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Influence of the spatial extent of the space-charge region in *c*-Si on the electric-field-induced second-harmonic-generation effect

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Second-harmonic-generation (SHG) spectroscopy can be used as an all-optical probe of space-charge regions (SCR) in semiconductors such as *c*-Si by exploiting the electric-field-induced second-harmonic-generation (EFISH) effect. To do so accurately, a thorough understanding of the EFISH effect is needed, and here a detailed model is presented, taking into account the so-far neglected spatial extent of the SCR on the spectral shape of the EFISH contribution. This shows that the spatial extent causes a significant phase shift in the EFISH contribution ranging from 0.1π rad to 0.4π rad with decreasing SCR strength. This predicted phase shift was verified by dedicated measurements of the spectral SHG phase and intensity of a series of samples covering the typical range of SCR strengths. The spectral SHG response of these samples indeed showed the predicted phase shift in the EFISH contribution and demonstrated that the extent of the SCR cannot be neglected. The obtained insights can result in improved accuracy in the determination of built-in charges near a *c*-Si interface, which is of interest in the context of semiconductor devices using SHG spectroscopy. Moreover, this refined understanding of the EFISH effect is beneficial in SHG experiments on 2D materials with *c*-Si serving as a substrate of Si-based photonic devices. © 2021 Optical Society of America

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1. INTRODUCTION

Second-harmonic generation (SHG) is a nonlinear optical process used to study (buried) interfaces of solids, a purpose for which SHG is particularly well suited due to its inherent interface and surface sensitivity [1,2]. With SHG it is possible to probe interface structure [3–5], electronic transitions at interfaces [6], local strain at interfaces [7], and adsorbates at surfaces [8,9], among other related properties. The sensitivity of the SHG process toward interface and surface properties stems from its second-order nonlinear nature: SHG is not allowed at a site with inversion symmetry (in the dipole approximation) [10,11]. Hence, SHG is forbidden in amorphous materials such as SiO₂ and Al₂O₃ and in the bulk of most crystalline solids including crystalline silicon (*c*-Si). Conversely, SHG is allowed at an interface or a surface where by definition inversion symmetry is broken [10,11].

Static electric fields in solids also break inversion symmetry and therefore can result in SHG, effectively making SHG an all-optical probe of electric fields. This electric-field-induced SHG (EFISH) effect was predicted by Bloembergen *et al.* and observed experimentally for *c*-Si by Lee *et al.* [12,13]. Of special interest are electric fields near interfaces of semiconductors caused either by an externally applied voltage over the material

or caused by built-in (fixed) charges near the interface. These fields can have an impact on the characteristics of the semiconductor interface affecting, e.g., its electronic properties and behavior [14]. Irrespective of the cause, the shape and strength of the (induced local) electric field in the semiconductor are described by the same set of equations. The EFISH effect solely interacts with the local electric field and not with the origin of the static electric fields [15,16]. Consequently, the cause of the electric fields does not have to be considered in the interpretation or the modeling of the EFISH effect.

In practice, the EFISH effect can dominate the SHG response of *c*-Si: a not uncommon built-in charge density of $5 \times 10^{12} \text{ cm}^{-2}$ at an *c*-Si interface, for example, leads to an EFISH contribution that is a factor ~ 20 larger than the signal originating from the *c*-Si interface itself [17]. In these cases, the EFISH contribution dominates over the interface contributions of *c*-Si and high-order effects such as quadrupole terms' contribution to SHG response [18]. As a result, the total SHG signal from a *c*-Si substrate might be significantly larger than expected solely considering interface contributions. There is a growing interest in SHG in areas such as the characterization of 2D transition metal dichalcogenides, which are often placed on *c*-Si substrates [19–26] and for (probing) Si-based photonic

structures [27,28], where the presence of the EFISH contribution can impact interpretation of SHG experiments. These examples underline the need for a thorough understanding of the different contribution of the SHG of *c*-Si and the EFISH effect in particular.

In the context of nanoelectronic fabrication, built-in charges near buried interfaces are of large technological importance given their impact on device performance. The charge density and polarity of the fixed charges can be probed by SHG via the EFISH effect in a contactless and virtually sample-preparation-free fashion [4,17,29–31]. This makes SHG particularly well suited as a diagnostic for *in situ* studies of (buried) interfaces and the characterization of built-in charges in an early stage before a fully functioning electrically device has been realized [29,32]. These capabilities set SHG apart from other approaches such as capacitance-voltage (CV) measurements. CV measurements are often used to characterize built-in charge density but require a function device or electrical circuit to function [33]. Therefore, the all-optical nature of SHG makes it an valuable and complementary addition to the established methodologies for the characterization of built-in charges near semiconductor interfaces, which are mostly based on electrical measurements.

Seminal work on the fundamentals of the EFISH effect in *c*-Si was conducted by Aktsipetrov *et al.* in a series of experiments studying the SHG response of metal-oxide-semiconductor (MOS) stacks [30]. Such MOS structures are well suited for this kind of studies because they form well understood (electric) system. When an external voltage is applied over a MOS structure, the strength of the electric field throughout the structure is known and can be calculated accurately. The applied voltage will give rise to a voltage drop over the oxide and the semiconductor, with the ratio of the two voltage drops depending on the exact details of the structure. Considering the semiconductor in the MOS structure, a large part of the voltage drop over the *c*-Si occurs near the interface of the *c*-Si with the oxide [14,34]. This results in a relatively strong electric field near the interface and as a consequence the free charge carriers in the *c*-Si rearrange to compensate for the external electric field. Effectively, either electrons or holes accumulate near the interfaces [14,34] with the affected region called the space-charge region (SCR). The depth and the shape of the SCR electric field mainly depend on the strength of the applied potential, the doping density, and to a lesser degree on the doping type among other factors [14].

The strength of the EFISH effect was predicted to be directly related to the strength of the electric field, and this was experimentally demonstrated by Aktsipetrov *et al.* [30]. They monitored the SHG response of the MOS structure at a single wavelength as a function of the applied voltage. The SHG intensity was found to scale quadratically with the electric field in the SCR caused by the external voltage [30]. The first *spectroscopic* SHG study was performed by Godefroy *et al.* using a similar configuration as Aktsipetrov *et al.* [35]. They found that the spectral response of the MOS structure changed significantly when varying the applied voltage over the MOS structure. For a *c*-Si substrate with a dielectric film on top, Rumpel *et al.* demonstrated that SHG spectroscopy is sensitive to *both* the strength and direction of the electric fields in the SCR: the strength of the electric field in the SCR is reflected by

the intensity of the EFISH signal, whereas the direction of the electric field is related to the phase of the EFISH signal [17].

The SCR causing the EFISH signal extends tens of nanometers into the *c*-Si. The impact of the spatial extent of the SCR on the EFISH contribution can be deduced by comparing the typical length scale of the SCR with the SHG probing depth. This is illustrated in Fig. 1 for the geometry typically used in SHG experiments showing the spatial dependence of the SCR electric field and the probing strength of SHG. For a moderately high fixed charge density of 10^{12} charges per cm^2 , the SCR extends up to 10 nm into the *c*-Si (n-type *c*-Si, $\rho = 2 \Omega \cdot \text{cm}$). The spatial extent of the SCR is on a similar scale for charge densities ranging from 10^{11} up to 10^{13} per cm^2 typical for metal-oxide/*c*-Si interfaces as also shown in Fig. 1. The probing depth of SHG in *c*-Si ranges from 10 nm for SHG light with a wavelength of $\lambda_{2\omega} = 360 \text{ nm}$ ($\alpha = 1.0 \cdot 10^6 \text{ cm}^{-1}$) to 400 nm for $\lambda_{2\omega} = 450 \text{ nm}$ ($\alpha = 2.4 \cdot 10^4 \text{ cm}^{-1}$); this is a wavelength range typical in spectroscopic SHG experiments covering the E_1 transition of *c*-Si situated at 3.4 eV. Therefore, in a typical SHG experiment, EFISH light will be generated throughout a large part of the SCR. Significant interference effects are expected because the $1/4\lambda$ of the SHG light in the *c*-Si also ranges between 15 and 19 nm (considering the refractive index ranging from $n = 6.4$ to $n = 4.6$) for the aforementioned wavelengths [36]. As a result, the shape of the electric field in the SCR and its spatial extent will have an influence on the phase and intensity of the EFISH response.

For single-wavelength experiments, the importance of the spatial extent of the SCR on the EFISH effect was already alluded to by Aktsipetrov *et al.* and more recently by Lei *et al.* and Chng *et al.* [15,16,30,37]. For the scenario of a fully depleted or fully accumulated (Schottky) SCR in a MOS structure, the impact of the spatial extent was modeled in the work of Aktsipetrov *et al.* in the context of a single-wavelength experiment. Yet so far the impact of the spatial extent of the SCR on the spectral shape of the EFISH contribution has not been considered despite its relevance for more elaborate spectroscopic SHG studies. In most studies (both spectroscopic and single-wavelength), the EFISH signal is considered as an infinitely thin sheet of polarization at or near the *c*-Si interface, i.e., not taking into account the actual spatial extent of the SCR [4,17,29,31]. From the geometric considerations mentioned above, it is clear that a more detailed description of the influence of the SCR on the spectral shape of the EFISH effect is needed.

In this work it will be shown how the spatial extent of the SCR significantly impacts the *spectral shape* of the EFISH contribution in *c*-Si. This effect will be discussed in the context of a SCR induced by built-in fixed charges; however, as stated before, the results are valid for the EFISH effect in *c*-Si irrespective of the cause of the SCR. First, the background of SHG and especially the EFISH effect in *c*-Si will be briefly discussed in Section 2. In Section 3, a mathematical description of the EFISH effect is given without making *a priori* assumptions about the shape of the electric fields in the SCR. Using this description, the impact of the spatial extent of the SCR is evaluated with the aid of a numerical model for the SCR electric fields. The outcome of this model is contrasted to an analytical model based on the Schottky approximation only valid for strong SCRs, and it is also compared to the common approach, neglecting the

Fig. 1. Electric-field-induced SHG occurs inside *c*-Si near the interface in the space-charge region (SCR) caused by, e.g., built-in fixed charge in a thin-film on top. (a) Cross-section TEM image of a typical sample consisting of a Si substrate with ALD Al₂O₃ film on top (scale corresponds to other panels); a spontaneously formed interfacial SiO_x layer can also be seen. The Al₂O₃ film contains negative built-in fixed charges that induce a SCR in the *c*-Si. The measured EFISH contribution is an integral of the local EFISH generation over the SCR, taking into account the highlighted position-dependent phase differences due to propagation. (b) The actual strength and shape of the electric field in the SCR shown for different charge densities (solid lines) and the assumed delta distribution of the electric field in the commonly used interface-only model (M1, see Section 2) represented by the round marker. (c) The normalized intensity of the EFISH signal emerging from the sample as a function of depth, taking into account the absorption of both fundamental and SHG radiation.

spatial extent of the SCR. Furthermore, the predictions of the numerical model are validated experimentally by combined spectral SHG phase and intensity measurements on samples with a varying amount of negative built-in fixed charge up to $\sim 10^{13} \text{ cm}^{-2}$. Furthermore, in Section 3 the main results will be discussed in a broader context, and an approach is proposed how these insights can be incorporated into the existing models used to interpret SHG spectra. The improvement that can be gained in the interpretation of SHG spectra of *c*-Si will be demonstrated by determining the built-in fixed charge of a set of simulated SHG spectra using the different models. In Section 4, earlier works are discussed in light of these new insights, and in Section 5 the main conclusions of the work are stated.

2. EFISH RESPONSE OF *c*-Si NEAR 3.3 eV E_1 CRITICAL POINT

The spectral SHG response of the *c*-Si interface with a metal-oxide such as SiO₂ or Al₂O₃ in the photon energy ($\hbar\omega$) range from 3 to 4 eV is dominated by three critical point (CP)-like resonances [4]. At 3.3 eV, the Si atoms at the interface bonded in

a tetrahedral fashion case a resonance labeled here as S_{E1} (S indicating a surface origin). A second resonance is present at 3.7 eV, labeled here as S_{SiSiO} , caused by nontetrahedrally bound Si-Si most likely backbonded to oxygen [4]. The EFISH contribution is situated at 3.4 eV, labeled B_{EFISH} (B indicating a bulk-like origin) and is caused by Si atoms in the SCR in conjunction with the SCR electric field. The bulk nature of the Si atoms in the SCR is reflected in the spectral position of the EFISH contribution corresponding to the energy of the bulk E_0/E_1 transition of *c*-Si [38]. The total spectral SHG response of the *c*-Si interface can be described by a coherent superposition of these resonances. The conventional description of the SHG polarization $\vec{P}(2\omega)$, caused by the fundamental light $\vec{E}_\omega$, is given by

$$\vec{P}_{2\omega} = \epsilon_0 \left(\sum_{S_x} \chi_{S_x}^{(2)}(2\omega) : \vec{E}_\omega, \vec{E}_\omega + \chi_{\text{scr}}^{(3)}(2\omega) : \vec{E}_\omega, \vec{E}_\omega, \vec{E}_{\text{scr}} \right). \quad (1)$$

In this equation, the $\chi_{S_x}^{(2)}$ tensors describe the spectral response of the surface contributions S_{E1} and S_{SiSiO} , with both tensors being of second rank and having a $3 \times 3 \times 3 \times 3$ shape. The EFISH contribution B_{EFISH} is described by the $\chi_{\text{scr}}^{(3)}$ tensor and the electric field $\vec{E}_{\text{scr}}$ in the SCR with the tensor being of third rank and having $3 \times 3 \times 3 \times 3$ shape. From this point onward, for simplicity only the dominant zzz component of the SHG tensor will be considered (dropping the zzz index for brevity), but the analysis can be repeated for all other tensor components as well. The spectral shape of all these resonances is assumed to be excitonic, which is incorporated in the (components) χ tensor

$$\chi(2\omega) = \frac{h \exp(i\phi)}{(2\omega - \omega_{\text{res}} + i\Gamma)} \quad (2)$$

with h the amplitude, ϕ the phase factor, ω_{res} the resonant energy, and Γ the broadening for each specific resonance, following the approach outlined by Daum *et al.* [4].

In Eq. (1) the spatial extent of the SCR is not accounted for (e.g., there is no dependence on z), and the EFISH response is written in the (same) form of an interface contribution, although in practice it is generated throughout the SCR. The **interface-only** approach, which is implicitly taken in Eq. (1), abstracts away the spatial extent and shape of the SCR electric fields. As a result, the E_{scr} Eq. (1) should be considered as an average value (using an unknown weighting function), which is at best proportional to the strength of the SCR. As a consequence, using Eq. (1) can be problematic when used to quantify the SCR strength from a (measured) SHG signal with an EFISH contribution.

In a more complete description, the total EFISH contribution is given by an integral of the *local* EFISH contribution over the whole SCR. In this integral, the interplay between the shape of the electric fields in the SCR $E_{\text{scr}}^{\text{SCR}}(z)$, the absorption of the (ω and 2ω) light, and the propagation phase shift of the light

are taken into account. The local EFISH polarization generated at position z is proportional to $\chi_{\text{EFISH}} : \vec{E}_\omega(z)^2 \vec{E}_{\text{dc}}^{\text{SCR}}(z)$. The strength of the local EFISH polarization depends on the strength of the fundamental light $\vec{E}_\omega(z)$, the local strength of the electric field of the SCR $\vec{E}_{\text{dc}}^{\text{SCR}}(z)$, and the χ_{EFISH} , which is a material constant. Finally, the propagation of the SHG signal generated by the EFISH polarization out of the c -Si has to be taken into account. The total EFISH signal ($P_{2\omega, \text{scr}}$) at the c -Si interface ($z = 0$), in reflection mode with the SHG signal propagating in the $-z$ direction, can be described by the following integral (considering a single component for brevity):

$$P_{2\omega, \text{scr}} = \epsilon_0 \chi_{\text{EFISH}} E_\omega^2(0) \int_0^\infty dz E_{\text{dc}}^{\text{SCR}}(z) \exp(iz(k_{2\omega} + 2k_\omega)), \quad (3)$$

using $E_\omega(z) = E_\omega(0) \exp(izk_\omega)$ with k_ω the propagation vector of fundamental radiation, and $k_{2\omega}$ is the propagation of the SHG radiation. The spatial shape $[E_{\text{dc}}^{\text{SCR}}(z)]$ of the electric field in the SCR is the only unknown that has to be established in order to evaluate Eq. (3).

Before considering several physical models for the electric fields in the SCR in the next section, it is now possible to comment on some of the implications of neglecting the spatial extent of the SCR. Information is lost when abstracting away the integral in Eq. (3) to a single term without z dependence as is the case for Eq. (1). This can be understood from the mean-value theorem, which shows that it is always possible to simplify Eq. (3) to Eq. (1) by choosing an appropriate $E_{\text{mean}}^{\text{SCR}}$ [30]. The information that is lost cannot be reconstructed, and the shape and strength of the SCR, needed to accurately determine the total charge, cannot be determined from $E_{\text{mean}}^{\text{SCR}}$ alone. This explains why Eq. (1) shows the right trends when using the EFISH effect to probe the strength of a SCR but will introduce errors in the actual quantification.

The mean-value theorem approach is beneficial when modeling SHG spectra. As will be shown later, we can also incorporate (to a large degree) the impact of the spatial extent of the SCR on the EFISH contribution into this effective EFISH tensor by parameterizing the insights from a full numerical model. Such a parameterization basically establishes the relation between SCR strength and $E_{\text{mean}}^{\text{SCR}}$. This results in a relatively easy-to-implement scheme, which is also numerically simple enough to be fitted to measured data. Note that this effective EFISH concept used in this fashion is a much broader than the **interface-only** (M1) description, which refers in this work to the representation of the EFISH effect as a sheet of polarization (i.e., a point source) situated at the interface with a phase of either 0 or π rad.

3. RESULTS

A. Interface-Only Model for EFISH (M1)

The **interface-only** model (M1) can be written in a form that is compatible with Eq. (3). Placing the EFISH contribution solely at the interface is equivalent to an SCR electric field that is only nonzero at the interface,

$$E_{\text{dc}}^{\text{SCR}}(z) = E_{\text{M1}}^{\text{SCR}} \delta(z). \quad (4)$$

Note that in this description $E_{\text{M1}}^{\text{SCR}}$ is not the actual strength of the electric field at the interface but an *average* electric field. In this approach it is assumed that $E_{\text{M1}}^{\text{SCR}}$ scales with Q , which is a oversimplification of the actual relation between the two. The phase and intensity of the EFISH contribution are now given by

$$I \propto |P_{2\omega, \text{SCR}}|^2 \propto |\chi_{\text{SCR}} Q|^2, \quad (5)$$

$$\Phi \propto \arg(\chi_{\text{SCR}}) + \arg(Q), \quad (6)$$

with $\arg(Q)$ equal to 0 or π depending on its polarity. In this approximation the EFISH intensity is proportional to the square of the built-in charge density Q , and the phase does not vary with the magnitude of Q .

B. Schottky Model for EFISH of Strong SCR (M2)

A often used and fairly accurate approximation for the electric field in the SCR $E_{\text{dc}}^{\text{SCR}}(z)$ for strong SCR ($Q_{\text{built-in}} > 10^{13} \text{ cm}^{-2}$) is given by the **Schottky model** and will be referred to as (M2). In the Schottky model, the semiconductor is assumed to be fully depleted or accumulated in the SCR and to have its “equilibrium carrier concentration” outside the SCR [14]. The charge distribution in the SCR is step-like, and the depth of the transition region (going from depletion to equilibrium) is assumed to be negligible compared to the SCR depth z_{sch} . Under the assumption that the doping in the c -Si is fully ionized, the depth z_{sch} of a SCR caused by areal charge density Q is given by $z_{\text{sch}} = \frac{|Q|}{N_D}$ with N_D the (active) doping density [14]. For this step-like charge distribution, the electric field can be calculated and is given by

$$E_{\text{SCR}}(z) = \begin{cases} \pm \frac{2eN_D}{\epsilon\epsilon_0} (z - z_{\text{sch}}) & 0 < z < z_{\text{sch}} \\ 0 & z > z_{\text{sch}} \text{ and } z < 0, \end{cases} \quad (7)$$

where the $+$ ($-$) sign has to be used in the expression for positive (negative) charges causing the SCR. Equation (3) can now be evaluated using Eq. (7) as input. The details of this calculation and the calculation of the corresponding EFISH phase Φ and intensity I are provided in the supporting information (SI). It is found that the SHG polarization generated by the EFISH effect is given by

$$P_{2\omega, \text{SCR}} \propto \chi_{\text{SCR}} N_D \frac{z_0 \beta - \exp(\beta z_0)}{\beta^2}, \quad (8)$$

where the combined absorption and retardation at ω and 2ω are given by $\beta = i(k_{2\omega} + 2k_\omega)$. The intensity of the EFISH contribution is given by

$$I \propto |P_{2\omega, \text{SCR}}|^2 \propto \left| \chi_{\text{SCR}} N_D \frac{z_0 \beta - \exp(\beta z_0)}{\beta^2} \right|^2 \propto |\chi_{\text{SCR}}|^2 Q^2 / \beta. \quad (9)$$

In the derivation of this equation it was used that $z_0 N_D = Q$ and $\exp(\beta z_0)$ was neglected with respect to βz_0 in the last step. From Eq. (9) it can be seen that the EFISH intensity scales with the square of the built-in charge causing the SCR in the Schottky approximation, in agreement with results from Aktsipetrov *et al.* [30]. The *effective* phase of the EFISH contribution is given by

$$\Phi = \arg(P_{2\omega, \text{SCR}}) \approx \arg(\chi_{\text{SCR}}) - \arg(\beta) + \arg(Q). \quad (10)$$

In this equation the $\arg(Q)$ is either 0 or π depending on the polarity. The *effective* phase of the EFISH contribution, Eq. (10), is $\approx 0.9\pi$ when evaluating the β term at a fundamental wavelength of 730 nm (1.7 eV) in *c*-Si for negative charges.

The results presented here are, of course, only valid for strong SCRs that can be described in the Schottky approximation. This limits the applicability of the model; however, the scaling of the EFISH contribution with Q is a good approximation for the general case. Furthermore, it is already observed that the *effective* phase of the EFISH contribution is lower than what is expected if the EFISH contribution originated from an infinitely thin layer at the interface in the interface-only model (M1). This lower phase, i.e., lagging behind the EFISH signal, can be understood when comparing the distance that the radiation has to traverse: in the **interface-only** (M1) description, the light is generated at the interface, whereas, if the light is generated throughout the SCR, on average it has to traverse some additional distance to the interface, resulting in a lag. In the next section a numerical model will be used to evaluate more detailed scenarios, taking into account more accurate shapes of the electric fields in the SCR and evaluating, e.g., the impact of doping density and type on the EFISH effect.

C. Numerical Model of EFISH of SCR (M3)

A more complete (numerical) model of the DC electric field in the SCR was used to study the influence of the strength and shape of the SCR on the EFISH response. This approach will be referred to as the **numerical model** or (M3). The equations governing the electric fields in a SCR are well known, and numerous models are available to simulate the electric fields in a SRC in semiconductors [14,34,39,40]. In this work the electric fields were calculated with the PC1D code [41]. The model in this code takes into account the charge density causing the SCR, the influence of the carrier mobility, and the doping level of the semiconductor. The SCR in silicon was modeled for each combination of the following properties: doping type (*n* or *p*), doping level (2, 5, 20 Ω cm), polarity of the charge causing the space-charge region (positive or negative), and density of the charge causing the space-charge region (1, 10, 40, 100, 200, 1000, and 10000 $\times 10^{10}$ cm $^{-2}$). This set of parameters is a superset of the combination of properties typically encountered samples consisting of a dielectric film on top of a *c*-Si substrate.

The EFISH response was calculated between 3 and 4 eV by evaluating Eq. (3)—determining both the phase and intensity SHG spectrum—using the SCR electric field obtained from PC1D for each of the aforementioned combination of parameters. An excitonic line shape was assumed for the spectral response of the local χ_{SCR} tensor resulting in Fig. 2. In essence, the evaluation of Eq. (3) gives the amplitude and phase of the $\chi_{\text{SCR}}(\omega)E_{\text{dc}}^{\text{mean}}E_{\omega}^2$ term as a function of built-in charge density. In addition to the result of the numeric model (M3) shown in Fig. 2, the spectral response of the EFISH contribution of the interface-only model (M1) and the Schottky model (M2) are also shown in the figure for comparison. The phase spectra shown in the upper panel of Fig. 2 calculated using the numeric model (M3) exhibits a shift of $\approx 0.1\pi$ rad for SCRs with high charge densities (around 10^{13} cm $^{-2}$) compared to the

Fig. 2. EFISH phase (upper panel) and intensity (lower panel) plotted as a function of wavelength, obtained from the numerical model (M3) for different SCR strengths. The intensity spectra are normalized to emphasize the differences in shape. The inset shows the relation between charge density causing the SCR and relative EFISH intensity at resonance normalized to the weakest signal, showing the expected large variation in strength. For comparison, the spectra associated with the interface-only (M1) (dashed line) model and the Schottky model (M2) (round markers) are also shown.

phase spectrum obtained with the interface-only model (M1). For weaker SCRs, caused by lower charge densities, this shift increases in magnitude up to 0.4π . The shape of the phase spectrum is quite similar for all wavelengths, i.e., the phase spectra undergo a nearly rigid shift. The lower panel of Fig. 2 shows the normalized spectral shape of EFISH intensity for the different SCRs. Only a slight change in the shape at the low-energy side of the spectrum can be seen. The inset in Fig. 2 shows the absolute EFISH intensity at 3.4 eV as a function of charge density, showing the expected variation in intensity caused by the differences in SCR strength.

The trend predicted by the numerical model (M3) in the phase of the EFISH contribution can be interpreted with the aid of Fig. 1. The electric field in the SCR caused by a large charge density, which rapidly decreases in strength, resembles more closely the electric field of (M1) the interface-only model (a delta distribution); a SCR caused by a weak charge density is more spread out. This also means that for a weak SCR the average origin of the EFISH radiation is farther into the material than for a strong SCR, and therefore the light is retarded by a larger amount (i.e., larger phase shift).

The quantitative trends in the phase of the EFISH contribution differ significantly for the three models and highlight the limited validity of the interface-only (M1) and Schottky (M2) model. Figure 3 shows the trend in the phase of the EFISH contribution as a function of the SCR strength in more detail for the different models; the experimental data in the figure will be discussed in the next section. For a strong SCR, as expected the analytical Schottky model (M2) and the numerical model (M3) converge to the same value for the EFISH phase. Both models yield a shift in the phase factor ϕ of 0.1π rad compared to the interface-only model. For weaker SCRs, the phase factor of the numerical model (M3) starts to deviate from the Schottky model (M2) and can deviate as much as 0.4π rad from the interface-only (M1) result. As expected, the Schottky model (M2) is only valid for strong SCRs, and the interface-only

Fig. 3. Phase of the EFISH contribution as given by the interface-only model (M1) (dashed line), the Schottky model (M2) (circles) and the numerical model (M3) (solid line) as a function of total charge density causing the SCR. The trend for a positive SCR is similar to that of a negative SCR with an offset of π rad. The CP phase factor determined in this work for a series of samples by combined SHG phase and intensity spectroscopic measurements are included in the figure (triangles) as well as the data set published by Terlinden *et al.*, simultaneously analyzing a large set of intensity-only spectra (squares) [32]. No data points are available in for positive fixed charge because the few thin films that exhibit a large positive fixed charge such as SiN_x also generate bulk SHG, complicating the interpretation of the spectra.

model (M1) always introduces a systematic error by neglecting the spatial extent of the SCR.

D. Validation EFISH Trends by Spectral Phase and Intensity SHG Measurements

The results of the modeling, and in particular the phase shift, were validated in a dedicated SHG experiment. A series of samples spanning the range of built-in charge of interest were prepared and measured using combined *phase and intensity* SHG spectroscopy. The complementary nature of the phase and intensity measurements enhances the sensitivity to changes in the phase and should suffice to detect a shift of 0.1π rad. For a detailed description of the setup and an evaluation of its sensitivity, see the SI and Terlinden *et al.* [32].

The samples consisted of a Si(100) substrate with different (stacked of) dielectrics on top. A sample with a strong SCR was fabricated by depositing a 30 nm Al_2O_3 film directly on *c*-Si (n-type, $5 \Omega \cdot \text{cm}$) by plasma-assisted atomic-layer deposition (PE-ALD) with a ~ 1 nm thick spontaneously formed interfacial SiO_x in between. This sample, labeled $\text{TF}_{\text{Al}_2\text{O}_3}$, prepared in this fashion is known to have a built-in charge density of $\sim 10^{13} \text{ cm}^{-2}$ [29,42]. Samples with intermediate built-in charge densities were fabricated by depositing a SiO_2 spacer in between the *c*-Si and the Al_2O_3 film. For these samples it is known that the charge density is inversely proportional with the SiO_2 thickness as shown by Dingemans *et al.* and Terlinden *et al.* [43,44]. Two samples were made: $\text{TF}_{\text{inter}5}$ with a 5 nm and $\text{TF}_{\text{inter}10}$ with a 10 nm SiO_2 film in between a Si(100) substrate and a 30 nm thick Al_2O_3 film. A sample with 47 nm of thermally grown SiO_2 on *c*-Si (n-type, $2-3 \Omega \cdot \text{cm}$) was also included, which is known for its low built-in charge density of $\sim 10^{11} \text{ cm}^{-2}$ labeled sample TF_{SiO_2} [45]. All the samples were annealed in a N_2 atmosphere at 400°C for 10 min to activate the built-in charge.

Fig. 4. Measured SHG spectra showing the phase (upper panel) and intensity (lower panel) of the 4 samples under investigation. The phase spectra are offset by π rad each for clarity, zero phase is shown by the dashed line. The simultaneous fit of all the phase and intensity spectra, as described in the text, is shown as the solid line. The inset shows the two samples with the weakest SHG intensity response on enlarged scale.

The SHG phase and intensity spectra of all samples were measured near the E1 CP of *c*-Si covering the two-photon range of 2.6–3.5 eV. A tunable, mode-locked optical oscillator (Spectra-Physics Tsunami, pulse duration 90 fs) was used to generate the fundamental radiation. For the detection of the SHG radiation, a photomultiplier tube (Hamamatsu R585) in single-photon counting mode was employed. The fundamental radiation was removed by a combination of a Pellin–Broca prism and glass absorption filters (Schott BG40). More experimental details can be found in the SI and elsewhere [44].

Figure 4 shows the resulting phase (upper panel) and intensity (lower panel) spectra of the four samples. Except for sample TF_{SiO_2} , which has virtually no EFISH contribution, the shape of the phase and intensity spectra are relatively similar but the absolute SHG intensities differ significantly with the SCR strength. The SHG response of the $\text{TF}_{\text{Al}_2\text{O}_3}$, $\text{TF}_{\text{inter}5}$, and $\text{TF}_{\text{inter}10}$ samples is dominated by the EFISH contribution resulting in this similarity showing the characteristic EFISH peak at 3.4 eV in the intensity spectra. The spectra were fitted and the EFISH phase was plotted in Fig. 3 versus the built-in charge density of the samples determined from the EFISH intensity. The model represents the combined phase and intensity spectra well (overall goodness of fit $R^2 = 0.90$); see also SI for more details on the fitting. Sample TF_{SiO_2} was omitted from the Fig. 3 due to the very weak EFISH contribution (negligible built-in charge) resulting in a large uncertainty in the EFISH phase. A good agreement is seen in Fig. 3 between the experimental results and the predicted trend from the **numerical model (M3)**. This is a strong argument that the shift in phase found from the numerical model does indeed occur and affects the SHG spectra and their interpretation.

Further confirmation of the phase shift in the EFISH contribution can be found in our earlier work [32]. In that work a similar trend in the phase was observed; however, at the time of writing the trend in the EFISH phase was not expected, and it was not interpreted further. In that work a large set of similar samples was measured by SHG spectroscopy probing only the intensity. In general, a single SHG intensity spectrum does not contain sufficient information to reliably determine the phase of the EFISH contribution. However, to increase the accuracy in the EFISH amplitude, this large sample set was fitted simultaneously, which also enhanced the sensitivity toward the EFISH phase. The EFISH phase data reported in that work are also shown in Fig. 3. Placing this data set in the context of the current work, good agreement between the predicted and measured trend is found, which further supports the trend in the EFISH phase found from the numerical model (M3) in this work.

E. Consequences for the Interpretation SHG Spectra

The relation between the SCR and the EFISH phase and intensity also has consequences for the interpretation and modeling of SHG spectra. In this section, we will briefly illustrate the impact of neglecting the spatial extent of the SCR when interpreting SHG spectra. Based on the insight for the numerical model M3, we will propose a simple yet accurate strategy to include the impact of the spatial extent of the SCR on the EFISH contribution in the interpretation of typical SHG data. In short, the outcome of the numerical model (M3) will be parameterized, resulting in (M3p), which can be used in Eq. (1). In a hypothetical scenario, we will evaluate the performance of the (M1), (M2), and (M3p) models to determine of the charge density near a *c*-Si interface determined by fitting simulated SHG spectra.

For this scenario, a (hypothetical) bare Si substrate without any thin films on top was considered with a charge density ranging from 10^{10} cm^{-2} up to 10^{13} cm^{-2} at the surface. Adding thin films to the simulation would only introduce additional (constant) factors describing the linear optical response of those films; they do not impact the accuracy of the SHG modeling if their properties are well known. The *total* SHG response of these samples was simulated by modeling the EFISH contribution but also the S_{E1} contribution in conjunction with a weak nonresonant background (e.g., representing a bulk quadrupole contribution). The EFISH contribution was described by the full numerical model (reflection geometry, angle 70°), and the S_{E1} contribution was represented by the typical excitonic line shape. The resulting simulated intensity spectra were treated as “experimental data” and fitted using interface-only (M1) and the Schottky (M2) model. Figure 5 shows the relative error in the built-in charge density determined using the different models, plotted as a function of the simulated built-in charge density. In this case the simulation with 10^{14} cm^{-2} was used a “calibration measurement” for the models with known charge (therefore not shown in Fig. 5). Both the interface-only model (M1) and the Schottky model (M2) overestimate the charge density, getting progressively less accurate for intermediate charge densities. For intermediate charge density the EFISH and S_{E1} contribution are roughly equally strong, and therefore phase plays a more important role in the superposition. From

Fig. 5. Relative discrepancy between the charge density Q_{fit} obtained from the fit of the simulated SHG spectra for charge density Q_{sim} . The interface-only (M1) model neglects the spatial extent of the SCR entirely, the Schottky (M2) model is only valid for strong SCRs, and the parameterized (M3p) model approximates the full numerical model (M3) valid for the full range of Q_{sim} .

this result, it is clear that neglecting the shape and extent of the SCR leads to a significant error in the determined charge density.

For various practical reasons, using the full numerical model (M3) is not feasible in the day-to-day interpretation of SHG spectra. However, a relatively accurate yet simple parameterization can be made that captures the essence of the impact of the spatial extent of the SCR, and this approach is labeled (M3p). The main impact predicted by the numerical model (M3) in the phase spectrum in Fig. 2 is a rigid shift of the phase spectra as a function of SCR strength. Or in other words, the spectral shape of the EFISH phase remains virtually the same and is simply shifted vertically. Furthermore, the shape of the EFISH intensity does not vary with as a function of the SCR strength and is virtually identical to the excitonic shape giving in Eq. (2). Hence, it is reasonable to model the EFISH contribution using the simple excitonic line shape, Eq. (2), incorporating the rigid shift of the phase into the ϕ factor via parameterization. Effectively, both the amplitude h and ϕ become a function of charge density constrained by the relation shown in the insets in Fig. 2 and Fig. 3, respectively. The simulated spectra were also fitted with the **parameterized (M3p)** model, resulting in the cross-shaped markers in Fig. 5. Clearly, this approach shows a significantly better prediction of the built-in charge density—especially for intermediate built-in charge densities—than the oversimplified interface-only (M1) and Schottky (M2) models. The **parameterized model M3p** strikes a good balance: it is hardly more complex than the interface-only model (M1) but yields significantly more accurate results. It can readily be adopted in the excitonic models typically used to fit SHG spectra [4,5,29,31,32,44,46–50].

4. DISCUSSION

The shift in the EFISH phase—as predicted by the modeling and experimentally confirmed from the combined SHG *phase and intensity* measurements in this work—will impact to some degree the modeling and interpretation of most SHG experiments involving *c*-Si. For the interpretation of *single-wavelength* experiments, these insights are essential since a

single-wavelength experiment is not capable of differentiating between changes in the EFISH amplitude or phase. Spectroscopic (intensity-only) SHG experiments are slightly more robust because changes in the EFISH phase *indirectly* impact the spectral shape of the SHG signal. Nevertheless, spectroscopic SHG intensity measurements only probe one half of the SHG response, resulting in a limited resolving power, possibly leading to an (erroneous) exchange of phase versus amplitude of a resonance. This limited sensitivity toward the EFISH phase is underlined in the previous section by the hypothetical scenario comparing the different models. It was shown that the fits of the (modeled) intensity spectra can lead to significant errors in the determined SCR strength if the impact of the SCR extent is not taken into account. The parameterized model presented in this work does take into account the complex relation between SCR strength and EFISH phase and intensity, effectively reducing the freedom of the fit by imposing this relation. The better performance of the parameterized model compared to the often-used interface-only model shows that a more detailed model of the EFISH contribution can lead to a more accurate interpretation of experimental results.

The impact of spatial extent of the SCR on the EFISH contribution can also be found back in previous experimental SHG work on *c*-Si. In some works investigating the SHG response of *c*-Si in the vicinity of the E1 critical point, a phase shift of the EFISH contribution was reported, i.e., they found a phase different from 0 or π rad. Rumpel *et al.* and Daum *et al.* report a phase shift of 0.1π rad for samples with a strong SCR caused by positive and negative built-in charge near the interface—in agreement with our model and results—but they do not interpret this phase shift further [4,17]. For weaker SCR their data does not show a clear agreement with our model; however, these *intensity-only* experiments most likely lack the sensitivity to accurately measure the phase for weaker SCR. Godefroy *et al.* did not model their SHG spectra of *c*-Si and therefore do not report on the phase of the EFISH contribution [35]. He *et al.* performed single-wavelength SHG measurements on a $\text{Si:H/SiO}_2/\text{c-Si}$ stacks that clearly show sensitivity toward the phase of the SHG signal by sweeping the applied external voltage [51]. However, they report a combined phase and did not deconvolute the phase of the EFISH contribution from the other contributions. As discussed before, in earlier work we analyzed an extensive series of samples covering a wide range of Q_f , both positive and negative, while also varying the doping density of the *c*-Si [32]. The main goal of the work was to demonstrate the quantification of the built-in charge in high- k stacks using SHG spectroscopy. To this end, a large number of spectra were fitted simultaneously to enhance the accuracy and reliability of the EFISH amplitude (directly related to the built-in charge), but this has the side effect of also enhancing the sensitivity toward the EFISH phase. The EFISH phase was found to vary with SCR strength, and the data shows excellent agreement with the trend in the phase found by the numerical model (M3) as can be seen in Fig. 3. To summarize, the impact of the spatial extent of the SCR has been observed in earlier work, and a more detailed understanding of the EFISH effect can lead to a more accurate interpretation of the (spectral) SHG response.

5. CONCLUSION

The results presented in this work show that the spatial extent of the SCR, which varies with SCR strength, has to be taken into account to accurately describe the EFISH contribution present in the SHG response of *c*-Si. The EFISH effect occurring in *c*-Si was described using a detailed numerical model, which yielded as the main insight that the phase of the EFISH contribution shifts by 0.4π rad going from a strong to a weak SCR. This shift in the EFISH phase was verified in a dedicated experiment performing complementary spectral SHG *phase and intensity* measurements on a series of samples covering the typical range of built-in charge densities. The experimental data did indeed show the same trend in the EFISH phase as predicted by the model. From the modeling it was also found that the intensity of the EFISH contribution was proportional with the square of the SCR strength, in line with earlier findings. Other parameters such as doping type and density do also impact the EFISH response to some degree, but these effects are small compared to the impact of the spatial extent of the SCR on the EFISH phase. The impact of the predicted shift in the EFISH phase was discussed in the context of the often-used interface-only model. This interface-only model neglects the spatial extent of the SCR on the EFISH effect and thus omits this significant phase shift. Doing so can introduce an appreciable error in the interpretation of SHG spectra as also illustrated by a hypothetical scenario evaluated in this work using different models to determine the built-in charge density of simulated SHG intensity spectra. This showed that using a model that neglects the significant shift in the EFISH phase—i.e., the main consequence of the spatial extent of the SCR—results in a significant error in the interpretation of the EFISH contribution.

The results presented in this work can explain the systematic variation of the phase of the EFISH contribution observed in spectral SHG measurements. Moreover, these insights are especially pertinent for single-wavelength SHG experiments where an accurate understanding of the EFISH effect is key to accurately interpret intensity changes, which are strongly affected by phase effects. The EFISH effect is also expected to occur in other semiconductors such as Ge or 2D materials such as MoS_2 , and the analysis presented in this work also applies to those materials. The latter is especially relevant given the recent interest in SHG of 2D materials [21–24,52–55] because these 2D materials are often supported on *c*-Si substrates during SHG experiments. In these experiments a significant SCR can be induced in the *c*-Si by the 2D materials, trapped charges in these materials and interfaces, or an external voltage applied over the samples in some of these experiments [56]. Furthermore, the results are also of importance in the context of the ongoing interest in *c*-Si-based photonic structures [57–61].

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