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Influence of the SiO\(_2\) interlayer thickness on the density and polarity of charges in Si/SiO\(_2\)/Al\(_2\)O\(_3\) stacks as studied by optical second-harmonic generation

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By accurately tuning the SiO\(_2\) interlayer thickness the density and polarity of charges in Si/SiO\(_2\)/Al\(_2\)O\(_3\) stacks can be controlled. We report on the number density, polarity, and physical location of charges present in the stacks as studied by optical second-harmonic generation (SHG). Depending on the SiO\(_2\) interlayer thickness (1–150 nm) the effective charge density in the Si/SiO\(_2\)/Al\(_2\)O\(_3\) stacks ranges from \(10^{13}\) to \(10^{11}\) cm\(^{-2}\) for both n- and p-type silicon. The polarity of the charges switches from negative to positive around a SiO\(_2\) interlayer thickness of 5–10 nm at which point the effective charge density in the stacks is negligible. This switch in polarity is apparent from spectroscopic, time-dependent, and azimuthal SHG measurements. The observed trends in charge density and polarity can be explained by tunneling of electrons into defect states at the SiO\(_2\)/Al\(_2\)O\(_3\) interface as well as the presence of fixed and bulk charges at the Si/SiO\(_2\) interface and in the SiO\(_2\), respectively. This charge mechanism appears to hold generally for Si/SiO\(_2\)/Al\(_2\)O\(_3\) stacks as similar results were observed for SiO\(_2\) films prepared by various techniques. © 2014 AIP Publishing LLC. [http://dx.doi.org/10.1063/1.4857075]

I. INTRODUCTION

Control over the density and polarity of built-in charges in (high-\(\kappa\)) dielectric thin films is essential for the performance of modern silicon-based microelectronic and optoelectronic devices. In metal-oxide-semiconductor field-effect transistors (MOSFETs) such control can be used to minimize the voltage required to obtain a flat band condition or to completely eliminate the presence of charges for stable and reliable device operation. 1–3 In case of silicon-based photovoltaics, control over the polarity and density of built-in charges affords the engineering of the silicon (Si) interface properties for different silicon doping types and densities, and the prevention of strong inversion conditions below the Si surface that can compromise solar cell performance. 4–6 To obtain such a high level of control, a fundamental insight into the influence of material properties and processing conditions/parameters on the built-in charge density and polarity is required. For example, such detailed insight for the Si/SiO\(_2\) system has led to the reliable and reproducible processing of silicon-based semiconductor devices in the past decades. 7,8 However, the current trend to combine new materials with novel semiconductor device concepts introduces new sources and physical locations for built-in charges. 1,2 One typical location for additional charge formation is at the interfaces between the new materials. 2,3 This is specifically the case for the interface between (high-\(\kappa\)) dielectric thin films and unintentionally formed interfacial oxide layers. 2,3 The properties of this interfacial oxide are usually not very well controllable and can be of poor quality in terms of surface passivation. 5 Because the growth of an interfacial oxide layer is generally difficult to suppress a high-quality oxide interlayer is often intentionally grown before preparing high-\(\kappa\) dielectric films as an intermediate solution. 2 Consequently, the influence of the properties of such intentionally grown interfacial oxide layers on the charge trapping behavior at the interlayer/high-\(\kappa\) interface is of high technological relevance.

Recently, we have shown that the density and polarity of built-in charges in Si/SiO\(_2\)/Al\(_2\)O\(_3\) stacks can be controlled by accurately tuning the SiO\(_2\) interlayer thickness. 9 Such straightforward control can be highly advantageous for applications of such stacks in both microelectronic and optoelectronic semiconductor devices. To our knowledge it was the first time that the role of the SiO\(_2\) interlayer on the built-in charge density was clearly established even though it has been often speculated that the presence of negative charges in Al\(_2\)O\(_3\) thin films on silicon is associated with the presence of interfacial SiO\(_2\) between the silicon and the Al\(_2\)O\(_3\). 10–13 In our previous work we did, however, not conclusively establish the origin and physical location of the charges in the stacks. Furthermore, the SiO\(_2\) interlayers (1–13 nm) were prepared solely by atomic layer deposition (ALD) and only n-type silicon wafers were used. In this paper, we show that tunneling of electrons through the SiO\(_2\) interlayer into defect states at the SiO\(_2\)/Al\(_2\)O\(_3\) interface is the prevailing charge mechanism for an interlayer thickness below 5–10 nm. Above this thickness the presence of fixed charges at the Si/SiO\(_2\) interface and bulk charges in the SiO\(_2\) film dominate the effective charge density. Extending our previous work, the SiO\(_2\)/Al\(_2\)O\(_3\) stacks were deposited on n- and p-type silicon wafers and the SiO\(_2\) interlayers (1–150 nm) were synthesized using both ALD and plasma-enhanced chemical vapor deposition (PECVD). It was found that the influence of the
SiO₂ thickness on the charge density in the stacks is independent of the deposition method of the SiO₂ interlayer. However, the behavior of the built-in charges in the thickness range for which tunneling occurs (0–10 nm) was found to depend on the doping type of the silicon wafer. These observations suggest that the overall charge mechanism for Si/SiO₂/Al₂O₃ stacks holds generally but with the tunneling process likely being sensitive to the doping type.

II. PREPARATION OF SiO₂/Al₂O₃ STACKS WITH VARIOUS SiO₂ INTERLAYER THICKNESSES

The SiO₂/Al₂O₃ stacks were deposited at both sides of float zone Si(100) wafers (n- or p-type, ~3 Ω·cm, 280 μm) preceded by a HF dip to obtain a H-terminated surface. Ultrathin SiO₂ films (~0.9–13 nm) were prepared by ALD using ultra-short doses (~100 ms) of H₂Si[SiC₂H₅]₂ and a few seconds of O₂ plasma exposure that were separated by Ar purges at a substrate temperature of ~200°C. Relatively thick SiO₂ films (~4–150 nm) were synthesized by PECVD in a radio frequency parallel plate reactor from the gas mixture of SiH₄, N₂O, and N₂ at a substrate temperature of ~300°C. In all cases the SiO₂ films were capped by an Al₂O₃ layer with a nominal thickness of ~30 nm as 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.

After deposition the complete stacks received a post-deposition anneal (PDA) for 10 min. at 400°C in N₂. It is notable that this PDA leads to a substantial increase in the overall charge mechanism for Si/SiO₂/Al₂O₃, which is likely being sensitive to the doping type of the silicon wafer. These observations suggest that the overall charge mechanism for Si/SiO₂/Al₂O₃ stacks holds generally but with the tunneling process likely being sensitive to the doping type.

To understand the mechanism of charge formation and its dependence on the SiO₂ interlayer thickness, it is essential to accurately determine the thickness of the deposited SiO₂ films within the Si/SiO₂/Al₂O₃ stack after annealing. Spectroscopic ellipsometry (SE) measurements have therefore been performed in reflection mode for a wavelength range of 190–1000 nm using a J.A. Woollam Co., Inc. M-2000U rotating compensator ellipsometer mounted on a variable angle stage. To extract the dielectric function and thickness of each film from the ellipsometry data an optical model was built-up in which each layer of the sample is represented (Fig. 1). The SiO₂ and Al₂O₃ films were modeled as a layer of finite thickness and their optical dispersion $n(\lambda)$ was parameterized according to the Sellmeier dispersion equation given by

$$n(\lambda) = \left(\frac{\varepsilon_{\text{inf}} + A_{\text{Sel}} \lambda^2}{\lambda^2 - \Gamma_{\text{Sel}}^2} - A_{\text{IRpole}} \lambda^2\right)^{0.5},$$

where $\varepsilon_{\text{inf}}$ is the relative permittivity at infinity, $A_{\text{Sel}}$ is the Sellmeier amplitude, $\Gamma_{\text{Sel}}$ is the Sellmeier broadening, and $A_{\text{IRpole}}$ is the amplitude of an infrared pole which accounts for absorption at large wavelengths $\lambda$. The silicon substrate was assumed semi-infinite, and tabulated values were used for its optical dispersion. Propagation of the radiation from the ellipsometer light source through the multilayer thin-film system was described by the Fresnel reflection and transmission coefficients taking optical interference into account. The model was fitted to the experimental data using a Levenberg-Marquardt algorithm to minimize the reduced-chi-squared value of the model fit by optimizing the fitting parameters, i.e., the film thicknesses and Sellmeier coefficients with $\varepsilon_{\text{inf}}$ and $A_{\text{IRpole}}$ fixed at 1.0 and 0.01, respectively.

The sensitivity to film thickness of this method comes only from the difference in phase between the directly reflected beam and the multiple reflected beam propagating through the film system. For ultrathin films the phase difference becomes negligible, and the sensitivity to film thickness drastically reduces. As a result the film thickness and refractive index of transparent films become strongly correlated for a typical film thickness <10 nm. In addition, the optical contrast between SiO₂ and Al₂O₃ is relatively poor because of their small refractive index difference (see Table I). This means that little refraction occurs at the SiO₂/Al₂O₃ interface.

<table>
<thead>
<tr>
<th>Film type</th>
<th>$t$ (nm)</th>
<th>$n (-)$</th>
<th>$A_{\text{Sel}}$ (–)</th>
<th>$\Gamma_{\text{Sel}}$ (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma ALD Al₂O₃</td>
<td>31.5</td>
<td>1.63</td>
<td>1.611</td>
<td>0.109</td>
</tr>
<tr>
<td>Plasma ALD SiO₂</td>
<td>Table III</td>
<td>1.45</td>
<td>1.174</td>
<td>0.094</td>
</tr>
<tr>
<td>PECVD SiO₂</td>
<td>Table III</td>
<td>1.48</td>
<td>1.077</td>
<td>0.091</td>
</tr>
</tbody>
</table>

TABLE I. The thickness $t$, refractive index $n$ (at 633 nm), and Sellmeier coefficients ($A_{\text{Sel}}$, $\Gamma_{\text{Sel}}$) obtained from the multi-sample analysis of the SE data for the films specified.

FIG. 1. Images that illustrate the strategy followed to model the spectroscopic ellipsometry data. (a) High-resolution TEM image of a film stack consisting of alternating SiO₂ and Al₂O₃ layers as synthesized by plasma ALD. The layer thicknesses in nanometer are indicated. (b) Optical model used to analyze the in situ ellipsometry data of each layer comprising the stack where the film thicknesses were fixed according to the TEM analysis and the optical dispersion $n(\lambda)$ of each layer was fitted. (c) Optical model used to analyze the ex situ ellipsometry data of single thick PECVD SiO₂ layers where the film thickness and optical dispersion $n(\lambda)$ were both fitted. (d) Optical model used to analyze the ex situ ellipsometry data of all Si/SiO₂/Al₂O₃ stacks simultaneously to accurately obtain the SiO₂ interlayer thicknesses using a fixed optical dispersion $n(\lambda)$ for the SiO₂ and Al₂O₃ films.
interface, and interference is therefore less pronounced for each layer. As film thickness is mainly deduced from interference, it is difficult to distinguish between the individual thicknesses of SiO2 and Al2O3. The latter could in principle have been overcome by modeling of the SiO2 interlayer prior to Al2O3 deposition and by using this information when modeling the stack. However, this is not entirely possible because of some additional SiO2 growth (~1 nm) during the initial stage of the SiO2 deposition and during the deposition process of the Al2O3 film. Especially for the thinnest SiO2 films, which are most critical when describing quantum tunneling (see Sec. V), this would result in a significant error in the acquired SiO2 thickness. We therefore used an advanced modeling strategy to obtain unique values for the SiO2 interlayer thickness.

First, the ellipsometry data have been obtained at three angles of incidence (65°, 75°, and 85°) to effectively vary the optical path length for the light propagating through the stack structure. This increased the accuracy with which the film thicknesses can be determined via interference enhancement. Second, the optical dispersion of the films was determined from separate SE measurements. For the plasma ALD SiO2 and Al2O3 this was done completely independent of film thickness by depositing a dedicated stack structure of alternating SiO2 and Al2O3 films of various thicknesses while performing in situ SE measurements after each successive deposition. A cross-sectional image of the structure was obtained with high-resolution transmission electron microscopy (TEM) to accurately determine the thickness (~0.3 nm) of each layer as shown in Fig. 1(a). These thicknesses were used as a fixed value while the optical dispersion of each layer was obtained by fitting the Sellmeier coefficients using the in situ SE data with the model of Fig. 1(b). The Sellmeier coefficients for the thickest films were assumed to be most accurate and used for the modeling of the actual stack data. Note that the combination of the TEM image with the SE data is essential for determining the optical constants of such ultrathin layers. In case of the PECVD SiO2 films, separate SE measurements were performed on single thick layers (~150 nm) such that both the optical dispersion (Sellmeier coefficients), and the film thickness could be obtained with good accuracy as illustrated in Fig. 1(c). The refractive index and Sellmeier coefficients determined for each type of film are listed in Table I.

Finally, a multi-sample fitting procedure was performed by simultaneously modeling the SE experimental data at each angle of incidence for all the stacks. In this procedure a unique fitting parameter was used for each SiO2 interlayer thickness while the Al2O3 thickness had a single parameter which was fixed to the value (31.5 ± 0.3 nm) determined via TEM [Fig. 1(d)]. The Sellmeier coefficients, describing the optical dispersion, were fixed to the a priori obtained values for plasma ALD and PECVD SiO2 and plasma ALD Al2O3. A slight increase in SiO2 thickness due to the aforementioned additional SiO2 growth during processing was taken into account using an interfacial oxide layer [Fig. 1(d)] with a single fit parameter for thickness and tabulated values for its optical dispersion. The SiO2 interlayer thickness resulting from this analysis for each Si/SiO2/Al2O3 stack is listed in Table III.

### III. SECOND-HARMONIC GENERATION TO PROBE BUILT-IN CHARGES

#### A. Second-harmonic generation experiments

To investigate the effective charge density and polarity in the Si/SiO2/Al2O3 stacks we used the nonlinear optical technique of second-harmonic generation (SHG). This technique is surface and interface specific for centrosymmetric media, such as amorphous films and crystalline silicon, and its signal is resonantly enhanced at optical transitions. SHG is therefore very well suited for the contactless and non-intrusive probing of the interface properties between silicon and thin films. Specifically, SHG is directly sensitive to the electric field in the space-charge region (SCR) of silicon as induced by built-in charges in the dielectric films. By carrying out spectroscopic SHG measurements both the strength and polarity of the electric field in the SCR can be determined under steady-state conditions which then reflects the density and polarity of the built-in charges. The intensity of the electric-field-induced (EFISH) contribution to the second-harmonic (SH) response scales quadratically with the effective charge density present in thin-film systems. This allows for the quantification of the effective charge density in the Si/SiO2/Al2O3 stacks. In this work the effective charge density $Q_{eff}$ is defined as the sum of the total negative charge density $Q_{neg}$ and the total positive charge density $Q_{pos}$ in the system that causes the space-charge field in the silicon. The values of charge density are given in units of elementary charge per unit of surface area (cm~2) and the sign indicates whether negative (−) or positive (+) charges are effectively present. In addition to the spectroscopic SHG measurements, time-dependent and azimuthal (i.e., rotating the sample around the surface normal) measurements at a single wavelength have been carried out to corroborate the interpretation of the spectroscopic data as these signals contain also a signature of the space-charge field.

SHG 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 ~1–9 μJ·cm~2 per pulse ($f_{rep} = 80$ MHz), 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 optical response of the system. The optical response comprises the optical transmission of the colored glass filters and the polarizer in the beam path after the sample 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 unless stated otherwise.

#### B. Charge density and polarity from second-harmonic intensity spectra

The effect of the SiO2 interlayer thickness on the SH spectral response of the stacks is shown in Fig. 2. It is
emphasized at this point that the resonant feature observed in all spectra originates from interband transitions in the vicinity of the $E_1$ critical point of silicon. No resonant SHG occurs at the $\text{SiO}_2/\text{Al}_2\text{O}_3$ interface or at the surface of $\text{Al}_2\text{O}_3$ due to the fact that there are no optical transitions of these amorphous materials within the fundamental and second-harmonic photon energy range. First we will qualitatively discuss the obtained SH spectra as this will facilitate the optical modeling of the data in Sec. IV from which the charge density can be quantified.

In case of the stacks deposited on $n$-type silicon wafers (Fig. 2, left panel) a rapid decrease in the SH intensity is observed initially for increasing $\text{SiO}_2$ interlayer thickness. Around 4–5.5 nm a minimum is obtained after which the SH intensity slightly increases reaching a constant level for interlayers between 27 and 51.9 nm. For the stacks deposited on $p$-type silicon wafers (Fig. 2, right panel) an initial decrease in the SH intensity is also observed for increasing $\text{SiO}_2$ interlayer thickness, but it is less pronounced compared to the $n$-type spectra. A minimum is obtained at $\sim$11 nm after which the SH intensity shows a similar increase towards a constant level for interlayers between 27 and 46 nm. At a $\text{SiO}_2$ interlayer thickness of $\sim$150 nm a further increase in SH intensity is clearly observed for both $n$- and $p$-type silicon wafers. To understand the effect of the interlayer thickness on the SH intensity other features of the spectra will be first discussed before returning to this point.

Clearly, the two minimum intensity spectra of the $n$-type series (Fig. 2, left panel), i.e., the spectra with interlayer thicknesses of 4 and 5.5 nm, are characterized by a red-shift of their peak position to a two-photon energy of 3.3 eV with respect to the 3.4 eV of all other spectra. As was addressed in our recent work the red-shift can be associated with a negligible effective charge density to be present in the films comprising the stack structure. In this case the SH signal originates only from interface contributions that are energy-shifted due to a loss of the silicon bulk properties near the vicinity of the film interface. It is notable that for both the ALD and PECVD interlayers a minimum SH intensity is obtained around 5 nm. The low intensity spectrum obtained for the 10.8 nm $\text{SiO}_2$ interlayer stack of the $p$-type series shows slightly different features compared to the ones of the $n$-type series. The intensity is slightly higher, the peak position is at a two-photon energy of 3.35 eV, and a small bump is visible on the right side of the peak. These observations indicate that the contribution causing the 3.4 eV peak still slightly contributes to the SH response for this sample.

A peak located at a two-photon energy of $\sim$3.4 eV, which is very similar to the resonance energy of the $E_1$ interband transition from bulk silicon, is a clear signature for EFISH. With no external electric field applied, the presence of an EFISH contribution implies that the films comprising the stack contain a certain amount of built-in charges which give rise to a space-charge field in silicon. The effective polarity of these charges, or actually the polarity of the induced silicon SCR, is reflected by the spectral shape. It is clear from Fig. 2 that the SHG spectra for interlayers with a thickness above 5–11 nm exhibit a broadening of the peak at its left side or even show a double peak. This is a spectral signature for constructive interference between the interface contributions and the EFISH contribution which is indicative for a negatively charged SCR. It can therefore be concluded that a positive charge density is effectively present in these stacks. In case of the SHG spectra for the thinnest interlayers (<5–11 nm) a distinct peak broadening is absent. On the basis of the fact that EFISH contributes to the SH response this is indicative for a positively charged SCR. Accordingly, a negative charge density is effectively present in stacks with an interlayer thickness below 5–11 nm. Considering the features of the 10.8 nm $\text{SiO}_2$ interlayer stack of the $p$-type series, a small amount of built-in charges is likely present. It is not possible to specify whether these charges are negative or positive without applying a model to the data.

It must be stressed that the effective charge density and prevailing polarity induces the electric field in the SCR, and that the EFISH intensity scales quadratically with the strength of this electric field. This also implies that so-called dipole charges, which could be present in the stack structure, do not contribute to EFISH because they do not affect the SCR. With this in mind the variation in SH intensity with $\text{SiO}_2$ interlayer thickness in Fig. 2 can be qualitatively explained in terms of the effective charge density present in the stacks: A large negative charge density is present for the thinnest interlayers ($\sim$1 nm). For increasing interlayer thickness this effective charge density reduces, becomes (virtually) zero around 5–11 nm thick interlayers, and subsequently increases again but with the opposite polarity. The fact that a minimum SH intensity is observed means that both negative and positive charges are present in the stacks and that their relative densities change with $\text{SiO}_2$ interlayer thickness.

![Optical SH spectra of SiO2/Al2O3 stacks on Si(100)](image)
C. Charge polarity from the time-dependent and azimuthal response

To corroborate the interpretation of the spectroscopic data concerning the charge polarity, complementary time-dependent and azimuthal SHG measurements have been performed for two selected stacks on n-type silicon wafers. The SiO₂ interlayer thickness of these samples was 0.9 and 18.4 nm, which is either below or above the thickness yielding a minimum SH intensity. Figure 3 shows the complementary measurements for the two samples as carried out at a fundamental photon energy of 1.71 eV.

The time-dependent SH signal reflects the process of multiple-photon-induced charge injection (see inset in Fig. 3) at high laser fluence (~5.8–8.6 µJ·cm⁻² per pulse). Both for SiO₂ and high-κ dielectrics on Si this process has been reported to occur via injection of electrons from the Si valence band into trap sites in either the film bulk, at the buried interface, or at the ambient surface. In case of Al₂O₃ the electrons are injected into defect states near the SiO₂/Al₂O₃ interface in the Al₂O₃ as indicated in the inset of Fig. 3. These states are related to point defects in the Al₂O₃ that have been tentatively identified by simulation studies. The most likely candidates for electron trapping are the oxygen interstitial Oᵢ and the aluminum vacancy Alᵥ. Both Oᵢ and Alᵥ produce defect states in the Al₂O₃ band gap below mid gap and can be negatively charged.

In our previous study, the charging process for Al₂O₃ films deposited directly on silicon has been shown to occur via two- and three-photon-induced electron injection through the interfacial oxide layer.

In case of the stack with a 0.9 nm thick interlayer a monotonous increase of the SH intensity as a function of laser radiation exposure time can be observed in Fig. 3(a) with a rapid initial increase (t < 3 min.) and subsequent slow increase towards a maximum level. The time-dependence for the 18.4 nm SiO₂ interlayer sample is quite different as shown in Fig. 3(b). After a rapid initial decrease (t < 3 min.) a minimum level in SH intensity is slowly reached (t ~ 24 min.) and eventually the intensity starts to increase again for continuing exposure of the sample to the laser radiation. The decrease in the rate at which the SH intensity changes for increasing exposure time is in both cases mainly caused by the saturation of the most favorable trap sites in Al₂O₃. Detrapping of the injected charges plays only a minor role. This was verified by measuring the change in SH intensity that occurs while blocking the laser beam for 30 min. after the samples were exposed to laser radiation for 60 min. (not shown). The low detrapping rate for the stacks agrees with our previous measurements for Al₂O₃ films deposited directly on silicon.

The fact that primarily electrons are injected, because hole injection requires at least one more photon, allows one to determine the polarity of the initial charge density in the sample from the charging behavior. A monotonous increase implies that the injected charges have the same polarity as the built-in charge density whereas a decrease means that they have the opposite polarity. It can thus be concluded that the 0.9 nm SiO₂ interlayer sample contains effectively a negative built-in charge density and the stack with an 18.4 nm thick interlayer a positive built-in charge density. The minimum observed in Fig. 3(b) can be explained as the point where the positive charge density present in the stack is nullified by the amount of injected electrons. Further charge injection then causes a negative charge density to be effectively present in the stack.

The EFISH intensity scales quadratically with the strength of the electric field in the SCR which itself scales linearly with charge density. When assuming that the changes of the SH intensity in Figs. 3(a) and 3(b) are solely caused by changes in the EFISH response, and, that the amount of injected charge (ΔQ) is related to the SH intensity as ΔQ = (Iₘₐₓ − Iₘᵢₙ)⁻¹, it can be inferred from the data that ΔQ is roughly equal for the two stack samples, i.e., ΔQ₈.₄ₙₘᵣ = ΔQ₉₉ₙₘᵣ. This implies that the total number of trap sites, and thus defect states, available at the SiO₂/Al₂O₃ interface is roughly the same for both samples. Consequently, the number of oxygen interstitials Oᵢ and aluminum vacancies Alᵥ in the Al₂O₃ is likely to be independent of the SiO₂ interlayer thickness.

Figures 3(c) and 3(d) show the azimuthal dependence of the SH intensity for the two stacks obtained by rotating the sample around the surface normal. The variation in the SH signal is related to anisotropic bulk contribution from the silicon due to nonlocal nonlinear interactions. The four-fold rotational symmetry reflects the 4 mm symmetry of the
Si(100) surface. The most noticeable difference between the 0.9 and 18.4 nm SiO₂ interlayer sample is that the azimuthal phase is shifted by 45° as indicated by the Δ-symbol in Fig. 3(c). When EFISH contributes to the SH response this shift of the azimuthal SH anisotropy pattern is directly related to a flip in the direction of the space-charge field, as has been shown in the literature.³⁶,³⁷ The effect is caused by the phase differences between the interface and bulk contributions. From the azimuthal response it can thus be concluded that the 0.9 nm SiO₂ interlayer sample contains an effective built-in charge density with an opposite polarity to the one of 18.4 nm. The level of the isotropic background around which the oscillation occurs is an approximate measure for the relative strength of the electric field in the SCR, when assuming that EFISH dominates the SH response. This means that the stack with a 0.9 nm SiO₂ interlayer contains a significantly higher built-in charge density than the 18.4 nm one.

In summary, both the time-dependent and azimuthal behavior of the SH response in Fig. 3 confirm the qualitative interpretation of the SH spectroscopic data shown in Fig. 2.

IV. MODELING OF THE SECOND-HARMONIC INTENSITY SPECTRA

A. Intensity and phase of the EFISH contribution

In general, it can be concluded from Fig. 2 that the influence of the SiO₂ interlayer thickness on the charge density in the stacks is independent of the deposition method and shows similar behavior for both n- and p-type silicon. This means that some universal mechanism should underlie the observed trends. To be able to determine this mechanism it is necessary to quantify the effective charge density in each stack. This can be done by isolating the EFISH contribution from the interfering SH contributions that are related to the silicon/film interface. For this purpose a critical-point (CP) model was used to deconvolute the SH spectra. The model reproduces the SH intensity by a coherent superposition of CP-like resonances with excitonic line shapes evaluated at the Si/SiO₂ interface as has been described extensively elsewhere.²²,³⁸ The excitonic line shape is characterized by an amplitude, a resonant energy, a linewidth (or broadening), and excitonic phase. Propagation of both the fundamental and SH radiation through the thin film system is also taken into account and includes linear optical phenomena, such as absorption, refraction, and interference due to multiple reflections.²⁹ To do this correctly the thickness and optical dispersion of each layer comprising the stack should be accurately known in advance. The comprehensive analysis of the ellipsometry data as discussed in Sec. II is therefore vital for the modeling of the SHG spectra.

In line with our earlier work,⁹,²¹,³⁴ three distinct excitonic resonances were used that are each assigned to interband transitions of Si for different configurations of Si-Si bonds: a Si-Si interface contribution (~3.3 eV), an Si-SiO₂ suboxide contribution (~3.6 eV), and, particularly important here, an EFISH contribution originating from the bulk SCR in Si at a typical resonance energy of ~3.4 eV.²³ The polarity of the electric field in the SCR is reflected by the excitonic phase of the EFISH contribution relative to the phase of the Si-Si interface contribution, i.e., ~0 rad for a negative and ~π rad for a positive SCR, respectively.²⁰ To improve the goodness of fit, the spectra in Fig. 2 were simultaneously analyzed using single fit parameters for the resonant energy and broadening of the Si-Si interface contribution, broadening of the EFISH contribution, and phase of the Si-SiO₂ sub oxide contribution. The resonance energy of the EFISH contribution was fixed to 3.39 eV which corresponds to the value of the E₁ transition of bulk Si.²⁴ Because the Si-SiO₂ suboxide contribution lies mostly outside our available photon energy range, its resonant energy and broadening were taken from the literature and kept fixed at 3.62 and 0.34 eV, respectively.²⁰ The initial parameter values for the model were estimated from the qualitative information obtained from the spectroscopic, time-dependent, and azimuthal data (Figs. 2 and 3). Especially, the strength and relative phase of the EFISH contribution could be well estimated. The values for the single fit parameters obtained from the multi-sample analysis of the SH spectra are listed in Table II. They are all consistent with values found for these parameters in the literature.²⁰,²³

The solid lines through the experimental points in Fig. 2 represent the model fits to the data using the three individual contributions. As can be seen the model reproduces the experimental data for all spectra well. No EFISH contribution was required in case of the two minimum intensity spectra from the n-type series, which confirms that the 4 and 5.5 nm thick interlayer stacks contain a negligible density of built-in charges, i.e., at least below the sensitivity limit of the experimental configuration and analysis method used in this work (Q<sub>eff</sub> < 10⁻¹⁴ cm⁻²). In case of the 10.8 nm SiO₂ interlayer spectrum (p-type) the EFISH contribution was still required, meaning that a limited number of built-in charges was present in this stack as expected. From the fitting parameters defining the excitonic line shape the EFISH intensity at a given two-photon energy can be calculated. The EFISH intensities (I<sub>EFISH</sub>) at an energy of 3.4 eV for each Si/SiO₂/Al₂O₃ stack, normalized at the value (see below) of the stack with 0.9 nm ALD SiO₂, are listed in Table III together with the relative phase of the EFISH contribution.

The top panel of Fig. 4 shows the values obtained for the EFISH relative phase as a function of SiO₂ interlayer thickness. It is observed that when the normalized EFISH intensity (see Sec. IV B) goes through its minimum value (Table III) that the EFISH phase changes by ~π rad. This confirms that the prevailing polarity of the built-in charges

### Table II. Values for the single fit parameters in the multi-sample analysis of the SH intensity spectra shown in Fig. 2.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>E&lt;sub&gt;Si,Si&lt;/sub&gt; (eV)</td>
<td>3.30 ± 0.02</td>
</tr>
<tr>
<td>Γ&lt;sub&gt;Si,Si&lt;/sub&gt; (eV)</td>
<td>0.08 ± 0.03</td>
</tr>
<tr>
<td>Γ&lt;sub&gt;EFISH&lt;/sub&gt; (eV)</td>
<td>0.11 ± 0.03</td>
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<tr>
<td>φ&lt;sub&gt;Si-SiO₂&lt;/sub&gt; (π rad)</td>
<td>0.36 ± 0.10</td>
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</table>
TABLE III. Summary of the obtained SiO2 interlayer thickness \( t_{\text{SiO2}} \), normalized EFISH intensity \( I_{\text{EFISH}} \), EFISH relative phase \( \varphi_{\text{EFISH}} \), and effective charge density \( Q_{\text{eff}} \) of the SiO2/Al2O3 stacks for both n- and p-type silicon and for SiO2 interlayers prepared either by ALD or PECVD.

<table>
<thead>
<tr>
<th>( t_{\text{SiO2}} ) (nm)</th>
<th>( I_{\text{EFISH}} ) (( \pi ) rad)</th>
<th>( \varphi_{\text{EFISH}} ) (( \pi ) rad)</th>
<th>( Q_{\text{eff}} ) (10(^{12}) cm(^{-2}))</th>
<th>( t_{\text{SiO2}} ) (nm)</th>
<th>( I_{\text{EFISH}} ) (( \pi ) rad)</th>
<th>( \varphi_{\text{EFISH}} ) (( \pi ) rad)</th>
<th>( Q_{\text{eff}} ) (10(^{12}) cm(^{-2}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALD SiO2</td>
<td>PECVD SiO2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>n-type</td>
<td>n-type</td>
<td>p-type</td>
<td>p-type</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.9 ± 0.5</td>
<td>1.2 ± 0.5</td>
<td>1.5 ± 0.5</td>
<td>2.6 ± 0.5</td>
<td>5.5 ± 0.5</td>
<td>13.1 ± 0.5</td>
<td>1.0 ± 0.5</td>
<td>1.5 ± 0.5</td>
</tr>
<tr>
<td>( I_{\text{EFISH}} ) (( \pi ) rad)</td>
<td>+0.88</td>
<td>+0.80</td>
<td>+0.79</td>
<td>+0.69</td>
<td>...</td>
<td>+0.87</td>
<td>+0.80</td>
</tr>
<tr>
<td>( \varphi_{\text{EFISH}} ) (( \pi ) rad)</td>
<td>( -Q_{\text{eff}} )</td>
<td>( -Q_{\text{eff}} )</td>
<td>( -Q_{\text{eff}} )</td>
<td>( -Q_{\text{eff}} )</td>
<td>( -Q_{\text{eff}} )</td>
<td>( -Q_{\text{eff}} )</td>
<td>( -Q_{\text{eff}} )</td>
</tr>
<tr>
<td>( Q_{\text{eff}} ) (10(^{12}) cm(^{-2}))</td>
<td>( (5.8 ± 0.3) \times 10^{11} )</td>
<td>( (3.5 ± 0.3) \times 10^{11} )</td>
<td>( (2.4 ± 0.3) \times 10^{11} )</td>
<td>( (0.8 ± 0.3) \times 10^{11} )</td>
<td>( (Q_{\text{eff}} &lt; 0) \times 10^{11} )</td>
<td>( (5.8 ± 0.3) \times 10^{11} )</td>
<td>( (3.7 ± 0.3) \times 10^{11} )</td>
</tr>
</tbody>
</table>

**FIG. 4.** Effective built-in charge density \( Q_{\text{eff}} \) (bottom panel) and EFISH relative phase \( \varphi_{\text{EFISH}} \) (top panel) as a function of SiO2 interlayer thickness for SiO2/Al2O3 stacks on both n-type (open markers) and p-type (closed markers) silicon wafers. The SiO2 films have been deposited either by ALD or PECVD. The lines in the bottom panel are fit to the data according to the model described by Eqs. (2)-(5) whereas in the top panel the lines serve as a guide to the eye. In the bottom panel two regimes are indicated for which the origin of \( Q_{\text{eff}} \) is predominantly related either to tunneling of electrons through the SiO2 interlayer or to charges that are intrinsically present in the SiO2 interlayer.

Changes from negative to positive. The fact that the absolute EFISH phase decreases with decreasing charge density is expected as can be derived from theoretical calculations of the strength and polarity of the space-charge field as a function of charge density. The analysis in terms of the EFISH intensity and phase is, therefore, in agreement with the quantitative discussion of the spectroscopic, time-dependent, and azimuthal data of Figs. 2 and 3.

### B. Determination of the absolute charge density in the stacks

Because the EFISH intensity is only a relative measure it needs to be related to the absolute charge density by performing a calibration measurement for at least one sample. The absolute charge density for the stack comprising an interlayer of 0.9 nm ALD SiO2 is \( (5.8 ± 0.5) \times 10^{12} \) cm\(^{-2}\) as determined by capacitance-voltage measurements. By normalizing the EFISH intensity of the other stack samples to that of the calibration sample their charge density can be quantified according to a previously established procedure. Following this procedure the effective charge density \( Q_{\text{eff}} \) for each Si/SiO2/Al2O3 stack has been obtained as listed in Table III. The polarity is given by the relative phase of the EFISH contribution whereby it should be recognized that the polarity of the charges is opposite to that of the SCR.

The bottom panel of Fig. 4 shows the absolute value of the effective charge density \( Q_{\text{eff}} \) in the stacks as function of the SiO2 interlayer thickness on a double logarithmic scale. The legend specifies whether the data points belong to stacks with an ALD or PECVD synthesized interlayer. For both n- and p-type silicon wafers the effective charge density \( (5.8 ± 0.3) \times 10^{11} \) cm\(^{-2}\) at \( t_{\text{SiO2}} \approx 1 \) nm decreases rapidly for increasing SiO2 interlayer thickness and reaches a minimum. As expected from the qualitative discussion of the SH intensity spectra (Sec. III B) this minimum is obtained at a thinner interlayer for the n-type series (\( ~5 \) nm) compared to the p-type series (\( ~11 \) nm). For completeness the effective charge density for the stacks with 4.0 and 5.5 nm SiO2 from the n-type series has been set to an arbitrary low level of \( 1 \times 10^{10} \) cm\(^{-2}\) in the log-log graph. However, as mentioned before, for these SiO2 thicknesses no EFISH contribution could be distinguished meaning that it can only be concluded that \( Q_{\text{eff}} < 10^{13} \) cm\(^{-2}\). Subsequently, for interlayers between 25 and 50 nm, the effective charge density increases towards a more or less constant level \( (+4 ± 1 \times 10^{11}) \) cm\(^{-2}\). Finally, a small increase in charge density \( (+7 ± 1 \times 10^{11}) \) cm\(^{-2}\) is...
observed for the 150 nm thick interlayer stacks. Values reported in the literature by Saito et al.\textsuperscript{41} for the effective charge density in Si/SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} stacks with dry thermal oxide interlayers in the thickness range 0.7–2 nm are between \(-2 \times 10^{13}\) and \(-5 \times 10^{12}\) cm\textsuperscript{-2}, respectively. Aboof et al.\textsuperscript{42} obtained values of \(-3 \times 10^{12}\) cm\textsuperscript{-2} for plasma oxidized interlayers in Si/SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} stacks with a SiO\textsubscript{2} thickness in the range of 23–100 nm. Compared to our data these values from the literature agree very well for both SiO\textsubscript{2} thickness ranges, especially, considering the fact that the interlayers have been prepared using different deposition methods.

V. DEPENDENCE OF THE EFFECTIVE CHARGE DENSITY ON THE INTERLAYER THICKNESS

A. Simple model to distinguish between various types of charges

It appears that the difference in the trend of effective charge density versus SiO\textsubscript{2} interlayer thickness (Fig. 4) for n-type and p-type silicon is mainly due to a difference in the negative charge density for very thin SiO\textsubscript{2} interlayers. This is most likely related to the origin of the charges itself, because effects caused by differences in the (ALD) processing conditions would be independent of doping type. To unravel the mechanism that explains the observed behavior it is necessary to develop a model that discriminates between the various types of charges that can be present in the stack. Without losing generality it can be stated that the effective charge density \(Q_{\text{eff}}\) in the stacks as function of SiO\textsubscript{2} interlayer thickness—from now on defined as \(t\)—can be written as

\[
Q_{\text{eff}}(t) = Q_{\text{AlO}_3}(t) + Q_{\text{SiO}_2}(t) + Q_n, (2)
\]

where \(Q_{\text{AlO}_3}\) and \(Q_{\text{SiO}_2}\) are the total charge density in the Al\textsubscript{2}O\textsubscript{3} and SiO\textsubscript{2} depending on \(t\), respectively. \(Q_n\) represents the charge density that is trapped in acceptor- and donor-type states at the Si/SiO\textsubscript{2} interface. This interface-state charge density is \(t\)-independent but depends on the interface state density \(D_{in}\), the occupation probability of the available states, and the doping type of the silicon. For all Si/SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} stacks presented in this work low \(D_{in}\) values (<\(10^{11}\) eV\textsuperscript{-1}cm\textsuperscript{-2}) have been obtained previously,\textsuperscript{9,43} which is attributed to the effective hydrogenation of electronically active interface defect states. A strong contribution of \(Q_n\) to the effective charge density is thus not expected. Moreover, according to the literature, the interface states (\(P_n\) centers) at the Si/SiO\textsubscript{2} interface are negatively charged for n-type silicon and positively charged for p-type silicon.\textsuperscript{44–47} A strong contribution of \(Q_n\) would, therefore, result in exactly the opposite effect on \(Q_{\text{eff}}\) in terms of silicon doping type compared to what is observed in Fig. 4 for \(t < 11\) nm. Consequently, \(Q_n\) will lead to a small offset at most. Such a small offset is effectively assimilated into the other charge contributions.

For dielectric thin films, a negative charge density is basically only encountered in case of Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{1,10,48–50} Significant presence of charge in the Al\textsubscript{2}O\textsubscript{3} bulk or at its surface is not expected and typically also not reported for the experimental conditions used in this work.\textsuperscript{10,49–51} It can therefore be assumed that all negative charge is present in the Al\textsubscript{2}O\textsubscript{3} near the SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} interface.\textsuperscript{10,49–51} The strong exponential-like decrease of negative charge with increasing \(t\) in Fig. 4 suggests that a tunneling process occurs in which the SiO\textsubscript{2} interlayer acts as a barrier for electron injection into the Al\textsubscript{2}O\textsubscript{3}. Such an exponential-like trend would be expected for tunneling processes where the transmission probability falls quickly with increasing barrier thickness. As mentioned earlier (Sec. III C), the electrons can be injected into defect states near the SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} interface in the Al\textsubscript{2}O\textsubscript{3} with the oxygen interstitial \(O_i\) and the aluminum vacancy \(A_v\) being the most likely candidates for electron trapping.\textsuperscript{31} The negative-to-positive charge transition at a relatively large thickness of \(t = \approx 5\) (n-type) and \(\approx 10\) nm (p-type) suggests that not only direct tunneling plays a role because this process becomes negligible for barriers larger than \(\approx 3\) nm.\textsuperscript{52} The tunneling process thus likely involves some kind of trap-assisted tunneling (TAT) mechanism, which, given the fact that a post-deposition anneal is required to activate a large negative charge density, might be thermally induced.\textsuperscript{53,54} Nevertheless, assuming that the tunneling process can be described by a direct-tunneling-like mechanism, the charge density at the SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} interface can be written as

\[
Q_{\text{AlO}_3}(t) = Q_0 T(t), \quad (3)
\]

with \(Q_0\) the charge density due to direct tunneling for \(t = 0\) and \(T\) the transmission probability for direct tunneling through a SiO\textsubscript{2} film with a thickness \(t\). The expression for the transmission probability can be obtained by using the Wenzel-Kramers-Brillouin (WKB) approximation for the tunneling of electrons through a constant potential barrier\textsuperscript{52}

\[
T(t) = \left(1 + 4^{-1}e^{-x^{-1}}\right)^{-2} e^{-x^{-1}}, \quad (4)
\]

with \(x\) the average tunneling decay length.

With negative charges in the Al\textsubscript{2}O\textsubscript{3} and a negligible contribution of interface-state charges, the only source for positive built-in charges in the SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} stacks is the SiO\textsubscript{2} interlayer. This is in agreement with literature reports as for SiO\textsubscript{2} films a positive charge density is generally obtained. A well-known type is that of fixed charges which are present in the SiO\textsubscript{2} within a few nanometers (<3 nm) from the Si/SiO\textsubscript{2} interface.\textsuperscript{7,55} This fixed charge density is independent of SiO\textsubscript{2} thickness and silicon doping type, but strongly depends on processing conditions and silicon orientation.\textsuperscript{7,8} Other charges can be present in the bulk of SiO\textsubscript{2} films.\textsuperscript{8,55} The total charge density in the SiO\textsubscript{2} interlayer can therefore be expressed as

\[
Q_{\text{SiO}_2}(t) = Q_f + \int_0^t \rho_b(z)dz = Q_f + \rho_b \times t, \quad (5)
\]

where \(Q_f\) is the fixed charge density in SiO\textsubscript{2} near the Si/SiO\textsubscript{2} interface, \(\rho_b\) the bulk charge density which is assumed to be independent of the SiO\textsubscript{2} thickness, and \(z\) is the direction perpendicular to the silicon surface with \(z = 0\) at the Si/SiO\textsubscript{2} interface.
B. Interpretation of the modeling results

By using the expressions of Eqs. (3)–(5) the effective charge density \( Q_{\text{eff}} \) in Eq. (2) can be written in an explicit form. The resulting model was fitted to the experimentally obtained \( Q_{\text{eff}} \) data in Fig. 4 using \( Q_{0}, \lambda, Q_{t}, \) and \( \rho_{b} \) as fit parameters. Initial values for \( Q_{0} \) and \( Q_{t} \) were estimated from Fig. 4 (bottom panel) at an appropriate interlayer thickness, \( \lambda \) was initially taken to be 1 nm, and \( \rho_{b} \) was initially set to zero. To pinpoint whether the difference in \( Q_{\text{eff}} \) between \( n \)- and \( p \)-type silicon can be explained by a different tunneling behavior both data-sets were simultaneously fitted using single fit parameters for \( Q_{0}, Q_{t}, \) and \( \rho_{b} \) but two independent fit parameters for the tunneling decay length \( \lambda \). The result of this analysis is shown as the lines through the data points in the bottom panel of Fig. 4. A good agreement between the model and the experimental data can be observed. The acquired fit parameter values are listed in Table IV. Besides a fixed charge density \( Q_{t} \) of \( +3.3 \times 10^{11} \) cm\(^{-2} \) for \( \text{SiO}_2 \), consistently with previously obtained values for our \( \text{SiO}_2 \) layers,\(^{9,43,56} \) also a bulk charge density \( \rho_{b} \) of \( 2.3 \times 10^{19} \) cm\(^{-3} \) in \( \text{SiO}_2 \) is required to match the data points at \( t = 150 \) nm. This low bulk charge density is in line with the expectations for \( \text{SiO}_2 \) films prepared by ALD and PECVD after annealing.\(^{57} \) It indicates that the films have a low density of bulk defect states. Nevertheless, the obtained bulk charge density is equivalent to a surface charge density of \( \sim 3.5 \times 10^{13} \) cm\(^{-2} \) for a film of 150 nm, which explains the observed increase of \( Q_{\text{eff}} \) in Fig. 4 for the \( \text{Si}/\text{SiO}_2/\text{Al}_2\text{O}_3 \) stacks with a 150 nm \( \text{SiO}_2 \) interlayer. The value of \( -1.1 \times 10^{13} \) cm\(^{-2} \) found for \( Q_{0} \) is consistent with negative charge densities of \( -(0.6–1.3) \times 10^{13} \) cm\(^{-2} \) typically obtained for plasma ALD \( \text{Al}_2\text{O}_3 \) films deposited directly on silicon for which, generally, an interfacial \( \text{SiO}_2 \)-layer of \( \sim 1 \) nm thickness is present.\(^{15,49,58} \)

A tunneling decay length \( \lambda \) of 1.5 and 3.5 nm was obtained for \( n \)- and \( p \)-type silicon, respectively. Both values are unrealistic for direct tunneling, for which \( \lambda \) is typically less than one nanometer,\(^{52} \) and the obtained decay lengths should thus not be interpreted strictly in terms of their physical meaning. They do reveal, however, that trap-assisted tunneling is very likely to occur and should be incorporated in the model when a detailed analysis of the tunneling process is required. Still, the fact that, in our simple model, both the \( n \)- and \( p \)-type data can be fitted with single parameters except for the decay length is a strong indication that the difference in \( Q_{\text{eff}} \) versus \( t \) for the different doping types is related to the tunneling process. Several factors that can influence tunneling are temperature, doping density, tunnel barrier height, density of states, and effective electron mass.\(^{52} \) Temperature is not likely the cause as the annealing process is very reproducible. Moreover, variations in annealing temperature would lead to changes in \( Q_{\text{eff}} \) independent of doping type. The doping density can also be ruled out as it is nearly equal for both wafer types. One difference between \( n \)- and \( p \)-type silicon is the band structure that is formed at the \( \text{Si}/\text{SiO}_2 \) interface when band bending occurs due to the presence of built-in charges. This difference could lead to a different effective tunneling barrier thickness. Whether differences in tunnel barrier height, density of states, and effective electron mass can cause the pronounced difference in tunneling behavior between \( n \)- and \( p \)-type silicon is not clear at present.

Altogether, it can be derived from the modeling that the trend in \( Q_{\text{eff}} \) as a function of \( \text{SiO}_2 \) interlayer thickness can be divided into two regimes as indicated in the bottom panel of Fig. 4. One that is dominated by the tunneling of electrons from the silicon through the \( \text{SiO}_2 \) into \( \text{Al}_2\text{O}_3 \) defects states near the \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) interface for an interlayer thickness below \( \sim 13 \) nm. The other regime, for \( t > 13 \) nm, is dominated by charges \( (Q_{t} \text{ and } \rho_{b}) \) that are intrinsic to the \( \text{SiO}_2 \) film. Because both \( Q_{t} \) and \( \rho_{b} \) depend on processing conditions it is expected that their absolute number densities will vary with the preparation method of the \( \text{SiO}_2 \) interlayers. Apparently, the ALD and PECVD prepared \( \text{SiO}_2 \) interlayers in this work have quite similar charge densities. For a \( \text{Si}/\text{SiO}_2/\text{Al}_2\text{O}_3 \) stack with a 41.3 nm \( \text{SiO}_2 \) interlayer prepared by wet thermal oxidation, however, a negligible built-in charge density was found to be present on basis of its SH intensity spectrum. This spectrum is shown in Fig. 5 together with the spectra of the 45.2 nm PECVD \( \text{SiO}_2 \) interlayer stack and the 5.5 nm ALD \( \text{SiO}_2 \) interlayer stack. It is clear that the spectrum for the stack with a 41.3 nm wet thermal \( \text{SiO}_2 \) interlayer closely resembles the 5.5 nm ALD \( \text{SiO}_2 \) interlayer one which was found to have a negligible effective charge density (Sec. IVB). This shows indeed that, unlike the

<table>
<thead>
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<td>( Q_{t} ) (cm(^{-1} ))</td>
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<td>( \rho_{b} ) (cm(^{-1} ))</td>
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<td>( Q_{0} ) (cm(^{-2} ))</td>
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<td>( \tilde{t}_{n} ) (nm)</td>
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</tr>
</tbody>
</table>

FIG. 5. SH spectra for \( \text{SiO}_2/\text{Al}_2\text{O}_3 \) stacks on \( \text{Si}(100) \) with \( \text{SiO}_2 \) interlayers prepared by wet thermal oxidation (41.3 nm), PECVD (45.2 nm), and ALD (5.5 nm). The \( \text{Al}_2\text{O}_3 \) films have a nominal thickness of \( \sim 30 \) nm.
45.2 nm PECVD SiO2 interlayer stack, the 41.3 nm wet thermal SiO2 interlayer does not contain a significant density of positive charges. A negative charge density in the Al2O3 is not expected on basis of a negligible tunneling for a 41.3 nm thick interlayer. The absence of built-in charges for the stack with 41.3 nm of wet thermal SiO2 is consistent with the literature as such oxides are known to contain a negligible Qs.1,8

This discussion shows that a theoretical model describing the presence of built-in charges in thin-film systems on silicon can provide detailed insight into the various types of charges contributing to the effective charge density and the prevailing charging mechanisms.

VI. CONCLUSIONS

SiO2/Al2O3 stacks were deposited on n- and p-type Si wafers with SiO2 interlayers in the thickness range of 1–150 nm as prepared by ALD and PECVD. The SiO2 interlayer thickness of each stack as well as the optical dispersion of the SiO2 and Al2O3 films were accurately determined from spectroscopic ellipsometry data by using an advanced modeling strategy. The effective density and prevailing polarity of built-in charges present in the Si/SiO2/Al2O3 stacks were probed by spectroscopic, time-dependent, and azimuthal SHG measurements. Depending on the SiO2 interlayer thickness the effective charge density in the Si/SiO2/Al2O3 stacks was found to vary between 1015 to 1011 cm−2 for both n- and p-type silicon. The polarity of the charges switched from negative to positive around a SiO2 interlayer thickness of 5–10 nm at which point the effective charge density in the stacks is negligible, i.e., the number densities of positive and negative charges in the stack are equal and nullify each other. To discriminate between various types of charges present in the Si/SiO2/Al2O3 stacks and to pinpoint their origin a simple model was developed describing the effective charge density as a function of SiO2 interlayer thickness. Using this model it was shown that tunneling of electrons through the SiO2 interlayer into defect states at the SiO2/Al2O3 interface is most likely the prevailing mechanism leading to built-in charges for an interlayer thickness below 5 and 10 nm. Above this thickness the presence of fixed charges (≈3.3 × 1011 cm−2) at the Si/SiO2 interface and bulk charges (≈2.3 × 1016 cm−3) in the SiO2 dominate the effective built-in charge density. This charging mechanism appears to hold generally as the trend was equal for the differently prepared SiO2 films. The difference found in the tunnel decay length between n-type (1.5 nm) and p-type (3.5 nm) silicon, as well as the relatively large values of the tunneling decay length, indicates the importance of trap-assisted tunneling for describing charge trapping in Si/SiO2/Al2O3 stacks.

Finally, it is emphasized that the methods presented in this work can be applied to other technologically and scientifically relevant material systems, including alternative dielectric films on silicon and germanium.

ACKNOWLEDGMENTS

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