DC-electric-field-induced and low-frequency electromodulation second-harmonic generation spectroscopy of Si(001)-SiO₂ interfaces

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Abstract

The mechanism of DC-Electric-Field-Induced Second-Harmonic (EFISH) generation at weakly nonlinear buried Si(001)-SiO₂ interfaces is studied experimentally in planar Si(001)-SiO₂-Cr MOS structures by optical second-harmonic generation (SHG) spectroscopy with a tunable Ti:sapphire femtosecond laser. The spectral dependence of the EFISH contribution near the direct two-photon $E_1$ transition of silicon is extracted. A systematic phenomenological model of the EFISH phenomenon, including a detailed description of the space charge region (SCR) at the semiconductor-dielectric interface in accumulation, depletion, and inversion regimes, has been developed. The influence of surface quantization effects, interface states, charge traps in the oxide layer, doping concentration and oxide thickness on nonlocal screening

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of the DC-electric field and on breaking of inversion symmetry in the SCR is considered. The model describes EFISH generation in the SCR using a Green function formalism which takes into account all retardation and absorption effects of the fundamental and second harmonic (SH) waves, optical interference between field-dependent and field-independent contributions to the SH field and multiple reflection interference in the SiO$_2$ layer. Good agreement between the phenomenological model and our recent and new EFISH spectroscopic results is demonstrated. Finally, low-frequency electromodulated EFISH is demonstrated as a useful differential spectroscopic technique for studies of the Si-SiO$_2$ interface in silicon-based MOS structures.

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I. INTRODUCTION

Optical Second Harmonic Generation (SHG) has been one of the most intensively studied phenomena in surface and interface optics [1–3] for the last decade. The interest in SHG stems from its unique sensitivity to the structural and electronic properties of surfaces and interfaces of centrosymmetric media. This unusually high surface/interface-sensitivity comes about because, in the electric dipole approximation, SHG is forbidden in the bulk of materials with inversion symmetry [4,5], but allowed at interfaces, where inversion symmetry is broken by the discontinuity of crystalline structure. Related nonlinear sources of SHG are localized in a thin (several nanometers thick) surface or interface layer. In semiconductors, inversion symmetry is also broken by the DC-electric Field (DCF) in the subsurface Space Charge Region (SCR), which is created by initial band bending and/or external bias application. The lack of inversion symmetry in the SCR results in DC-Electric-Field Induced Second-Harmonic (EFISH) generation, which manifests itself through electromodulation of the SHG intensity. Thus, all important properties of surfaces, buried interfaces and subsurface layers - their charge [6–8], electronic surface state density [9–11], roughness (morphology) [12,13], adsorption (adatom and admolecule surface density) [14–17], initial band bending [18–20], etc. - can, in principle, be determined by means of the SHG probe.

The technological importance of Si(001)-SiO$_2$ interfaces stems from their ubiquitous presence in Metal-Oxide-Semiconductor (MOS) structures and MOS Field Effect Transistors (MOSFET). EFISH generation provides a promising noninvasive, in situ technique for characterizing interfacial imperfections and charge defects at the Si(001)-SiO$_2$ interface. Moreover, the relative simplicity of the description of the SHG response from the Si(001) face, originating from the small number of tensor components of the interface quadratic susceptibility and the rotationally isotropic interfacial SHG response, makes Si(001)-SiO$_2$ interface among the most important for investigation of fundamental aspects of the EFISH phenomenon.

The 1967 discovery of EFISH generation by Bloembergen and co-workers [21] at Si-
electrolyte and Ag-electrolyte interfaces in electrochemical cells remained largely unnoticed for a number of years. The 1981 discovery of surface-enhanced SHG by Shen and co-workers [22] rejuvenated interest in this effect. Surface-enhanced EFISH generation at a silver-electrolyte interface was observed shortly afterward [23]. Since 1984 EFISH has been systematically studied at Si(111)-electrolyte interfaces [24,25], and to a lesser extent at other semiconductor-electrolyte interfaces: Cd$_3$P$_2$ (111) [29], CdIn$_2$S$_4$ (111) [30], GaN (001) [31], TiO$_2$ [32]. These studies revealed that the strength of the DC-electric field which could be applied electrochemically was limited by interface electrochemical reactions, such as oxidation of a silicon surface at anodic potential. To circumvent this restriction, EFISH generation studies were extended to Si-SiO$_2$ MOS structures with bias applied by a ring metal [33] or semitransparent Cr [19,34] gate electrode, and to GaAs-based MOS structures [35].

A simple phenomenological model of EFISH based on the "interface field approximation" - which assumes linear dependence of the DC-field-induced nonlinear polarization on interface DCF strength and yields quadratic dependence of EFISH intensity on bias voltage - was developed for the Si-SiO$_2$-electrolyte interface in Refs. [25,26]. Since clear deviations from a quadratic bias dependence were observed [33,34], this model was improved by taking into account the nonlinear interference of DC-field induced and field-independent contributions to the nonlinear quadratic polarization as well as retardation and absorption effects [34]. Further improvement resulted from considering the spatial inhomogeneity of the DCF and the DC-electric-field-induced contribution to the nonlinear polarization [34]. These effects were later analyzed with a Green-function formalism [36,37]. At present, the most comprehensive description of the EFISH phenomenon is presented in Ref. [37]. However, this analysis remains incomplete on three points. First, it is restricted to the depletion regime of the SCR, whereas experimentally applied biases have included accumulation and inversion regimes. Moreover, as we demonstrate in this paper, the transition from depletion to inversion to accumulation drastically changes the EFISH response. Second, surface quantization effects originating from strong field localization in inversion and accumulation regimes, as
well as the role of interface states, should be taken into account. Third, multiple reflection
interference in the SiO$_2$ layer, which significantly affects the SHG intensity from Si-SiO$_2$
structures [38–40], was neglected.

In this paper we present a comprehensive phenomenological model of EFISH generation
supported by experimental spectroscopic studies of p- and n-type Si(001)-SiO$_2$-Cr MOS
structures. The key features of our model are: 1) a detailed electrophysical model of the
SCR in the accumulation and inversion regimes, which takes into account interface states
and oxide charge traps and their effect on the spatial DCF distribution in the SCR; 2) a
rigorous nonlinear optical model of EFISH in the SCR, based on a Green-function formalism,
which takes into account all retardation effects, absorption of the fundamental and SH
radiation, multiple reflection interference of both the fundamental and SH waves in the
oxide and optical interference between field-dependent and field-independent contributions
to the quadratic nonlinear polarization. The key feature of our experiments is comprehensive
observation of the dependence of SHG on numerous parameters, including applied bias,
azimuthal sample rotation, wavelength near the direct two-photon $E_1$ transition, doping
concentration, and oxide thickness. These combined dependences allow us to deconvolve
the EFISH contribution fully from field-independent contributions. The non-quadratic bias
dependence of the EFISH intensity predicted in Refs. [32,37], and its variation with doping
concentration, oxide thickness, interfacial state density, and wavelength, is observed and
analyzed in detail.

II. THEORETICAL BACKGROUND

A. Quadratic optical response of the Si-SiO$_2$ system

In the presence of a DCF the nonlinear polarization of a centrosymmetric semiconductor
at the second-harmonic (SH) wavelength is given by [11,42]:

$$ P^{NL} = P^S + P^{BQ} + P^{BD}, $$ (1)
where \( P^S \) is the surface nonlinear polarization, \( P^{BQ} \) is the bulk quadruple contribution, and \( P^{BD} \) is the bulk dipole DCF induced polarization. The last contribution is governed by the fourth-rank cubic susceptibility tensor \( \chi^{(3)} \) and can be written phenomenologically as

\[
P^{BD} = \chi^{(3),BD}(2\omega;\omega,\omega,0) : E(\omega)E(\omega)E_0,
\]

where \( E(\omega) \) and \( E_0 \) are the amplitudes of the fundamental radiation and DCF strength inside the semiconductor, respectively. For crystals such as Si and Ge of point group symmetry \( O_h \), \( \chi^{(3),BD} \) has 21 nonzero tensor components \([20]\), of which only three are nonequivalent.

The bulk quadrupole contribution in the plane-wave approximation is given by

\[
P^{BQ} = \chi^{(2),BQ}(2\omega;\omega,\omega) : E(\omega)ik(\omega)E(\omega),
\]

where \( \chi^{(2),BQ} \) is a fourth-rank tensor which represents the quadrupole contribution to the quadratic nonlinear susceptibility from spatial dispersion and \( k(\omega) \) is the wavevector of the fundamental radiation in the semiconductor. \( \chi^{(2),BQ} \) has the same symmetry properties as \( \chi^{(3),BD} \).

For the surface contribution to \( P^{NL} \) the multipole expansion is hardly expected to be valid, and we suppose that \([43]\): 

\[
P^S = \chi^{(2),S}(2\omega;\omega,\omega) : E(\omega)E(\omega),
\]

where \( \chi^{(2),S} \) is a third-rank tensor representing an effective quadratic susceptibility of the surface layer, which includes a local part from breaking of inversion symmetry at the surface, and a nonlocal part from the discontinuity of the normal electric field component at the surface. The structure of \( \chi^{(2),S} \) depends on the particular crystalline face under consideration.

The SH electromagnetic field \( E(2\omega) \) is found by solving the inhomogeneous wave equation for propagation of the SH wave with \( P^{NL} \) as a source term \([43,44]\). The solution can be written formally in terms of the tensorial Green-function \( \tilde{G}(\mathbf{r},\mathbf{r}',2\omega) \), which is defined to be the solution of the wave equation with a point source at \( \mathbf{r}' \). Since translational symmetry in the interface plane is assumed, the SH field is given by
where \( k_{||} \) is the in-plane component of the SH wavevector. Hereafter we use the \( xyz \) coordinate frame with the \( xy \) plane coinciding with the interface and the positive \( z \)-axis directed toward the semiconductor bulk. Expressions for the components of \( \hat{G} \), are calculated in Refs. [43,44]. The DCF induced part of the SH field is given by:

\[
E_{BD}(z, k_{||}, 2\omega) = F_{2\omega} F_{\omega}^{2} \chi_{BD}^{eff} I_{\omega} \times \int_{0}^{+\infty} E_{0}(z') \exp \left(i \left(k_{2\omega,z} + 2k_{\omega,z}\right) z'\right) dz'
\]

where the scalar factor \( \chi_{BD}^{eff} \) is a linear combination of components of \( \chi_{BD}^{(3)} \) which depends on the experimental geometry, \( I_{\omega} \) is the intensity of the fundamental radiation, \( k_{\omega,z} \) and \( k_{2\omega,z} \) are the normal wavevector components of the fundamental and SHG radiation, respectively, in the semiconductor, the unit vector \( p \) defines the polarization of the EFISH field, and \( F_{\omega} \) and \( F_{2\omega} \) are the transmission factors which include Fresnel coefficients and a correction for multiple reflection in the silicon oxide at both \( \omega \) and \( 2\omega \). Eq.(6) properly takes into account retardation, the penetration depth of the fundamental wave, the escape length of the SH wave and multiple reflection interference effects in oxide layer.

**B. DC-electric-field spatial distribution**

To perform the integration in Eq.(6) one must know the spatial distribution \( E_{0}(z) \) across the SCR. In this section we consider the screening of this DCF within the framework of Fermi carrier statistics [45–47]. The spatial distribution of the electrostatic potential \( \varphi(z) \) in the planar semiconductor-dielectric system can be found as a solution of the one-dimensional Poisson equation:

\[
\frac{\partial}{\partial z} \left( \epsilon \frac{\partial}{\partial z} \varphi \right) = 4\pi n,
\]

where \( \epsilon \) is the static dielectric constant of the semiconductor (dielectric) and \( n = n(z) \) is the space charge density. The boundary conditions for Eq.(7) are:
\[ \varphi(+\infty) = \mu, \]

\[ \varphi(-D) = \mu + \varphi_0, \quad (8) \]

where \( \mu \) is the chemical potential of the semiconductor and \( D \) is the thickness of the oxide film. The first equation in (8) is a statement of charge neutrality in the bulk of the semiconductor. The second equation takes into account the application of external potential \( \varphi_0 \) to the metal electrode with respect to the semiconductor. We divide the charge density into field independent and field dependent terms:

\[ n = n_{fi} + n_{fd}, \quad (9) \]

where \( n_{fi} \) includes the density of the ionized donors \( N_D \) and acceptors \( N_A \), and fixed charge \( n_{ox} \) trapped in the oxide layer near the semiconductor-dielectric interface:

\[ n_{fi} = N_D + N_A + \delta(z + 0)n_{ox}, \quad z \geq 0. \quad (10) \]

Hereafter \( z = +0 \) and \( z = -0 \) denote positions near the interface just inside the semiconductor and just inside the dielectric, respectively.

The spatial distribution \( n_{fd}(z) \) is, in principle, a nonlinear functional of the potential \( \varphi \) at all points inside the semiconductor. However, first we find expressions for \( n_{fd}(z) \) and \( E_0(z) \) within the model of local screening of the DCF in a Fermi electron-hole gas, in which \( n_{fd}(z) \) depends on the potential \( \varphi \) at point \( z \), i.e. \( n_{fd}(\varphi) = n_{fd}(\varphi(z)) \). The field-dependent part of charge density consists of the concentration of holes \( n_h \), electrons \( n_e \), and interface traps \( n_{it} \), which depend on the interface potential:

\[ n_{fd}(z) = n_h(\varphi(z)) + n_e(\varphi(z)) + \delta(z - 0)n_{it}(\varphi(z = +0)), \quad z \geq 0. \quad (11) \]

Since we assume that the SHG response comes from the semiconductor or semiconductor-dielectric interface, we treat charges in the oxide layer as an effective fixed trapped charge \( n_{ox} \). Since at \( z > 0 \) the variable \( z \) does not enter into Eq.(10,11) explicitly and the charge density \( n_{fd} \) depends on the coordinate via \( \varphi(z) \), the Poisson equation (7) has the first integral:
\[ E_0^3(\varphi) = \frac{8\pi}{\epsilon} \int_{\varphi + \mu}^{\mu} n(\varphi') d\varphi'. \]  

(12)

Using the charge neutrality condition in the bulk of the semiconductor for completely ionized donors and acceptors yields

\[ N_D = e N_C \Phi \left( \frac{\mu - \varepsilon_C}{kT} \right), \]  

(13)

\[ N_A = -e N_V \Phi \left( \frac{\varepsilon_V - \mu}{kT} \right). \]  

(14)

Eqs. (10, 11) have the form:

\[ n_{fd}(\varphi(z)) = e N_V \Phi \left( \frac{\varepsilon_V - \varphi}{kT} \right) - e N_C \Phi \left( \frac{\varphi - \varepsilon_C}{kT} \right) + \delta(z + 0)n_{it}, \]  

(15)

\[ n_{fi} = e N_C \Phi \left( \frac{\mu - \varepsilon_C}{kT} \right) - e N_V \Phi \left( \frac{\varepsilon_V - \mu}{kT} \right) + \delta(z - 0)n_{ox}, \]  

(16)

where

\[ \Phi(\tau) = \frac{2}{\sqrt{\pi}} \int_{0}^{\infty} \sqrt{x} \left(1 + \exp (x - \tau)\right)^{-1} dx, \]  

(17)

is the Fermi-Dirac integral; \( N_V \) and \( N_C \) are the density of states in valence and conduction bands, respectively, which depend on density-of-state and effective mass of electrons or holes; \( \varepsilon_V \) and \( \varepsilon_C \) are the energies of the upper level of the valence band and the lower level of the conduction band, respectively; \( k \) is the Boltzmann constant, and \( T \) is the temperature.

Interface traps are charged mid-gap states at the semiconductor-dielectric interface resulting from interruption of the semiconductor lattice structure or interface imperfections. As the interface electrostatic potential changes, the trap levels move up or down while the Fermi level remains fixed. Interface trap density \( n_{it} \) is defined in terms of the energy distribution \( L^{A,D}(E) \) of trap levels across the semiconductor band gap:

\[ n_{it}(\varphi) = e \int_{\varphi}^{\varepsilon_C} \left(L^D(E - e\varphi)F^D(\mu - E + e\varphi) - L^A(E - e\varphi)F^A(\mu - E + e\varphi)\right)dE, \]  

(18)

where superscripts \( A,D \) denote acceptor or donor traps, and \( F^A \) and \( F^D \) are Fermi distribution functions.
\[ F^{A,D}(\tau) = \left( 1 + g^{A,D} \exp\left( \pm \frac{\tau}{kT} \right) \right)^{-1}, \quad (19) \]

where coefficients \( g^A = 1/4 \) and \( g^D = 2 \) reflect the ground-state degeneracy of the acceptor and donor levels. The specific form of \( L^{A,D}(E) \) depends on the preparation of the semiconductor-dielectric system. In the calculations we model this distribution as a set of Lorentz functions.

Figure 1 shows the distributions \( \varphi(z) \) and \( E_0(z) \) across the SCR of p-doped silicon modelled within the above framework. In the depletion regime, where the Schottky approximation is valid, \( \varphi(z) \) is close to a parabolic function. For larger applied bias corresponding to inversion, the SCR divides into a thin subsurface region of rapidly changing potential, and a long tail of gradually decreasing potential. The transition depth \( z_0 \) between these two regions lies at several nanometers. In the accumulation regime, \( \varphi(z) \) drops completely within \( z_0 \).

C. The role of surface quantization effects in the subsurface region

The large gradient of the subsurface \( \varphi(z) \) for accumulation and inversion regimes requires that quantum effects be considered in the screening of the DCF. We take them into account via self-consistent calculations \[48\], using the Hartree-Fock (HF) approach to describe the exchange electron interaction. In the following we consider the screening of a ”positive” (in the above notation) external potential in the subsurface region by electrons, with negligible contribution from holes. The opposite case of ”negative” potential is treated similarly.

The HF equation for the single-electron wave function \( \psi_i(\mathbf{r}) \) is given by:

\[
\frac{\hat{p}^2}{2m} \psi_i(\mathbf{r}) + e^2 \sum_{j \neq i} < \psi_j(\mathbf{r}) | (\epsilon | \mathbf{r} - \mathbf{r}' |)^{-1} | \psi_j(\mathbf{r}') > \psi_i(\mathbf{r}) -
\]

\[
- e^2 \sum_{j \neq i, |\text{spins}|} < \psi_j(\mathbf{r}') | (\epsilon | \mathbf{r} - \mathbf{r}' |)^{-1} | \psi_i(\mathbf{r}') > \psi_j(\mathbf{r}) + U_0(\mathbf{r}) \psi_i(\mathbf{r}) = E_i \psi_i(\mathbf{r}), \quad (20)
\]

where \( U_0(z) = -E_0 z + \int n_{fi}(\mathbf{r}') (\epsilon | \mathbf{r} - \mathbf{r}' |)^{-1} d^3 r' \) and the sum in the exchange (third) term is over states with parallel spins; brackets denote averaging over the stationary state.
Because of translation symmetry in the $x, y$-plane $\psi_i(r) = \tilde{\varphi}_i(z) e^{i p_i r ||}$. We consider the case in which only one energy state for the subsurface electronic-motion is responsible for most of the screening. This is confirmed by the numerical results. We also assume $\tilde{\varphi}_i(z) = \tilde{\varphi}(z)$ to be independent from $p_i$. Then Eq.(20) may be written in the form of a Schrödinger equation with self-consistent potential $U_z$:

$$E\tilde{\varphi}(z) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial z^2} \tilde{\varphi}(z) - U(z)\tilde{\varphi}(z),$$

where

$$U(z) = -E_0 z + \int \frac{n(r')C(r, r') + n_{fi}(r')}{e|\mathbf{r} - \mathbf{r}'|} d^3 r',$$

$$n(r) = \langle \hat{n}(\mathbf{r}) \rangle = e \sum_{\mathbf{K}} \psi_{\mathbf{K}}(\mathbf{r}) \psi_{\mathbf{K}}^*(\mathbf{r}) f(E_{\mathbf{K}}),$$

$$\hat{n}(\mathbf{r})$$ is the density operator, $f(E_k) = 1/(1 + e^{(E_k - \mu)/kT})$ is the Fermi occupation factor,

$$C(\mathbf{r} - \mathbf{r}') = 1 - \frac{e^2}{n(\mathbf{r})n(\mathbf{r}')} \sum_{j \neq i, ||\text{spins}} f(E_j) f(E_i) e^{i(p_i - p_j)(\mathbf{r} - \mathbf{r}')}.$$

$C(\mathbf{r} - \mathbf{r}')$ can be interpreted physically as a correlation function for the in-plane motion of electrons. Boundary conditions for the wave function are given by

$$\tilde{\varphi}(0) = 0, \quad \tilde{\varphi}(z_0) = 0.$$

From the equations above one can show that the potential $U(z)$ obeys the following equation for the 2D-system under consideration:

$$\frac{dU}{dz} = -E_0 + \frac{2\pi}{\epsilon} \int dz' (n(z') F(z - z') + n_{fi}(z') \text{sgn}(z - z')),$$

where

$$F(z) = \int \frac{\text{sgn}(z)C(\rho||z|)}{(1 + \rho^2)^{3/2}} \rho d\rho.$$

The electrostatic potential $\varphi(z)$ obeys the equation

$$\frac{d\varphi}{dz} = -E_0 + \frac{2\pi}{\epsilon} \int dz' (n(z') + n_{fi}(z')) \text{sgn}(z - z'),$$
which can be derived from the Poisson equation.

Eqs. (26, 28) differ one from another by the factor $F(z)$ in Eq. (20). It can be shown that since $C(r) \to 1$ at $r \to \infty$, $F(z) \to 1$ at $z \to \infty$. Therefore, the self-consistent potential $U(z)$ is closely related to $\varphi(z)$. Moreover, remote charge layers contribute equally to $U(z)$ and $\varphi(z)$. Nevertheless, the electrostatic and self-consistent potentials are distinguished by the role of quantum-correlation effects in the electron plasma. The electrostatic potential describes interactions of a charged probe particle with other charges only via the electromagnetic field. The self-consistent potential $U(z)$ also includes the electron’s tendency to "wedge" itself into other electrons and repulse them via the exchange interaction, and therefore differs fundamentally from $\varphi(z)$. On the other hand, the EFISH bias dependence is expressed in terms of the classical potential $\varphi(z)$, because the major contribution to the semiconductor optical response comes from bound electrons, whereas screening in the semiconductor is caused by free carriers, and there are no correlation effects between these two different types of particles.

Summarizing this section, we have obtained a set of Eqs. (21, 23, 24) for the self-consistent potential $U(z)$, electron wave function $\psi_i(r)$ and charge density $n(z)$. These equations describe the screening in the immediate subsurface region $z < z_0$. This approach takes into account correlation effects in the electronic liquid via the factor $F(z)$ which is related to the in-plane correlation function $C(|r|| - r'||)$.

D. Numerical experiment

In this section the model bias dependence of the EFISH intensity is found by numerical integration of the Poisson equation and the wave equation. First, the dependence of the EFISH intensity on the doping of the semiconductor is taken into account. Then, the influence of parameters of the semiconductor-insulator interface on the amplitude of the EFISH wave is considered.

To find the DCF induced SH field amplitude $E^{BD}$ for applied bias $U$, $E_0(z)$ has been
calculated by numerically solving the first integral of the Poisson Equation (7) with the charge densities given by Eqs.(15,16). The boundary condition at the surface of the metal electrode of MOS structure is given by $\varphi_0 = U$. $U$ is related to the interface field $E_{\text{int}} = E_0(z = +0)$ and interface potential $\varphi_{\text{int}} = \varphi(z = +0)$, by

$$U = \epsilon_s \epsilon_d^{-1} E_{\text{int}}(\varphi_{\text{int}}) D + \varphi_{\text{int}}. \quad (29)$$

The parameters of silicon, which is used as a model semiconductor, have been taken from Ref. [49]. According to Eq.(6), the EFISH field $E^{BD}$ is a product of the integral

$$I(U) \equiv I_1 + iI_2 = \int_0^{+\infty} E_0(z) \exp(i (k_{2\omega,z} + 2k_{\omega,z}) z) dz, \quad (30)$$

and the complex factor $F_{2\omega} F_{\omega}^{2\chi_{eff}}$, which is a bias-independent constant for a given fundamental wavelength. This allows us to neglect the complex value of the latter term and simulate the bias dependence of $I_1(U)$ and $I_2(U)$ by the bias dependence of Re$E^{BD}$ and Im$E^{BD}$ in units of $|F_{2\omega} F_{\omega}^{2\chi_{eff}}|$. This notation is used in the numerical experiment shown in Figs. 2, 4 and 5. Figure 2 shows Re$E^{BD}$ and Im$E^{BD}$ as functions of the bias applied to the MOS structure, calculated by evaluating the integral in Eq.(3) for different dopant concentrations of a n-type silicon wafer covered by silicon oxide film 19 nm thick. The fundamental radiation wavelength is presumed to be 730 nm.

Two important trends in these curves are noteworthy. First, Im$E^{BD}$ depends strongly on the bias only in the region of negative biases between 0 V and a saturation bias we denote as $U_0$. Outside of this interval the amplitude of the EFISH field saturates. This strongly contradicts the previous phenomenological assumption that the amplitude of the EFISH field depends linearly (and the EFISH intensity quadratically) on the applied bias. The saturation of the imaginary part of the EFISH field amplitude for $U < U_0$ and $U > 0$ is attributed to the inversion and accumulation regimes of the external bias screening in the SCR (see inset in Fig. 1) as the DCF is mostly localized inside a thin subsurface layer of nm-scale thickness. Since the imaginary part of the Green’s function is equal to zero exactly at the interface, Im$E^{BD}$ becomes practically insensitive to the DCF inside the inversion and...
accumulation layers. Thus $U = U_0$ and $U = 0$ define end-points of a bias region which corresponds to the depletion regime; the interface potential $\varphi_0$ for external bias $U_0$ is equal to $2(\varepsilon_i - \mu)$, where $\varepsilon_i$ is the midgap energy [50].

Second, decrease of dopant concentration leads to the decrease of the absolute value of $U_0$ and $E_{BD}$. Figure 3 shows the dependence of the absolute value of $U_0$ on the dopant concentration of the n-type silicon wafer for various oxide thicknesses. For dopant concentrations larger than $10^{16} \text{ cm}^{-3}$, the absolute value of $U_0$ scales approximately as the square root of $N_D$, while for smaller doping levels $|U_0|$ scales as $\ln N_D$, as is clearly shown in the inset of Fig. 3. Applied bias $U_0$ according to Eq.(29) consists of voltage drops $\varepsilon_sc \varepsilon_d^{-1} E_0(\varphi_0)D$ across the oxide film, and $\varphi_0$ across the silicon SCR. Within the Schottky approximation for the SCR [47], the interface potential $\varphi_0$ and interface field $E_0$, corresponding to applied bias $U_0$ are given by

$$E_0 = 2\sqrt{\xi \varphi_0}, \quad \varphi_0 = 2(\varepsilon_i - kT \ln(N_D N_C^{-1})), \quad \xi = 2\pi e N_D \varepsilon_{sc}^{-1}. \quad (31)$$

Therefore, for high doping levels the applied bias mostly drops across the oxide layer and $U_0(N_D) \propto E_0(N_D) \propto \sqrt{N_D \ln(N_D N_C^{-1})}$. For low doping the interface potential dominates and $U_0(N_D) \propto \varphi_0(N_D) \propto \ln(N_D N_C^{-1})$. For thinner oxide layers, less of the applied voltage is dropped across the oxide and the transition from a logarithmic to a square root doping dependence of $U_0$ occurs at a higher doping level.

Figure 4 shows the EFISH amplitudes for applied bias $U_0$ as functions of donor concentration, $N_D$. Over a wide range of concentrations Re$E^{BD}$ and Im$E^{BD}$ depend on the square root of $N_D$. The latter can be explained by integrating Eq.(11) with a linear DCF $E(z) = E_0 - 2\xi z$ across the SCR, as in the Schottky model. This integration yields the following expressions for the EFISH field:

$$\text{Re}E^{BD} \propto E_0 \Delta_2 + 2\xi \frac{\Delta_1^2 - \Delta_2^2}{\Delta_1^2 + \Delta_2^2}; \quad (32)$$

$$\text{Im}E^{BD} \propto E_0 \Delta_1 - 4\xi \frac{\Delta_1 \Delta_2}{\Delta_1^2 + \Delta_2^2}; \quad (33)$$
where $\Delta_1 = \text{Re}(2k_\omega + k_{2\omega})$ and $\Delta_2 = \text{Im}(2k_\omega + k_{2\omega})$. Since the interface field $E_0 = 2\xi W$ depends linearly on the width of the SCR, the restrictions $W\Delta_1 >> 1$ and $W\Delta_2 >> 1$ lead to the following expression for the complex SH field: $E^{BD} \propto E_0(\Delta_2 + i\Delta_1) \propto \sqrt{N_D \ln(N_D N_C^{-1})}$. Thus $\text{Re}E^{BD}$ and $\text{Im}E^{BD}$ scale approximately as the square root of $N_D$. Furthermore, $\text{Im}E^{BD}/\text{Re}E^{BD} = \Delta_1 \Delta_2^{-1}$, i.e. the ratio of $\text{Re}E^{BD}$ to $\text{Im}E^{BD}$ is the ratio of the characteristic length scale of absorption, $\Delta_2^{-1}$, to that of retardation, $\Delta_1^{-1}$, for the SH waves. As the energy of the 365 nm SH photon used in our calculations is close to the $E_1$ critical point of silicon, $\Delta_1 = (1/5.7)\text{nm}^{-1}$ and $\Delta_2 = (1/21.5)\text{nm}^{-1}$ are sufficiently large to satisfy the conditions $W\Delta_1 >> 1$ and $W\Delta_2 >> 1$ for dopant concentrations up to $10^{18}\text{cm}^{-3}$ (Fig. 4). As shown in the inset of Fig. 4, the ratio $\text{Im}E^{BD}/\text{Re}E^{BD}$ is close to the value of $\Delta_1\Delta_2^{-1} = 3.89$.

E. The role of interface states in the EFISH phenomenon

A sheet of charged interface states changes the relationship between a potential drop across silicon and an applied bias due to the boundary condition for normal components of the electric displacement vector $D$. To demonstrate the role of interface traps in the EFISH phenomenon we consider the distribution of trap levels across the silicon band gap as a set of Lorentz’s functions. The charge density of interface traps $n_{it}$ as a function of the interface electrostatic potential is given by

$$n_{it}(\varphi(z = 0)) = e \int_{E_V}^{E_C} dE \sum_M \text{sgn}(n_{it}^M) F^M(\mu + e\varphi - E) \times$$

$$\times \sum_j N_{M,j} \delta_{M,j}^2 \left(\delta_{M,j}^2 + (E - \varepsilon_{0M,j})^2\right)^{-1}, \quad (34)$$

where $M = A, D$, $j$ numerates Lorentz functions of the energy distribution of the trap levels. $N_{M,j}, \delta_{M,j}$ and $\varepsilon_{0M,j}$ denote the effective number of traps per unit area, the width and central position of $j$-th Lorentz peak, respectively. These Lorentz functions simulate the continuous energy distribution of traps. By setting $\delta_{M,j} \to 0$ one can account for discrete levels.

Figure 5 shows the bias dependence of $\text{Re}E^{BD}$ and $\text{Im}E^{BD}$ for the MOS structure used in our experiment which is comprised of n-type Si with a donor concentration of $10^{18}\text{cm}^{-3}$.
and a 19-nm thick thermal SiO$_2$ layer. Interface traps are presumed to be acceptors with $N_A = 10^{13} \text{traps} \cdot \text{cm}^{-2} \text{eV}^{-1}$ and $\delta_A = 0.5 \, kT$. Different central positions are considered: $\varepsilon_{0A} = \mu$ (thin lines), $\varepsilon_{0A} - \mu = -10 \, kT$ (thick lines) and $\varepsilon_{0A} - \mu = -20 \, kT$ (dashed lines). The distribution of such traps across the silicon band gap is sketched at the inset in Figure 5. The dotted lines are presented for comparison to the same field components in the absence of traps. For negative biases in the inversion regime, bands are bent in such a way that all the trap levels are above the Fermi energy, acceptor traps are empty and bias dependence of the SH field components is unaffected by the presence of these uncharged traps. As the magnitude of the negative bias is decreased, the bands are bent less and trap levels begin to fall below the Fermi energy, first the traps with low energy levels, then those with higher energy. Consequently, the bias dependence of $\text{Re} E^{BD}$ and $\text{Im} E^{BD}$ for low energy acceptor traps starts to deviate from the dependence for $N_A = 0$, demonstrating the saturation-like feature. This is attributed to the pinning of the Fermi level. As the level of the neutral traps crosses the Fermi energy, the charge density of interface traps changes and application of a smaller bias leads to a decrease in the voltage drop across the oxide film while the interface potential and the DCF spatial distribution remain fixed until the trap level is completely filled. The bias dependence of $\text{Re} E^{BD}$ and $\text{Im} E^{BD}$ for $N_A \neq 0$ passes through the SHG intensity zero-point for a flatband voltage $U_{fb}$, which depends linearly on the interface charge $n_{it}$. In the case of donor interface traps the same effects are obtained, but the bias dependence of $\text{Re} E^{BD}$ and $\text{Im} E^{BD}$ for $N_D = 0$ and $N_D \neq 0$ differ in the inversion regime.

III. RESULTS AND DISCUSSION

A. Experimental

For the EFISH experiments the output of an unamplified Ti-Sapphire laser ranging from 710 to 800 nm was used. The Ti-sapphire laser generates 120-fs pulses with average power
of 200 to 300 mW, which is well below the damage threshold of the semiconductor. The p-polarized beam was focused onto the sample at a 45° angle of incidence. Reflected p-polarized SHG signal was selected by the use of appropriate filters and directed into a photon-counting system. High intensity, high repetition rate, short pulses provided a good signal-to-noise ratio in our experiments while avoiding significant sample heating. A small split off portion of the fundamental beam was focussed through a z-cut quartz crystal that provided a reference SHG signal.

The MOS structures were fabricated from two types of Si(001) wafers: (I) - a highly-doped n-type (10^{18} cm^{-3}, Sb doped) wafer covered by a 19 nm thick SiO_2 film, and (II) - a low-doped p-type (1.5 \cdot 10^{15} cm^{-3}, B doped) wafer with a 8.7 nm thick SiO_2 film. A 3 nm semitransparent chromium cap layer, and an ohmic aluminum backside electrode were evaporated onto the samples. Single-wavelength ellipsometry was used to measure the SiO_2 thicknesses. As an independent calibration of the flatband voltage, spatially resolved surface photovoltage measurements were performed on the same samples. The external bias voltage was applied between the chromium and aluminum electrodes. The SHG response from the chromium layer was verified to be negligible in comparison with the SHG signal from the buried Si(001)-SiO_2 interface.

The bias dependence of the rotational azimuthal anisotropy of the EFISH intensity was measured over a wide range of the bias voltages at various fundamental wavelengths from 710 nm to 800 nm. Figure 6 shows the azimuthal dependence of the EFISH intensity measured for an n-Si(001) MOS structure. The pronounced four-fold symmetric anisotropy of the EFISH intensity superimposed on a significant isotropic (i.e. independent from the azimuthal angle) background was observed at most biases. Variation of the applied voltage changes the amplitudes of both the four-fold symmetric and isotropic contributions, both of which increase with increasing the absolute value of the bias. At the center of the applied bias region near -2.75 V (upper panel) azimuthal dependence possesses a significant eight-fold symmetric component, which appears to be comparable with isotropic and four-fold components for the same bias. As the applied voltage passes through this bias the phase of the anisotropy shifts
by \(\pi/4\). Similar features of the field-induced rotational anisotropy were observed throughout the studied spectral range. Figure 7 shows the azimuthal dependence for a p-MOS structure which demonstrates similar behavior, except that the eight-fold symmetric component is observed at -1.2 V and the isotropic component is appeared to be quite larger than the four-fold one.

**B. EFISH at Si(001)-SiO\(_2\) interface: Role of the spatial DCF distribution**

The azimuthal angular dependence of the SHG intensity from the Si(001)-SiO\(_2\) interface in the presence of the DCF can be described phenomenologically as optical interference of DC-field dependent, isotropic and DC-field independent, four-fold symmetric components of the SH field:

\[
I_{2\omega}(\psi, V) = |a(V) + b \cos(4(\psi - \psi_0))|^2 = 
\]

\[
= c_0(V) + c_4(V) \cos(4(\psi - \psi_0)) + c_8 \cos(8(\psi - \psi_0)),
\]

(35)

where \(\psi_0\) is the azimuthal angle of a maximum of rotational anisotropy, \(a\) and \(b\) are the amplitudes of isotropic and anisotropic components of the SH field. The surface, \(P^S\), and the bulk DCF induced, \(P^{BD}\), components of the nonlinear polarization, \(P^{NL}\), contribute to the isotropic component \(a\) while the four-fold symmetric component originates from the bulk quadruple polarization, \(P^{BQ}\). For the sake of simplicity we put the amplitude \(b\) of the four-fold symmetric anisotropic component as a real quantity and define the phase of the isotropic component \(a = a' + ia''\) with respect to \(b\). As a result the dependence of the EFISH intensity on the azimuthal angle, \(\psi\), is given by a Fourier expansion (35) with 0-th, 4-th and 8-th Fourier components:

\[
c_0 = a'^2 + a''^2 + \frac{1}{2}b^2, \quad c_4 = 2a'b, \quad c_8 = \frac{1}{2}b^2.
\]

(36)

Figure 8 shows the bias dependence of the isotropic Fourier component of the EFISH intensity (left panel) and of the normalized four-fold Fourier component \(c_4\left(2\sqrt{2c_8}\right)^{-1}\) (right
panel), which is exactly the $a'$ component of the EFISH field. The eight-fold symmetric component, $c_8$, appears to be field-independent throughout the range of applied biases. The error bars are the averaged amplitudes of Fourier components $c_1$ and $c_3 \left(2\sqrt{2}c_8\right)^{-1}$. The component $c_0(U)$ is quadratic with a minimum at -3.1 V. The $a'$ component passes through zero-point also at about -3.1 V and depends on bias nearly linearly with pronounced deviations from linearity at the edges of the bias range. These bias dependences have been fitted within the model described above with the amplitude of the field-independent part of $a$ and the flatband voltage $U_{fb}$ as adjustable parameters. Figure 8 shows the model results with $U_{fb} = 0.7$ V by solid curves which agree well with the experimental data. The obtained value of the flatband voltage significantly differs from either minimum of $c_0(U)$ or the bias for which $a' = 0$. This difference is attributed to the optical interference of the DCF dependent (bulk) and DCF independent (surface) contributions to $a$. For this highly doped MOS structure the entire 8 V range of applied biases of corresponds to the depletion regime.

Figures 9 and 10 show the bias dependence of $c_0$ and $a'$ for the p-MOS structure. The quadratic behavior of $c_0(U)$ with a minimum at -1.25 V and approximately linear dependence of $a'(U)$ with deviations at the limits are similar to the trends of the n-MOS structure. The model of the experimental data with dopant concentration of $1.5 \cdot 10^{15}$ cm$^{-3}$, shows a clear step-like feature near the center bias which corresponds to the depletion regime of the SCR in p-type silicon. However, such peculiarity has not been observed experimentally. This discrepancy between the model and experiment occurs for the surface-quantization calculation as well, because at these small biases the surface-quantization effects are not of importance.

One possible explanation for the experimentally measured bias dependences is the influence of photoinduced effects on the EFISH intensity. The absorption of femtosecond laser pulses leads to the excitation of electron-hole pairs in the SCR. The DCF in the SCR separates these photo-induced carriers and the density of the charge injected into SCR for the pulse duration $\tau \sim 120$ fs is on the order of $10^{17}$ cm$^{-3}$ [6]. The presence of these extra charges should lead to a decrease of the SCR width. Systematic theoretical description of this effect
requires a model that rigorously accounts for the kinetics of electron-hole recombination in the subsurface layer. In our model the parameter responsible for the SCR width is the dopant concentration. Therefore, photoinduced effects can be *effectively* taken into account by variation of $N_D$. Thick curves in Figures 9 and 10 show the fit with $N_D = 10^{17}$ cm$^{-3}$, which is two orders of magnitude larger than the actual dopant concentration. For such a doping level the range of biases which correspond to the depletion regime is sufficiently larger (about 4 V) and the transition from depletion to inversion and accumulation occurs more gradually than for a lower doping level. Much better agreement of the model with experimental data is achieved.

For biases larger then 4 V, which correspond to the strong inversion regime, clear deviations of the model from experimental data are obtained. This is attributed to the strong localization of DCF inside a very thin subsurface layer where the bulk description of the DCF screening is hardly expected to be valid and one should take into account surface quantization effects. The dashed curve shows the approximation of the data by the model with quantum corrections, which demonstrates a better agreement with experimental data points in this bias region.

**C. The EFISH spectroscopy: Bulk origin of DC-field-induced contribution**

Tuning the fundamental wavelength in the vicinity of the direct two-photon $E_1$ transition allows measurement of the spectrum of the EFISH intensity and deconvolution of the bulk and red-shifted surface contributions to the SHG signal [9,11,51]. Figure 11 shows the bias dependence $c_4(U)$ for various wavelengths of the fundamental radiation, $\lambda_\omega$. Tuning of $\lambda_\omega$ from 800 nm to the two-photon resonance near 3.4 eV ($\lambda_\omega = 730$ nm) produces stronger bias dependence of both $c_4(U)$ and $c_0(U)$. Further decrease of $\lambda_\omega$ results in a reduced bias dependence. The bulk quadrupole component of the SH field, $b \equiv E_{anis}^{BQ}$, contributes to both the isotropic, $c_0$, and the four-fold symmetric, $c_4$, Fourier components. To extract the spectral dependence of the EFISH field, $E_{BD}$, one must find the spectrum of $|E_{anis}^{BQ}|$. The
latter has been obtained from the spectrum of the eighth Fourier component $c_8$ averaged over the entire bias region. Integration of the product of the Green’s function and the bulk quadrupole polarization, according to Eq. (3), gives the spectral behavior of $|E^{BQ}_\text{anis}|$ in the form:

$$
|E^{BQ}_\text{anis}(\Omega)| = I_\omega \left| \frac{k^2_{w,z}(\Omega)}{k_{2w,z}(\Omega) + 2k_{w,z}(\Omega)} \right| \left| F^2_\omega(\Omega) F_{2\omega}(\Omega) \right| \left| \chi^{(2),BQ}(\Omega) \right|. \quad (37)
$$

Hereafter, $|\chi^{(2),BQ}(\Omega)|$ is the magnitude of a combination of $\chi^{(2),BQ}$ tensor components responsible for the four-fold symmetric part of $P^{BQ}$. $I_\omega$ is the fundamental intensity. Figure 12 shows the spectrum of the magnitude of the effective quadruple susceptibility $|\chi^{(2),BQ}(\Omega)|$. The filled symbols in Figure 12 show the spectral dependence of the effective cubic susceptibility $\chi^{(3),BQ}$ extracted from the set of the bias dependences $c_0(V, \lambda)$. Both spectral dependences of $|\chi^{(2),BQ}(\Omega)|$ and $|\chi^{(3),BD}(\Omega)|$ peak at approximately 3.4 eV and have been fitted by a single Lorentz function with a real spectral background:

$$
\chi^M(\Omega) = \alpha + \frac{\beta}{\Omega - \omega_M + i\delta}, \quad (38)
$$

with $M = BQ, BD$. The solid curves in Figure 12 show the spectral fits of $|\chi^{(2),BQ}(\Omega)|$ and $|\chi^{(3),BD}(\Omega)|$ by Eq. (38) with the parameters presented at Table I. The values of resonance positions obtained are shown to be close to 3.38 eV. This is consistent with the energy of the bulk $E_1$ critical point as known from linear spectroscopy and fully indicates a bulk origin of the EFISH response.

**D. Low-frequency electromodulation SHG spectroscopy of Si(001)-SiO₂ interface**

Modulation techniques are widely used in optical spectroscopy [52] because of their sensitivity. The right side of Fig. 13 shows the schematic of the low-frequency electromodulation of the SHG signal from Si-SiO₂ interface in a MOS structure by the application of the superposition of DC-bias $U$ and low-frequency squarewave modulation voltage $\Delta U(\Omega)$ with the amplitude $\Delta U$ and frequency $\Omega$. Microwave frequency and pulse-voltage modulation of the
SHG response in Si-based MOS structures were studied in Refs. [37] and [33], respectively. Low-frequency electromodulation SHG from GaN surface in electrochemical cell was studied in Ref. [31].

The efficiency of the modulated SHG signal \( \alpha(U, \Omega) \) at certain DC-bias \( U \) can be defined by a relative increment of the EFISH intensity while applying the modulation voltage \( \Delta U(\Omega) \):

\[
\alpha(U, \Omega) = \frac{2(I_{2\omega}(U + \Delta U) - I_{2\omega}(U - \Delta U))}{(I_{2\omega}(U + \Delta U) + I_{2\omega}(U - \Delta U))} \approx \frac{dI_{2\omega}(U) \Delta U(\Omega)}{dU} I_{2\omega},
\]

and appears to be a differential characteristic of the EFISH phenomenon which is complementary to the static EFISH dependence \( I_{2\omega}(U) \).

Figure 13 shows the experimental static (DCF-induced) EFISH bias dependence \( I_{2\omega}(U + \Delta U) \) measured at p-Si(001) MOS structure for \( \Delta U = 0.6 \) V which is typically featureless for the DCF induced SHG. Figure 14 shows the experimental bias dependence \( \alpha(U) \) (open symbols) of the efficiency of the modulated EFISH for for \( \Delta U = 0.6 \) V, and \( \Omega = 100 \) Hz at an azimuthal angle \( \psi = 0 \) that minimizes the anisotropic EFISH intensity. This dependence shows a flat feature in the vicinity of \( U = 0 \) V. This feature is not seen on the bias dependence of the numerical derivative of \( I_{2\omega}(U) \) function shown in Fig. 14 (solid symbols). The bias dependence \( \alpha(U) \) as calculated in the framework of the phenomenological model above (Sections A and B in Part II) is presented in Fig. 14 (solid curve). This curve does not show a flat feature in the vicinity of \( U = 0 \). This flat-like feature in the experimental differential bias dependence is likely coming from the large modulation amplitude, which could not be reduced for technical reasons.

The inset in Fig. 12 shows the spectral dependence of the modulation efficiency in the tuning region of the Ti:Sapphire laser. A peak in the spectral dependence \( \alpha(\lambda_\omega) \) is observed at the two-photon energy \( 2\hbar\omega = 3.41 \) eV with half-width \( \hbar\Delta\omega = 0.023 \) eV. The spectral position of this peak is close to the bulk \( E_1 \) resonance. This confirms once again the bulk origin of the DCF-induced term of the nonlinear polarization in Eqs. (1) and (2). The spectral half-width of the resonance in the differential response \( \alpha(\lambda_\omega) \) is smaller than the
half-width of the resonances of the electrostatic (DCF-induced) EFISH terms in Fig. 12. This shows the increased sensitivity of the EFISH modulation spectra to density of states in the semiconductor valence and conduction bands.

IV. CONCLUSIONS

In summary, the DC-electric-field-induced SHG and the low-frequency electromodulation SHG spectroscopy of Si(001)-SiO$_2$ interfaces in p- and n-type Si(001)-SiO$_2$-Cr MOS structures have been studied. The dependences of the DC-electric-field-induced SHG intensity on the applied bias are shown to be sensitive to the doping concentration of silicon, oxide thickness and fundamental and SHG wavelengths. From spectroscopy of the anisotropic EFISH dependences the field-induced contribution has been extracted and the spectrum of the cubic susceptibility $\chi^{(3)}$ appears to be peaked at the energy of the bulk $E_1$ critical point. The presence of significant EFISH contribution at an unbiased Si(001)-SiO$_2$ interface due to the initial band bending has been observed. This initial band bending contribution should be taken into account in the further interpretation of the spectroscopic SHG measurements at Si(001)-SiO$_2$ interfaces [3,61].

A general phenomenological model of the EFISH phenomenon is developed. This includes a comprehensive analyses of the generation and the propagation of the EFISH wave in the silicon space charge region taking into consideration the retardation and absorption effects, optical interference of the DC-field-dependent and DC-field-independent contributions to the SH waves and interference of multiple reflections in the oxide layer. The spatial distribution of the DC-field-induced bulk dipole nonlinear polarization is calculated using the rigorous DCF distribution across the SCR taking into account surface quantization effects. The influence of the silicon doping level, oxide thickness, interface states and oxide charge traps on the screening of the external DCF in the SCR is studied. We have demonstrated the sensitivity of the EFISH probe to the charge characteristics of the Si(001)-SiO$_2$ interface which makes this technique promising as a noninvasive sensor of the MOS devices for the
mapping of interface charge distribution.

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|       | $BQ$   | $BD$      |
|-------|--------|-----------|
| $\alpha$, rel.un. | -0.005 | -1.216    |
| $\beta$, rel.un. | 0.006  | 0.378     |
| $\delta$, eV      | 0.054  | 0.053     |
| $\omega_M$, eV     | 3.382  | 3.384     |

Spectral parameters of $|\chi^{(2),BQ}(\Omega)|$ and $|\chi^{(3),BD}(\Omega)|$.

Fig. 1: The spatial electrostatic potential (left panel) and DC-electric field (right panel) distribution across the SCR of p-doped silicon (doping concentration of $1.5 \cdot 10^{15} \text{ cm}^{-3}$) for different values of interface potential: +0.95 V (inversion), +0.6 V (depletion) and -0.33 V (accumulation). The upper panel is the sketch of the potential and field distribution across the MOS structure.

Fig. 2: The bias dependences of the real (left panel) and imaginary (right panel) parts of the EFISH field $E^{BD}$ for different doping levels of silicon wafer. Parameters of MOS structure used are in the text. The flatband voltage is supposed to be zero. Insets: the bias dependences in the vicinity of zero-point bias.

Fig. 3: The absolute value of the depletion bias $U_0$ vs. the doping concentration $N_D$ of the n-Si wafer for Si- SiO$_2$- metal MOS structures with different SiO$_2$ thicknesses: 1 nm (filled squares), 8.7 nm (open squares), 19 nm (filled circles), and 50 nm (open circles). Solid curves are guides to the eye. Inset: dependence $U_0(N_D)$ for MOS structure with 1 nm thick oxide in the linear scale.

Fig. 4: The real (open circles) and imaginary (filled circles) part of $E^{BD}$ for the depletion bias $U_0$ vs. the doping concentration $N_D$ of the silicon wafer with 19 nm thick oxide film. Solid curves are guides to the eye. Inset: the doping dependence of the ratio of $\text{Im}(E^{BD})/\text{Re}(E^{BD})$.

Fig. 5: The bias dependences of the real (left panel) and imaginary (right panel) part of the EFISH field $E^{BD}$ for different parameters of acceptor interface states. The energy spectrum of interface states is simulated by Lorenzian function with density of $N_A = 10^{13} \text{ traps cm}^{-2} \text{ eV}^{-1}$, width of $\delta_A = 0.5 kT$, and different central positions - $\varepsilon_{0A} = \mu$ (thin curves), $\varepsilon_{0A} - \mu = -10 kT$ (thick curves) and $\varepsilon_{0A} - \mu = -20 kT$ (dashed curves) and sketches on the inset. The dotted curves present for comparison the same dependences.
without traps. Parameters of the MOS structure are in the text.

Fig. 6: p-in,p-out SHG signal from n-Si(001) MOS structure at several biases for $\lambda_\omega = 725$ nm ($2\hbar\omega = 3.43$ eV) vs. sample azimuthal angle. Solid curves are fits to data by the 0-th, 4-th and 8-th Fourier components.

Fig. 7: p-in,p-out SHG signal from p-Si(001) MOS structure at several biases for $\lambda_\omega = 730$ nm ($2\hbar\omega = 3.41$ eV) as a function of sample azimuthal angle. Solid curves are fits to data by the 0-th, 4-th and 8-th Fourier components.

Fig. 8: Bias dependences of isotropic $c_0$ and normalized four-fold $a' = c_4 \left(2\sqrt{2c_8}\right)^{-1}$ SHG Fourier amplitudes from n-Si(001) MOS for $\lambda_\omega = 725$ nm ($2\hbar\omega = 3.43$ eV). Solid curves are fits to data using the model presented.

Fig. 9: Fig. 8. The isotropic SHG component from p-Si(001) MOS structure for $\lambda_\omega = 730$ nm ($2\hbar\omega = 3.41$ eV) as a function of applied bias. Curves are fits to data using the model of the DCF screening within “classical” approach for $N_A = 1.5 \cdot 10^{15}$ cm$^{-3}$ (thin curve) and $N_A = 10^{17}$ cm$^{-3}$ (thick curve) and with surface quantization corrections (dashed curve).

Fig. 10: The normalized four-fold symmetric SHG component $a' = c_4 \left(2\sqrt{2c_8}\right)^{-1}$ from p-Si(001) MOS structure for $\lambda_\omega = 730$ nm ($2\hbar\omega = 3.41$ eV) as a function of applied bias. Curves are fits to data using the model of the DCF screening within “classical” approach for $N_A = 1.5 \cdot 10^{15}$ cm$^{-3}$ (thin curve) and $N_A = 10^{17}$ cm$^{-3}$ (thick curve) and with surface quantization corrections (dashed curve). Inset: voltage dependences near zero-point of bias.

Fig. 11: The bias dependences of the four-fold symmetric anisotropic SHG component $c_4(U)$ for several wavelengths of the fundamental radiation and their fit presented by solid lines.

Fig. 12: The spectral dependence of module of cubic dipole and quadratic quadruple susceptibility around the direct two-photon $E_1$ transition extracted from the spectra of the EFISH azimuthal dependences. Solid lines are fits to data by the Lorenz function with real background. Inset: the spectral dependence of the efficiency of modulated EFISH for $\Delta U = 0.6$ V, $\Omega = 100$ Hz in p-Si(001) MOS structure.

Fig. 13: The experimental static bias dependence of the SHG intensity. The right side shows the schematic of the low-frequency electromodulation of the SHG signal by the application
of the superposition of DC-bias $U$ and low-frequency squarewave modulation voltage $\Delta U(\Omega)$ with the amplitude $\Delta U$ and frequency $\Omega$.

Fig. 14: The bias dependence of the efficiency of modulated EFISH signal in p-Si(001) MOS structure: open symbols are experimental dependence of $\alpha(U)$ for $\Delta U = 0.6$ V, $\Omega = 100$ Hz; solid symbols are numerical derivative of the static (DCF-induced) bias dependence of the EFISH intensity; solid line is the model calculation in accordance of Sections A and B in Part II.
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The graph shows the relationship between the real and imaginary parts of $E^{BD}$ and doping concentration. The real part $\text{Re} E^{BD}$ and the imaginary part $\text{Im} E^{BD}$ are plotted on a log-log scale. The graph indicates that $\text{Im} E^{BD}$ remains relatively constant while $\text{Re} E^{BD}$ increases linearly with the doping concentration. The concentration approaches $N_D^{1/2}$.
SHG Intensity (arb. un.)

Ω = 100 Hz
ΔU = 0.6 V

Ω(t) = U_0 + ΔU(Ω)

Applied Bias (V)
