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Electric field induced second harmonic generation spectroscopy on a metal-oxide-silicon structure

P. Godefroy, W. de Jong, C. W. van Hasselt, M. A. C. Devillers, and Th. Rasing^{a)}
*Research Institute for Materials, University of Nijmegen, Toernooiveld, NL 6525-ED Nijmegen,
 The Netherlands*

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Spectroscopic electric-field-induced second harmonic generation on a Si(111)-SiO₂-Cr metal-oxide-silicon structure shows a bias-independent “interface” resonance at 3.25 eV and a “bulk” resonance at 3.43 eV which is strongly bias dependent. The symmetry forbidden bulk dipole contribution becomes observable, and even dominating, due to the bias-induced band-bending that breaks the bulk inversion symmetry. The origin of these resonances is discussed, as well as the prospects for using second harmonic generation as a probe of metal-oxide-silicon characteristics.

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Over the last decade second harmonic generation (SHG) and sum-frequency generation (SFG) have been developed into sensitive surface and interface probes.¹⁻⁵ One of the main advantages of an all-optical technique like these, is the possibility to study buried interfaces, like the technologically important Si-SiO₂ interface. After the initial work by Tom⁶ on Si, the sensitivity of SHG to interface steps,⁷ strain⁸ and preparation of Si-SiO₂ interfaces⁹ has been studied. Daum⁴ performed SHG and SFG spectroscopy on clean and oxidized Si surfaces, interpreting a strong resonance at 3.3 eV in terms of strained layers of Si at the Si-SiO₂ interface. We will call this the interface resonance in the remainder of the paper. The sensitivity of SHG to surfaces can be enhanced by applying an electric field across the interface. Recently, electric field induced second harmonic generation (EISHG) on a Si-SiO₂ interface using a metal-oxide-silicon (MOS) structure was reported.¹⁰ In this letter we report the first spectroscopic EISHG experiment on a Si(111)-SiO₂-Cr MOS structure. For zero applied bias a resonance at ~3.25 eV is observed, in agreement with Daum.⁴ When the MOS capacitor is in inversion, apart from the bias-independent interface resonance at 3.25 eV, a strongly bias-dependent resonance at 3.43 eV appears, corresponding to the bulk *E*₁ direct bandgap transition in Si.¹¹ In the accumulation regime no changes are observed.

For the (111) face of Si, the *p*-polarized SHG intensity under *m*-polarized excitation *I*_{*m,p*} (*m* indicating *s* or *p*) can be written, in the electric dipole approximation, as^{6,12,13}:

$$I_{m,p} = |A_{m,p} + B_{m,p} \cos(3\psi)|^2, \quad (1)$$

where ψ is the azimuthal angle, and *A* and *B* are the total isotropic and anisotropic contributions respectively. *A* and *B* are determined by the contributing elements of the nonlinear susceptibility tensor $\tilde{\chi}^{(2)}$ and contain the Fresnel factors, taking into account multiple reflections in the SiO₂ film.^{14,15}

If a bias is applied across the Si-SiO₂ interface, the nonlinear polarization $\tilde{P}^{NL}(2\omega)$ can be written as¹⁰

$$P_i(2\omega) = \chi_{ijk}^{(2)} E_j(\omega) E_k(\omega) + \chi_{ijkl}^{(3)} E_j(\omega) E_k(\omega) E_l(0), \quad (2)$$

where $\vec{E}(0)$ is the static electric field due to the applied bias,

and $\chi_{ijkl}^{(3)}$ is a fourth-rank tensor describing the third-order nonlinear susceptibility. Note, that the static electric field does not change the resonant properties of $\tilde{\chi}^{(2)}$ and $\tilde{\chi}^{(3)}$, as it acts as a scaling factor. At the Si-SiO₂ interface, band bending will break the bulk inversion symmetry.¹⁶ For zero applied bias, this cannot be distinguished from the “real” interface contribution. By applying a bias, the band bending and thus the electric-field-induced bulk dipole term can be varied.

The frequency dependence of the nonlinear susceptibility $\tilde{\chi}^{(2)}$ reflects the interface electronic structure and can be expressed in terms of eigenstates of this electronic system and the dipole moment \vec{d} .¹⁷ If the SHG frequency 2ω is close to resonance and the fundamental frequency ω is far from any resonance of the system (as is the case in our experiment) we can write^{4,17}

$$\chi_{ijk}^{(2)} \sim \frac{\langle g | d_i | n \rangle}{(2\omega - \omega_{ng} + i\Gamma_{ng})} C(\omega) + \chi_{ijk, \text{nonres}}^{(2)}, \quad (3)$$

where $|g\rangle$ is the electronic groundstate, $|n\rangle$ is an excited state, Γ is a damping constant, and *C*(ω) contains matrix elements and a frequency denominator that change very little for the frequency range used. $\tilde{\chi}_{\text{nonres}}^{(2)}$ is the nonresonant contribution to the total $\tilde{\chi}^{(2)}$.

Our MOS structure consists of a low-doped ($\sim 5 \times 10^{15} \text{ cm}^{-3}$) *p*-type Si(111) wafer with a high quality 300 nm thick thermal oxide, an aluminum backcontact, and a semitransparent 30 Å Cr top-electrode. We have characterized these kind of samples extensively with linear and nonlinear optics.^{14,15} In the linear optical functions, measured with spectroscopic ellipsometry, no bias-dependences were observed for the voltages used, thereby excluding linear electro-optical effects. High- and low-frequency capacitance-voltage (C-V) measurements showed the well-known MOS characteristics^{18,19} and a density of interface traps *D*_{it} at mid-gap of $\sim 2 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$, which is reasonable for a Si(111)/SiO₂ MOS capacitor.²⁰

For the SHG experiment we used a mode-locked titanium sapphire laser that produces 100 fs pulses at 82 MHz repute. The wavelength was varied between 710 nm and 850 nm, and the incident power was 100 mW. The incoming

^{a)}Electronic mail: theoras@sci.kun.nl

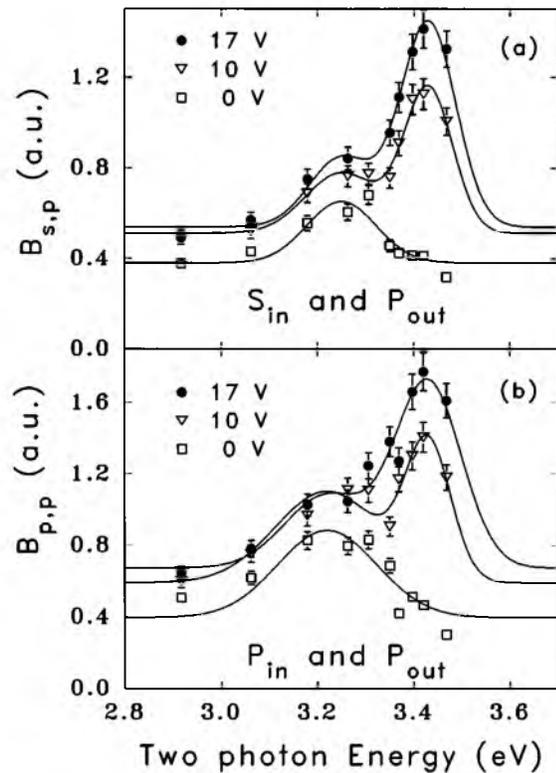


FIG. 1. Spectra of the anisotropic amplitudes for the p -polarized SH intensity under (a) s -polarized excitation ($B_{s,p}$), and (b) p -polarized excitation ($B_{p,p}$) as a function of gate bias.

linearly polarized light was focused to a $100 \mu\text{m}$ spot under an angle of incidence on the sample of 45° . The SHG signal was generated in reflection from the MOS capacitor, through the thin Cr electrode. SHG measurements on a 1000 \AA Cr film, prepared in the same way as the electrode, showed negligible, isotropic, SHG signals. In all measurements the well-known anisotropies for the Si(111) surface were observed,^{6,12,13} indicating that we are probing the buried Si-SiO₂ interface (and possibly the Si bulk). The SHG signal was quadratic for all powers used. This means that laser-induced carrier excitation and band bending,¹⁶ which in principle is possible because the laser photonic energy is greater than the bandgap energy of Si, does not play a significant role. A monochromator was used to check that the signal was at the SHG wavelength. As the spectral resolution was determined by the frequency width of the 100 fs pulses ($\sim 7 \text{ meV}$), the monochromator was left out in the actual measurement, in order to get the best signal-to-noise ratio. All measurements were normalized to a quartz second harmonic (SH) signal. A bias was applied to the MOS capacitor, while the sample was rotated to measure the SH anisotropy. Great care was taken to keep optical alignment constant at all times.

Figure 1 shows the spectra of the anisotropic amplitudes for the p -polarized SH intensity under both s -polarized ($B_{s,p}$) and p -polarized excitation ($B_{p,p}$) [see Eq. (1)], with the gate bias as a parameter. The symbols are measured data, and the solid lines are qualitative fits to the data using Lorentzian line shapes for the resonances as given by Eq. (3). The known resonances at 3.3 eV and 3.4 eV (Ref. 4) are used as starting values for the fit. The error bars have been ob-

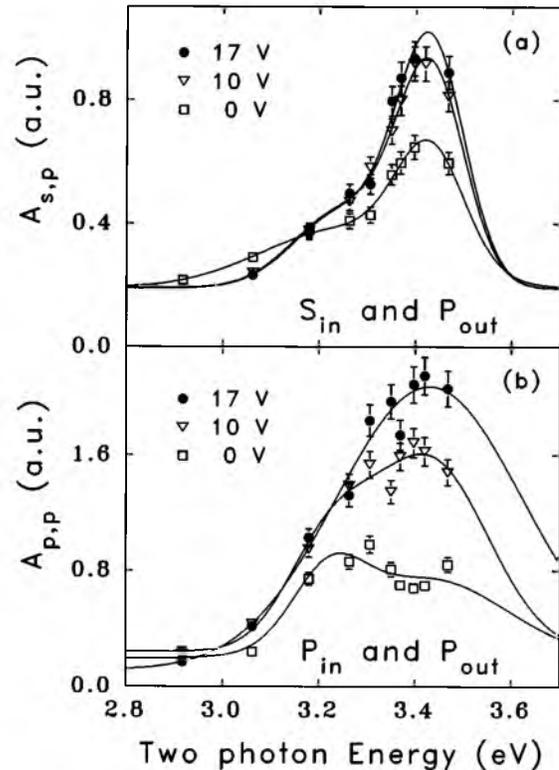


FIG. 2. Spectra of the isotropic amplitudes for the p -polarized SH intensity under (a) s -polarized excitation ($A_{s,p}$) and (b) p -polarized excitation ($A_{p,p}$) as a function of gate bias.

tained from repeated SHG rotational anisotropy measurements. For both polarizations we observe at zero bias only one resonance at $\sim 3.25 \text{ eV}$, whereas a strong bias-dependent resonance appears at 3.43 eV .

Figure 2 shows the spectra of the corresponding isotropic amplitudes. In this case both resonances are already present at zero bias. The 3.25 eV peak dominates the p,p response while the 3.43 eV dominates the s,p response. For both cases, the 3.43 eV peak strongly increases with gate bias, whereas the 3.25 eV peak is bias-independent within experimental error. It has been shown by a combination of SHG and SFG studies that these are two-photon resonances.^{4,21}

These results can be understood qualitatively in the following way. The anisotropic response is governed by a single component $\chi_{\xi\xi\xi}$ for both polarization combinations,^{6,12,13} which accounts for their similar frequency and bias dependence. The zero bias peak at $\sim 3.25 \text{ eV}$ likely corresponds to the 3.3 eV interface resonance observed by Daum *et al.*⁴ They attributed this peak to an interface mode, induced by strain in the direction perpendicular to the Si-SiO₂ interface, which is strongly coupled to χ_{zzz} . Uniaxial strain is known to cause a splitting and shift of the E_1 direct bandgap transition in bulk Si.²² As the splittings are very small and difficult to observe experimentally, the redshift is due to the hydrostatic component of the strain.^{23,24} In this way the out-of-plane strain also couples to the in-plane anisotropic tensor component $\chi_{\xi\xi\xi}$, as was also observed by Meyer.²¹ The 3.43 eV resonance corresponds to this E_1 direct bandgap transition in bulk Si. This mode will become symmetry-allowed if the inversion symmetry is

lifted by a (bias-induced) band offset. It is clear from Fig. 2 that this mode is already strongly present in the isotropic s,p response, even at zero bias, whereas it is weakly present in the p,p response. The interface resonance at 3.3 eV disappears for a H -terminated Si surface,⁴ which is consistent with the fact that the strain is relieved.²⁵ However, for the H -terminated surface, no resonance at 3.4 eV was observed.⁴ This justifies our neglect of resonantly enhanced nonlocal bulk contributions and shows that the 3.43 eV resonance we observe in the isotropic components is an electric-field-induced bulk dipole contribution. The appearance of the E_1 mode in the zero bias spectra indicates that the inversion symmetry is already lifted in this case. This can be understood from the band bending at the Si–SiO₂ interface that is induced by the Cr electrode, due to workfunction differences. With this Cr electrode and for zero applied bias, the MOS capacitor is in depletion/weak inversion, whereas without it the bands would be nearly flat.^{18,19}

The isotropic response of $I_{s,p}$ is governed only by the tensor component $\chi_{\perp\parallel\parallel}$,^{6,12,13} where \perp indicates the direction perpendicular to the interface (z), and \parallel indicates a direction parallel to the interface (x,y). The isotropic $I_{p,p}$ signal results from $\chi_{\perp\parallel\parallel}$ as well as from $\chi_{\perp\perp\perp}$ and $\chi_{\parallel\perp\parallel}$.^{6,12,13} From this we conclude that the $\chi_{\perp\parallel\parallel}$ term is responsible for the 3.43 eV peak in both polarization combinations, whereas it also couples weakly to the interface resonance. For $I_{p,p}$, the $\chi_{\perp\perp\perp}$ and $\chi_{\parallel\perp\parallel}$ components contribute as well, resulting in a stronger appearance of the interface mode at 3.25 eV. This shows that different tensor components probe different properties of the electronic structure of the Si–SiO₂ interface.

Since the interface resonance is bias-independent, it is clear that the electric-field-induced bulk dipole term at 3.43 eV must be generated in a volume that is large compared to that of the layer of strained Si. From x-ray reflectivity²⁶ and ellipsometry²³ studies, the thickness of the strained Si layer was estimated to be about 1.5 nm. Numerically solving the Poisson equation for our MOS capacitor, we found an inversion layer width of about 10 nm, which changes little with gate bias.^{18,19} Since for zero applied bias our MOS capacitor is already close to inversion, the depletion layer width is already near its maximum value, and increasing the gate bias only increases the electric field in the inversion layer.^{18,19} At the 3.43 eV resonance we measured a linear dependence of the anisotropic and isotropic amplitudes on gate bias, which can be explained by a model based on Eq. (2), assuming that the EISHG is generated only in the inversion layer. This is because only the amplitude of the electric field in the inversion layer changes with gate bias and not the width of the inversion layer.^{18,19}

Thus, the observed resonances and their bias-dependencies can be explained with a simple model that combines the well-known theory for MOS structures with that of SHG. Our results are in agreement with Daum's interpretation of a resonance at 3.3 eV due to a strained layer of Si close to the Si–SiO₂ interface, but not with his assign-

ment of the responsible tensor components. By a combination of bias and polarization selection, we show how different tensor components probe different structural properties of the Si–SiO₂ interface. This result opens new perspectives to study these important buried interfaces that are hardly accessible by other techniques.

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