. 4. *p*-polarized SHG intensity under *s*-polarized excitation reflected from native SiO_2/Si(111) interface as a function of the tensile strain. The solid curve is fitted, and the fitting function can be expressed as $I_{s\to p} = 3.0656 \times 10^6\varepsilon_0^2 + 0.0004 \times 10^6\varepsilon_0 + 106693$.

the tensile strain of wafer center, calculated as follows for SiO_2/Si(111) interface [4], [10]:

$$\chi^{(2),strain}_{zyy}(esu) = 1.03 \times 10^{-6}\varepsilon_0 \tag{3}$$

from (2), it can be seen that

$$\frac{|c_{sp}(\text{strain})|^2}{|c_{sp}(0)|^2} = \frac{\left|i\chi^{(2),strain}_{zyy} + K_{2z}\zeta\right|^2}{|K_{2z}\zeta|^2} = 1 + \left|\frac{\chi^{(2),strain}_{zyy}}{K_{2z}\zeta}\right|^2. \tag{4}$$

The coefficients a_{sp} and c_{sp} are determined by Fourier analysis and Fourier transform of the SH azimuthal dependence, as shown in Fig. 3(b). It can be seen from Fig. 3(b) that $|c_{sp}(\text{strain})|^2/|c_{sp}(0)|^2 = 1.54$ when strain is 2.41×10^{-4}. Considering $K_{2z}\zeta = 4.0 \times 10^{-10}$ esu [4], we can calculate the strain at the center as 2.86×10^{-4} from (3). The magnitude of the tensile strain is readily altered by continuous strain scanning, which leads to quantitative determination of the relation between SH intensity and known strains [Fig. 4].

Exerting a force with the ring instead of the ball from the front side of the wafer induces a compressive strain, from which a change in the type and magnitude of the strain in the built-in native SiO_2/Si interface can be expected. The SH intensity is found first to reduce with the increase of the external compressive strain, and then to increase in the course of strain scanning. A knee point appears, as indicated in Fig. 5. The occurrence of the minimum of SH intensity at a compressive strain of 3.07×10^{-4} is surprising, but is well understandable. That is, the external compressive strain has the opposite sign of the intrinsic strain, which is consistent with the result of tensile strain scanning, and at the minimum point, the built-in tensile strain is completely compensated by the external compression. The same phenomenon has been experimentally observed with high reproducibility from the different points of a wafer and from different wafers when a compressive force is added from zero to a maximum, beyond which the wafer would break. In the entire strain-scanning

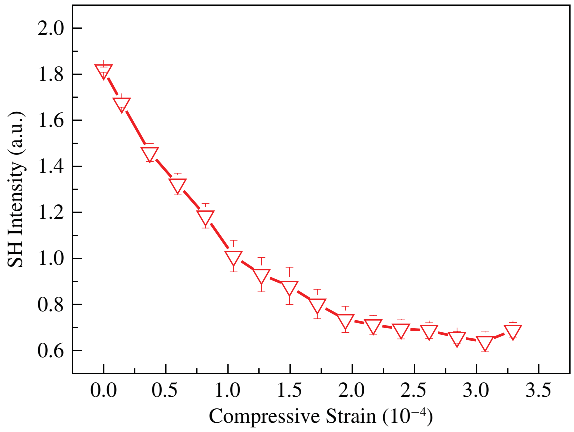

Fig. 5. Intensity of the p-polarized SHG under s-polarized excitation reflected from native SiO_2/Si(111) interface as a function of the compressive strain. The compressive strain that corresponds to the minimum of SH intensity is equal to 3.07×10^{-4}.

process, the built-in tensile strain is first reduced because of the less deformation of the silicon lattice at the interface, then is minimized because of the minimal lattice deformation, and the final increase should be the result of enhanced lattice distortion due to compressive strain. There are three points that are worthy of mentioning: 1) the nonzero level of the minimum should be associated with other contributions (such as the surface dipolar polarizations, bulk electric quadrupole, the contributions induced by the dc electric field built-in SiO_2/Si(111) interface) that are independent of strain-induced SH contribution; 2) the occurrence of the minimal point in the compressive strain scanning is highly reproducible from various samples, but increase in the external force leads to wafer fracture; and 3) the strain resolution of the strain scanning, associated with the screwing step of the propeller micrometer and the measurement accuracy of the deflected beam spot is 10^{-5}, which is similar to the SHG detection accuracy.

IV. Conclusion

In conclusion, this paper demonstrated an SS-SHG technique that is useful for weak strain measurement. As an application example, we continuously exerted tensile and compressive strains onto a native SiO_2/Si interface, and as a result its built-in strain was determined as tensile with a magnitude of 3.07×10^{-4}. This technnique may find broad application in surface studies, particularly, of silicon micro-nano devices in the integrated circuit industry.

References

[1] G. Lüpke, D. J. Bottomley, and H. M. van Driel, "SiO_2/Si interfacial structure on vicinal Si (100) studied with second-harmonic generation," *Phys. Rev. B*, vol. 47, no. 16, pp. 10389–10394, Apr. 1993.

[2] W. Daum, H. J. Krause, U. Reichel, and H. Ibach, "Identification of strained silicon layers at $Si - SiO_2$ interfaces and clean Si surfaces by nonlinear optical spectroscopy," *Phys. Rev. Lett.*, vol. 71, no.8, pp. 1234–1237, Aug. 1993.

[3] H. Ibach, "The role of surface stress in reconstruction, epitaxial growth and stabilization of mesoscopic structures," *Surf. Sci. Rep.*, vol. 29, nos. 5–6, pp. 195–263, 1997.

[4] J. Y. Huang, "Probing inhomogeneous lattice deformation at interface of $Si(111)/SiO_2$ by optical second-harmonic reflection and Raman spectroscopy," *Jpn. J. Appl. Phys.*, vol. 33, no. 7A, pp. 3878–3886, Jul. 1994.

[5] F. H. Pollak and M. Cardona, "Piezo-electroreflectance in Ge, GaAs, and Si," *Phys. Rev.*, vol. 172, no. 3, pp. 816–837, Aug. 1968.

[6] B. C. Larson, C. W. White, T. S. Noggle, and D. Mills, "Synchrotron X-ray diffraction study of silicon during pulsed-laser annealing," *Phys. Rev. Lett.*, vol. 48, no. 5, pp. 337–340, Feb. 1982.

[7] F. J. Himpsel, F. R. McFeely, A. Taleb-Ibrahimi, J. A. Yarmoff, and G. Hollinger, "Microscopic structure of the SiO_2/Si interface," *Phys. Rev. B*, vol. 38, no. 9, pp. 6084–6096, Sep. 1988.

[8] M. Niwano, H. Katakura, Y. Takeda, Y. Takakuwa, N. Miyamoto, A. Hiraiwa, and K. Yagi, "Photoemission study of the SiO_2/Si interface structure of thin oxide films on Si(100), (111), and (110) surfaces," *J. Vac. Sci. Technol. A*, vol. 9, no. 2, pp. 195–200, Mar. 1991.

[9] C. W. van Hasselt, M. A. Verheijen, and T. Rasing, "Vicinal Si(111) surfaces studied by optical second-harmonic generation: Step-induced anisotropy and surface-bulk discrimination," *Phys. Rev. B*, vol. 42, no. 14, pp. 9263–9266, Nov. 1990.

[10] J.-H. Zhao, Q.-D. Chen, Z.-G. Chen, G. Jia, W. Su, Y. Jiang, Z.-X. Yan, T. V. Dolgova, O. A. Aktsipetrov, and H.-B. Sun, "Enhancement of second-harmonic generation from silicon stripes under external cylindrical strain," in *Proc. Extended Abstract 6th Nat. Photon. Conf.*, Chongqing, China, Oct. 2008.

[11] E. Liiarokapis and W. Richter, "Design of two devices for biaxial stresses and their application to silicon wafers," *Meas. Sci. Technol.*, vol. 3, no. 4, pp. 347–351, Apr. 1992.

[12] S. P. Timoshenko and S. Woinowsky-Krieger, *Theory of Plates and Shells*. New York: McGraw-Hill, 1989.

[13] E. Liarokapis, D. Papadimitriou, and J. Rumberg, "Raman and RAS measurements on uniaxially strained thin semiconductor layers," *Phys. Status Solidi (B)*, vol. 211, no. 1, pp. 309–316, Jan. 1999.

[14] D. Papadimitriou and W. Richter, "Highly sensitive strain detection in silicon by reflectance anisotropy spectroscopy," *Phys. Rev. B*, vol. 72, no. 7, pp. 075212-1–075212-11, Aug. 2005.

[15] G. L. Bir and G. E. Pikus, *Symmetry and Strain-Induced Effects in Semiconductors*. New York: Wiley, 1974.

[16] S. V. Govorkov, V. I. Emel'yanov, N. I. Koroteev, G. I. Petrov, I. L. Shumay, V. V. Yakovlev, and R. V. Khokhlov, "Inhomogeneous deformation of silicon surface layers probed by second-harmonic generation in reflection," *J. Opt. Soc. Am. B*, vol. 6, no. 6, pp. 1117–1124, Jun. 1989.

[17] J. E. Sipe, D. J. Moss, and H. M. van Driel, "Phenomenological theory of optical second- and third-harmonic generation from cubic centrosymmetric crystals," *Phys. Rev. B*, vol. 35, no. 3, pp. 1129–1141, Jan. 1987.

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