Second-harmonic intensity and phase spectroscopy as a sensitive method to probe the space-charge field in Si(100) covered with charged dielectrics

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Second-harmonic intensity and phase spectroscopy as a sensitive method to probe the space-charge field in Si(100) covered with charged dielectrics

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A space-charge region (SCR) can develop in silicon due to the presence of built-in charges in dielectric thin films that are used in silicon-based device architectures. To study both the strength and polarity of the electric field in such a SCR, the authors performed second-harmonic (SH) generation spectroscopy in the vicinity of the \( E_1 \) critical point (2.7–3.5 eV) of silicon. As multiple contributions add coherently to SH intensity spectra, the electric-field-induced contribution cannot always be distinguished unambiguously from the intensity data in the absence of complementary phase information. Combined SH intensity and phase measurements were therefore performed to resolve this ambiguity. Using a coherent superposition of critical-point-like resonances with excitonic line shapes, the intensity and phase spectra of several SiO\(_2\)- and Al\(_2\)O\(_3\)-based samples were simultaneously modeled. This analysis reveals that not only the polarity of the space-charge field can be determined unambiguously but also that the sensitivity to the electric field strength is significantly enhanced. © 2014 American Vacuum Society. [http://dx.doi.org/10.1116/1.4862145]

I. INTRODUCTION

The performance of modern silicon-based semiconductor devices is highly affected by the presence (either intentionally or not) of built-in charges in (high-\(\kappa\)) dielectric thin films. This is mainly due to the fact that such charges lead to the development of a space-charge region (SCR) in crystalline silicon at the dielectric interface.\(^1\)–\(^5\) A fundamental insight into the influence of built-in charges on the silicon SCR is therefore of prime importance. This implies that it is desirable to directly measure the strength and polarity of the space-charge field with high sensitivity. A very suitable technique in this respect is optical second-harmonic generation (SHG) due to its contactless and background-free character.\(^6\)–\(^10\) Besides being directly sensitive to the electric field in the silicon SCR, through the effect of electric-field-induced SHG (EFISH), this technique is also interface specific for centrosymmetric media such as crystalline silicon and amorphous materials.\(^11\) To characterize the space-charge field under steady-state conditions, it is necessary to carry out spectroscopic second-harmonic (SH) intensity measurements.\(^12\)–\(^14\)

In case of silicon covered with transparent oxide films, the frequency dependence of the SH intensity is typically composed of multiple contributions that are related to the silicon interface and to the electric field in the silicon SCR.\(^11\)–\(^12\) Due to interference phenomena caused by the phase difference between the various contributions, it is virtually impossible to directly distinguish between them from the spectroscopic data. Moreover, when only performing SH intensity measurements direct information on the phase of each contribution is lost by definition.\(^15\) This implies that the strength of the space-charge field, which is related to the EFISH intensity, and the polarity of the space-charge field, which is related to phase of the EFISH contribution, can also not be determined directly.\(^12\)–\(^16\) One way to isolate the interfering contributions is by using a critical-point (CP) model, which describes the SH intensity spectrum by a coherent superposition of CP-like resonances with excitonic line shapes.\(^17\) These line shapes are defined by an amplitude, a resonance energy, a linewidth (or broadening), and excitonic phase. The excitonic parameters of each contribution are used to fit the model to the intensity data. However, due to the large number of adjustable parameters, the various contributions can still not be unambiguously isolated. Information can then only be extracted when certain parameters of the excitonic line shapes are known in advance, for example, the resonance energy, or when other sound assumptions can be made, for example, about the absence of a specific contribution depending on the experimental configuration. Furthermore, the excitonic phase in the model is an indirect parameter with respect to the SH intensity. To solve the ambiguity, the measurement of the complementary phase of the SH radiation is required.\(^18\)–\(^19\)

In this paper, we show that combined second-harmonic intensity and phase spectroscopy allows for the unambiguous determination of the polarity of the space-charge field and also leads to a significant enhancement in the sensitivity to the field strength.

II. SAMPLE CHOICE AND PREPARATION

SH intensity and phase spectra were obtained for four SiO\(_2\)- and Al\(_2\)O\(_3\)-based samples. These samples were selected because they contain different number densities of built-in charges. This sample choice allows us to highlight the benefit of simultaneously modeling intensity and phase data in terms of extracting the EFISH intensity and phase. Table I shows the details of each sample, their built-in charge density \(Q_{\text{built-in}}\), and the sample names for further reference. All sample structures are of relevance for photovoltaic and microelectronic devices.\(^2\)–\(^23\)
Table I. Properties of each sample. Sample A is an Al₂O₃ film deposited directly on silicon with an interfacial SiO₂ present. Samples B and C are ALD-prepared stacks of Si/SiO₂/Al₂O₃ with intentionally grown SiO₂ interlayers. Sample D is a SiO₂ film obtained from wet thermal oxidation of silicon, which contains no Al₂O₃ film. The film thicknesses were obtained from spectroscopic ellipsometry (Ref. 43). Note that the negative built-in charges in the dielectric films induce a positive space-charge region in silicon for all samples. The strength of the corresponding space-charge field reduces from samples A to D.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Silicon type</th>
<th>t_Al₂O₃ (nm)</th>
<th>SiO₂ type</th>
<th>t_SiO₂ (nm)</th>
<th>Q_{bulk,in} (cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>p</td>
<td>1.5 ± 0.5</td>
<td>Interfacial</td>
<td>31.5 ± 0.5</td>
<td>-5.8 × 10¹²</td>
</tr>
<tr>
<td>B</td>
<td>p</td>
<td>4.7 ± 0.5</td>
<td>Plasma ALD</td>
<td>31.5 ± 0.5</td>
<td>-1.4 × 10¹⁰</td>
</tr>
<tr>
<td>C</td>
<td>p</td>
<td>10.8 ± 0.5</td>
<td>Plasma ALD</td>
<td>31.5 ± 0.5</td>
<td>-2.0 × 10¹⁰</td>
</tr>
<tr>
<td>D</td>
<td>n</td>
<td>47.0 ± 0.5</td>
<td>Wet thermal</td>
<td>—</td>
<td>-7.8 × 10¹⁰</td>
</tr>
</tbody>
</table>

aValue from Ref. 21.
bValue from Ref. 43.
cValue estimated in this work.

Ultrathin SiO₂ films were prepared by atomic layer deposition (ALD), at a substrate temperature of ~200 °C, using ultrashort doses (<100 ms) of H₂Si[N(C₂H₅)₂]₂ (SAM.24, Air Liquide) and a few seconds of O₂ plasma exposure that were separated by Ar purges. A thicker SiO₂ film was grown by wet thermal oxidation via the exposure of a silicon wafer to H₂O vapor at a substrate temperature of ~900 °C. Thin Al₂O₃ films with a nominal thickness of (31.5 ± 0.5) nm were prepared by plasma ALD, at a substrate temperature of ~200 °C, using Al(CH₃)₃ as the metal precursor and O₂ as the plasma gas. The films were deposited at both sides of float zone Si(100) wafers (n- or p-type, 2–3 Ω cm, 280 μm) preceded by a HF dip to obtain a H-terminated surface. After deposition, samples A, B, and C received a post-deposition anneal for 10 min. at 400 °C in N₂, whereas sample D received a forming-gas anneal for 10–20 min. at 400 °C using a mixture of 10% H₂ in N₂.

Note that the samples have been characterized “as-processed” without fabricating a device structure, which might impact the intrinsic sample properties.

III. PHASE-SENSITIVE MEASUREMENTS

A. Principles

SH phase-sensitive techniques are generally based on the principle of interference between a SH reference pulse and the SH pulse generated at the sample of interest. The interference can be either recorded in the time domain variant or in the spectral domain. For the work described here, we adopted the time-domain variant. In this variant, the SH reference pulse is typically generated in a spectrally flat nonlinear film (e.g., indium tin oxide or tricyanovinylaline polymer) on a glass substrate, which is placed in the incident fundamental beam of a narrowband pulsed laser. The SH reference pulse generated in transmission interferes with the SH pulse generated at the sample in reflection. By changing the optical phase delay between the fundamental and SH reference pulses a time-domain interferogram is obtained from which the total phase of the interfering SH radiation can be deduced. In our work, the phase delay is changed by sequentially changing the distance between the reference and the sample as schematically depicted in Fig. 1. The phase difference (φ) between the SH reference pulse and the SH pulse generated in the sample of interest is measured. Note that the optical phase delay (Δk⋅d) is predominantly introduced due to the difference in propagation velocity between the fundamental and SH reference pulse in the medium (air in this work) that is present between the reference and sample.

B. Implementation of the interferometric setup

To change the distance between the reference and the sample a computer-controlled translation stage (Thorlabs LTS300S, Δ = 300 mm, δ = 4 μm) is used. As the phase reference sample we use a (100 ± 25) nm thick film of indium tin oxide (ITO) on a ~1 mm thick glass substrate. According to Dolgova et al., the choice of ITO, with this thickness, satisfies the conditions for a reference sample that is (1) thin enough to avoid Maker fringes in the SH response while tuning the fundamental wavelength, (2) optically inactive to conserve the polarization state of the fundamental radiation as it passes through it, and (3) has no resonant features.
within the wavelength range of both the fundamental and SH radiation applied in this work. Figure 2 shows a schematic representation of the interferometric setup.

The phase reference sample, from this point onwards referred to as the reference, is placed in the incident fundamental beam between the lens and the sample with the ITO film facing the sample. Positioning the reference in this way ensures that the phase shift remains small since the SH radiation generated in the ITO by the fundamental beam does not pass through the highly dispersive glass substrate. Furthermore, the reference sample is placed at an oblique angle to prevent SH radiation from multiple passes of the fundamental beam in the ITO film to become part of the primary transmitted reference pulse. The reference signal is collinear with the fundamental beam and as such reflected by the sample. After passing through the reference the focused fundamental beam generates also a SH signal at the sample in reflection. The SH signal of both the reference and sample are directed toward the detector where their interference effect, which causes the oscillations, is lost. In the situation that the reference signal would be dominant an exponential-like [cf. Eq. (1)] increase is observed for decreasing distance. Because, in the case of the interferograms in Fig. 3, the oscillations dominate even when the two-photon energies.

Spectroscopic measurements were performed using p-polarized femtosecond (~90 fs) laser radiation from a Ti:sapphire oscillator (Spectra-Physics Tsunami), tunable in the 1.33–1.75 eV photon energy range, and focused on the sample at a 35° angle of incidence to a beam waist of ~100 μm. SH radiation generated in reflection, using a fluence at the sample of ~1–4 μJ·cm⁻² per pulse, was separated from the fundamental radiation using optical and spatial filtering and detected in p-polarization with a photomultiplier tube (PMT) connected to single photon counting electronics. The SHG data are represented in terms of the SH intensity as calculated from the detected SH signal after correction for the applied laser intensity and the response of the optical system. The optical response comprises the optical transmission of the colored glass filters and the polarizer in the exit beam path and the quantum efficiency of the PMT. In all experiments, the Si(100) substrates were oriented with the [011] crystal axis parallel to the plane of incidence of the laser beam. In case of the phase measurements, the SH intensity is obtained at every set position of the translation stage for each fundamental wavelength. This results in a spectrum of interferograms from which a phase spectrum can be extracted.

C. Analysis of the interferometric data

Figure 3 shows the type of interferograms typically obtained from the interferometric measurements at four different two-photon energies. The data is obtained from a SiO₂/Al₂O₃ thin film stack on a silicon substrate (sample B in Table I). For clarity, the interferograms are offset vertically. They all clearly show the expected oscillations of the SH intensity as a function of the reference position. More specifically, it can be observed that the amplitude of the oscillations increases when the distance between the reference and the sample becomes smaller. This is due to the fact that the focusing on the reference improves when moving it toward the sample, which leads to an enhanced SH response from the reference. It is important, however, that the signal from the sample and reference remain more or less equal. If either of the two signals dominates the total response, the interference effect, which causes the oscillations, is lost. In the situation that the reference signal would be dominant an exponential-like [cf. Eq. (1)] increase is observed for decreasing distance. Because, in the case of the interferograms in Fig. 3, the oscillations dominate even when the two-photon energies.
reference is closest to the sample, the ratio between the signals appears to be fairly optimal. It can be also seen that the amplitude of the oscillations depends on the two-photon energy. This is primarily caused by the change in the ratio between the signal from the sample and the reference due to the spectral response of silicon. The oscillation period is determined by the optical dispersion of air. In Fig. 3(a), the exact position of the minima and maxima depend on the optical dispersion as well as the total SH relative phase. By plotting the SH intensity as function of the dimensionless parameter \( \Delta k \cdot d \), with \( \Delta k \) the phase-mismatch parameter, only the total SH relative phase \( \phi \) determines the position of the extrema. The shift in the extrema between the different two-photon energies is now directly related to the change in total SH relative phase \( \Delta \phi \) as indicated in Fig. 3(b).

To extract the total SH relative phase \( \phi \) from each individual interferogram, the data are reproduced by

\[
I^{2\omega}(d) = \left| E^{2\omega}_{\text{sample}} \right|^2 + \left| E^{2\omega}_{\text{reference}} \right|^2 \frac{E^{2\omega}_{\text{sample}}}{1 + (d/d_0)^2} + 2 \left| E^{2\omega}_{\text{sample}} \right| \left| E^{2\omega}_{\text{reference}} \right| \cos(\Delta k \cdot d + \phi),
\]

where \( d \) is the distance between the two samples (see Fig. 2) and \( I^{2\omega}(d) \) is the distance-dependent SH intensity. In this equation, \( E^{2\omega}_{\text{sample}} \) and \( E^{2\omega}_{\text{reference}} \) are the SH electric fields generated at the sample and at the reference, respectively. The total SH relative phase is given as

\[
\phi = \phi_{\text{sample}}^{2\omega} + \phi_{\text{prop}}^{2\omega} - \phi_{\text{ref}}^{2\omega} - \phi_{\text{prop}}^{2\omega},
\]

with \( \phi_{\text{sample}}^{2\omega} \) and \( \phi_{\text{ref}}^{2\omega} \), the relative phase of the SH signal from the sample and reference, respectively, and \( \phi_{\text{prop}}^{2\omega} \) and \( \phi_{\text{prop}}^{2\omega} \) the phase shifts caused by the propagation of the SH radiation through the thin-film-system. The factor \( 1 + (d/d_0)^2 \) in Eq. (1) describes Gaussian beam focusing, in which \( d_0 \) is the Rayleigh length, and it corrects for the changing spot size on the reference when traversing the distance \( d \). The phase-mismatch parameter \( \Delta k \) describes the propagation delay in air between the fundamental and SH radiation from the reference and is defined as

\[
\Delta k = \frac{4\pi}{\lambda_0} \Delta n = \frac{4\pi}{\lambda_0} (n_{\text{air}}^{2\omega} - n_{\text{air}}^{2\omega}),
\]

where \( \lambda_0^{2\omega} \) is the fundamental wavelength in vacuum, and \( \Delta n \) is the difference between the refractive index of air at the SH \( (n_{\text{air}}^{2\omega}) \) and fundamental \( (n_{\text{air}}^{\omega}) \) wavelength. Using tabulated dispersion data for the refractive index of air the oscillation length can be calculated.\(^{30}\) This can be used to estimate the number of oscillation periods expected for a given travel range of the stage. With a travel range of \( \sim 8 \) cm in our experiments, the number of oscillation periods expected for a fundamental wavelength of 800 nm is approximately one and a half. This is indeed observed for the curve in Fig. 3 at a two-photon energy of 3.1 eV which corresponds to a fundamental wavelength of 800 nm. At least one oscillation period should be acquired to accurately obtain the total SH relative phase from fitting Eq. (1) to the interferometric data. Consequently, the number of oscillation periods between one and two in our data, as depending on the fundamental wavelength, is sufficient.

The solid lines in Fig. 3 are the result of fitting Eq. (1) to the experimental data using \( E^{2\omega}_{\text{sample}}, E^{2\omega}_{\text{reference}}, d_0, \Delta k, \) and \( \phi \) as fit parameters. Starting values for the parameters are estimated from the characteristics of the interferograms and from Eq. (3) using known values for the refractive index of air. Each interferogram is fitted separately because all parameters depend on the photon energy. Although the SH response of the reference is expected to be spectrally flat this is not \( a \ priori \) imposed by using a single fit parameter \( E^{2\omega}_{\text{reference}} \) for all interferograms.\(^{19,28}\) Thus, if the tail of the resonance of ITO at \( \sim 6.5 \) eV has some influence on the measurements within the applied two-photon energy range (2.9–3.5 eV) it can be accounted for. An excellent agreement between the data and the model can be observed for all the interferograms. By performing the analysis for each wavelength at which an interferogram has been measured, the frequency dependence of the fit parameters of interest can be obtained. Figure 4 shows the total SH relative phase \( \phi \), the phase-mismatch parameter \( \Delta k \), and the SH intensity of the

![Figure 4](image-url)

**Fig. 4.** (Color online) Total SH relative phase \( \phi \) (top panel), the SH intensity \( I^{2\omega} \) (middle panel), and phase-mismatch parameter \( \Delta k \) (bottom panel) as a function of two-photon energy. The individual data points were acquired by fitting the interferograms obtained for sample B using Eq. (1). The solid line in (b) represents intensity data of the sample acquired from separate intensity measurements. The solid line in the bottom panel was calculated via Eq. (3) using tabulated values for the refractive index of air.

of the sample, \( I_{2\omega_{\text{sample}}} = |E_{2\omega_{\text{sample}}}|^2 \), and reference, \( I_{2\omega_{\text{reference}}} = |E_{2\omega_{\text{reference}}}|^2 \), as a function of the two-photon energy for sample B.

A change in the total SH phase of \( \sim 1.2\pi \) radians occurs within the two-photon energy range of 2.9–3.5 eV as is visible in Fig. 4(a). The change is largest around the region of 3.3–3.5 eV, which indicates that a resonant feature is present in this energy range. This is also clear from the extracted SH intensity spectrum of the sample (diamond markers) as shown in Fig. 4(b) with a maximum intensity at \( \sim 3.4 \) eV. This two-photon energy coincides with the resonance energy of the \( E_1 \) interband transition of bulk silicon. 31 Note that the ITO reference sample has a flat spectral response (circular markers) which is consistent with the literature. 19,28 It must be stressed that both the SH intensity and phase spectrum can be simultaneously obtained from the interferometric measurements as represented by the data markers. The sensitivity to both intensity and phase originates from the convenient choice of placing the ITO reference sample behind the lens that focuses the fundamental beam on the sample (Fig. 2). Depending on the position of the reference, the focusing of the laser beam on the reference changes, which causes the intensity from the reference to vary with respect to the intensity of the sample during an interferometric measurement. This enables the model to effectively discriminate between the signal from the sample and reference. The solid line in Fig. 4(b) represents intensity data of the sample, which was acquired with high accuracy from separate intensity measurements. It is evident that the two data-sets overlap almost exactly. As can be seen in Fig. 4(c), the values of the phase-mismatch parameter \( \Delta k \) extracted from the interferograms (markers) match with the trend (solid line) calculated via Eq. (3). The beam waist \( w_0 \), as calculated from the obtained Rayleigh lengths via \( d_0 = \frac{\pi w_0^2}{\lambda} \), is about 90 \( \mu \)m for the wavelengths \( \lambda \) used in this experiment, which is in agreement with the previously measured value. 29

In summary, the data in Fig. 4 clearly validate the interferometric technique and the analysis of the interferograms on the basis of Eq. (1). In the following sections, SH phase spectra obtained from the interferometric data for all samples in Table I as well as their independently acquired SH intensity spectra will be considered. A critical-point model will be used to simultaneously reproduce the intensity and phase data. This allows us to demonstrate that by exploiting the complementary phase information the goodness of the model fit improves and that the EFISH contribution can be accurately isolated from the overall intensity spectrum.

IV. RESULTS AND DISCUSSION

A. Second-harmonic intensity and phase spectra

Figure 5 shows the SH intensity (bottom panel) and phase (upper panel) spectra of all samples in the two-photon energy range of 2.6–3.6 eV. It must be stressed at this point that the SH response is dominated by bulk-type interband transitions at critical points (CP) of the bulk Brillouin zone of crystalline silicon. 12,13,32,33 No resonant SHG occurs at the SiO\(_2\)/Al\(_2\)O\(_3\) interface or at the surface of either SiO\(_2\) or Al\(_2\)O\(_3\) due to the fact that the band gap of these amorphous materials lies outside the fundamental and second-harmonic photon energy range.

Pronounced differences in the SH intensity (Fig. 5, bottom panel) can be observed between the samples. The intensity decreases in magnitude from samples A to D with a factor of \( \sim 46 \) between the lowest and the highest value. From the inset, it can be seen that the spectrum of sample D has an asymmetric peak shape. The maximum intensity for sample A and B is obtained at a two-photon energy of \( \sim 3.4 \) eV, which is very similar to the resonance energy of the \( E_1 \) interband transition of bulk silicon. This indicates that the EFISH contribution from the silicon SCR dominates the spectral response, as is indeed expected for these two samples with a high built-in charge density (Table I). However, the peak position of sample C and D are red-shifted to 3.35 and 3.3 eV with respect to 3.4 eV, respectively. This suggests that for these samples the EFISH contribution is less dominant, or absent, such that the interband contributions have more influence on the overall SH spectrum. These contributions are energy-shifted due to the loss of the silicon bulk properties in the vicinity of the interface. 12,34 The red-shift and low intensity for sample C and D are consistent with their relatively low number densities of built-in charges as listed in Table I. The determination of the charge density value for sample D is described in Sec. IV C. Due to the almost negligible EFISH contribution, this determination from the SH data is only possible by modeling the intensity and phase data simultaneously.
The SH phase spectra in the top panel of Fig. 5 show a general trend of increasing total phase for increasing two-photon energy. Note that for clarity a vertical offset has been applied to the data of samples A, B, and C. Subtle differences between the samples can be observed in terms of absolute phase, total phase increase within the two-photon energy range, and overall shape of the phase spectrum. This shows that the variation in sample properties, most distinctly the changes in built-in charge density, not only influence the SH intensity but also has a visible impact on the spectral phase response. Sample D has a clearly different phase spectrum compared to the other samples with a strong decrease in total phase at a two-photon energy of ~3.5 eV.

### B. Critical-point modeling of the spectroscopic data

To extract more quantitative information from the spectroscopic data in Fig. 5, the obtained spectra need to be described by a model. The SH response of silicon to the driving electric field is determined by the second-order susceptibility tensor \( \chi^{(2)}(2\omega) \) of the interface. The frequency dependence of the components of this interface second-order susceptibility can be approximated by a coherent superposition of CP-like resonances with excitonic line shapes as

\[
\chi_{ijk}^{(2)}(2\omega) = \sum_q \chi_q^{(2)}(2\omega) \propto \sum_q \frac{h_q e^{i\phi_q}}{2\omega - \omega_q + i\Gamma_q},
\]

where \( i,j,k \in \{x,y,z\} \) and \( h_q \) denotes the (real) amplitude, \( \omega_q \) the resonance frequency, \( \Gamma_q \) the linewidth (or broadening), and \( \phi_q \) the excitonic phase of resonance \( q \). This equation shows clearly the phase dependent summation of the different contributions \( q \) that contribute to the overall SH spectral response. It can be intuitively shown that the intensity and phase are complementary to each other by isolating a single excitonic resonance from the summation term in Eq. (4). For such a single excitonic transition, the quantity that would be measured when performing intensity measurements is

\[
I_{SH} \propto |\chi_q^{(2)}|^2 = \frac{|h_q|^2}{(2\omega - \omega_q + i\Gamma_q)^2}.
\]

The SH intensity \( I_{SH} \) in Eq. (5) scales quadratically with \( h_q \), which is therefore a “direct” parameter. Note, however, that the excitonic phase \( \phi_q \) does not appear, which means that the SH intensity contains no explicit information on the relative phase. In case of phase measurements, the quantity that would be measured for a single excitonic transition scales with the SH phase \( \phi_{SH} \) as

\[
\phi_{SH} \propto \arg\left(\chi_q^{(2)}\right) = \phi_q - \arctan\left(\frac{\Gamma_q}{2\omega - \omega_q}\right),
\]

in which the excitonic phase \( \phi_q \) is the “direct” parameter while the amplitude \( h_q \) does not appear. However, this clear separation between amplitude and phase in case of a single resonance is not so strict when multiple contributions are present. In that case, the amplitudes \( h_q \) lead to a weighted summation of the total phase, and the excitonic phases \( \phi_q \) lead to a weighted summation of the intensity [cf. Eqs. (7) and (8)]. The latter is the reason why, in general, intensity spectra “indirectly” contain information about the excitonic phase of the various contributions.

With the expression for the interface second-order susceptibility given in Eq. (4), the frequency dependence of the SH intensity and total SH relative phase can be written as

\[
I_{SH}(2\omega) \propto \left|A(\omega,\theta) \sum_q \frac{h_q e^{i\phi_q}}{2\omega - \omega_q + i\Gamma_q}\right|^2 I_m(\omega),
\]

and

\[
\phi_{SH}(2\omega) \propto \arg\left(B(\omega,\theta) \sum_q \frac{h_q e^{i\phi_q}}{2\omega - \omega_q + i\Gamma_q}\right),
\]

respectively, with \( I_m(\omega) \) the intensity of the fundamental radiation at frequency \( \omega \). The complex function \( A(\omega,\theta) \), where \( \theta \) is the angle of incidence, describes the propagation of both the fundamental and SH radiation through the thin film system, and includes linear optical phenomena such as refraction, absorption, and interference due to multiple reflections. The complex function \( B(\omega,\theta) \) is slightly different from \( A(\omega,\theta) \) as it also takes into account the propagation of the SH radiation from the reference sample through the thin film system. To compute \( A \) and \( B \) the thickness and linear optical properties of the \( \text{SiO}_2 \) and \( \text{Al}_2\text{O}_3 \) films need to be known in advance. For this reason, spectroscopic ellipsometry measurements (190–1000 nm) were performed using a J.A. Woollam Co., Inc M-2000U rotating compensator ellipsometer mounted on a variable angle stage.

Equations (7) and (8) were simultaneously fitted to the SH intensity and phase spectra in Fig. 5. The data were analyzed only in terms of tensor element \( \chi_{zzz}^{(2)} \) although also the elements \( \chi_{zzx}^{(2)} \) and \( \chi_{zzy}^{(2)} \) contribute to SHG for \( p \)-polarized fundamental and SH radiation. It has been shown in the literature, however, that \( \chi_{zzz}^{(2)} \) dominates and that the spectral parameters show only minor differences in fits for each of the three tensor elements. Following the approach of Rumpel et al., three distinct contributions were taken into account. These are each assigned to interband transitions of Si for different configurations of Si-Si bonds. More specifically, a Si-Si interface contribution (~3.3 eV) and EFISH contribution (~3.4 eV) around the bulk \( E_1 \) resonance, and a Si-SiO suboxide contribution (~3.7 eV), which is resonant in between the \( E_1 \) and \( E_2 \) resonances of bulk Si. The parameters describing the excitonic line shape, i.e., amplitude, resonance energy, broadening, and phase, for each contribution are used to fit the model to the SH intensity and phase spectra. Because the Si-SiO suboxide contribution lies mostly outside our available photon energy range, its resonance energy and broadening were taken from the literature and kept fixed at 3.6 and 0.30 eV, respectively. The broadening of the Si-Si interface contribution was not fitted but manually optimized to obtain the best fit result taking typical
values found in the literature into account.\textsuperscript{12,13} The excitonic phases of the various contributions are determined relative to the excitonic phase of the Si-Si interface contribution. This phase cannot be set to zero, as is usually done for the modeling of intensity-only data, because the total SH phase is determined relative to the unknown SH phase of the reference sample [see Eq. (2) and Fig. 1]. To facilitate comparison of the excitonic phases obtained in this paper with previously obtained values, and those reported in the literature, the excitonic phase of the Si-Si interface contribution is subtracted from the excitonic phases for all contributions after modeling. To account for silicon resonances at high photon energy ($E_2 \approx 4.5$ eV and $E_1'$ at $\approx 5.3$ eV) a nonresonant contribution was added to the description for the second-order nonlinear susceptibility given by Eq. (4) with only an amplitude and a phase, i.e., $h_{nr} e^{i\phi_{nr}}$.

A multisample fitting procedure was employed to improve the stability and goodness of the fit. This means that the data of all samples were simultaneously modeled with a single variable for certain model parameters. The multisample fitting procedure allows for unconstraint model parameters without their values becoming unrealistic. The solid lines through the experimental points in Fig. 5 represent the model fits to the data. An excellent agreement between the lines through the experimental points in Fig. 5 and the data has been obtained for both the SH intensity and phase data of all samples with appropriate weighting factors. The parameter values resulting from the analysis are listed in Table II for each sample. Those values which are printed in italic had a single variable in the multisample fitting procedure and those printed in bold were fixed. Unlike the modeling for the intensity only data in our previous works only few of the model parameters need to be fixed.\textsuperscript{14,37,38}

### Table II. Excitonic parameters of the various contributions to the SH response as obtained from simultaneously modeling the SH intensity and phase spectra using a multisample fitting procedure. After modeling, $\phi_1$ was subtracted from all excitonic phases. Parameter values printed in italic had a single variable in the multisample fit and those printed in bold were fixed.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Si-Si interface contribution ($E_1$)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$h_1$ (arb. unit)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>$h_{01}$ (eV)</td>
<td>3.32</td>
<td>3.32</td>
<td>3.32</td>
<td>3.32</td>
</tr>
<tr>
<td>$\Gamma_1$ (eV)</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
<td>0.09</td>
</tr>
<tr>
<td><strong>EFISH contribution ($E_1$)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$h_0$ (arb. unit)</td>
<td>3.1</td>
<td>1.2</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>$h_{02}$ (eV)</td>
<td>3.39</td>
<td>3.39</td>
<td>3.39</td>
<td>3.39</td>
</tr>
<tr>
<td>$\Gamma_2$ (eV)</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>$\phi_2$ ($\pi$ rad)</td>
<td>0.6</td>
<td>0.5</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td><strong>Si-SiO interface contribution</strong></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$h_3$ (arb. unit)</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
</tr>
<tr>
<td>$h_{03}$ (eV)</td>
<td>3.60</td>
<td>3.60</td>
<td>3.60</td>
<td>3.60</td>
</tr>
<tr>
<td>$\Gamma_3$ (eV)</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>$\phi_3$ ($\pi$ rad)</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
</tr>
</tbody>
</table>

### C. Interpretation of the modeling results

The resonance energy and broadening obtained for the Si-Si interface and EFISH contributions agree very well to the values typically found in the literature.\textsuperscript{12,13,32,34} A constant amplitude of the Si-Si interface contribution as well as the Si-SiO suboxide contribution was obtained for all samples. The excitonic phase of the Si-SiO suboxide contribution is the same for all samples. However, the obtained values are not consistent with those found by Rumpel et al. for thermally oxidized silicon.\textsuperscript{13} This might be related to a difference in the Si/SiO$_2$ interface characteristics for our samples compared to those in the literature. Since the Si-SiO interface contribution is supposed to be very sensitive to the bond configuration at the Si/SiO$_2$ interface its resonance parameters can be expected to depend on the exact processing conditions. On the other hand, the value for the phase of the Si-SiO interface contribution specified by Rumpel et al. was determined only from intensity data that contain no direct information about the excitonic phases. The complementary phase data in this work improve the sensitivity of the model to the excitonic phases and it may therefore be expected that their values can be obtained more accurately.

The trend in the obtained EFISH amplitudes matches the trend in the charge densities for all samples listed in Table I. From the EFISH phase, the polarity of the space-charge field and, thus, the built-in charges can be determined, i.e., $\sim 0$ radians is positive charge and $\sim \pi$ radians is negative charge, depending slightly on the strength of the electric field.\textsuperscript{13,39} A negative charge density is therefore present in all samples. Although expected for samples A, B, and C, this appears to be also the case for sample D. In general, however, thermally grown SiO$_2$ films are known to contain positive charges.\textsuperscript{40} The charges in sample D originate therefore most likely from charged interface states at the Si/SiO$_2$ interface. In case of $n$-type silicon, these states, which are primarily caused by $P_b$ defect centers, are negatively charged.\textsuperscript{41} This intuitively explains the presence of negative charges in sample D for which an $n$-type silicon substrate was used. Moreover, the relatively low defect density of $\sim 10^{10}$ eV$^{-1}$ cm$^{-2}$ typically obtained for thermally grown SiO$_2$ films accounts for the low absolute number density of charged interface states found.\textsuperscript{5,42}

Using a previously established procedure, the charge density in sample D can be determined from the parameters of the EFISH contribution.\textsuperscript{14} Via this procedure a charge density of $\sim 7.8 \times 10^{10}$ cm$^{-2}$ is obtained, which corresponds to an electric field at the Si/SiO$_2$ interface of $\sim 10$ kV cm$^{-1}$. This is a factor two lower compared to the lower limit of $\sim 20$ kV cm$^{-1}$ previously obtained using the critical-point modeling for intensity data only.\textsuperscript{14} The combined SH intensity and phase modeling thus improves the sensitivity of EFISH to the strength of the electric field in the SCR. To the best of our knowledge, the minimum detectable electric field strength reported for EFISH is on the order of $\sim 1$ kV cm$^{-1}$.\textsuperscript{17} However, this value was obtained using an externally applied bias voltage on a special sample structure while having the sample orientation and input polarization such that
FIG. 6. (Color online) Visualization of the impact of intentional changes in the EFISH relative phase $\phi$ on the model fit. The individual points represent the experimental data obtained for sample A. The solid lines are the results obtained from the combined intensity and phase modeling, whereas the dashed lines are the results for the intensity-only modeling with $\phi_{\text{EFISH}}$ fixed in both cases. (a) The total SH relative phase spectrum, (b) the SH intensity spectrum, and (c) the reduced chi-squared $\chi^2_{\text{reduced}}$ as function of $\delta$.

The sensitivity to the electric field strength of our approach is demonstrated by the simultaneous SH intensity and phase modeling, i.e., $\phi_{\text{EFISH}}$ fixed, the model has been fitted only to the intensity data as well as simultaneously to both the intensity and phase data. From the parameter values obtained for the intensity-only fit, the corresponding SH phase spectrum has been simulated. The result of repeating this procedure for different values of $\phi_{\text{EFISH}}$ is shown in Fig. 6 using the data of sample A. As can be seen in Fig. 6(a) small variations in EFISH relative phase have quite an impact on the modeled SH phase spectra, i.e., most of the calculated curves do not match the data at all. Strikingly, however, the SH intensity spectrum is hardly affected by the EFISH relative phase values as shown in Fig. 6(b). To quantify the impact of the complementary phase data on the goodness of fit the reduced-chi squared $\chi^2_{\text{reduced}}$ has been calculated as a function of the change in EFISH relative phase ($\delta$) for both the combined and the intensity-only modeling. Figure 6(c) shows that in case of the combined modeling a sharp and low minimum in $\chi^2_{\text{reduced}}$ is obtained and its average value is significantly higher than for the combined modeling.

In summary, the results in Fig. 6 demonstrate that by the simultaneous modeling of SH intensity and phase spectra the goodness of the model fit is significantly improved. This means that without the SH phase data the model parameters will not always be uniquely determined. Nevertheless, our conclusions drawn from the modeling results in our previous works for intensity-only data are still reliable as additional information on some of the fit parameters was present. Despite the improved goodness of fit when using the complementary phase information, it was not possible to perform a fit with all parameters released because this leads to unphysical parameter values. This is the result of the small photon energy range used for the spectroscopic measurements and could, therefore, be resolved by extending the range up to the resonance energy ($\sim 4.5$ eV) of the $E_2$ transition of bulk silicon.

V. CONCLUSIONS

The phase of SH radiation contains complementary information with respect to the SH intensity. To acquire the phase information, we implemented a SH phase-sensitive experimental setup based on the interference between a SH reference signal and the SH signal from the sample of interest. Using this setup, time-domain interferograms were acquired at various two-photon energies. From the analysis of these interferograms, the frequency dependence of the total SH relative phase was obtained. Combined SH intensity and phase spectroscopy was performed for four SiO2- and Al2O3-based samples that contain different number densities of built-in charges. This sample choice allowed us to highlight the benefit of simultaneously modeling SH intensity and phase spectra in terms of isolating the EFISH contribution from interfering contributions. The analysis revealed that the polarity of the space-charge field can be unambiguously determined and that the sensitivity to the electric field strength is also significantly enhanced. This makes second-harmonic generation spectroscopy more powerful for the characterization of the SCR in semiconductors as induced by charged dielectric films or otherwise.

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