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RAPID COMMUNICATION

First comparison of electric field induced second harmonic of near-infrared femtosecond laser pulses in reflection and transmission generated from Si/SiO_2 interfaces of a silicon membrane

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Abstract For the first time electric field induced second harmonic (EFISH) generation of femtosecond (fs) laser pulses ($\lambda = 800$ nm, $\tau = 75 \pm 5$ fs, rep. rate = 80 MHz, $E_{\text{pulse}} \le 10$ nJ) is observed in transmission through a thin free-standing silicon (Si) membrane of 10-µm thickness and compared to the well-known EFISH results in reflection by use of the z-scan technique. EFISH in reflection and transmission unequivocally originate from the front and rear Si/SiO_2 interfaces, respectively, with SiO_2 being the natural oxide on the Si surfaces. Frequency conversion is enhanced by photoinduced electric fields across the Si/SiO_2 interfaces caused by charge-carrier injection from Si into the oxide. The z-scan results and time-dependent measurements allow comparison of the EFISH signal amplitudes and time constants detected in transmission and reflection, demonstrating the need for further investigation.

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1 Introduction

Optical second harmonic generation (SHG) is well known for its atomic scale surface and interface sensitivity if applied to centrosymmetric materials like silicon (Si), for which SHG is dipole forbidden in the bulk. It is contactless, non-intrusive with in situ abilities of monitoring electronic defects during UV irradiation [1], chemical contamination [2], interfacial roughness [3, 4], and the dc electric field resulting from charge separation across the Si/SiO_2 interface [5–10]. In the presence of interfacial electric fields, frequency conversion is enhanced significantly so that the electric field induced second harmonic (EFISH) generation process dominates [10]. The interfacial electric fields are caused by photoinduced charge transfer across the Si/SiO_2 interface and depend on the intensity and duration of fs laser irradiation [10]. In this paper, the term EFISH is used to refer to this specific phenomenon of second harmonic generation at the Si/SiO_2 interface induced by interfacial electric fields established by photoinduced charge transfer across the interface.

In all previous EFISH investigations of photoinduced electric fields in Si/SiO_2 the second harmonic (SH) signal was detected in reflection geometry. Typically, femtosecond (fs) laser irradiation in the near-infrared (NIR) range (700 to 900 nm) is absorbed by intrinsic Si on the 10- to 100-µm length scale. Its second harmonic, however, is strongly absorbed within sub-µm distances. Therefore, buried interfaces of Si devices are not accessible by EFISH detection in reflection with Si structures of more than 0.5-µm thickness. With optically transparent substrates, on the other hand, EFISH detection in transmission should be accessible and provide a useful probe for the study of buried interfaces.

SHG in transmission was previously demonstrated using free-standing porous Si films [11] or externally biased bulk

Si samples [12]. In both experiments the SH signals measured in transmission were time independent and originated from the bulk of the samples. The strong influence of phase matching on the SH signal in the porous Si is characteristic of SHG in bulk material. The centrosymmetry of the bulk is broken by alignment of the pores [11] and the externally applied electric field [12], making SHG in bulk Si a dipole-allowed process.

In this paper, we present a proof of principle experiment on EFISH from Si/SiO_2 interfaces measured in transmission. A free-standing Si membrane of 10-µm thickness with practically identical Si surfaces covered with ultra-thin natural oxide layers (thickness <5 nm [13]) is investigated by EFISH detection in transmission and in reflection. The signals measured in transmission showed the characteristic temporal evolution, azimuthal angular variation, and insensitivity to phase matching similar to known EFISH generation in reflection. This differentiates our investigation from previous studies of SHG in the bulk of silicon using detection in transmission.

The optical nonlinearity of EFISH generation makes it very sensitive to temporal and spatial fs laser pulse deformations and beam distortions that may occur during transmission through the Si structure when measuring EFISH in transmission. While two-photon absorption (TPA) will flatten the spatial and temporal intensity profiles of a Gaussian-shaped beam, self-focusing or self-defocusing will increase or decrease the intensity at the laser beam centre, respectively. In order to investigate the role of these processes, the z-scan method [14–16] was applied using both the fundamental fs laser frequency and its second harmonic generated by EFISH on both oxidized Si surfaces. The z-scan method using the EFISH signals in reflection and in transmission selectively probes the front and rear Si/SiO_2 interfaces of the Si membrane, respectively. This renders it a tool for providing comparative measurements before and after beam propagation through bulk Si. Time-dependent measurements further serve to characterize the EFISH phenomena. These results constitute, to our knowledge, the first EFISH detection in transmission through a thin Si structure and the first comparison of EFISH detection in reflection and transmission from the same sample.

2 Experimental

Figure 1a shows a schematic diagram of the experimental setup used to measure the EFISH signals in transmission and reflection from a Si membrane (modification of setup described earlier [10]). The output from a mode-locked Ti–sapphire laser source (Spectra Physics, 3941-M3S, Tsunami, 800 nm, 75 ± 5 fs, rep. rate = 80 MHz, $E_{pulse} \leq 10$ nJ) is tightly focused onto the sample using an achromat lens ($f = 35$ mm) which can achieve intensities of up to 100 GW/cm^2. The average output power of the laser is measured by a power meter (Coherent FieldMaster 33-0506-000 with detector sensor LM-3). The transmitted and reflected fundamental beams from the sample are blocked by a set of filters (Schott AG, Mainz, Germany, BG-39, short-pass filter for 350 nm $\leq \lambda \leq$ 590 nm and $<0.01\%$ transmission for $\lambda > 700$ nm), which allow the EFISH signal to pass through and be detected by two identical photomultiplier tubes (Hamamatsu Photonics, Japan, H678003 amplified by Hamamatsu Photonics, C5594). To enhance the signal-to-noise ratio, a lock-in-amplifier (Ithaco Inc., New York, USA, Dynatrac model 393) is used in combination with a 500-Hz light chopper (Thorlabs MC1000A). Computer-controlled translation of the achromat lens and data acquisition were

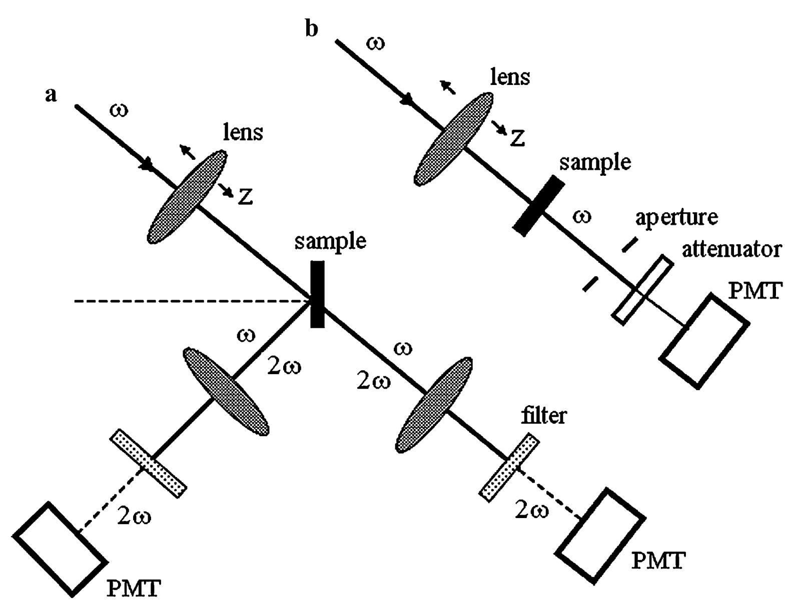

Fig. 1 Experimental configuration for (**a**) EFISH z-scan measurements in transmission and reflection from a free-standing Si membrane and (**b**) z-scan measurements at the fundamental wavelength

employed providing a temporal resolution of 0.2 s. All the EFISH experiments were performed in the p–p polarization (p for parallel to the incident plane) configuration for excitation and detection. The sample was always positioned to be measured at the maximum of the azimuthal rotation anisotropy pattern. Based on the previous EFISH results [7, 10] and those of Fig. 5 in this paper, the EFISH z-scans were recorded in the proper time regime (∼1000 s after onset of irradiation) to allow for saturation of the photoinduced electric fields.

To additionally investigate nonlinear absorption and refractive-index changes in the sample caused by the fundamental laser beam, the setup was modified to the standard setup for open and closed aperture z-scans [14–16] as illustrated in Fig. 1b. The sample was positioned perpendicular to the laser beam and the position of the lens with $f = 60$ mm in this case was scanned, while measuring the transmission of the fundamental wavelength with or without an aperture in front of the detector.

An array of Si membranes (4×4 mm^2 each) of about 10-µm thickness was fabricated by wet chemical etching of a moderately p-doped (3.2×10^{16} to 6.5×10^{17} cm^{-3}) Si(100) wafer using a low stress silicon nitride mask layer and a tetramethylammonium hydroxide solution at ∼ 60°C under clean room conditions [17]. After about 72 h the silicon nitride mask was chemically removed and the surface roughness found to be ∼12 Å using atomic force microscopy. The membrane thickness was determined from profilometer records and optical transmission spectra in the visible range. The membranes were chemically degreased and treated with hydrofluoric acid to remove the existing oxide on both sides. The samples were subsequently placed in the dark at room temperature and under atmospheric pressure for at least 48 h to allow a new native oxide layer to grow and reach equilibrium thickness [10] on both sides, that is, the etched and the original wafer surfaces of the membrane. During the z-scan measurements, the membranes were irradiated on the original polished side. But, it was also verified that irradiation of the etched surface did not significantly change the results.

3 Results and discussion

The standard z-scan experiment at the fundamental wavelength of the fs laser (Fig. 1b), with orthogonal irradiation of the Si membrane and detection of the fundamental beam in transmission was applied to characterize the nonlinear optical properties of the Si membrane and the laser beam parameters. Figure 2 shows the results of an open aperture z-scan. According to Bristow et al. [18], the transmittance for a Gaussian beam in an open aperture technique is given by

$$T_{\text{open}}(z) = 1 - \frac{1}{2\sqrt{2}} \frac{\beta I_0 L_{\text{eff}}}{1 + (z/z_0)^2}, \quad (1)$$

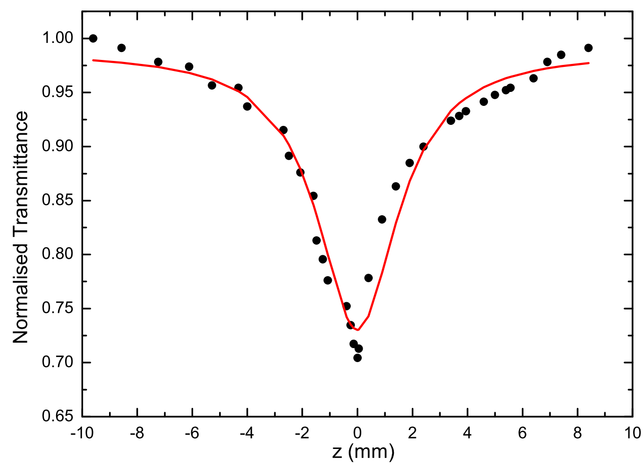

Fig. 2 An open aperture z-scan trace showing the transmittance of the fundamental beam as the beam waist position (z) is scanned longitudinally. At $z = 0$ the beam waist (focal point) is centred in the Si membrane. The *solid line* is a fitting according to equation (1)

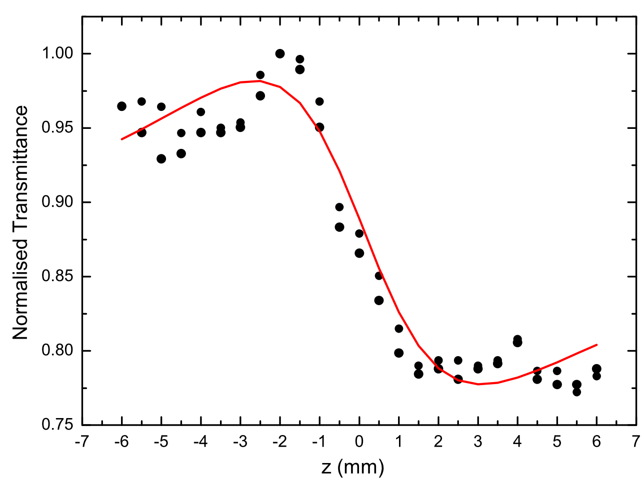

Fig. 3 A closed aperture z-scan trace showing the change in transmittance of the fundamental beam as the beam waist position is scanned. The *solid line* is a fitting according to the appropriate equation from Bristow et al. [8]

where z is the longitudinal scan distance between the beam waist (the focal point) and the sample, I_0 the on-axis intensity at the beam waist, β the TPA coefficient, z_0 the confocal beam parameter, $L_{\text{eff}} = \alpha^{-1}(1 - \mathrm{e}^{-\alpha L})$ the effective optical path length, α the linear absorption coefficient, and L the sample thickness. Fitting (1) to the data of Fig. 2 and using the value $\alpha = 604$ cm^{-1} [19], a TPA coefficient value of $\beta = 9.7 \pm 1.2$ cm/GW was obtained for the Si membrane. Data fitting applied to the closed aperture results (Fig. 3) following Bristow et al. [18] yielded values for the nonlinear refractive index $n_2 = (1.7 \pm 1.5) \times 10^{-4}$ cm^2/GW, the Rayleigh length $z_R = 1.6$ mm, and the beam waist radius $\omega_0 = 20$ µm.

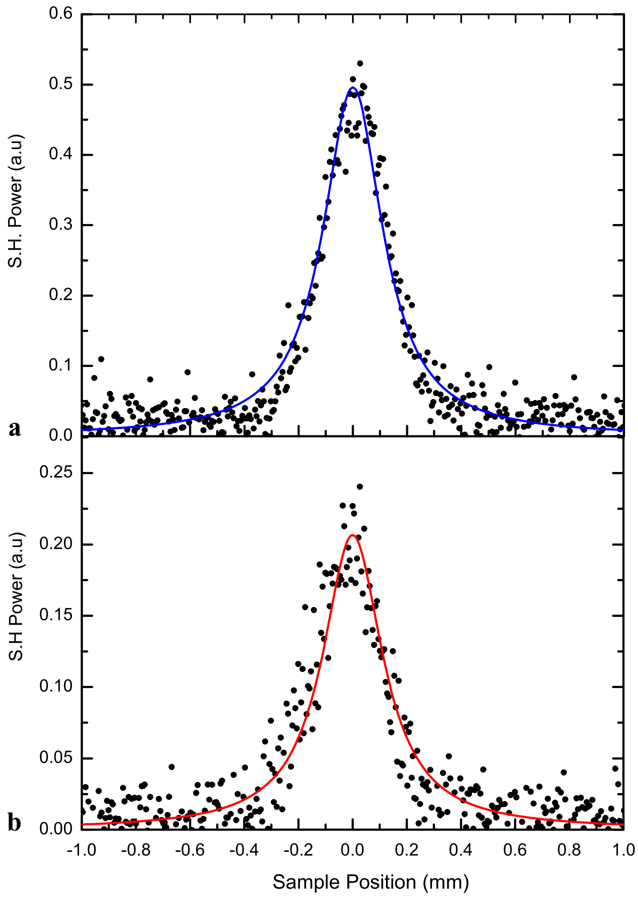

Fig. 4 Open aperture EFISH z-scan traces showing the SH yield as the beam waist position is scanned, measured in (**a**) transmission and (**b**) reflection at 14 GW/cm^2 and 34 GW/cm^2 incident intensity at the focus on the rear and the front interfaces, respectively

With the setup sketched in Fig. 1a and irradiation of the thin Si membrane at $\theta = 40^\circ$ angle of incidence, z-scans based on EFISH measurements were performed in both configurations, i.e. in transmission and in reflection (Fig. 4). The data in Fig. 4 were fitted using the formula for second harmonic power as function of beam waist position (z) derived for an intensity distribution of an elliptical Gaussian beam [20]

$$P_{2\omega}(z) = \frac{z_R K}{z_R^2 + z^2}, \quad (2)$$

where $K = \gamma P_\omega^2 \cos\theta/\lambda$, γ the efficiency of the EFISH generation, z_R the Rayleigh length of the fundamental beam, θ the angle of incidence, and P_ω the fundamental beam power. The values for the Rayleigh length (z_R) and the waist radius (ω_0) of the fundamental beam extracted from the EFISH z-scan in transmission (Fig. 4a) are 0.13 mm and 5.8 µm, respectively, and are similar to values extracted from reflection data (Fig. 4b).

EFISH generation in reflection at the front interface (laser entrance) has been demonstrated and applied by various groups [5–10]. EFISH generation and detection in transmission has become amenable in this study by using the thin Si membrane ($d \approx 10$ µm), since the penetration depth of about 16.6 µm [19] for the fundamental beam is greater than the sample thickness. The sample transparency is evidently high enough to provide the high laser intensity required to induce EFISH generation at the rear interface (laser exit). EFISH generation in transmission at the front interface as well as EFISH generation in reflection at the rear interface may also occur. But, in both these cases the SH photons cannot be detected due to their short penetration depth of about 100 nm in Si [19]. For this reason, EFISH in reflection and in transmission are generated independently of each other and unequivocally originate from the front and the rear interfaces of the membrane, respectively. Therefore, the values of z_R and ω_0 extracted from the transmission and reflection measurements can be attributed to the rear and front interfaces, respectively.

The Rayleigh length $z_R = 1.6$ mm and the beam waist radius $\omega_0 = 20$ µm obtained from the fundamental wavelength z-scans and the related values $z_R \approx 0.13$ mm and $\omega_0 \approx 5.8$ µm obtained from the EFISH z-scans cannot be compared quantitatively due to different focusing lenses, applied intensities, and experimental geometries (e.g. angle θ of incidence).

The laser intensity incident on the rear Si/SiO_2 interface relevant for EFISH generation in transmission can be estimated by taking into account the laser beam refraction at the front surface (resulting angle of incidence on rear surface $\approx 10^\circ$) as well as the beam transmittance through the front surface and its attenuation by absorption in the bulk of the Si membrane. With 34 GW/cm^2 maximum intensity inside the front Si/SiO_2 interface, the calculated value of the intensity on the rear interface amounts to about 14 GW/cm^2 after taking into account Fresnel reflection on the front and rear Si/SiO_2 interfaces.

The change in the refractive index of bulk Si caused by the extracted value of n_2 at the peak intensity $I_0 =$ 34 GW/cm^2 is $\Delta n \approx 0.01$ using the formula $n = n_0 + n_2 I_0$ [21], where $n_0 = 3.65$ is the linear refractive index and I_0 is the peak intensity. Following [16], the corresponding focal length due to the induced nonlinear refractive index is estimated by

$$f = \frac{n_0 w_0^2}{4 n_2 I_0 L}, \quad (3)$$

which yields a value of approximately 560 µm. This induced focal length is much larger than the sample thickness and therefore there is no difference in the beam spot sizes of the fundamental beam on the two interfaces of the membrane. This result is confirmed by the identical beam spot sizes calculated from the EFISH z-scan results in reflection and transmission, respectively.

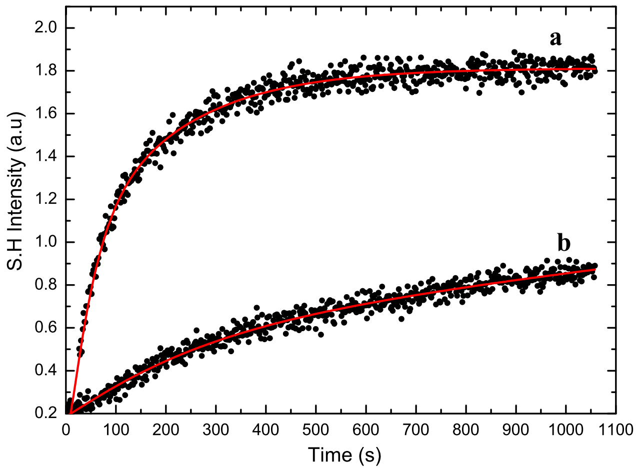

Fig. 5 The time-dependent EFISH response from Si/SiO_2 interfaces of the Si membrane measured in (**a**) transmission and (**b**) reflection for the incident intensities of $14\ GW/cm^2$ and $22\ GW/cm^2$ on the rear and the front interfaces, respectively. Both these incident intensities correspond to a laser power of 100 mW measured before the light interacts with the sample

The attenuation of the fundamental beam in the Si membrane by single-photon absorption is about 45%. In the presence of TPA at a peak intensity of $34\ GW/cm^2$ inside the front Si/SiO_2 interface, the absorption increases to approximately 60% using the β value obtained in this study and the formula [20]

$$I(z) = \frac{\alpha I_0 e^{-\alpha z}}{\alpha + \beta(1 - e^{-\alpha z}) I_0}. \tag{4}$$

We assume that the increase in absorption caused by TPA does not cause significant spatial and temporal beam distortions. The EFISH peak intensity measured in transmission was found to be higher than that in reflection, despite the lower local intensity of the fundamental beam at the rear interface.

Furthermore, the time-dependent EFISH measurements were performed on a virgin sample spot by setting the beam waist position $z = 0$ and recording the EFISH signals in transmission and reflection over 1050 s of fs laser irradiation. The results obtained with an incident laser power of 100 mW, as shown in Fig. 5, show a higher EFISH yield and a faster increase in the signal after onset of irradiation in the case of transmission than in reflection. The time constants extracted from the time-dependent curves using a bi-exponential function fit [7, 10] for transmission were obtained as $\tau_1(t) = 17.6 \pm 0.6$ s and $\tau_2(t) = 150 \pm 4$ s and for reflection $\tau_1(r) = 338 \pm 68$ s and $\tau_2(r) = 1573 \pm 92$ s. The signal increase originates from the build-up of the photoinduced interfacial electric fields [10]. The time constants τ_1 and τ_2 correspond to the processes of electron injection into the oxide and electron trap generation in the oxide, respectively [7].

We conclude that the EFISH results obtained in our measurements in transmission and reflection are characteristic of EFISH generation from a Si/SiO_2 interface where the interfacial electric field is the result of photoinduced charge transfer. We suggest that both the fast signal rise time and the high EFISH amplitude observed in transmission may be related to the dynamics of the build-up of the interfacial electric field at the rear interface of the Si membrane. A more detailed description of these phenomena based on further experiments with free-standing Si membranes is currently in preparation and will be published in a forthcoming paper.

4 Summary and conclusion

EFISH detection in transmission from Si/SiO_2 interfaces of a thin, free-standing Si membrane (10-µm thick with natural oxide) is reported for the first time and compared to EFISH detection in reflection of the same sample using the z-scan method. The EFISH signals in reflection and transmission originate from the front and rear Si/SiO_2 interfaces, respectively. The z-scan measurements at the fundamental laser frequency and those with EFISH detection in transmission and reflection confirm that distortion of the fundamental beam by self-focusing or TPA in the Si membrane is not significant and does not affect the EFISH generation at the rear interface. The results from the z-scan and time-dependent EFISH measurements in transmission and reflection are qualitatively similar. However, the rise times and saturation values of the EFISH signals in reflection and transmission show remarkable differences, which motivate further investigation.

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