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Silicon interband transitions observed at Si(100)-SiO_2 interfaces

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We report on a type of Si interband transitions at Si(100)-SiO_2 interfaces that has no equivalent in the bulk of crystalline silicon. These transitions, leading to strong resonances in optical second-harmonic-generation spectra with energies of 3.6–3.8 eV, are energetically located between the E_1 and E_2 critical points of bulk Si. We assign these transitions to Si atoms without T_d lattice symmetry at the boundary between crystalline Si and the SiO_x transition region. We also report on a strong blueshift of the E_2 transitions at the interface. [S0163-1829(98)51428-2]

Owing to the undiminished importance of metal-SiO_2-Si heterostructures in current semiconductor device technology, the physical and chemical properties of the Si-SiO_2 interface continue to be a field of active research.[1] One important issue addresses the electronic excitations of a well-ordered Si-SiO_2 interface and the related question of whether optical spectroscopy can be used for a characterization of structural order at the interface. Recently, both linear[2,3] and nonlinear optical (i.e., second-harmonic generation) techniques[4–8] have been applied to study the effect of the oxide on the energetic position of the E_0' and E_1 critical points (CP's) of direct optical band-gap transitions in the near-interface Si layers. To explain observed energy shifts of these transitions at the Si-SiO_2 interface it was proposed that the Si layers beneath the interface are strained, either as a result of a long-range mechanical stress due to the different coefficients of expansion for Si and SiO_2,[2] or as a result of lattice relaxations due to a charge transfer from the near-interface Si layers to the oxide.[4]

In this paper we report on our observation of a type of Si interband transitions in second-harmonic-generation (SHG) spectra of Si(100)-SiO_2 interfaces with a resonance energy between 3.6 and 3.8 eV. We attribute these transitions, which do not occur in the bulk of crystalline silicon, to Si atoms without T_d lattice symmetry located at the interface between crystalline Si and the SiO_x transition region. Our observations have been made possible by extending the spectral range of our SHG experiments up to 5 eV, thereby covering the full range of the fundamental interband transitions in Si up to the E_2 CP. We also report on an unexpectedly large blueshift of the E_2 transitions at the interface that cannot be explained by any strain effect. To excite the interband transitions at the interface we used optical SHG that is a particularly interface-sensitive spectroscopy because it is forbidden in the bulk of centrosymmetric materials in the electric-dipole approximation.

Our samples were cut from (100)-oriented silicon wafers with different doping concentrations, which were either investigated as received from the manufacturer or subjected to different thermal oxidation procedures. For comparison we also investigated amorphous silicon, which was plasma deposited on Si(100) substrates at temperatures between 400 and 550 °C, using SiH_4 or SiD_4 as precursors. The SHG spectra were measured with a tunable ps parametric generator/amplifier laser system similar to that described in Ref. 9. The spectra were normalized against the SHG signal from an index-matched suspension of urea crystallites, which was recorded simultaneously with the sample signal. All spectra shown here were obtained at an angle of incidence $\theta = 65°$ and with p-polarized fundamental and second-harmonic beams (p-in/p-out).

In Fig. 1 we show the SHG spectrum of a Si(100) sample (p doped, $\rho = 2-10\ \mathrm{k}\Omega\ \mathrm{cm}$) covered with a native oxide, in comparison with the spectrum of amorphous silicon (deposited at 450 °C, precursor SiD_4, film thickness 0.7 μm). The Si(100) sample exhibited comparatively strong resonant SHG, while the spectrally flat signal from the amorphous Si sample was at least one order of magnitude smaller in the range of the strongest Si interband transitions (3.2–4.4 eV). For the Si(100) sample we observed two pronounced resonances: the resonance with a maximum at about 3.3 eV is derived from the E_0'/E_1 CP transitions in bulk Si.[10] This resonance, due to the lowest energy direct transitions, has been the subject of previous SHG studies.[4–8] The resonance with a maximum at about 4.3 eV corresponds to transitions

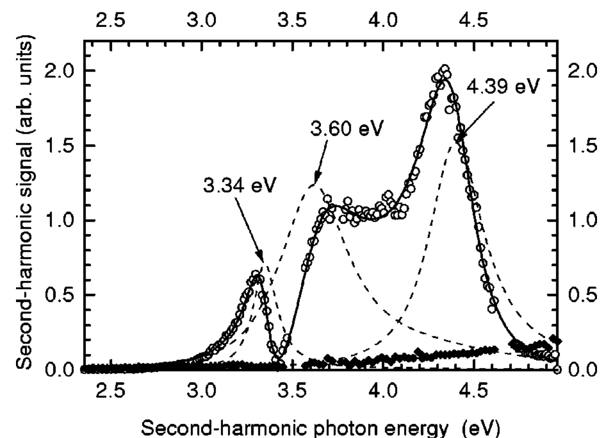

FIG. 1. SHG spectrum of a Si(100) sample with a native oxide (open symbols), compared to a spectrum of amorphous Si with a native oxide (solid symbols). Solid line: fit of three CP resonances to the data. Dashed lines: SHG intensities separately calculated from the fit parameters of each resonance. The resonance energies obtained from the fit are indicated.

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that cause the E_2 CP in bulk Si.[10] In addition to these bulk-derived resonances, the SHG spectrum of the crystalline Si(100) sample in Fig. 1 exhibits appreciable resonant intensity between 3.6 and 4.0 eV. Obviously, there are strong interband transitions at the Si-SiO_2 interface that do not occur in the bulk of crystalline Si and must therefore be attributed to the unique bonding configuration of Si atoms at the interface.

To extract the energies of the resonant transitions involved in the SHG process, we reproduced the measured frequency dependence of the SHG intensity $I(2\omega)$ by a coherent superposition of CP-like resonances for the second-order nonlinear susceptibility $\chi_s^{(2)}$ of the interface:

$$I(2\omega)\propto\left|\sum_{k=1}^{3} A_k(\omega,\theta)\frac{f_k\exp(i\psi_k)}{2\omega-\omega_k+i\gamma_k}\right|^2, \tag{1}$$

with the resonance frequencies ω_k, linewidths γ_k, amplitudes f_k, and phases ϕ_k being fit parameters. The physical grounds for the ansatz (1) will be discussed in more detail in a forthcoming paper.[11] The analytic form (1) for the spectral dependence of the resonances is referred to as an excitonic line shape that represents the best approximation for the E_1 CP in the linear dielectric function of bulk Si,[10] but which we also used for the analysis of the other transitions. The coefficients $A_k(\omega,\theta)$ take into account the linear propagation of the fundamental and second-harmonic beams through the sample, including multiple reflections in the oxide layer. They were obtained using a matrix formalism[12,13] and depend on the fundamental frequency ω and angle of incidence θ as well as on the tensor elements of $\chi_s^{(2)}$.[11]

The solid line in Fig. 1 is a fit of Eq. (1) to the data with three resonances, using the coefficient $A_k(\omega,\theta)$ of the tensor element $\chi_{s,zzz}^{(2)}$. The dashed lines represent the SHG intensity if only one single resonance were to contribute to the spectrum. The good agreement between experimental data and fit suggests that the SHG spectrum in Fig. 1 is indeed composed of three interband resonances with resonance energies of 3.34 eV, 3.60 eV, and 4.39 eV. The deviations of the resonance energies from the maximum intensity positions in the spectrum is a well-known phenomenon in nonlinear optics and results from the phase-dependent, nonlinear superposition of the resonances in Eq. (1). An additional nonresonant contribution to $\chi_s^{(2)}$ is not needed for a good fit to the data, indicating that transitions at higher energies (such as those of the E_1' critical point at 5.3 eV in bulk Si) (Ref. 10) do not significantly contribute to this spectrum. We note that $\chi_{s,zzz}^{(2)}$ is not the only interface tensor element measured in the p-in/p-out configuration. The interface tensor elements $\chi_{s,xxz}^{(2)}$ and $\chi_{s,zxx}^{(2)}$, the quadrupole bulk susceptibilities ζ and γ,[14] and third-order bulk terms due to the electric field in the space-charge region[7] also contribute to the spectrum. The relevance of the various contributions for the spectral positions of the three resonances will be discussed in a subsequent paper.[15] We quote error margins of about 0.04, 0.10, and 0.03 eV for the above values of the three resonance energies, respectively. These error margins result from the different frequency dependencies of the coefficients $A_k(\omega,\theta)$ of those tensor elements that were not considered in the fits but also contribute to the SHG. We point out that these error margins do not affect the general conclusions of the present paper.

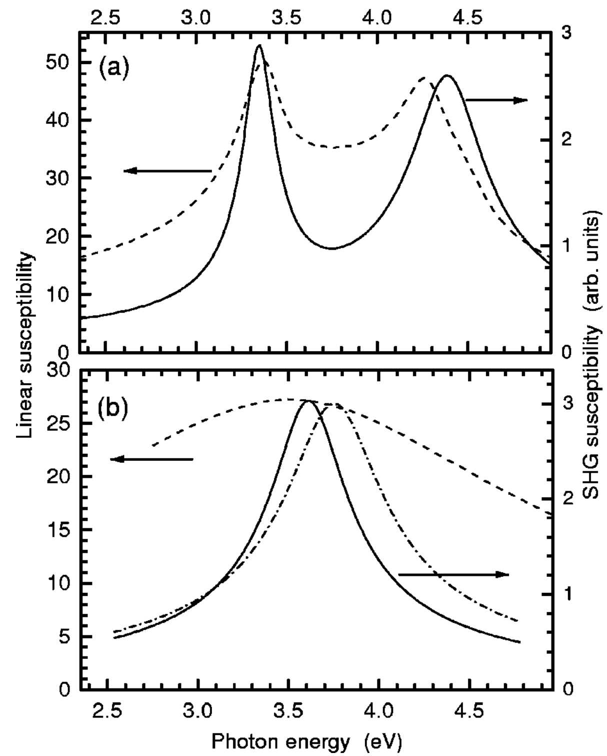

FIG. 2. (a) Solid line: magnitude $|\chi_s^{(2)}|$ of the E_1- and E_2-type resonances from Fig. 1. Dashed line: magnitude $|\chi^{(1)}|$ of the linear bulk susceptibility of crystalline silicon. (b) Solid and dash-dotted lines: magnitude $|\chi_s^{(2)}|$ (not to scale) of the new resonance as obtained from the fits in Figs. 1 and 3(c), respectively. Dashed line: magnitude $|\chi^{(1)}|$ of the linear bulk susceptibility of amorphous silicon.

Figure 2(a) displays a comparison of the magnitude of the linear optical susceptibility $|\chi^{(1)}|$ of crystalline Si, as calculated from spectroscopic ellipsometry data,[16] with the magnitude of the nonlinear susceptibility $|\chi_s^{(2)}|$, as obtained from the fit in Fig. 1 for the two resonances at 3.34 and 4.39 eV. The overall frequency dependence is surprisingly similar, lending further support of an assignment to transitions in Si atoms with a bulklike structure, although there are significant differences regarding the resonance energies and linewidths. The third band at 3.60 eV in Fig. 1, which was not observed in s-in/p-out and p-in/s-out polarization combinations, obviously has no equivalent in the linear susceptibility of crystalline Si.

The effect of the interface on all three resonances is demonstrated in Fig. 3, where we compare SHG spectra of three different Si(100) samples cut from the same wafer (n doped, $\rho=0.08-0.12\ \Omega$cm), which have been subjected to different oxidation procedures. Thus any changes in the spectra must be attributed to the different oxidation treatments. Sample (a), covered with a thin native oxide, was studied as received. Sample (b) was oxidized at 1000 °C in a dry oxygen atmosphere to yield an oxide of about 60 nm thickness. Sample (c) with a 105 nm thick oxide was prepared in a dry/wet/dry oxidation cycle at 1050 °C and subsequently annealed in argon at 1100 °C for 15 min. All three spectra

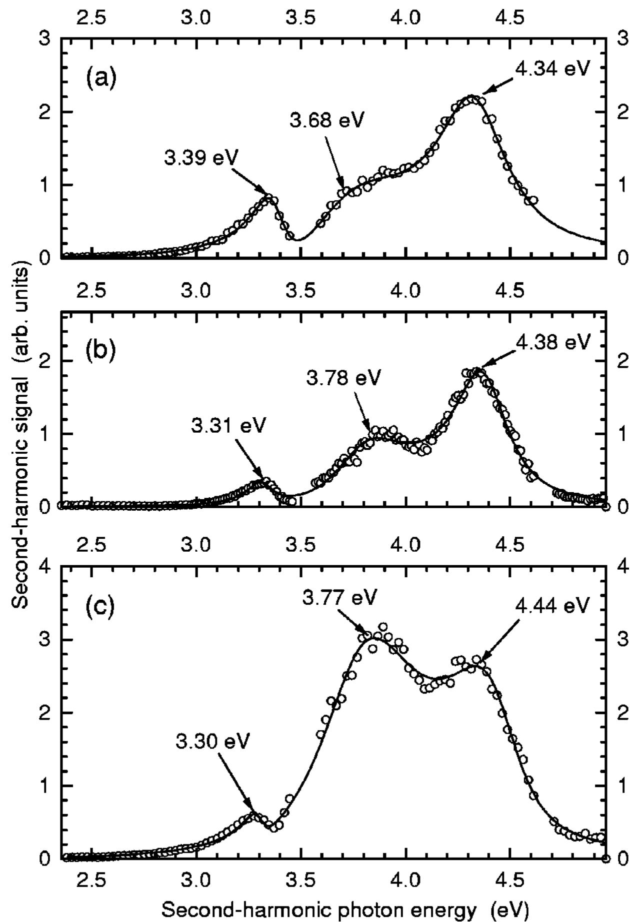

FIG. 3. SHG spectra of three differently oxidized samples cut from the same Si wafer: (a) native oxide, (b) 60 nm oxide after thermal oxidation, and (c) 105 nm oxide after dry/wet/dry thermal oxidation and postannealing in argon. Solid lines: fits of three CP resonances to the data. The resonance energies obtained from the fits are indicated.

exhibit the same three resonances as in Fig. 1. However, strong energy and intensity variations of these resonances as a result of the different oxidation procedures can be seen in Fig. 3. In particular, the new resonance energetically located between the bulklike transitions becomes the dominant spectral feature for sample (c).

Before turning to this resonance we discuss the energy variations of the E_1 and E_2 transitions in Fig. 3. It was recently shown that the electrostatic field of the space-charge region at the Si-SiO_2 interface in metal-SiO_2-Si structures causes a contribution to the SHG spectrum with resonant excitations of E_1 transitions within the space-charge region (''electric-field-induced SHG'').[7,8] Since we cannot vary the electrostatic field strength in our Si-SiO_2 samples, a strict separation of this effect from SHG due to loss of structural symmetry at the interface is not possible. However, the energy of 3.39 eV for sample (a) is very close to the spectrally unresolved E_0'/E_1 CP at 3.37 eV and to the E_1 CP at 3.40 eV of bulk Si.[10] Therefore, it is not unreasonable to assume that this band in spectrum (a) acquires most of its amplitude from Si bulk transitions in the space-charge region through dc-field-induced SHG. Since the density of defects at Si-SiO_2 interfaces is lower for thermally oxidized and postannealed wafers than for a native oxide on an as-received wafer, band bending and the associated electrostatic field are also expected to be lower in samples (b) and (c) than in sample (a). This is consistent with the much lower intensity of the E_1 band for samples (b) and (c). In addition, its resonance energy is considerably redshifted from the bulk value to about 3.30 eV for these samples. Consequently, we assign the E_1 band in Figs. 3(b) and 3(c) primarily to transitions in Si layers near the interface, with only a weak contribution from dc-field-induced SHG. The redshift in energy can be explained by oxide-induced lattice strain in these layers, leading to weakening of Si-Si bonds in these layers, on an average.[4] For the E_2-type excitations we observed the opposite behavior. Their resonance energy is substantially higher than the bulk E_2 CP at 4.27 eV [Fig. 2(a)] and increases from (a) to (c). Since dc-field-induced bulk SHG should be weakest for sample (c), the observed resonance energy of 4.44 eV must be considered characteristic of E_2 transitions at the interface.

At present we do not have a conclusive explanation for the very strong blueshift of 130 meV and more for the E_2 transitions. In any case, strain at the interface cannot be responsible for this shift because the strain dependence of the E_2 CP is lower than that of the E_1 CP,[17] and the shifts are in opposite directions. We observed the same strong blueshift in SHG spectra of strained $Si_{0.85}Ge_{0.15}$ alloy layers grown on Si(100) by molecular beam epitaxy. Since the bulk E_2 energy of $Si_{1-x}Ge_x$ alloys is virtually identical to that of pure Si,[18] the shift must be a genuine interface effect. We point out that the linear optical properties of bulk Si in this energy range are dominated by the $E_2(X)$ CP at 4.27 eV. The comparatively weak contributions of the $E_2(\Sigma)$ CP at 4.5 eV (Ref. 10) could become more significant, however, at the interface and could cause the observed blueshift of the E_2 interband transitions.

The new interband resonance with energies between 3.68 and 3.77 eV in Fig. 3 is broader than the E_1- and E_2-derived bands. It has no equivalent in crystalline bulk Si and was not observed in linear optical spectra of oxidized Si surfaces, presumably because of the lower interface sensitivity of linear optical probes. The strong influence of the oxidation procedure on its intensity clearly demonstrates its interface character. We point out that the splitting of the bulk Si interband transitions into two bands E_1 and E_2 is a consequence of the T_d symmetry of the Si lattice. The SHG resonance between these two bands therefore represents Si atoms lacking this type of long-range bulk symmetry. Structural models of the Si(100)-SiO_2 interface that have been derived from the tridymite modification of crystalline SiO_2 attached to Si(100) and that contain all observed intermediate oxidation levels of Si atoms within a thin (5 Å) suboxide transition region have been discussed recently.[19] The most likely candidates for the band around 3.7 eV are the Si atoms right at the boundary between Si and SiO_x. Since most of these atoms still have four Si atoms as nearest neighbors, their excitation energies are within the range of bulk Si interband transitions, but the reduced symmetry, accompanied with strong distortions of bond angles and lengths due to the influence of the suboxide, cause a breakdown of the bulk band structure description for the interband transitions in these atoms. The comparatively large width of the resonance probably reflects the finite distribution of bond angles and lengths.

A well-known example for the breakdown of a band structure description of interband transitions in condensed Si is amorphous Si. The dielectric function of amorphous Si (Ref. 20) exhibits a broad distribution of transitions with a maximum between the E_1 and E_2 CP's of crystalline Si [Fig. 2(b)]. Nevertheless, we consider the appearance of a strong band between 3.6 and 3.8 eV indicative of a well-ordered Si-SiO_2 interface for three reasons. First, the SHG spectrum of a mostly disordered Si-SiO_2 interface, the interface between amorphous Si and its native surface oxide (Fig. 1), exhibited only very weak intensity in comparison with the Si(100) sample. Second, disorder at clean and oxidized interfaces of crystalline Si has been shown to cause a strong decrease of the SHG signal.[21,22] Third, SHG spectra of strained $Si_{0.85}Ge_{0.15}$ alloy layers on Si(100) (Ref. 11) also showed the same broad band at a slightly lower energy of 3.6 eV with comparable intensity as in Fig. 3(c). These structures were grown under ultra-high-vacuum conditions, and their surfaces showed well-ordered $(2\times n)$ dimer reconstructions as revealed by scanning tunneling microscopy and low-energy electron diffraction.[23] Transfer of the samples from the molecular beam epitaxy chamber to the SHG experiment through the ambient leads to the formation of a very thin native oxide on the surface. Therefore we do not believe that the atomic layers beneath the oxide of these samples are particularly disordered. In future work we hope to explore how the strength of the 3.7 eV SHG resonance can be used to characterize structural order at the Si-SiO_2 interface.

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