Nonlinear Optical Spectroscopy of Suboxides at Oxidized Si(111) Interfaces

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Native oxidation of the Si(111)(1 × 1)H surface causes the appearance and disappearance of second-harmonic generation (SHG) resonances related to specific bonding configurations of Si atoms at the interface. Resonances at 3.52 eV two-photon energy observed in p-polarized SHG spectra are indicative of a Si suboxide configuration present in a partially oxidized Si surface bilayer. Similar resonances are observed in spectra of thermally oxidized Si(111) and point to Si^{2+} suboxide states at the buried interface.

The atomic structure of Si-SiO_2 interfaces is not only of fundamental importance in semiconductor technology but also the subject of ongoing research aiming at a microscopic understanding of the structural transition from a crystalline semiconductor to an amorphous oxide [1,2]. While most work focused on the technically important Si(001)-SiO_2 interface, the Si(111)-SiO_2 interface has recently attracted considerable interest as a model system for an atomically abrupt interface [3–5]. Different to (001)-terminated Si where all Si-Si bonds have both components perpendicular and parallel to the surface, the bilayer structure of (111)-terminated Si (Fig. 1) is highly anisotropic with respect to the surface normal: Si bonds between two bilayers are strictly vertical while bonds within a bilayer have a small vertical but a large parallel component. Proposed models for an ideal, atomically abrupt Si(111)-SiO_2 interface include structural elements of interbilayer and intrabilayer oxide termination to account for the observation of Si^{+1} and Si^{+3} suboxide states in photoelectron spectra [3,5,6]. In these models, Si^{+2} suboxide states appear at boundaries between the two different terminations (Fig. 1).

In the present work we applied second-harmonic generation (SHG) as an optical spectroscopy to detect oxygen-induced changes of Si-Si bonds during native oxidation of the Si(111)(1 × 1)H surface. While SHG as a surface-sensitive spectroscopy has been applied to Si-SiO_2 interfaces in previous work [7–12], the results of the present study allow for the first time an identification of resonant features in SHG spectra with specific bonding configurations at Si(111) interfaces. Our work represents a novel spectroscopic *in situ* approach to characterize Si bonding and suboxides at Si interfaces under typical oxide growth conditions. We also demonstrate application of this technique to the buried Si(111)-SiO_2 interface. Buried SiO_2 layers, for example, are of fundamental importance in the formation of high-K gate dielectrics on Si [13].

In our experiments native oxidation of the Si(111) surface started from a well defined, atomically flat, hydrogen-terminated Si(111)(1 × 1)H surface. In previous studies it was concluded that water molecules are predominantly involved in the oxidation of this surface in air [14,15], and it was suggested that organic surface contaminations from the air are physisorbed and do not take part in a chemical bond formation [15]. Under conditions of low air humidity our H-terminated samples were stable against native oxidation in air for several hours, and the time (~2 h) to complete a SHG spectrum from 2.5 to 5 eV two-photon energy was small on the time scale of significant changes in the spectra (~1 day). The samples were cut from undoped Si wafers ($n < 1.3 \times 10^{12}$ cm^{-3}). Our experimental setup and the analysis of the spectra using model functions have been described elsewhere [16]. SHG spectra were acquired for different polarizations (p, s) of the laser beam and of the second-harmonic beam (P, S) and are presented as nonlinear intensity reflection coefficients $R_{aB} = I_B^{2\omega}/(I_a^{\omega})^2$ with $a = p, s$ and $B = P, S$. The sample azimuth was oriented with the plane of incidence parallel to the [1$\bar{1}$0] direction. With this orientation the second-harmonic surface susceptibility tensor element $\chi_{s,xxx}^{(2)}$ (see below) does not contribute to the SHG signal in p/P and s/P spectra
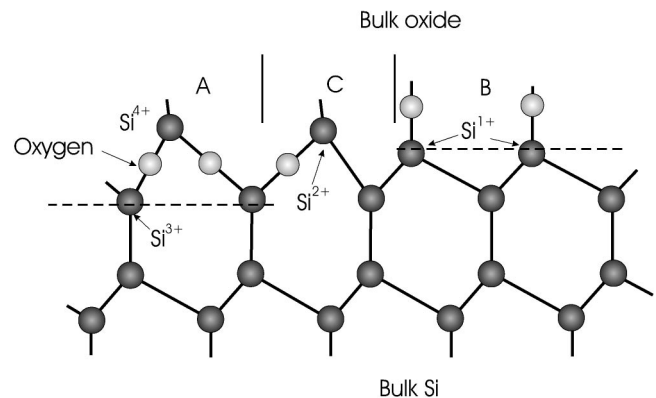

FIG. 1. Simplified model for Si suboxide states at an atomically abrupt Si(111)-SiO_2 interface.

and is maximized in p/S spectra. The angle of incidence was 65°.

In Fig. 2(a)–2(c) we present SHG spectra for polarization combinations p/P, s/P and p/S obtained at different times after exposing the H-terminated surface to air. The p/P spectrum of the pristine $Si(111)(1 \times 1)H$ surface exhibits two-photon resonances of Si critical-point (CP) interband transitions. The spectrum is reproduced by a fit of three bands with energies of 3.39 eV, 4.28 eV and 4.52 eV that agree with the energies of the E_0'/E_1, $E_2(X)$ and $E_2(\Sigma)$, respectively, CP interband transitions in bulk Si within experimental error. In addition, in the fits it was necessary to include a fourth, spectrally broad resonance with an energy set to 5.18 eV to reproduce the very low SHG intensity at 5 eV by destructive interference with the E_2 band [17]. We assign the latter contribution to transitions from occupied surface states of the $Si(111)(1 \times 1)H$ surface [18] to Si conduction band states. The initial native oxidation of the $Si(111)(1 \times 1)H$ surface caused the following changes in the p/P spectrum: (1) the intensity of the CP resonances decreased, (2) the SHG signal at 5 eV increased, and most importantly, (3) a new resonance at about 3.52 eV appeared after 6 days which decreased in intensity after 40 days. A closer analysis revealed that most of the changes of the Si CP resonances can be related to interference with the 3.52 eV band. The solid lines represent fits with the same spectral parameters and nearly constant amplitudes of the E_1 and E_2 transitions for all p/P spectra. The changes mainly originate from the evolution of the 3.52 eV band with time and from a decrease of the 5.18 eV contribution. Apparently, the oxidation did not significantly affect the strength of the CP transitions in the p/P spectra but caused the appearance of a new band which must be related to the changed structure of the oxidized surface.

The s/P spectrum measured 6 hours after sample preparation exhibits only a weak feature around 3.52 eV, but a strong increase in intensity for energies close to 5 eV. After 6 days the weak feature developed into a pronounced band at 3.52 eV and the SHG signal close to 5 eV decreased strongly. Paralleling the observation in the p/P spectrum, the intensity of the 3.52 eV band decreased after 40 days. Note that bulk-type E_1 and E_2 transitions are absent in all s/P spectra.

The p/S spectrum obtained 5 hours after sample preparation shows a resonance at 3.50 eV. Different to the 3.52 eV bands in the s/P and p/P spectra, the intensity of this band decreased monotonically as oxidation of the surface proceeded. Therefore, the bands at 3.50 and 3.52 eV have different origins although their energies are very close. After 33 days the intensity of the 3.50 eV band decreased substantially, and a new resonant feature at
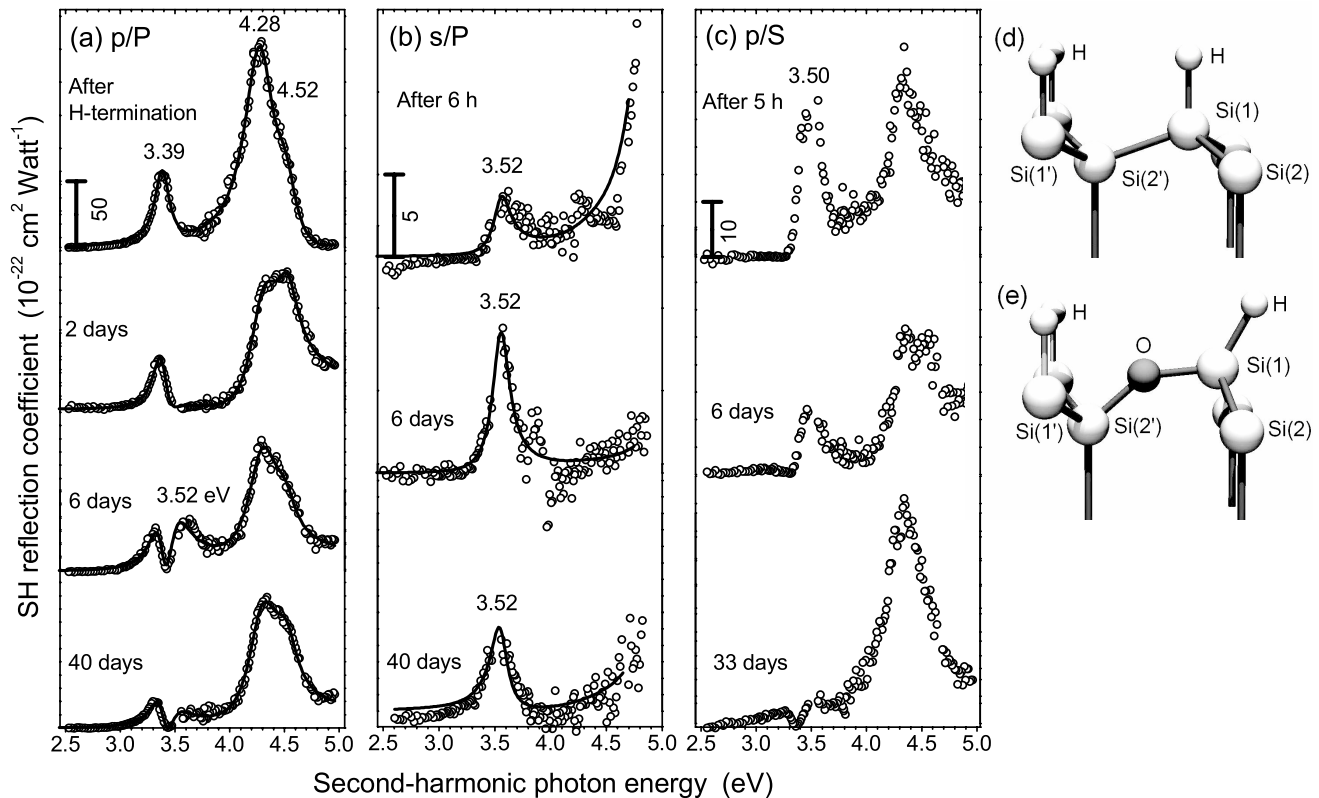

FIG. 2. (a)-(c) SHG spectra of the initial stage of oxidation of $Si(111)(1 \times 1)H$ at room temperature in air. Solid lines are fits to the data. (d) bilayer structure of the unoxidized surface. (e) bilayer structure with relaxed orientation of the two Si(1)-Si(2) bonds due to bridging of the Si(1) and Si(2′) atoms by an oxygen atom.

lower energy, about 3.3 eV, emerged [8]. A second resonance in the p/S spectra around 4.3 eV shows some non-monotonic intensity variation with time but is not nearly as strongly affected by the oxidation as the 3.50 eV band.

Auger electron spectroscopy of a sample with maximum s/P intensity of the 3.52 eV resonance (similar to the 6-day spectrum in Fig. 2) revealed that at this stage (1) surface oxidation did not proceed below the first three Si monolayers, (2) only $\sim 18\%$ of the first Si bilayer was completely oxidized as indicated by the Si 76 eV Auger line, and (3) the first Si bilayer contained additional oxygen atoms. The amount of the additional oxygen can account for the oxidation of roughly one third of the Si-Si bonds in the first bilayer.

Taking into account the geometry of the Si bonds at the surface, the polarizations of the fundamental and second-harmonic light and the different dependencies of the features in the spectra on the degree of surface oxidation, the two bands at 3.50 and 3.52 eV can be assigned to electronic transitions related to Si-Si bonds in the topmost bilayer. We first discuss the 3.50 eV resonance in the p/S spectra which was also observed at slightly lower energy (~ 3.47 eV) in a recent study by Mitchell et al. [11]. This band was strongly affected by surface oxidation and must be assigned to a resonance of $\chi_{s,xxx}^{(2)}$ which is the only nonlinear surface susceptibility element contributing to the p/S spectrum of the Si(111) surface. Here, x and z denote coordinates parallel and perpendicular to the surface, respectively. For $\chi_{s,xxx}^{(2)}$ to be nonzero, the dipole moment matrix elements of both the nonresonant one-photon excitation and the resonant two-photon deexcitation in the SHG process [19] must have a component parallel to the surface. This is obviously the case for electrons in the first bilayer where the Si-Si bonds have a large parallel component [Fig. 2(d)]. Electrons in the vertical Si-H bonds and in the vertical bonds between the second and the third Si layer do not contribute to $\chi_{s,xxx}^{(2)}$ by symmetry. It has been shown [20–22] that the first step of oxidation of the Si(111)(1 × 1)H surface is oxidation of the back bonds of the top layer Si atoms, leaving the Si-H bonds intact [Fig. 2(e)]. The decrease of the 3.50 eV band in Fig. 2(c) for longer oxidation times can be attributed to the decrease of the number of unoxidized Si-Si bonds in the first bilayer.

Next we discuss the 3.52 eV band which is absent in the p/P and s/P spectrum of a pristine Si(111)(1 × 1)H surface [23]. In the s/P configuration, surface SHG originates from the tensor element $\chi_{s,zxx}^{(2)}$. The absence of a significant SHG signal below 4 eV in the s/P spectrum of the unoxidized Si(111)(1 × 1)H surface points to a small z-component of the transition dipole moments for electrons in Si-Si bonds of the first bilayer. However, during the oxidation of the first Si bilayer, the SHG resonance at 3.52 eV showed up in p/P and s/P spectra. The appearance of this resonance can be related to changes in the bonding structure of the first bilayer when oxygen atoms bridge neighboring Si surface atoms as indicated in Fig. 2(e). Relaxations of the oxidized Si atoms do not only cause tilting of the Si(1)-H bond away from the surface normal but also tilting of the two Si(1)-Si(2) bonds as shown in Fig. 2(e). The vertical component of the latter bonds increases, and transitions related to these bonds become observable through $\chi_{s,zxx}^{(2)}$. In addition, the lack of inversion symmetry of the H-Si(1)-Si(2)-Si(3) group with respect to the center of the Si(1)-Si(2) bond is dramatically enhanced by the oxidation, causing stronger SHG. The increase of SHG intensity near 5 eV in the topmost s/P spectrum can be related to transitions involving surface states of the H-terminated surface [18] which are also affected by the surface oxidation. As $\chi_{s,zxx}^{(2)}$ also contributes to the p/P spectrum, the 3.52 eV resonance is observed in the 6-day spectrum in Fig. 2(a) as well. Our assignment of this resonance to Si(1)-Si(2) bonds of the O-Si(1)-(H, 2 × Si(2)) suboxide group is consistent with the observed decrease of the intensity at 3.52 eV for samples which were exposed to air for longer times (40 hours in Fig. 2) as more Si atoms in the top layer are converted to oxidation states higher than that of the Si(1) atom in Fig. 2(e) and, as a consequence, the number of Si(1)-Si(2) bonds decreases. Auger electron spectra of such samples showed that a much larger fraction of the first bilayer than 18% is oxidized to SiO_2.

We point out that our conclusion on the nature of the Si suboxide species at the initial stage of oxidation of the Si(111)(1 × 1)H surface is at variance with results of previous infrared studies of Si-H vibrations [21,22] showing that dry oxidation of this surface by O_2 at elevated temperatures (573 and 643 K, respectively) produces predominantly H-SiO_2 and H-SiO_3, but only little H-SiO. However, our conclusion is consistent with infrared spectra exhibiting the H-SiO vibrational band before H-SiO_3 is formed when the surface is oxidized at room temperature in humid air [14].

The E_1 and E_2 bands in the p/P spectra cannot be explained by transitions in an atomically thin surface layer, for the splitting of the E_2 band in X and Σ transitions is a clear indication of a 3D band structure. The bulklike character of these SHG resonances can be understood in terms of an effective quadrupole-type surface nonlinearity that originates from large gradients of the perpendicular optical field components at the interface [24] and that is most relevant for $\chi_{s,zzz}^{(2)}$. Taking into account that screening in a semiconductor is weaker than in a metal, the field gradients should extend over a number of atomic layers beneath the surface, and the resulting quadrupole-type nonlinearity should not be very sensitive to the oxidation of the topmost Si atoms, in accordance with our experimental observation.

In Fig. 3 we present p/P and s/P spectra of Si(111) with 86 nm SiO_2 grown by dry thermal oxidation of a
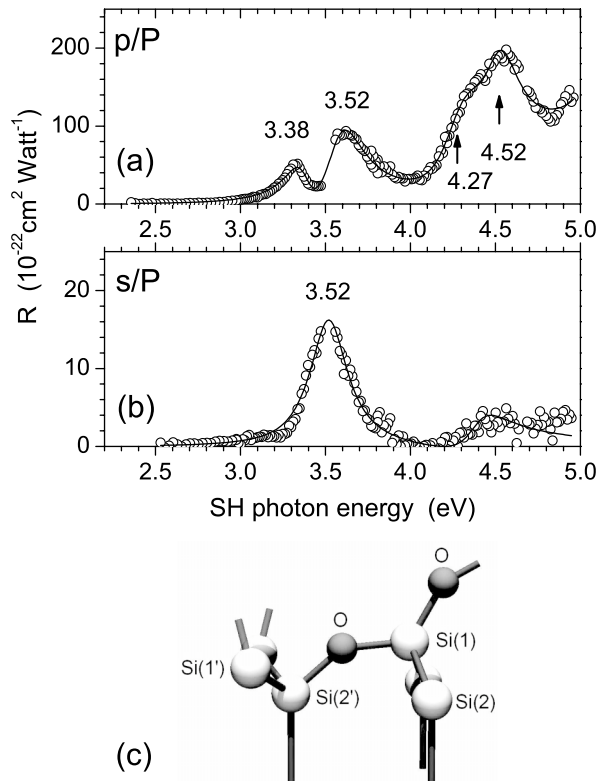
FIG. 3. (a), (b) SHG spectra of thermally oxidized Si(111) with 86 nm SiO$_2$. Solid lines are fits to the data. (c) suboxide group with tilted Si(1)-Si(2) bonds proposed as the origin of the 3.52 eV band in (a) and (b).

sample cut from the same undoped wafer. Besides bulk-type CP transitions at 3.38 eV (E'_0/E_1), 4.27 eV ($E_2(X)$), and 4.52 eV ($E_2(\Sigma)$), the p/P spectrum exhibits a well-developed band at 3.52 eV. In addition, a resonance at 5.32 eV which can be attributed to Si E'_1 CP transitions had to be included in the fit to reproduce the increase in SHG intensity above 5 eV [12]. The s/P spectrum consists of a single band at 3.52 eV and has negligible contributions from Si bulk CP transitions. Note how similar these spectra of thermally oxidized Si(111) are to the spectra of Si(111)(1 × 1)H after 6 hours exposure to air [Fig. 2(a) and 2(b), respectively]. We therefore conclude that the Si(111)-SiO$_2$ interface contains structural units similar to those in the partially oxidized surface Si bilayer of Si(111)(1 × 1)H. Hence we assign the 3.52 eV band of the Si(111)-SiO$_2$ interface to transitions localized in the tilted Si(1)-Si(2) bonds of the Si(2′)-O-Si(1)-(O, 2 × Si(2)) group shown in Fig. 3(c). This group differs from that in Fig. 2(e) only by a second Si(1)-O bond instead of H termination. Also note that the Si(1) atom in Fig. 3(c) represents a Si^{+2} suboxide state that appears at boundaries separating interface regions with interbilayer oxide termination (Si^{+1} suboxides) from regions with intrabilayer oxide termination (Si^{+3} suboxides, see Fig. 1).

In conclusion, we have demonstrated the potential of SHG as a purely optical *in situ* probe to characterize structure and bonding at Si(111) surfaces and buried interfaces with monolayer depth resolution. Analysis of the strong polarization and time dependence of SHG spectra of the oxidizing Si(111)(1 × 1)H surface reveals that suboxide groups in a partially oxidized Si(111) surface bilayer give rise to a characteristic SHG band at 3.52 eV two-photon energy. Our results for thermal oxides on Si(111) strongly suggest that similar groups, which have Si^{+2} suboxide character, are essential constituents of Si(111)-SiO$_2$ interfaces and indicate frequent changes of interbilayer and intrabilayer oxide terminations at the interface.

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