

# Determination of interface layer strain of Si/SiO<sub>2</sub> interfaces by reflectance difference spectroscopy

Z. Yang,<sup>a)</sup> Y. H. Chen,<sup>b)</sup> and Jacob Y. L. Ho

Department of Physics, the Hong Kong University of Science and Technology, Clearwater Bay, Kowloon, Hong Kong

W. K. Liu<sup>c)</sup>

Department of Physics and Astronomy and Laboratory of Electronic Properties of Materials, University of Oklahoma, Norman, Oklahoma 73019

X. M. Fang and P. J. McCann

School of Electrical and Computer Engineering and Laboratory of Electronic Properties of Materials, University of Oklahoma, Norman, Oklahoma 73019

(Received 10 March 1997; accepted for publication 6 May 1997)

Detailed studies of the often-observed resonance feature near 3.4 eV in the reflectance difference spectrum of Si/SiO<sub>2</sub> interfaces and Si surfaces show that the resonance is due to the intrinsic local-field effect, and that its energy position coincides with the  $E_1$  energy of bulk Si. Using the energy position of the resonance of the pseudomorphically grown Si/CaF<sub>2</sub> interfaces as a reference point, the strain-induced resonance energy shift of the Si interface layer at several Si/SiO<sub>2</sub> interfaces are obtained and the strain in these layers is determined. The results show that the interface layers are highly strained with an equivalent hydrostatic pressure of 0.79 GPa, but still maintain a high degree of order. © 1997 American Institute of Physics. [S0003-6951(97)05027-4]

The demand for further dimension reduction of Si-based integrated circuits has imposed even greater challenges to the growth of thinner gate oxides of high quality. One of the critical concerns is the strain at the interface between Si and the oxides. Various techniques have been developed to study the strain in both the oxide layer and the Si layer near the interface. The thickness-averaged strain in the oxide layers, studied by the laser deflected beam technique and by infrared spectroscopy,<sup>1</sup> was found to be closely related to the interface state density at the Si midgap. To measure the strain in the Si interface layer, several optical techniques, including photoreflection (PR),<sup>2</sup> spectroscopic ellipsometry (SE),<sup>3</sup> and nonlinear optical spectroscopy, such as second-harmonic generation (SHG),<sup>4,5</sup> have been employed. The main effort has been concentrated on the measurement of the strain-induced energy shift of the  $E_1$  critical energy of Si. These techniques, though quite successful, had their limits. The PR signals from the Si interface layer were very weak, and a line-shape fit was required to extract the value of  $E_1$ .<sup>2</sup> The SHG signals were also quite weak, and measurements at several crystal orientations were needed.<sup>4,5</sup> Furthermore, the effects of high excitation in SHG experiments on  $E_1$  energy were not all clear. The SE technique required high-precision measurements of the combined optical function of the oxide/interface/Si system and careful least-square fitting of several samples with presumably identical interfaces but different oxide layer thicknesses.<sup>3</sup> From the peaks of the dielectric function, the value of  $E_1$  could then be obtained. Due to

these limitations, the uncertainty of the strain measured so far has been quite large, and improved techniques are certainly in demand.

We demonstrate that the reflectance difference/anisotropy spectroscopy (RDS/RAS) is a more effective technique in studying the strain in the Si interface layer of Si/SiO<sub>2</sub> interfaces. First, we will show that the resonance often observed in Si surface and Si/SiO<sub>2</sub> interface RD spectra near 3.4 eV (Ref. 6) is due to the local field effect of well-ordered Si surfaces and interfaces.<sup>7</sup> The strain in the Si interface layer of a Si/SiO<sub>2</sub> interface can then be determined by comparing the strain shifted RD resonance with that of a Si/CaF<sub>2</sub> interface served as a reference, because Si and CaF<sub>2</sub> are almost lattice matched.

Several (211) and (111) vicinal orientation Si/SiO<sub>2</sub> interfaces with either native oxide or formed by dry oxidation were studied. The samples with native oxide were as-received wafers without further treatments. Normal dry-oxidation procedures for metal-oxide-semiconductor devices were followed to prepare the oxide layers of about 10 nm thickness. The wafers were first cleaned in 10:1 sulfuric-acid/hydrogen-peroxide solution, and then were etched twice for 1 min in 1:50 HF solution. The oxidation was carried out at 950 °C with dry oxygen. Some of the dry-oxidized samples were subjected to rapid thermal annealing (RTA) in pure argon gas for 100 s at 1050 °C immediately after the oxidation. All the Si/SiO<sub>2</sub> interfaces were formed on 2 in. *p*-type (~0.1 Ω cm) wafers. The (111) wafer was unintentionally miscut, and was found by x-ray diffraction measurement to be 2° off towards the [211] direction plus 0.6° towards the [011] direction.

The CaF<sub>2</sub>/Si(111) heterostructures were grown by molecular beam epitaxy using an Intevac modular Gen II system. The Si (111) substrates with ~3° misorientation prepared using a modified Shiraki etch<sup>8</sup> followed by a 10% HF

<sup>a)</sup>Electronic mail: phyang@usthk.ust.hk

<sup>b)</sup>On leave from the Laboratory of Semiconductor Materials Science, Institute of Semiconductors, Chinese Academy of Sciences, Box 912, Beijing 100083, People's Republic of China.

<sup>c)</sup>Present address: Quantum Epitaxial Designs, Inc., 119 Technology Drive, Bethlehem, PA 18015. Electronic mail: amy@qedmbe.com

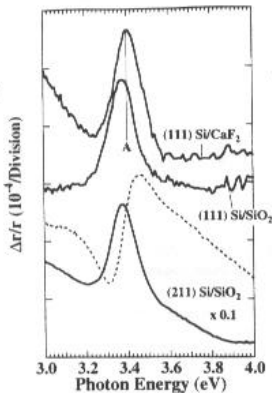


FIG. 1. The RD spectrum of several Si/insulator interfaces. The dashed curve represents the real RD spectrum of the (211)-oriented Si/SiO<sub>2</sub> interface, while the solid curves are the imaginary RD spectrum of the interfaces being investigated. The spectra have been shifted vertically for clarity.

dip exhibited well-defined Si(111)-(7×7) reflection high-energy electron diffraction patterns after *in situ* thermal cleaning at 700 °C. A high-purity polycrystalline CaF<sub>2</sub> source was evaporated from a graphite-coated pyrolytic boron nitride crucible at around 1280 °C. This produced a beam equivalent pressure of  $\sim 7.0 \times 10^{-8}$  Torr and a growth rate of  $\sim 0.1$  ML/S. The substrates were rotated at 10 rpm to improve film uniformity. A background pressure of  $\sim 10^{-10}$  Torr was maintained throughout the growth. The sample was grown pseudomorphically using a two-stage growth procedure,<sup>9</sup> where a single monolayer of CaF<sub>2</sub> was first grown at 700 °C before the growth of the following 4 ML ensued at a reduced substrate temperature ( $\sim 100$  °C).

The RDS measurements were carried out after the oxide layers were formed. The RDS apparatus was virtually the same as the one in Ref. 10. Low-temperature RDS was carried out in a cold finger cryostat with a stress-free quartz window. No noticeable birefringement effects from the window were observed in the RDS spectra when the setup was tested with a singular (001) Si wafer. The two principal axes of the RDS were the [0,1,1] and the [1,1,1] directions for the (211) oriented interface, and along and perpendicular to the tilt direction for the vicinal (111) interfaces.

A common feature often observed in the real RD spectrum of a well-ordered Si surface is the derivativelike structure near 3.4 eV. This feature has been observed for a number of Si surfaces terminated with H or O and several Si/SiO<sub>2</sub> interfaces.<sup>6,11</sup> The energy position and the shape of the structure resemble well the theoretical ones based on the local-field effect.<sup>7</sup> We have also observed this feature in the real RD spectrum of all the samples studied, and a typical one for the (211)-oriented Si/SiO<sub>2</sub> interface is shown as a dashed curve in Fig. 1. A corresponding line-shaped resonance appears at the same energy in the imaginary RD spectra (solid curves), as expected.<sup>12</sup> The intensity of the resonance for the (211) interface is about ten times of that of the (111) vicinal interfaces. This is because a singular (111) in-

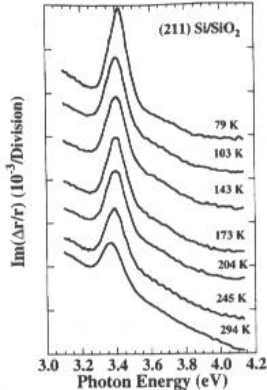


FIG. 2. The imaginary RD spectra of the (211)-oriented Si/SiO<sub>2</sub> interface at low temperatures showing the change of the dominant resonance.

terface is expected to be isotropic. The observed optical anisotropy is caused by the misorientation and the magnitude of which is roughly proportional to the misorientation angle.<sup>11</sup> The influence of the optical activity inside the oxide layer or the CaF<sub>2</sub> layer to the RD spectra can be neglected since the layers are less than 15 nm thick.

We propose, based on the following observations, that the resonance near 3.4 eV is due to the intrinsic surface local-field effect of a well-ordered anisotropic Si surface or interface layer. The resonance is a dominant feature in the RD spectra of almost all the Si surfaces and interfaces reported so far, and it is not sensitive to the type of chemical species covering the surface. The resonance had been observed in the RD spectrum of (011) surfaces covered with H,<sup>6</sup> (001) vicinal surfaces covered with O,<sup>6</sup> a number of Si/SiO<sub>2</sub> interfaces of different orientations,<sup>11</sup> and the (111) vicinal Si/CaF<sub>2</sub> interface shown in Fig. 1. The energy position and the line shape of the resonance fit the theory well,<sup>7</sup> which predicts that the resonance is due to the combined contribution of the  $E'_0$  and the  $E_1$  critical energies of bulk Si. For further verification, we performed low-temperature RDS to see whether the energy shift of the resonance follows that of the  $E'_0$  and the  $E_1$  critical energies. Figure 2 shows the low-temperature RDS spectra of the (211) sample subjected to RTA at 1050 °C. Lowering the temperature at which the RDS was taken shifts the resonance to higher energy and enhances the amplitude, while the linewidth narrows only slightly. The resonance of the (111) vicinal Si/SiO<sub>2</sub> and the Si/CaF<sub>2</sub> samples behave the same. Figure 3 shows the resonance energy of the (111) Si/CaF<sub>2</sub>, the (211) Si/SiO<sub>2</sub>, and the (111) Si/SiO<sub>2</sub> interfaces as a function of temperature. Apart from a temperature-independent energy shift of 37 meV for the Si/CaF<sub>2</sub> interface, all the data points form a single line with a common slope of  $-(0.20 \pm 0.05)$  meV/K. This value is consistent with the  $E_1$  temperature coefficient of  $-0.21 \pm 0.10$  meV/K for bulk silicon.<sup>13</sup> The fact that the resonance energy of all three interfaces have the same temperature coefficient indicates that the origin of the resonance for the three interfaces is the

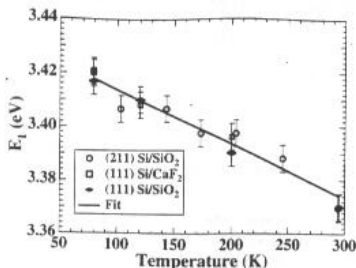


Fig. 3. The energy position of the resonance as a function of temperature of the (211)-oriented Si/SiO<sub>2</sub> interface, the (111) vicinal Si/SiO<sub>2</sub> interface, and the (111) vicinal Si/CaF<sub>2</sub> interface. The data points of the Si/CaF<sub>2</sub> interface have been shifted downwards by 37 meV.

same. The amplitude of the resonance keeps increasing without saturation down to 79 K. This linewidth and intensity change is also consistent with that of the  $E_1$  peak of the Si dielectric function.<sup>13</sup> The temperature dependence of the resonance strongly suggests that it is closely related to the  $E'_0$  and the  $E_1$  critical energies of bulk Si, and that it is due to the interface local-field effect.

Silicon is almost lattice matched to CaF<sub>2</sub> (<0.6% at 300 K), so that the Si interface layer next to the thin layer of pseudomorphically grown CaF<sub>2</sub> is not strained. The energy position of the RDS resonance (see Fig. 1) at  $3.407 \pm 0.005$  eV, therefore, represents the  $E_1$  energy of unstrained Si,<sup>13</sup> and can be used as a reference point to determine the strain in the Si/SiO<sub>2</sub> interface system. This value is almost identical to the reference  $E_1$  energy value of  $3.408 \pm 0.010$  eV obtained by PR in Ref. 2. The  $E_1$  energy shift of the Si/SiO<sub>2</sub> interfaces studied here is  $37 \pm 10$  meV. The shift for the native oxide interface is slightly smaller than that of the dry-oxidized one. This is probably because the native oxide is not as dense as the one formed by the well-controlled dry-oxidation process. The energy shift indicates a highly strained Si interface layer with an equivalent hydrostatic pressure of 0.79 GPa. This value is smaller than, but is within the experimental error of, that reported in Refs. 2 and 3, which ranges from 0.81 to 1.4 GPa with an error of  $\pm 0.4$  GPa. The interface layer still maintains a high degree of order so that the local-field effect is manifested in the RD spectra. The fact that the linewidth of the Si/SiO<sub>2</sub> interface is comparable to that of the Si/CaF<sub>2</sub> interface indicates that the strain distribution within the interface layer is uniform. Since

a gradual change of strain in the direction perpendicular to the interface into the Si substrate is expected, the narrow linewidth suggests that only a very thin Si interface layer is being probed by the RDS. The resonance for the as-grown (211) Si/SiO<sub>2</sub> interface is almost identical in position and intensity as the ones subjected to RTA, indicating that RTA has virtually no influence on the strain. This is consistent with previous findings.<sup>4,5</sup>

In summary, we have demonstrated that the RDS technique is a useful tool to study the strain in the Si interface layer of Si/SiO<sub>2</sub> interfaces. The RDS spectra are easy to interpret because only the peak position and the intensity are involved. The strain values so obtained are of good accuracy because the resonance line is well defined, and unlike SE, no fitting process to an optical model is needed. Our results show that the interface layer of Si is highly strained with an equivalent hydrostatic pressure of 0.79 GPa, but the interface layer still maintains a high degree of order. The interface layer, which is uniformly strained, is probably confined to a few monolayers of Si atoms. The scope of RDS application can be extended to other Si-based interfaces, such as Si/SiN<sub>x</sub> interfaces as well.

Helpful discussions with D. A. Aspnes are gratefully acknowledged. The work at Hong Kong University of Science and Technology was supported by the Research Grant Council Grant No. 609/95P from the Hong Kong Government, and the experiments were performed in the William Mong's Semiconductor Cluster Laboratory.

<sup>1</sup> C. H. Bjorkman, J. T. Fitch, and G. Lucovsky, *Appl. Phys. Lett.* **56**, 1983 (1990).

<sup>2</sup> J. T. Fitch, C. H. Bjorkman, and G. Lucovsky, *J. Vac. Sci. Technol.* **B 7**, 775 (1989).

<sup>3</sup> N. V. Nguyen, D. Chandler-Horowitz, P. M. Amirtharaj, and J. G. Pellegrino, *Appl. Phys. Lett.* **64**, 2688 (1994).

<sup>4</sup> W. Daum, H.-J. Krause, U. Reichel, and H. Ibach, *Phys. Rev. Lett.* **71**, 1234 (1993).

<sup>5</sup> C. Meyer, G. Lupke, U. Emmerichs, F. Wolter, H. Kurz, C. H. Bjorkman, and G. Lucovsky, *Phys. Rev. Lett.* **74**, 3001 (1995).

<sup>6</sup> T. Yasuda, L. Mantese, U. Rossow, and D. E. Aspnes, *Phys. Rev. Lett.* **74**, 3431 (1995); D. E. Aspnes and A. A. Studna, *ibid.* **54**, 1956 (1985).

<sup>7</sup> R. Del Sole, W. L. Mochan, and R. G. Barrera, *Phys. Rev. B* **43**, 2136 (1991).

<sup>8</sup> A. Ishizaka and Y. Shiraki, *J. Electrochem. Soc.* **133**, 666 (1986).

<sup>9</sup> N. S. Sokolov, J. C. Alvarez, and N. L. Yakovlev, *Appl. Surf. Sci.* **60/61**, 421 (1992).

<sup>10</sup> Z. Yang, I. K. Sou, Y. H. Yeung, G. K. L. Wong, Jie Wang, Cai-xia Jin, and Xiao-Yuan Hou, *J. Vac. Sci. Technol. B* **14**, 2973 (1996).

<sup>11</sup> T. Yasuda, D. E. Aspnes, D. R. Lee, C. H. Bjorkman, and G. Lucovsky, *J. Vac. Sci. Technol. A* **12**, 1152 (1994).

<sup>12</sup> Tat-Kun Kwok and Z. Yang, *J. Appl. Phys.* **80**, 4621 (1996).

<sup>13</sup> A. Daunois and D. E. Aspnes, *Phys. Rev. B* **18**, 1824 (1978).