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## → Optical Casimir Nonlocality as a Source of a Macroscopic Effect during the Generation of the Second Harmonic in a Si(111)–SiO<sub>2</sub> System

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During the generation of the second harmonic (SH) in centrosymmetric semiconductors, the violation of the central symmetry of the medium near surfaces and internal interfaces, which manifests itself in such factors as a rupture of the crystal lattice [1], the presence of internal stresses in the near-surface layer [2] and an initial bending of semiconductor energy bands [3], the presence of a crystalline transition layer [4], etc., are primarily responsible for the appearance of nonlinear polarization.

For a dimensional dependence of the magnitude of the SH on the thickness  $D$  of the oxide in the system Si(111)–SiO<sub>2</sub>, two characteristic scales are known:  $l_{\mu} \sim 1$  nm given by the microscopic structure of the interface and  $l_{\text{opt}} \sim 100$  nm defined by an optical-field discontinuity. In the limiting cases  $D \geq l_{\text{opt}}$  and  $D \sim l_{\mu}$ , microscopic and macroscopic (interference) effects are substantially separated in the problem; a change in the microstructure of the interface changes its quadratic susceptibility, whereas a scale  $l_{\text{opt}}$  enters into the solution of the problem of the electromagnetic-field propagation [5]. The aim of this paper is to investigate the intermediate case  $l_{\mu} \leq D \leq l_{\text{opt}}$ , which has not yet been studied systematically.

We investigated experimentally the intensity of the optical SH generated in the Si(111)–SiO<sub>2</sub> system as a function of the oxide thickness within the range 2–300 nm. The experimental conditions rule out contributions from the mechanisms described in [1–4] to the thickness dependence under consideration. To interpret the experimental results, we use a formalism borrowed from the theory of the Casimir effect; the dimensional effect is explained by the specific nonlocality of the nonlinear response caused by electron–electron interactions through long-wavelength modes of the quantized electromagnetic field.

1. The principal features of the experimental scheme are the following:

The preparation procedure provides the production of samples with various oxide thicknesses and with an identical structure of the Si(111)–SiO<sub>2</sub> interface.

In order to rule out multiple reflections, the measurements were carried out for a  $p, p$  combination between the polarizations of the pumping radiation and the SH and for an angle of incidence of the pumping beam equal to the Brewster angle for the SiO<sub>2</sub>–air interface.

In order to investigate the role of the SiO<sub>2</sub>–air interface, the measurements in air were supplemented by those for a sample submerged in liquid whose index of refraction was nearly equal to that of the oxide.

The samples investigated were Si(111) wafers ( $\pm 0.5^\circ$ ) of the  $p$  type (2–5 Ohm cm), on which an oxide layer 300 nm thick was grown previously at 1000°C in an oxygen ambient. In order to obtain a sharp Si–SiO<sub>2</sub> interface, the wafers were annealed at higher temperature in an N<sub>2</sub> ambient. The wafers annealed in one batch were etched in a buffer solution of NH<sub>4</sub>F/HF at a rate of  $\sim 25$  nm/s; the samples obtained after this procedure included  $3 \times 3$  or  $5 \times 5$  regions with the thickness  $D$  ranging from 2 to 300 nm. This value was measured by ellipsometric techniques with the use of a He–Ne laser (632.8 nm).

The source of the pumping radiation in the experiment on the SH generation was a pulsed YAG : Nd<sup>3+</sup> laser (1064 nm) with a pulse width of 10 ns and a peak power density of up to 5 MJ/cm<sup>2</sup>. The detection setup involved a monochromator, a photomultiplier, and a gated electronic system. The experiments were performed with a  $p, p$  combination of polarizations for an incidence angle of the pumping beam of  $55.5^\circ$  very close to the Brewster angles for the SiO<sub>2</sub>–air interface for the pumping radiation ( $55.3^\circ$ ) and for the SH ( $55.7^\circ$ ). The thickness dependence was investigated for both a sample in air and for one immersed in twice-distilled

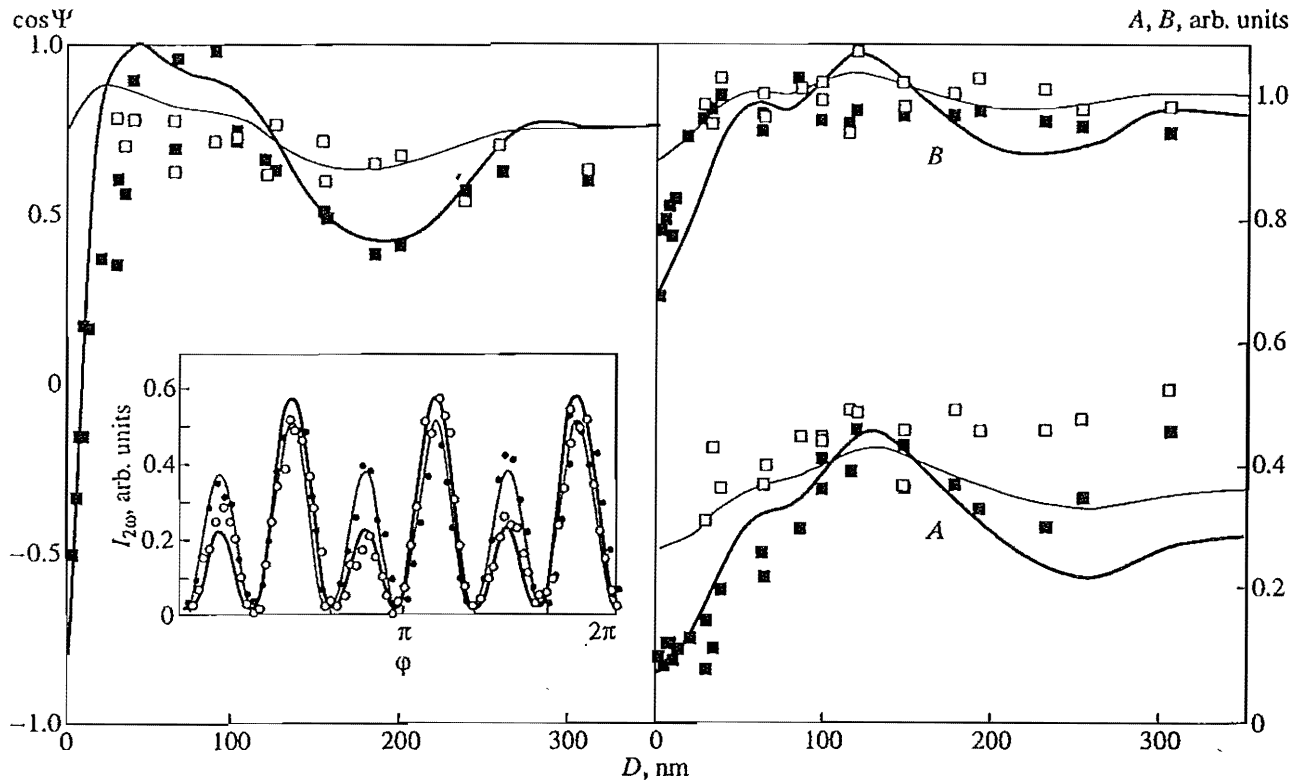


Fig. 1. Isotropic (A) and anisotropic (B) components of the SH and the cosine of the phase shift  $\Psi$  between these components as functions of the oxide thickness  $D$  for a sample in air (open symbols and thin lines correspond to experimental and theoretical values, respectively) and for a sample immersed in water (closed symbols and thick lines, correspond to experimental and theoretical values, respectively). Insert: the rotational anisotropy of the SH intensity for oxide thicknesses of 34 nm (closed symbols and thin line) and 65 nm (open symbols and the thick line).

water, whose index of refraction (1.33) was close to that of  $\text{SiO}_2$  (1.45).

Plots of the SH intensity  $I_{2\omega}^{p,p}$  as a function of the sample-rotation azimuthal angle for two different oxide thicknesses are shown in Fig. 1 for the case of a sample in air. This relationship can be described by the expression

$$I_{2\omega}^{p,p}(D, \varphi) = |A(D) + B(D)e^{i\Psi(D)}\cos 3\varphi|^2, \quad (1)$$

where  $A(D)$ ,  $B(D)$  and  $\Psi(D)$  are the oxide-thickness-dependent moduli of isotropic and anisotropic components of the SH and the phase shift between them, respectively. The quantities  $A$ ,  $B$  and  $\cos \Psi$  are shown as a function of the oxide thickness in Fig. 1. For the case of a sample in air, all three quantities reveal a strong thickness dependence with a scale of  $\sim 100$  nm; this dependence is substantially suppressed if the sample is immersed in water.

2. The following five mechanisms cannot be used to explain the effect, because they do not correspond to the whole range of experimental data. The thickness dependence is not the result of the multibeam interference [5], since the use of the Brewster angle and the  $p, p$  combination of polarizations rules out this effect. The thickness dependence of the internal stresses [2]

and of the initial bending of energy bands [3] does not disappear when the sample is immersed in water throughout the entire oxide-thickness range 2–300 nm under investigation; the SH sources associated with the crystallinity of the transition layer do not contribute to the thickness dependence for  $D > 10$  nm [4]. Finally, even though the assumption about the presence of the interference between two dipole sources located at the  $\text{Si}(111)\text{-SiO}_2$  and  $\text{SiO}_2\text{-air}$  interfaces makes it possible to explain the suppression of the dependence when the sample is submerged (hence a significant part of the nonlinearity of the interface is associated with the near-surface jump of normal components of the field [6]), the corresponding interference pattern would have too low a contrast with respect to that observed experimentally, because the nonlinearity of the  $\text{SiO}_2\text{-air}$  interface is 2–3 orders of magnitude less than that of  $\text{Si-SiO}_2$  [6].

3. The interpretation we propose is based on describing the dimensional effect as a manifestation of a macroscopic optical nonlocality that arises due to interaction between the electron subsystem of the layered medium and modes of the quantized electromagnetic

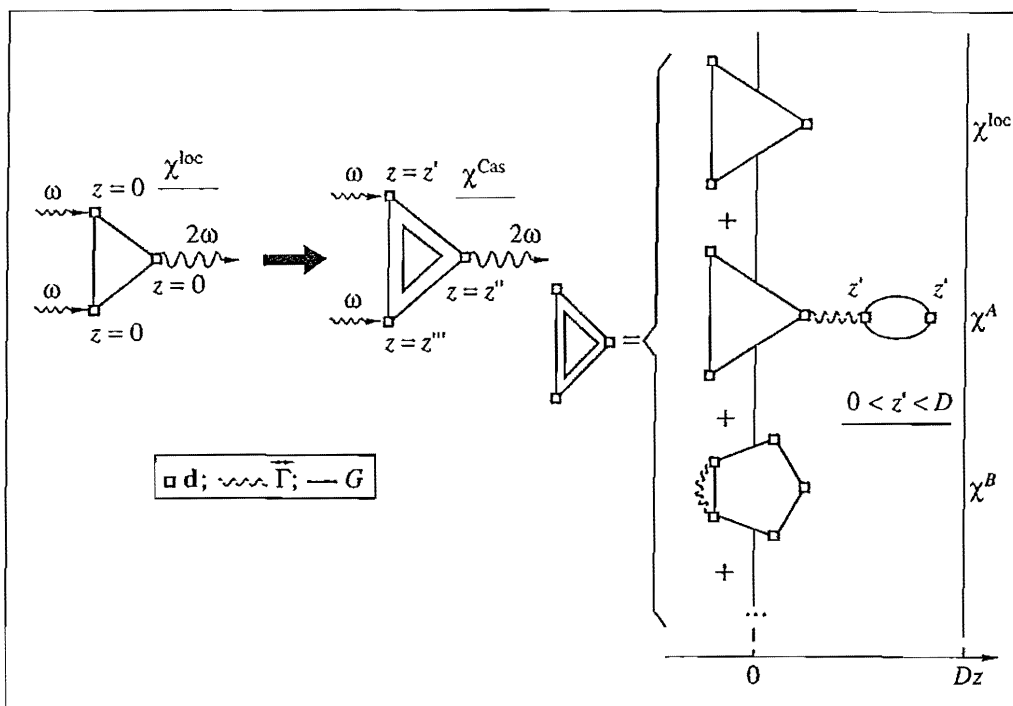


Fig. 2. Diagrams that represent various terms of the series of the perturbation theory for  $\chi^{\text{Cas}}$ . Elements of the diagrams:  $\mathbf{d}$  is the matrix element of the dipole moment for electron transitions;  $G$  is the one-particle Green function for electrons.

field. We consider the general expression for the nonlinear quadratic susceptibility in the dipole approximation [7]:

$$\chi_{\alpha\beta\gamma}^{(2)} \sim \int_0^{\infty} \int_0^{\infty} d\tau \int_0^{\infty} d\tau' \exp(2i\omega\tau + i\omega\tau') \quad (2)$$

$$\times \text{Sp} \{ [ [d_{\alpha}(t), d_{\beta}(t-\tau)], d_{\gamma}(t-\tau-\tau') ], \rho_0 \}.$$

Here,  $\alpha, \beta, \gamma = x, y, z$ ,  $\rho_0$  is the unperturbed matrix of the system density at  $T = 0$ , and  $d(t)$  is the operator of a dipole moment in the representation of the interaction. In a traditional semiclassical consideration, we should have  $H = H_0$ , where  $H_0$  includes the short-range interaction between particles due to field modes with the frequencies  $\geq c/r_0$ . This approximation leads to the local quadratic susceptibility  $\chi^{\text{loc}}$ , which vanishes everywhere except in the layer  $\sim r_0$  thick that includes the Si-SiO<sub>2</sub> interface. We use the formalism taken from the theory of the Casimir effect [8]; this formalism explicitly takes into account optical modes of the quantized field in the Hamiltonian:

$$H = H_0 + W + \sum_{\Lambda} \hbar\omega_{\Lambda} a_{\Lambda}^{\dagger} a_{\Lambda}, \quad (3)$$

where  $a_{\Lambda}^{\dagger}$  and  $a$  are the operators of the creation and destruction of a photon for an optical mode  $\Lambda$  with

the frequency  $\omega_{\Lambda}$ ;  $W = -\int \mathbf{P}(\mathbf{r})\mathbf{E}(\mathbf{r})d^3r$  is the operator of the interaction between the quantized field and the electron subsystem; and  $\mathbf{E}(\mathbf{r}) = \sum_{\Lambda} \mathbf{E}_{\Lambda}(\mathbf{r})a_{\Lambda} + \text{h.c.}$

and  $\mathbf{P}(\mathbf{r})$  are the operators of the electric field and the macroscopic polarization, respectively.

The quadratic susceptibility  $\chi^{\text{Cas}}$  given by (2) with the Hamiltonian (3) can be calculated by a perturbation-theory series expansion in powers of  $W$ , every term of which can be represented by a diagram (Fig. 2) with an odd number of vertices. Due to the symmetry-based selection rules for the matrix elements of the dipole moment, compact electron sections of the diagram with an odd number of vertices differ from zero only in the layer of thickness  $\sim r_0$  near the Si-SiO<sub>2</sub> interface. On the other hand, the electron sections with an even number of vertices differ from zero in the bulk of both Si and SiO<sub>2</sub>. For this reason, the diagrams containing at least one section with an even number of vertices (for example, diagram  $\chi^A$  in Fig. 2) contribute nonlocally to  $\chi^{\text{Cas}}$ . We refer to this type of spatial nonlocality in the optical susceptibility as a Casimir nonlocality.

The relationship  $I_{2\omega}(D)$  is most pronounced in the region of thicknesses  $r_0 \ll D \ll \lambda = c/\omega$ , where the relationship  $I_{2\omega}(D)$  in the principal term with respect to  $r_0/\lambda$  and  $D/\lambda$  is defined by the term  $\chi^A$ . Retaining only

$\chi^{\text{loc}}$  and  $\chi^A$  in the expansion for  $I_{2\omega}(D)$  and considering the incident radiation as a plane monochromatic wave with a frequency  $\omega$  and with a projection  $q_{\parallel}$  of the wave vector on the plane of the sample surface, we find

$$\begin{aligned}
 I_{2\omega} &\sim \left\{ r_0 \Gamma_{ij}(\infty, 0, 2q_{\parallel}, 2\omega) (P_j^{\text{bare}} + P_j^{\text{surf}}) \right. \\
 &\quad \left. + \int_{-\infty}^D \Gamma_{ij}(\infty, z', 2q_{\parallel}, 2\omega) P_j^{\text{bulk}}(z') dz' \right\} \cdot \{c. c.\}, \\
 P_i^{\text{bare}} &= \chi_{ijk}^{\text{bare}} E_j^{(\omega)}(0) E_k^{(\omega)}(0), \\
 P_i^{\text{surf}} &= \int_{-\infty}^D \chi_{ijk}^A(0, z', q_{\parallel}) E_j^{(\omega)}(z') dz' E_k^{(\omega)}(0), \\
 P_i^{\text{bulk}}(z) &= \chi_{ijk}^A(z, 0, 2q_{\parallel}) E_j^{(\omega)}(0) E_k^{(\omega)}(0), \\
 \chi_{ijk}^A(z, z', \mathbf{k}) &= \int X_{ijl}^{(2)}(\Omega) \Gamma_{ln}(z, z', \mathbf{k}, \Omega) X_{nk}^{(1)}(\Omega) d\Omega, \\
 \bar{\Gamma}(z, z', \mathbf{k}, \Omega) &= \iint \exp(ik\rho - i\Omega t) \bar{\Gamma}^R(z, z', \rho, t) dt d^2\rho, \quad (4)
 \end{aligned}$$

where  $E^{(\omega)}$  and  $\bar{\Gamma}^R$  are the local field at the frequency  $\omega$  and the Green's function of the electromagnetic field [8] (calculated for the zeroth order with respect to the value of the perturbation  $W$ ), respectively; a radius vector  $\rho$  lies in the surface plane with the axis  $z$  perpendicular to this plane. Explicit expressions for the tensors  $X^{(1)}$  and  $X^{(2)}$  that correspond to two- and three-vertex electron sections of the diagram for  $\chi^A$  (Fig. 2) are omitted for simplicity. These expressions are similar in structure to those for the linear and quadratic susceptibilities of the medium calculated for the zeroth order with respect to  $W$ .

Thus, the Casimir nonlocality leads to the appearance of a new type of the dipole quadratic polarization described by two  $D$ -dependent terms  $P^{\text{bulk}}$  and  $P^{\text{surf}}$ . To emphasize the sources of these dependences, we can rewrite (4) as

$$\begin{aligned}
 I_{2\omega}(D) &\sim \left| \mathbf{P}^{\text{bare}} + \int_{-\infty}^0 \mathbf{F}_{\text{Si}}(\dots, \bar{\Gamma}(\dots, \Omega, D)) dz' \right. \\
 &\quad \left. + \int_0^D \mathbf{F}_{\text{SiO}_2}(\dots, \bar{\Gamma}(\dots, \Omega, D)) dz' \right|^2, \quad (5)
 \end{aligned}$$

where  $\mathbf{F}_{\text{SiO}_2}$  and  $\mathbf{F}_{\text{Si}}$  are the known functionals of the Green's function  $\bar{\Gamma}$  for a virtual photon, which depends on  $D$  as a parameter. Furthermore,  $D$  enters explicitly

into the second integral in expression (5) as the upper limit.

4. For a quantitative analysis of the contribution of the Casimir nonlocality to the thickness dependence of the SH, it is necessary to know either the morphologic and electronic structure of the interface or detailed spectroscopic information about the phenomenological constants describing the quadratic response of the interface. Since neither is known, we used the following simplified model to compare with the experimental data, which still retains all the qualitative features of the phenomenon: the first integral in (5) is assumed to be independent of  $D$ ; in the second integral,  $X^{(1)}$  is replaced by the linear susceptibility of the medium; and the third-rank tensor  $X^{(2)}$  is approximated by the expression  $X_{ijk}^{(2)} = M_{ijk}(\nu)\mu(\Omega)$ , where the tensor  $M$  dependent on a fitting parameter  $\nu$  has the same symmetry as  $\chi^{\text{loc}}$ , whereas the spectral function  $\mu(\Omega)$  represents the superposition of two Lorentz peaks with resonance frequencies, half-widths, and amplitudes still to be fitted.

The results of the fitting procedure are presented in Fig. 1 [the resonance frequencies of the peaks in  $\mu(\Omega)$  correspond to 5 and 10 eV, while the half-widths are 0.5 and 5 eV, respectively]. The curves agree well with the experimental data for the entire range of oxide thicknesses investigated. The behavior of the spectral function  $\mu(\Omega)$ —a narrow peak at the background of a wide pedestal—appears to be reasonable compared to the known experimental data [2] and the results of numerical calculations [9] taking into account the simplicity of the model in use.

5. Thus, the experimentally observed dimensional effect in the SH of the Si-SiO<sub>2</sub> structure is explained as a manifestation of the nonlocality of the quadratic susceptibility with a macroscopic length scale, i.e., the Casimir nonlocality. Obviously, such a nonlocality can be explained by the existence of correlations in the electron motion, which are associated with the interaction via the electromagnetic field; in this case, the characteristic linear scale is the wavelength that corresponds to frequencies of electron transitions in the system. The type of nonlocality considered here represents a substantially multiparticle effect that owes its origin to an effective electron-electron interaction via the modes of the optical-range electromagnetic field.

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