Identification of Strained Silicon Layers at Si-SiO$_2$ Interfaces and Clean Si Surfaces by Nonlinear Optical Spectroscopy

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Optical second-harmonic and sum-frequency spectra of clean and oxidized Si(100) and Si(111) samples reveal a strong resonance band at 3.3 eV photon energy. It is concluded that the resonance arises from direct transitions between valence and conduction band states in a few monolayers of strained silicon at the Si-SiO$_2$ interface and at the selvedge of clean reconstructed silicon surfaces.

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The Si-SiO$_2$ interface as an essential constituent of metal-oxide-semiconductor (MOS) devices is certainly the most investigated interface between two solid materials. Crucial parameters of such devices are chemical composition and structural order of the Si-SiO$_2$ interface [1]. Important types of interface defects which detrimentally affect the electrical characteristics of MOS structures have been identified by different spectroscopies in the past: The existence of silicon suboxide species on the SiO$_2$ side of the interface has been shown by x-ray photoelectron spectroscopy [2]. Nonsaturated bonds of silicon atoms at the interface induce chargeable interface states of amphoteric character close to the middle of the silicon band gap [3]. These dangling bond states act as paramagnetic (P_b) centers and have been identified by electric-field-controlled electron paramagnetic resonance (EPR) [4]. The density of these states can be considerably reduced by annealing procedures, leaving behind a residual, U-shaped distribution of interface gap states with steeply increasing tails towards the bulk valence and conduction band edges, as commonly observed in capacitance-voltage (C-V) measurements [5]. In order to reproduced such a U-shaped background distribution of gap states by model calculations, strained and weakened Si-Si bonds at the interface have been proposed [6,7]. In this Letter we present direct evidence for a thin Si layer with strained bonds at Si-SiO$_2$ interfaces and in the selvedge region of clean reconstructed Si(100)2×1 and Si(111)7×7 surfaces.

We used frequency-dependent second-harmonic generation (SHG) and sum-frequency generation (SFG) which are nonlinear optical techniques with high interface sensitivity and which have been shown to be effective probes of semiconductor interfaces [8,9]. They are directly applicable to the Si-SiO$_2$ interface as SiO$_2$ is transparent for optical wavelengths, and destructive sample preparations like oxide etching or substrate thinning are not required. The interface sensitivity of these nonlinear techniques is based on the selection rule, valid in the dipole approximation, that the second harmonic and the sum frequency cannot be generated in materials with inversion symmetry such as amorphous SiO$_2$ and crystalline silicon. At the interface, however, these nonlinear optical processes are allowed. Particularly, a layer of distorted or reconstructed silicon will lift the inversion symmetry of the bulk silicon crystal, giving rise to the generation of second-harmonic and sum-frequency photons.

Our experiments were performed with boron-doped, 0.02 Ω cm and 30–50 Ω cm Si(100) and Si(111) wafers. We investigated different kinds of oxides. Differences due to sample treatment will, however, not be discussed in this paper. Clean and hydrogen-terminated surfaces were studied in an ultrahigh vacuum system with a base pressure of 3×10^{-10} mbar. The system was equipped with facilities for low energy electron diffraction and Auger electron spectroscopy, as well as with viewports for the incoming laser beam and outgoing second-harmonic photon beam. Hydrogen-terminated Si(111) and Si(100) surfaces were prepared in a NH$_4$F solution [10,11] and introduced into the vacuum system via an air lock. These samples displayed a (1×1) diffraction pattern indicative of a nonreconstructed, bulklike surface termination. Clean, reconstructed Si(100)2×1 and Si(111)7×7 surfaces were obtained by heating the hydrogen-terminated surfaces or samples covered with native oxides for a few seconds above 1000 °C.

Our tunable laser system has been described in detail elsewhere [12]. Briefly, tunable laser pulses with 14 ps duration at a repetition rate of 10 Hz were produced by optical parametric generation and amplification in LiB$_3$O$_5$ crystals pumped by the third harmonic of a mode-locked Nd:YAG laser. For sum-frequency experiments on oxidized silicon samples we mixed the tunable laser pulses with laser pulses of 2.33 eV photon energy (0.532 μm). The second-harmonic (SH) and sum-frequency (SF) photons were detected using color filters, monochromator, photomultiplier, and gated electronics. The spectra were normalized against the energy of the pump pulses and the spectral characteristics of the detection system. In our experiments we used p-polarized laser beams and measured the power of the generated SH and SF photons with p-polarization (p in, p out). For (111)-oriented samples the scattering plane was chosen at an azimuthal orientation rotated by 30° against the $[\bar{2}11]$

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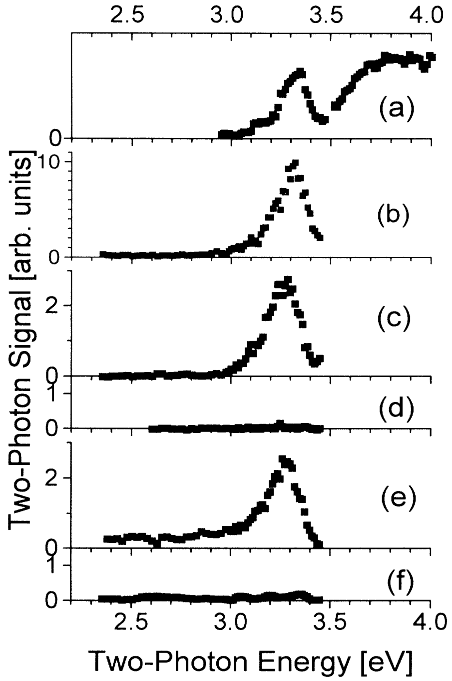

FIG. 1. SGF (a) and SHG (b)-(f) spectra of differently oxidized (a)-(d), clean (2×1)-reconstructed (e), and H-terminated (f) Si(100) samples. Spectra (a) and (b) were measured from the same 2 nm oxide. Samples (c) (700 nm oxide) and (d) (770 nm oxide) were thermally oxidized, sample (d) was annealed in N_2 at 1025 °C after oxidation.

direction. With this orientation the anisotropic surface contribution ($\chi^{(2)}_{\xi\xi\xi}$) and (higher order) bulk contributions (ζ) to the SH signal are zero, and only isotropic contributions are measured [13]. (100)-oriented samples were investigated with the scattering plane aligned parallel to the [100] direction. Here an anisotropic contribution is generated only in the bulk [13], but it turned out to be negligible compared to the resonant isotropic signal from the interface.

Figure 1 shows a series of SFG and SHG spectra from differently oxidized and from clean and hydrogen-terminated Si(100) samples. The oxide of Figs. 1(a) and 1(b) was approximately 2 nm thin and prepared by chemical oxidation of a clean, HF-etched surface in H_2O_2 [11] and subsequent annealing at 500 °C in ultrahigh vacuum. Both SFG (a) and SHG (b) spectra display a strong resonance band at 3.3 eV two-photon energy. A very similar spectrum was obtained from a 700 nm oxide grown at 1100 °C (c) while a 770 nm oxide postannealed in N_2 at 1025 °C revealed no appreciable intensity (d). The band was also absent for the hydrogen-covered, bulk-like terminated Si(100) surface (f), but appeared after heating this surface above 1000 °C to desorb the hydrogen and generate a clean, reconstructed Si(100)2×1 surface (e). Similar spectra not shown here were obtained from Si(111) surfaces. By performing SHG measurements with varying angles of incidence, we identified $\chi^{(2)}_{zzz}$ to be the responsible nonlinear susceptibility tensor element for the observed resonance.

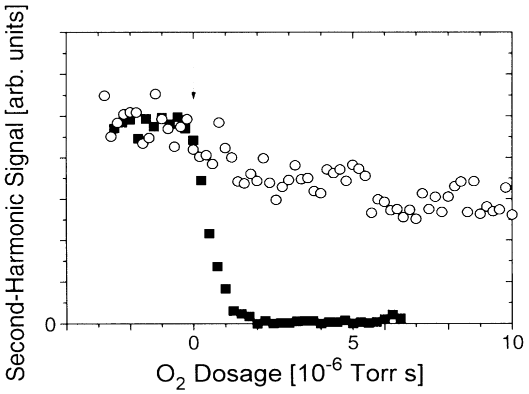

FIG. 2. Dependence of the SHG signal from a Si(111)7×7 surface on O_2 dosage. Photon energies of the exciting laser pulses were 1.17 eV (3 mJ pulse energy, filled symbols) and 1.65 eV (250 μJ pulse energy, open symbols). The arrow marks the beginning of the dosage.

From Fig. 1 it is obvious that the reason for the resonance at 3.3 eV in our spectra must be the same for oxidized and clean surfaces. Therefore a possibly crystalline SiO_2 interface layer [14,15] or SiO_x-induced static field effects [14] cannot be responsible for our results on oxidized Si samples. We note that the anisotropic SHG response from vicinal (100) Si-SiO_2 interfaces was recently investigated by Lüpke, Bottomley, and van Driel employing a SH photon energy of 3.26 eV [15]. These authors, however, used a polarization configuration (s in, p out) where the resonant isotropic contribution $\chi^{(2)}_{zzz}$ was not measured. The spectra in Fig. 1 lead to the conclusion that the resonance band at 3.3 eV is generated in a silicon layer at the Si-SiO_2 interface and at the surface of the clean Si samples where the structure is different from the centrosymmetric bulk structure of Si. The most significant structural deviations from the bulk are, of course, the 7×7 and 2×1 reconstructions of the clean Si surfaces, leading to the appearance of adatoms in the case of Si(111)7×7 and dimers in the case of Si(100)2×1 as the prominent structural elements of the reconstructions. Thus one might be tempted to relate the observed resonance to transitions involving occupied or unoccupied surface states of the dangling bonds (or back bonds) of the adatoms and dimers which constitute the outermost atomic layers of the two silicon surfaces. This interpretation seems, however, very unlikely as the surface state band structures of Si(111)7×7 and Si(100)2×1 are substantially different [16,17]. By performing SHG measurements during adsorption of molecules that are known to quench the surface states we have proved that surface states are in fact not responsible for the resonance at 3.3 eV. In Fig. 2 we show the results of such measurements on the Si(111)7×7 surface for two different wavelengths. While for excitation with 1.17 eV photons the SH signal drops dramatically to zero upon oxygen adsorption, indicating a dominant influence of surface states of SHG at this energy, the change is only minor for excitation with 1.65 eV photons ($2\omega = 3.3$ eV). Also, the spectrum did not change significantly after adsorption. Similar results were obtained for water adsorption on Si(100). These results clearly prove that the resonance is not caused by the top layer atoms of the reconstructed surfaces but arises from transitions in a *subsurface layer* that lacks inversion symmetry. It is also very unlikely that the static electric field of the space-charge region near the surface is responsible for the resonant enhancement in our spectra: Oxidation of the Si(111)7×7 surface drastically decreases the high density of dangling bond states which pin the Fermi level of the clean surface at 0.63 eV above E_v [18]. The resulting diminution of the space-charge region should lead to a strong decrease of SHG intensity which we did not observe in corresponding experiments. Furthermore, the resonance was observed independent of the doping concentration (3×10^{14} and 3×10^{18} cm^{-3}).

To infer more on the nature of the resonant transitions at 3.3 eV we compare in Fig. 3 the measured frequency dependence of $|\chi_{zzz}^{(2)}(2\omega)|^2$ derived from spectrum (c) in Fig. 1 with that of $|\chi(2\omega)|^2$ where $\chi(2\omega) = \varepsilon(2\omega) - 1$ is the (linear) susceptibility of bulk silicon [19]. In comparing $|\chi_{zzz}^{(2)}(2\omega)|^2$ with $|\chi(2\omega)|^2$ we utilize the fact that the frequency dependence of the nonlinear susceptibility close to a resonance at 2ω is approximately that of the linear susceptibility of the interface if two conditions are satisfied [20]: The nonresonant contribution to the SH signal is negligible, and no resonance at ω interferes. Apparently our spectra satisfy both conditions. The resonance band at 3.37 eV in the linear susceptibility of bulk silicon is caused by the well-known E_1 direct band gap transitions in silicon [21]. The energetic position of the band at 3.3 eV is very close to this bulk band, leading to the conclusion that direct transitions between valence and conduction band states are also responsible for the resonant enhancement in our spectra. These transitions must then take place in a perpendicularly strained or distorted silicon layer at the interface. Furthermore, the redshift of the band indicates an expansion of Si-Si bond lengths close to the interface.

Distortions of the Si lattice with increased Si-Si bond lengths at Si-SiO$_2$ interfaces can be caused by different effects: transfer of electronic charge to the oxygen atoms of the interface resulting in short-range structural relaxations of the Si atoms underneath (about 2–4 atomic layers), and long-range elastic strain due to intrinsic stress in thermally oxidized Si. The latter has been the subject of previous experimental investigations [22,23] and refers to a thin-film stress which depends on oxidation temperature and oxide thickness and causes an elastic strain gradient in the adjacent Si lattice extending about 100 Å or more of the interface [23]. Previous SHG results obtained from thermally oxidized Si samples at $2\omega = 2.33$ eV were indeed referred to the presence of inhomogeneous mechanical stress at the interface [24]. The SH photon energy employed in these studies was, however, distinctly away from the resonance in our spectra. Thus a different effect could be responsible for our observations. In fact, it appears difficult to interpret our spectra in terms of a purely elastic deformation since the relative change in volume must be larger than 1% in order to shift the E_1 feature from 3.4 to 3.3 eV [23]. Furthermore, the spectral position of the band at 3.3 eV in our SHG spectra does not significantly depend on oxide thickness or oxide preparation (Fig. 1) and thus not on the amount of elastic strain. Since the largest deviations from the Si bulk structure have to be expected in the immediate proximity of the interface, we conclude that vertical relaxations of a few atomic Si layers at clean, reconstructed surfaces and at Si-SiO$_2$ interfaces are responsible for the appearance of the resonance in our spectra. This conclusion is also supported by ion backscattering channeling experiments by Haight and Feldman who found a 1–2 monolayer thin region of distorted silicon at (111) Si-SiO$_2$ interfaces with a major displacement of the Si atoms in the vertical direction [25].

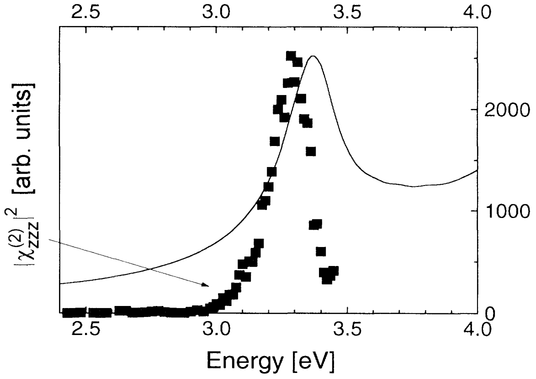

FIG. 3. Spectral dependence of $|\chi_{zzz}^{(2)}|^2$ (filled symbols) evaluated from spectrum (c) in Fig. 1 and of $|\chi|^2$ (solid line) calculated from the dielectric function of Si.

Significant vertical expansions not only between the adatoms and the first layer, but also between the first and second layer (9%) and between the second and third layer (2.6%) have been reported in a recent x-ray reflectivity study of the Si(111)7×7 surface by Robinson and Vlieg [26]. Bulk Si interlayer spacings were found for atoms in layers deeper than the fourth. Substantial subsurface distortions involving at least 3 monolayers have also been reported for the clean Si(100)2×1 surface in a previous ion-scattering study by Stensgaard, Feldman, and Silverman [27]. From our SHG spectra of hydrogen-terminated Si surfaces we conclude that the structure of the silicon layers underneath the surface of these samples must be very close to the structure of bulk silicon. Therefore, inversion symmetry is conserved, except for the top-layer Si atoms. This interpretation of our spectra is consistent with the results of a recent calculation of structure and surface stress of the H-terminated Si(111)1×1 surface [28].

In conclusion, we have studied the frequency dependence of the second-harmonic and sum-frequency generation from Si-SiO_2 interfaces and clean Si surfaces. The pronounced resonance around 3.3 eV photon energy in our spectra is indicative of direct band gap transitions in a few monolayer thin Si region at the Si-SiO_2 interface with increased Si interlayer spacings. Likewise, strained Si-Si bonds are also identified in the subsurface region of clean Si(100)2×1 and Si(111)7×7 samples. This work demonstrates that SHG and SFG are sensitive to distortions of the cubic bulk structure of Si at interfaces. Therefore, these nonlinear optical techniques should be also applicable to the spectroscopy of strained layers at interfaces of other semiconductors like Ge or Si-Ge compounds.

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