Optical second-harmonic generation induced by a dc electric field at the Si–SiO$_2$ interface

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For what is to our knowledge the first time, electric-field-induced optical second-harmonic generation (SHG) is studied at the Si–SiO$_2$ interface by the use of a metal-oxide-semiconductor (MOS) structure. The crystallographic anisotropy of this phenomenon is studied for MOS structures. Experimental results indicate that the MOS technique of dc electric-field application to the Si–SiO$_2$ interface can be effectively used for studying electroinduced effects on SHG.

The technique of optical second-harmonic (SH) generation (SHG) was shown to be an effective probe for studying surfaces of centrosymmetric media.[1–3] SHG is forbidden in a bulk of a media with the inversion symmetry in the electrodipole approximation. Thus sources of SH radiation placed directly at the surface lead to an exceptionally high sensitivity of SHG to nonlinear optical properties of the surface layer. The advantages of the SHG method can be significantly enlarged as the nonlinear surface properties are modulated by the dc electric field, i.e., for studying the electric-field-induced surface SH (EISH) generation. This phenomenon was discovered by Lee *et al.*[4] and has been intensively studied at the metal–electrolyte interface since 1982.[5] Later numerous similar experiments were performed, and the same results were obtained by Richmond *et al.*,[6] and the mechanism of this phenomenon for a metal–electrolyte interface was discussed.[7]

EISH generation at the Si–SiO$_2$ interface was previously studied in an electrochemical cell.[8,9] In this Letter we suggest quite a different method of experimental studies of EISH generation at the Si–SiO$_2$ interface: the metal-oxide-semiconductor (MOS) structure. The voltage φ in this case is applied between the semiconductor and the metallic electrode that overcoats the SiO$_2$ layer, so that the electric-field strength $\mathcal{E}$ inside the semiconductor can reach values as high as 10^5 V/cm.

When considering the process of SHG at the Si–SiO$_2$ interface, one should take into account bulk and surface contributions to the nonlinear polarization $\mathbf{P}^{\mathrm{NL}}(2\omega)$ at the double frequency 2ω of the fundamental radiation[1]: dipole surface and bulk and quadropole surface and bulk contributions. The dipole bulk contribution is caused when the Si inversion symmetry is broken as the dc electric field $\mathcal{E}$ is applied to the Si surface. The corresponding contribution to $\mathbf{P}^{\mathrm{NL}}(2\omega)$ is given by $\mathbf{P}^{\mathrm{DBE}}(2\omega) = \hat{\chi}^{(3)}(2\omega; \omega, \omega, 0)\mathbf{E}(\omega)\mathbf{E}(\omega)\mathcal{E}$, where $\mathbf{E}(\omega)$ is the electric field of the fundamental radiation. It was shown that the value of $\mathbf{P}^{\mathrm{DBE}}(2\omega)$ can significantly exceed the contributions to $\mathbf{P}^{\mathrm{NL}}(2\omega)$ that are due to other mechanisms and depends on the density of the Si surface states, the electric charge embedded in the SiO$_2$ layer, etc.[9]

In our experiments the fundamental radiation of a Q-switched YAG:Nd^{3+} laser was used with a 1.064-μm wavelength, a 15-ns pulse duration, and a 12.5-Hz repetition rate. The SH radiation at 532 nm, which was polarized parallel to the fundamental one, was detected in transmission through the sample by the use of a photomultiplier tube and gated electronics. Experimental samples were prepared from an n-type (111) Si wafer 0.1 mm thick with a thermal SiO$_2$ layer 0.53 μm thick. The dc electric field was applied when the voltage φ was imposed between the Si substrate and the metallic In–Ga electrode that overcoated the SiO$_2$ layer. Positive φ values corresponded to the positive potential of the Si. The liquid In–Ga electrode was formed as a ring with a hole inner diameter of ~0.1 cm (Fig. 1, inset). The thickness of the metallic electrode was large enough (~0.1 cm) to produce the more homogeneous dc electric field

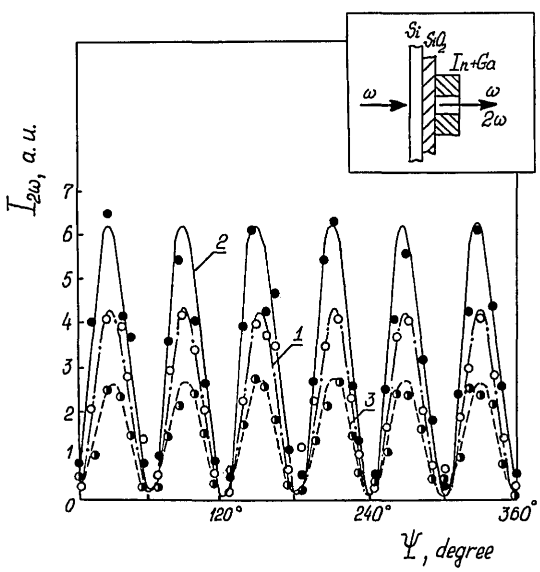

Fig. 1. Angular azimuthal dependences of the SH intensity at the Si–SiO$_2$ interface in the MOS structure for various φ values: 1, 0 V; 2, +0.5 V; 3, −1.3 V. The inset shows the schematic of the MOS structure.

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inside the hole. The SH signal was generated by the $Si-SiO_2$ interface and the internal side of the metallic electrode. The contribution of the liquid electrode to the SH radiation was nearly zero, as its thickness was large enough to absorb the SH radiation generated at the SiO_2–metal interface. The fundamental radiation was absorbed by the metallic electrode too; hence there was no contribution to the total SH signal from the external side of the metal. Thus the SH radiation detected was generated by the $Si-SiO_2$ interface.

To study the electroinduced SH generation at the $Si-SiO_2$ interface, one should take into account the anisotropy of the nonlinear response that results from the anisotropic character of the $\hat{\chi}^{(3)}$ tensor. In our experiments this anisotropy was studied as the sample was rotated on the azimuthal angle ψ measured between the plane of incidence and the X axis of the coordinate system XYZ attached to the MOS sample. The XYZ system was chosen such that the X, Y, and Z axes were parallel to the $[2\bar{1}\bar{1}]$, $[01\bar{1}]$, and [111] directions of the Si single-crystal substrate, respectively.

The dependence $I_{2\omega}(\psi)$ in the absence of the voltage φ is completely anisotropic (Fig. 1, curve 1) and has sixfold symmetry. The application of the voltage φ just leads to changes of amplitudes of all the maxima (Fig. 1, curves 2 and 3). It is well known[10] that for a (111) surface of the $m3m$ single crystal in the transmission geometry, as the polarization of the fundamental radiation was parallel to the SH one, the value of $\mathbf{P}^{\mathrm{NL}}$ can be written as $\mathbf{P}^{\mathrm{NL}} \sim \chi_{xxx} \sin(3\psi)$, where χ_{xxx} is the anisotropic surface contribution to $\hat{\chi}^{(2)}$; hence the $I_{2\omega}(\psi)$ dependence has sixfold symmetry. As the dc electric field is applied to the crystal along the [111] direction, in analogous conditions (the transmission geometry and parallel polarizations of fundamental and SH beams) the value of $\mathbf{P}^{\mathrm{DBE}}$ is given by $\mathbf{P}^{\mathrm{DBE}} \sim \chi_{xxxz} \sin(3\psi)$, where χ_{xxxz} is the anisotropic component of $\hat{\chi}^{(3)}$. Thus the $I_{2\omega}(\psi)$ curve in the presence of the dc electric field is completely anisotropic and has sixfold symmetry. The influence of the electric field should result in the modulation of anisotropic maxima amplitudes that was observed in our experiments (Fig. 1, curves 2 and 3).

The following measurements of the electric-field dependences of the SH intensity were performed for the orientation of the MOS structure that corresponded to the maximum of the anisotropic dependence. This typical dependence $I_{2\omega}(\varphi)$ is presented in Fig. 2 (filled circles) as the voltage φ is varied in the interval (−4 V, +1 V). The significant modulation of the SH intensity caused by the dc electric field is observed, and the maximum value of the SH intensity is 4.5 times larger than the minimum $I_{2\omega}$ value. Analogous to the linear electroreflectance, the relative index $\beta_{2\omega}$ is introduced by $\beta_{2\omega}(\varphi) = [I_{2\omega}(\varphi) - I_{2\omega}(\varphi_0)]/I_{2\omega}(\varphi_0)$, where $I_{2\omega}(\varphi)$ is the SH intensity at the voltage φ and $I_{2\omega}(\varphi_0)$ is the minimum value of the SH intensity of the $I_{2\omega}(\varphi)$ dependence. In terms of $\beta_{2\omega}$ the EISH results are shown in Fig. 2 (open circles) for $\varphi_0 = -1.4$ V.

The voltage φ applied to the MOS structure involves two terms: the voltage φ_{ox} inside the SiO_2 layer and the voltage φ_{sc} inside the space-charge region (SCR) of the Si wafer. As the EISH intensity is $I_{2\omega} \sim (\mathbf{P}^{\mathrm{DBE}})^2$ and the electric-field strength inside the SCR is $\mathcal{E} \sim (\mathrm{d}\varphi_{\mathrm{sc}}/\mathrm{d}z)$, one can find that $I_{2\omega} \sim (\mathrm{d}\varphi_{\mathrm{sc}}/\mathrm{d}z)^2$. To obtain the spatial distribution $\varphi_{\mathrm{sc}}(z)$ one should solve the Poisson equation with corresponding boundary conditions. However, for estimates of $I_{2\omega}(\varphi)$ dependence analogous to Ref. 9 we assume that, inside the SCR, $\varphi_{\mathrm{sc}}(z)$ is the step function. In this case $I_{2\omega} \sim (\mathrm{d}\varphi_{\mathrm{sc}}/\mathrm{d}z)^2 \sim (\varphi_{\mathrm{sc}} - \varphi_{\mathrm{sc}}^{\mathrm{fb}})^2$, where $\varphi_{\mathrm{sc}}^{\mathrm{fb}}$ is the flatbands' potential. Hence $I_{2\omega}(\varphi)$ and $\beta_{2\omega}(\varphi)$ near the value of $\varphi = \varphi_{\mathrm{sc}}^{\mathrm{fb}} + \varphi_{\mathrm{ox}}$ should have a quasi-parabolic shape. Indeed, the experimental curve $\beta_{2\omega}(\varphi)$ (Fig. 2) may be expressed to a good approximation by the quasi-parabolic function, except for the voltage region near −1 V, where the intermediate peak was obtained.

In our opinion this intermediate peak can be attributed to the recharging of surface states at the $Si-SiO_2$ interface or to the redistribution of the electric charge embedded in the SiO_2 layer.

To try to understand the peak origin, we also studied the EISH generation by applying voltage pulses to the MOS structure as the time delay τ of the laser pulse after the leading edge of the voltage pulse was varied. The $\beta_{2\omega}(\varphi)$ curve for time delay $\tau = 80\ \mu$s and a pulse duration of 150 μs is shown in Fig. 3. One can see that there are no differences in the modulation depth of the $\beta_{2\omega}(\varphi)$ curve compared with the static voltage application, whereas a significant shift of the $\beta_{2\omega}(\varphi)$ curve intermediate peak to more negative φ values is observed. It is possible that, starting with certain voltage φ_{ox}, the charge embedded in the SiO_2 layer (ions of Na^+ and K^+ that arise from the thermal procedure of the oxidation) redistributes inside the SiO_2 film, shifts to the $Si-SiO_2$ interface, and decreases φ_{sc}. The shift of the peak in the case of the pulse voltage application could be associated with the low mobility of the embedded charge and, hence, with the necessity for application of a significant effective potential φ_{ox}. Apparently the significant concentration of mobile ions distinguishes the

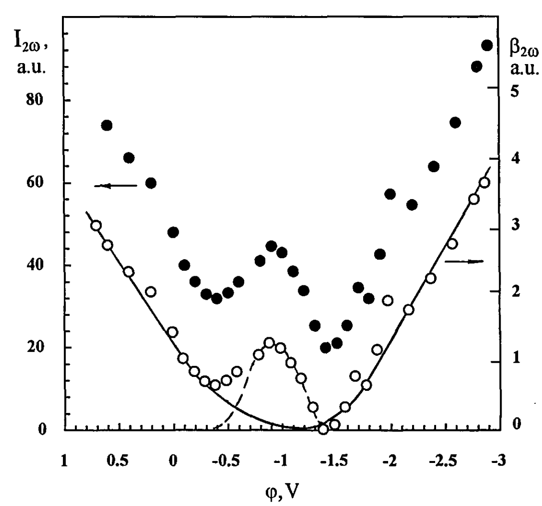

Fig. 2. Dependences of $I_{2\omega}$ (filled circles) and $\beta_{2\omega}$ (open circles) on the voltage φ. The solid curve represents the quasi-parabolic dependence, and the dashed curve indicates the intermediate peak.

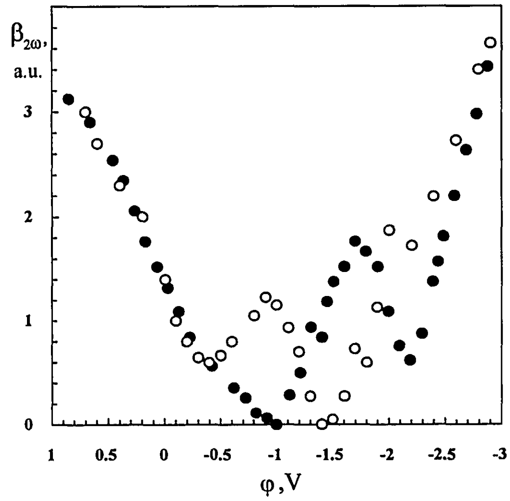

Fig. 3. Dependence of $\beta_{2\omega}$ (filled circles) on pulsed voltage φ, time delay $\tau = 80\ \mu s$, and pulse duration 150 μs. Open circles represent the reference dependence $\beta_{2\omega}$ on the static voltage φ from Fig. 2.

SiO_2 film in MOS structure from the SiO_2 film that covered the Si wafer in the case of a Si–electrolyte interface.[9] Unfortunately, the unambiguous origin of a intermediate peak has not yet been experimentally found yet.

In conclusion, our experimental data on EISH generation indicate that the described procedure of the dc electric-field application to the $Si-SiO_2$ interface gives the deep electroinduced modulation of the SH intensity and can be effectively used for studying the EISH phenomenon.

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