

Second harmonic generation probing of dopant type and density at the Si/SiO₂ interface

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(Received 8 February 2010; accepted 4 October 2010; published online 25 January 2011)

Time-dependent second-harmonic generation (TD-SHG) is shown to be a sensitive, noncontact probe of dopant type and concentration at Si/SiO₂ interfaces. TD-SHG signal magnitude increases for n-Si(111)/SiO₂, while for p-Si(111)/SiO₂ TD-SHG is nonmonotonic. This behavior is interpreted as a consequence of SHG sensitivity to electric fields induced by interfacial charge transfer and trapping. © 2011 American Institute of Physics. [doi:10.1063/1.3505356]

Semiconductor-device operation depends critically on dopant density and distribution. Silicon-device fabrication could be greatly facilitated with a nondestructive, noncontact *in situ* probe of doping. Doping characterization using electrical means can destroy the device and requires considerable surface area for contacts. Second harmonic generation (SHG) is a noninvasive, *in situ* interfacial probe.¹ The SHG response of Si–SiO₂, GaAs, SiGe–SiO₂, and metal-capped structures have revealed sensitivity to dc-electric fields and/or doping, explained by the electric-field-induced second harmonic (EFISH) contribution to the SHG.^{2–6}

EFISH is governed by a third-order susceptibility tensor, $\chi^{(3)}$. EFISH adds to the usual second harmonic field of the semiconductor in the absence of an electric field, as shown in Eq. (1):^{7–10}

$$I(2\omega) \propto |P_{2\omega} + P_{2\omega}^{\text{EFISH}}|^2 = |\chi^{(2)} + \chi^{(3)}E_{\text{DC}}|^2 I^2(\omega), \quad (1)$$

where $I(2\omega)$ and $I(\omega)$ are, correspondingly, the intensities of the SHG and the fundamental; $P_{2\omega}$ and $P_{2\omega}^{\text{EFISH}}$ are the nonlinear polarizations at the second-harmonic wavelength due to the surface-dipole and EFISH contributions, respectively; $\chi^{(2)}$ and $\chi^{(3)}$ are the nonlinear susceptibility tensors governing the surface-dipole and EFISH contributions, respectively, and E_{DC} is the electric field across the interface. In the space-charge region, E_{DC} is determined by the density and nature of surface states (surface property) and the doping of the semiconductor (bulk property).^{11,12} $\chi^{(2)}$ and $\chi^{(3)}$ are complex, and therefore, the phase between the $\chi^{(2)}$ and $\chi^{(3)}$ must be considered in Eq. (1).^{2,6,13,14}

To investigate SHG as a potential probe of semiconductor doping, SHG experiments were performed on Si(100)/SiO₂ samples using a laser system providing sub-100-fs pulses in 100 mW of p-polarized average input power (1.3 GW/cm² peak power, 9.1 kW/cm² average irradiance) and p-polarized second-harmonic detection, as detailed elsewhere.^{15,16} Time-dependent SHG (TD-SHG) was carried out at a fundamental wavelength of 730 nm,¹⁵ which is 2-photon resonant with the E₁ transition of Si at 3.4 eV.¹⁷ TD-SHG experiments were performed by irradiating the sample continuously for 3 min (“irradiation” stage) followed by blocking the laser beam and periodically sampling the SHG recovery (“recovery” stage).^{8,10,18,19} To provide maximum sensitivity to laser-induced interfacial charging, TD-

SHG was monitored at a major maximum of the SHG rotational-anisotropy pattern as determined at 800 nm to minimize laser-induced electronic processes from the E₁ resonance.^{15,16} Prior to SHG experiments, Si/SiO₂ (native oxide) samples were degreased by successive sonication (10 min each) in trichloroethylene, acetone, and methanol, thus avoiding oxide etching and additional trap formation that might result from other cleaning methods.¹⁰ Si samples were n-doped by phosphorus or p-doped by boron.

TD-SHG was observed from oxidized Si interfaces by van Driel *et al.* and was ascribed to electron transfer across the Si–SiO₂ interface.^{8,18} Subsequent trapping and detrapping of electrons lead to a variation in the interfacial charge, and therefore, a change in the effective nonlinear susceptibility.^{8,18,19} The sensitivity of SHG to bulk boron dopant concentration has been reported for unoxidized Si(001) epitaxial films.³ H-termination of Si(001) surfaces essentially rendered SHG insensitive to boron dopant concentration, emphasizing the importance of interfacial effects on the SHG.³ Our recent discovery that TD-SHG can distinguish trapped electrons from trapped holes²⁰ provided the motivation to inquire whether TD-SHG would be sensitive to dopant concentration and type. A recent study of TD-SHG on Si/SiO₂ interfaces compared the time evolution of SHG from B- and Sb-doped samples and found that B-doped samples exhibited a nonmonotonic behavior of TD-SHG,²¹ reminiscent of the bi-tonic behavior of the UV-irradiated Si/SiO₂ interfaces in our previous study.²⁰

We extend the Park *et al.* study,²¹ by: (i) systematically investigating both p-doped and n-doped Si at various dopant concentrations, (ii) exploring charge-relaxation dynamics at the interface after the removal of laser irradiation, and (iii) proposing a “metric” for estimating the dopant type and concentration from the SHG intensity. We find that the shape of the TD-SHG clearly reveals the dopant type (p or n). Specifically, TD-SHG is bitonic for p-doped samples and monotonic for n-doped samples, Fig. 1. Furthermore, we quantified the sensitivity of the quiescent SHG intensity to dopant concentration and investigated the charge-relaxation dynamics after laser irradiation is ceased.

The initial (t=0) SHG intensity increases with dopant density above 10¹⁷ cm⁻³ for both n- and p-type Si(111) (Fig. 2). This trend can be explained by SHG sensitivity to doping-amplified interfacial charge. The density of the surface charge trapped at surface states, Q_s, increases with dopant density (N_d) according to the equation Q_s

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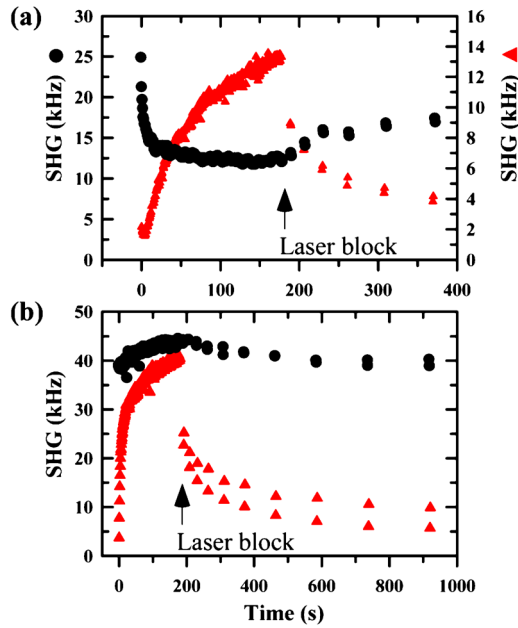


FIG. 1. (Color online) TD-SHG from Si(111)-SiO₂ samples at various doping levels and types. (a) p-Si(111): circles (left axis) $N_d=9 \times 10^{18} \text{ cm}^{-3}$; triangles (right axis) $N_d=10^{12} \text{ cm}^{-3}$ (note the transient drop of TD-SHG around $t=0$); (b) n-Si(111): circles $N_d=4 \times 10^{19} \text{ cm}^{-3}$; triangles $N_d=10^{12} \text{ cm}^{-3}$.

$= \pm \sqrt{2\epsilon_0\epsilon_b|V_s|e_0N_d}$, where ϵ_0 is the vacuum permittivity, ϵ_b is the material dielectric constant, V_s is the band bending, and e_0 is the elementary charge.^{11,12} Consequently, E_{DC} can be estimated by the Schottky approximation, Eq. (2), assuming that the magnitude of band bending (V_s) varies slowly with doping as has been previously suggested,^{1,12,22}

$$E_{DC} = -\nabla V = -\frac{dV}{dz} = \frac{2|V_s|}{z_{dep}^2}(z_{dep} - z) = \frac{N_d e_0}{\epsilon_0 \epsilon_b} \left(\frac{\sqrt{2\epsilon_b \epsilon_0 |V_s|}}{\sqrt{N_d e_0}} - z \right), \quad (2)$$

where z_{dep} is the extent of the space-charge region, z is the distance from the interface, and the sign of E_{DC} arising from Q_s is omitted.

With identical preparation of sample surfaces, the doping alone should be responsible for any changes in surface po-

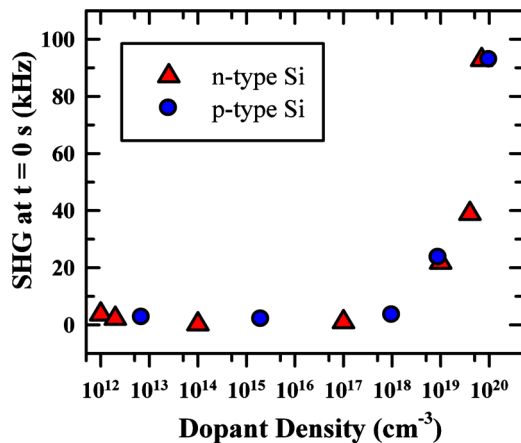


FIG. 2. (Color online) Initial signal of TD-SHG of Si(111)/SiO₂ as a function of doping.

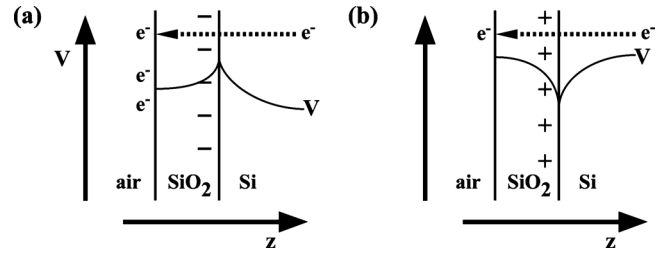


FIG. 3. Schematic for electron injection of electrons from Si to SiO₂ (dotted arrows), following three-photon excitation to Si conduction band, illustrating the potential (V) vs distance from the interface (z), i.e., band bending, in heavily doped (a) n-type and (b) p-type Si.

tential (V), and in E_{DC} with distance from the interface (z). If the sample is moderately doped, the Fermi level is closer to the mid-band gap, where the density of surface states is relatively small.²³ Thereby, in moderately doped samples, the charge density accumulated at the interface and the $|E_{DC}|$ are correspondingly smaller than in heavily doped samples.²³ As the doping increases, one expects $|E_{DC}|$ and the accumulated interfacial charge to increase [Eq. (2)],²³ amplifying the magnitude of the SHG response, [Eq. (1)].

To estimate the EFISH contribution to SHG, one has to integrate E_{DC} over the space-charge region while taking into account the retardation effects of the fundamental and second harmonic, which, in turn determine the effective SHG probe depth.^{7,24} For a wide range of dopant concentrations, the SHG probe depth is smaller than the extent of the space-charge region. Thus, the initial magnitude of E_{DC} can be taken as an approximation of the EFISH contribution to the SHG.²⁴ Therefore, lighter doping leads to a smaller effective $|E_{DC}|$ and a lower quiescent TD-SHG (Fig. 2); the independence of the initial signal from the sign of E_{DC} will be discussed later.

The change in the TD-SHG magnitude relative to the initial, quiescent value during the continuous “irradiation” stage, becomes smaller as the dopant density increases for n-type Si(111) [Fig. 1(b)], presumably because heavier doping leads to an increased charge density at the interface and, consequently, to a Coulombic barrier for electron injection into SiO₂ [Fig. 3(a)]. In previous studies, it was suggested that electron injection into the silicon-oxide conduction band occurs through a multiphoton process and that the barrier for this process grows with increased charge density at the interface, following the theoretical model by Kane.^{19,25,26} Therefore, the rate of laser-induced electron injection into interfacial traps is slowed with increasing n-dopant density. After photoexcitation, the electrons thermalize and diffuse to the interface, thereby modifying the effective interfacial charge. The charge carried by the photoinjected electrons adds to the interfacial charge in the case of n-doped Si, thereby effectively increasing E_{DC} , and the SHG according to Eq. (1).

The TD-SHG of p-doped Si is particularly interesting [Fig. 1(a)] as it initially drops and then slowly rises, a behavior that is more prominent in heavily doped p-type Si. We attribute the initially higher SHG signal in the more heavily doped samples to a larger EFISH contribution arising from the positive charge accumulated at the interface [Fig. 3(b)]. The laser-induced decrease in the SHG signal can be interpreted as originating from the injection of photoexcited electrons that screen the field associated with the accumulated positive charges. This charge screening decreases E_{DC} in the

space-charge region and its corresponding EFISH contribution to the SHG, thereby decreasing the overall signal in a time-dependent manner as electrons are steadily injected. The SHG decrease continues until effective cancellation of E_{DC} is attained, at which point the SHG signal is determined mainly by the $\chi^{(2)}$ contribution. Additional photoinjected electrons then build up $|E_{DC}|$ so that the SHG increases again. The initial drop of the TD-SHG is fast [Fig. 1(a)], suggesting that the promotion of electrons to the interface and subsequent trapping is facilitated by downward band-bending, i.e., the “attraction” of electrons to the positive charge at the interface [Fig. 3(b)], that rapidly captures electrons to neutralize the E_{DC} induced by positive interfacial charges.

Two hypotheses can be suggested to account for the observation that the SHG at $t=0$ is independent of dopant type (Fig. 2). One involves $\chi^{(3)} E_{DC} \gg \chi^{(2)}$ so that effectively $I(2\omega) \sim |\chi^{(3)} E_{DC}|^2 I(\omega)^2$, as suggested in previous studies.^{27,28} However, in this case, the cancellation of E_{DC} in p-doped samples should lead to a much larger change in the TD-SHG signal than observed in our experiments. A second hypothesis is that the phase between $\chi^{(3)} E_{DC}$ and $\chi^{(2)}$ is around $\pi/2$, so that the resulting magnitude of the second-order polarization is independent of the sign of the E_{DC} . The latter hypothesis explains both the independence of the SHG($t=0$) from the sign of E_{DC} and the relatively small change in TD-SHG of p-doped samples. It is to be noted that $\chi^{(2)}$ might change with doping as suggested by the different values of SHG minima for the samples with different doping, as seen in Fig. 1(a). This observation is consistent with previous findings.²¹

TD-SHG recovers upon blocking the laser irradiation; this process is attributed to the relaxation of the electrons, photoinjected into SiO_2 , by tunneling back into Si.^{8,18,19} The detrapping times in heavily doped Si samples were found to be almost an order of magnitude larger than those in lightly doped Si. The slowing of this TD-SHG “recovery” stage with heavy doping in n-type samples, Fig. 1(b), suggests that electrons tunnel less efficiently across the Si/SiO₂ interface where negative charge due to n-type doping is accumulated and acts as a repulsive barrier to electrons returning to Si from the SiO₂/ambient interface, as illustrated in Fig. 3(a). Conversely, in heavily doped p-type Si(111), electrons do not detrapp (recover) quickly because they are retained by an attraction to the positive interfacial charges [Fig. 3(b)], as manifested by the slow increase in SHG after the laser is blocked [Fig. 1(a)].

In conclusion, the time evolution of SHG from Si/SiO₂ interfaces clearly reveals the dopant type (p or n). Dopant concentration can be estimated through the magnitude of the quiescent SHG at time $t=0$ s. Furthermore, the dynamics of

charge injection and relaxation after laser irradiation is sensitive to the dopant type and concentration.

The authors acknowledge the generous support of the National Science Foundation.

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