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Probing the silicon–silicon oxide interface of Si(111)–SiO_2–Cr MOS structures by DC-electric-field-induced second harmonic generation

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Abstract

The buried Si(111)–SiO_2 interface has been studied in transmission through planar Si–SiO_2–Cr MOS structures using DC-electric-field-induced second-harmonic generation (EISHG). The rotational anisotropy and oxide thickness dependence of EISHG have been measured. Multiple reflections in the oxide layer and interference effects between field-dependent and field-independent contributions to the nonlinear polarization are shown to affect the shape of the EISHG bias dependence. From a simple model the relative size of field-dependent and field-independent contributions can be estimated. In this way, information about the interface charge distribution can be obtained.

Keywords: Interfaces; Metal–oxide–semiconductor (MOS) structures; Second harmonic generation

1. Introduction

Optical second harmonic generation (SHG) is a powerful tool for the investigation of buried interfaces [1,2]. We show here that SHG can effectively be used to study the charge distribution near the buried Si(111)–SiO_2 interface. DC-electric-field-induced SHG (EISHG) at a Si–SiO_2–electrolyte interface was discovered by Lee et al. already in 1967 [3] and has been intensively studied again since 1984 [4,5]. Since for electrolytic interfaces the range of field values is restricted by oxidation processes that occur at the silicon surface for anodic potentials, the investigation of EISHG for metal–oxide–semiconductor (MOS) structures seems more promising [6,7]. In this paper we study EISHG in transmission through Si(111)–SiO_2–Cr MOS structures with varying oxide thickness. A strong parabolic dependence of the SHG intensity on the applied external bias voltage is observed. The minimum of this parabolic dependence in the EISHG intensity is shown to be shifted with respect to the flatband potential due to nonlinear interference between electric-field-dependent and

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independent contributions to the nonlinear polarization. This was used to estimate the relative sizes of these terms. The influence of the electric field spatial distribution in the silicon space charge region (SCR) and of trapped oxide charges located at the Si(111)–SiO_2 interface on the EISHG is demonstrated.

2. Theory

SHG is symmetry forbidden in the bulk of cubic centrosymmetric crystals within the electric dipole approximation, and the SHG response in transmission arises from the surface electric dipole P^{SD} and the bulk electric quadrupole P^{BQ} contributions [8,9]. An external DC electric field, applied to the crystal, breaks its inversion symmetry and allows an electric-field-induced bulk dipole contribution, produced in the SCR:

$$P^{BD}(2\omega) = \chi^{(3)}(2\omega;\omega,\omega,0) : E(\omega)E(\omega)E_{DC}, \quad (1)$$

where E_{DC} and $E(\omega)$ are the amplitudes of the DC electric field and the fundamental radiation, respectively, and $\chi^{(3)}$ is the cubic tensor susceptibility. In the transmission geometry used in our experiments, the SHG intensity can be written as:

$$I_{2\omega}^{trans} = |L_\omega^2 L_{2\omega}(P^{SD} + P^{BD} + P^{BQ})|^2, \quad (2)$$

where L_ω and $L_{2\omega}$ are the linear Fresnel factors at ω and 2ω, respectively. In general, the nonlinear polarization vectors P^{SD}, P^{BQ} and P^{BD} are complex quantities that will give rise to interference effects. Since the DC electric field, applied perpendicularly to the surface, varies appreciably along the penetration depth of the SH radiation $z_{2\omega}$, a more rigorous expression for the effective P^{BD} has the form:

$$P_{eff}^{BD}(2\omega) \sim \chi^{(3)} : E(\omega)E(\omega)\int E_{DC}(z)\, dz, \quad (3)$$

where the integration is taken over $z_{2\omega}$. The SHG from Si–SiO_2 interfaces depends on the silicon oxide thickness due to multiple reflections in the SiO_2 layer [11,12]. The SiO_2 layer also affects the electric field inside the Si through the voltage drop across the oxide and because of the presence of charge located at the buried Si–SiO_2 interface and/or trapped in the SiO_2 layer.

3. Experimental

The sample was low-doped p-type (5×10^{15} cm^{-3} boron) Si(111) (±0.5°) wafer, polished to a thickness of 0.16 mm. A thermal oxide with a thickness of 300 nm was grown on this wafer at 1000°C. A buffered NH_4F solution was used to etch the SiO_2 layer, and different oxide thicknesses ranging from 8 to 280 nm were prepared on the single Si substrate in a checkerboard configuration. Single-wavelength ellipsometry with a HeNe-laser was used to measure the SiO_2 thicknesses prior to and after etching. The MOS was prepared by evaporation of a 3 nm thick semi-transparent Cr top-electrode, and a strip Al back-electrode near the edge of the wafer. High-frequency C–V measurements were performed on an identically prepared wafer to characterize the prepared MOS structures. For the SHG experiments we used the output at 1064 nm of a Q-switched Nd:YAG laser, generating 8 ns pulses at 10 Hz with 24 mJ in a 4.5 mm diameter spot, well below the damage threshold. The signal was detected by a monochromator, photomultiplier and gated electronics. SHG was studied in transmission for perpendicular polarizations of the fundamental and SH radiations, with the beam focused onto the polished rear side of the samples along their normal. The observed SHG signal was purely anisotropic, so we can neglect the possible isotropic contribution from the Cr electrode. The EISHG was measured at the maximum of this anisotropy. The SHG intensities for different oxide thicknesses were normalized, taking into account the multiple reflections in the oxide film, and the multiple reflections in the Si substrate for the fundamental beam [11,12].

4. Results and discussion

Fig. 1 shows the dependences of the SHG intensity on the applied bias voltage for various oxide thicknesses. Parabolic dependences are observed near the minimum of the bias dependence, although deviations from this are seen at larger biases for all but the thickest oxide. Here we will concentrate on the parabolic dependence. The results of least-squares fitting of the experimental data of Fig. 1 to parabola near the minima are presented in Fig. 2. To compare

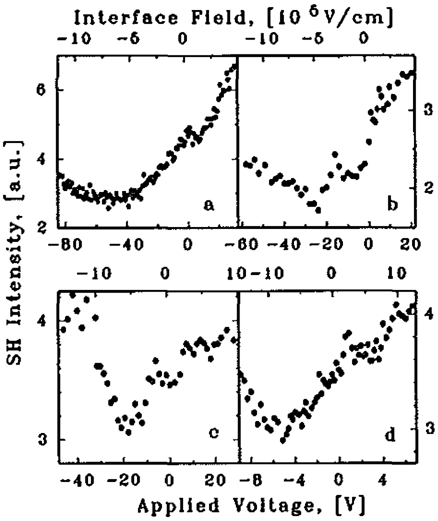

Fig. 1. The SHG intensities $I_{2\omega}$ versus applied bias voltage V (lower axes) and interface DC-electric-field E_{sc} (upper axes) for MOS samples with various oxide thicknesses: (a) 234 nm, (b) 158 nm, (c) 101 nm, (d) 18 nm.

the results for various oxide thicknesses the parabolic dependences in Fig. 2 are presented in units of the relative coefficient $\beta(V) = (I_{2\omega}(V) - I_{2\omega}(V_0))/I_{2\omega}(V_0)$, with V_0 the applied bias at the minimum of the SHG intensity. The minimum of the EISH bias dependence becomes sharper and shifts towards lower biases as the oxide thickness is decreased.

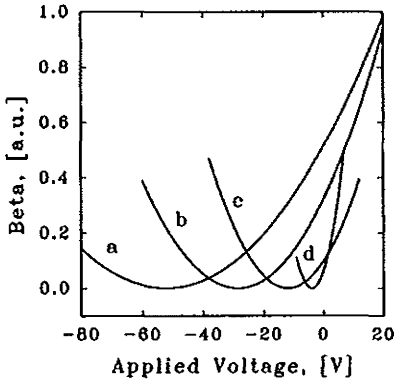

Fig. 2. The results of the fit of the experimental data presented in Fig. 1. The coefficient β (see text) is used to compare the EISHG curves for various oxide thickness.

Since according to Eq. (1) P^{BD} is proportional to the electric field, we should calculate the corresponding electric field values. This means solving the Poisson equation with appropriate boundary conditions [10]. From the C–V measurements it was found that the densities of interface states D_{it} ($\sim 10^{11}$ eV^{-1} cm^{-2}) and mobile charges were small compared to the number of interfacial fixed charges Q_f ($\sim 5.5 \times 10^{11}$ cm^{-2}), and therefore could be neglected. The Q_f influence can be taken into account by the boundary condition at the interface, and the charge density in the bulk oxide was assumed to be zero. Using this, we have rescaled the bias voltages in Fig. 1 to electric fields by numerically solving the Poisson equation, assuming Boltzmann statistics. We start with a simple nonlinear-optical model, in which it is assumed that P^{BD} is proportional to the electric field E_{sc} in the SCR just at the interface. It implies that the real field distribution $E_{DC}(z)$ in the SCR is changed by E_{sc} inside a layer of effective length z_0 that is comparable with the SCR width. We call this the "interface field approximation". The E_{sc} depends almost linearly on the applied bias [10] for the oxide thicknesses used, and the EISHG intensity should be quadratic in both the bias and the electric field, as is indeed observed in the data. The same quadratic dependence was also observed for thin oxides [5,13,14], though in that case this approximation is not expected to be valid. For such oxides the details of the spatial charge distribution should be taken into account. Due to interference between the various sources of SHG, the minimum of the bias dependence can be shifted from the flatband voltage V_{fb}. Using this shift we can estimate the relative sizes of the various contributions to Eq. (2) with a simple model. We will write $P^{SD} = a$, $P^{BD} = b \exp(i\Phi_1)$ and $P^{BQ} = c \exp(i\Phi_2)$, where $\Phi_{1,2}$ are the phases of bulk dipole and quadrupole polarizations with respect to the surface dipole one, and the real numbers a, b, c are their modules with b being a function of $V - V_{fb}$. Suppose for simplicity that $\Phi_1 = 0$ and $\Phi_2 = \pi/2$, which seems reasonable since in the plane-wave approximation $\nabla_i E_j(\omega) = ik_i E_j(\omega)$, where k_i is the ith component of the wave vector of the fundamental radiation inside the silicon (assuming $\chi^{(3)}$ to be real). Thus, the dependence of the SHG intensity on applied bias voltage will have the form $I_{2\omega}(V) \sim (a+b)^2 + c^2$. From the experimental data the values of c/a and $\chi^{(3)}/\chi^{(2)}$ can be found, if the flatband voltages for the MOS structures are known. These were determined from the *C–V* measurement. In Fig. 3 the position of the minimum of the EISHG parabolic dependence (right axis), and the flatband voltage (left axis) are plotted as a function of oxide thickness. A linear dependence is found in both cases, as is predicted by the model. Under the assumption that all the nonlinear susceptibilities are independent of the oxide thickness we find that $c/a = 2.9 \pm 0.4$ and $\chi^{(3)}_{xxxz}/\chi^{(2)}_{xxx} = (0.78 \pm 0.09) \times 10^{-5}$. Using these values it is possible to estimate the interfacial charge for differently prepared Si–SiO$_2$ interfaces. This suggests an interesting application of EISHG, namely as a contactless local probe of the in-plane variations of the interface charge distribution of silicon wafers. These results also indicate that for the fundamental wavelength used (1.064 μm) the bulk quadrupole term dominates the surface SHG response from Si–SiO$_2$ interfaces.

We have so far used the "interface field approximation", leading to a quadratic dependence of the SHG signal on applied bias. For all but the thickest oxide, however, clear deviations from parabolic behaviour are observed for large biases. This can be explained by taking into account the real spatial distribution of the electric field in the SCR. We have performed these calculations that will be published elsewhere.

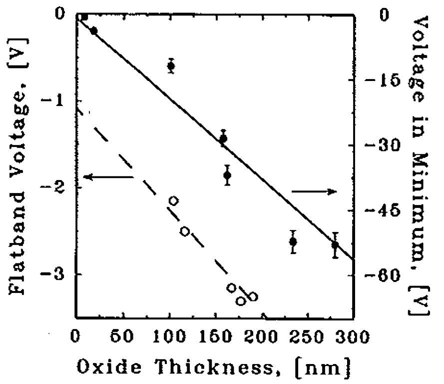

Fig. 3. Position of the minima of the experimental EISHG dependences V_0 (right axis) and the flatband voltage V_{fb} (left axis) versus the oxide thickness L_d. Lines present the model curves.

5. Conclusions

We have shown that the EISHG from Si(111)–SiO$_2$ buried interface with thick oxides can be described with a simple "interface field" model. The nonlinear interference effects between field-dependent and independent contributions to the nonlinear polarization have been taken into account. By using the measured flatband voltages we have made an estimate of the relative size of field-independent and field-dependent contributions to the EISHG. This in turn indicates that EISHG could be used to probe (variations in) the interface charge distribution.

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