Optical second harmonic generation as a probe for internal electric fields at the Si/SiO_2 interface

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The second harmonic signal generated in native Si/SiO_2 interfaces using femtosecond laser pulses (80 ± 5 fs, 10.5 nJ, 1.59 eV) is time dependent. The temporal evolution of the electric field-induced second harmonic signal (EFISH) shows a steady incline and subsequent saturation for incident laser peak intensities below ~45 GW/cm^2 due to electron injection and trapping as well as defect generation in the SiO_2 layer. We used second harmonic generation imaging to visualize defect sample areas. In contrast, a drastically different behaviour of the time-dependent SH response of Si/SiO_2 interfaces was observed for peak intensities above ~45 GW/cm^2. The SH signal rose to a maximum and showed a subsequent decline over many minutes. We suggest hole injection into the ultra-thin SiO_2 layer as an interpretation of this observation.

Introduction

Because of the advances in femtosecond laser technology over the last decade, optical second harmonic generation (SHG) has been developed into a versatile tool to investigate systems with broken inversion symmetry. SHG applications in basic as well as in applied science have become a vast field of research. SHG is non-intrusive and can be used as an *in situ* method. It has proved to be sensitive to surface orientation, defects, steps, strain and roughness of crystalline structures.[1] The Si/SiO_2 interface in particular has been investigated extensively owing to its outstanding importance in MOS technology. Charge trapping and defect generation in gate oxides lead to long-term drift and performance degradation of silicon-based electronic devices. The underlying microscopic mechanisms are not fully understood.[2]

The SH intensity generated in native Si/SiO_2 interfaces has been found to be time dependent.[3] The observed increase of the SH intensity is attributed to a laser-induced charge separation process yielding an internal electric field over the interface. SHG is thus sensitive to the internal field[3–5] and a key to the understanding of charge carrier dynamics and trap generation in Si/SiO_2 interfaces.

Theory

In general, the ith component of the polarization of a medium P_i due to an electric field can be expanded in a power series as follows:

$$P_i = \varepsilon_0 \left(\sum_j \chi_{ij}^{(1)} E_j + \sum_{j,k} \chi_{ijk}^{(2)} E_j E_k + \sum_{j,k,l} \chi_{ijkl}^{(3)} E_j E_k E_l + \ldots \right), \quad (1)$$

with E_i being the electric field components and χ^n the nth-order optical susceptibility tensors.

In the special case of an electric field-induced second harmonic (EFISH), the time-dependent second harmonic intensity $I^{(2\omega)}(t)$ can be expressed as:[5]

$$I^{(2\omega)}(t) = \left| \chi_0^{(2)} + \chi^{(3)} E(t) \right|^2 (I^{(\omega)})^2, \quad (2)$$

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with $I^{(\omega)}$ being the incident laser intensity, $E(t)$ the interfacial electric field, and $\chi_0^{(2)}$ and $\chi^{(3)}$ the interfacial second- and third-order susceptibilities, respectively. The equilibrium second harmonic intensity is a linear measure for the total trapped charge density n_c:[6,7]

$$n_c \propto \left| \chi_{i,\,\mathrm{eff}}^{(2)} \right| \propto \sqrt{I^{(2\omega)}}. \quad (3)$$

Here, $\chi_{i,\,\mathrm{eff}}^{(2)}$ is the effective photo-induced second-order susceptibility.

Experimental

For this study, a commercial Ti:sapphire oscillator was used. By means of a custom-built autocorrelator, the pulse width was determined to be 80 ± 5 fs. The photon energy was chosen to be 1.59 eV (782 nm). The maximum pulse energy was 10.5 nJ at a repetition rate of 80 MHz. The beam was focused onto the sample at an incident angle of 45 degrees. Employing the z-scan technique, the beam diameter at the sample position was determined to be 13 ± 2 μm.

Figure 1 is a schematic illustration of the experimental setup. A lock-in amplifier in combination with a 500-Hz light chopper was used to improve the signal-to-noise ratio. The second harmonic was separated from the fundamental frequency by a suitable set of filters and detected by a photomultiplier tube. All measurements were performed under p-polarized excitation as well as detection (p-p) at a fixed azimuthal angle.

All Si(100) samples were degreased and treated with HF to remove the oxide, then given at least 48 hours under dark normal conditions to grow a native oxide layer and reach equilibrium (<5 μm). All SHG measurements were performed in air at room temperature.

Results

Time-dependent SHG experiments

We performed time-dependent SHG experiments on native Si/SiO_2 interfaces with laser peak intensities up to the estimated damage threshold of crystalline silicon of 100 GW/cm^2.[1] Figure 2 shows the time evolution of the SH intensity for different incident peak intensities. Each measurement was taken at a virgin sample position. For peak intensities lower than ~45 GW/cm^2, the signal shows an incline on a time scale of minutes and subsequent saturation. This behaviour is well known as electric field-induced second harmonic generation and is attributed to the excitation of hot electrons inside the silicon and subsequent injection into the oxide conduction band. The latter process leads to charge separation as well as photo-induced trap generation[3,5,7] (see Discussion in ref. 5).

For peak intensities higher than ~45 GW/cm^2 the time evolution showed dramatically different behaviour. The SH signal rose to a maximum within 1–2 minutes and then declined for at least 15 minutes. The decline was more pronounced the higher the incident laser peak intensity.

SHG defect imaging

Photo-induced trap generation in Si/SiO_2 is irreversible.[7] Figure 3 shows an SHG image of a Si/SiO_2 sample, which was pre-irradiated at 5 positions with a laser peak intensity of 100 GW/cm^2 for a time interval of 900 s. The dwell time at each sample position was 0.2 s at a step size of 5 μm. The scanning laser intensity was 100 GW/cm^2. The pre-irradiated sample spots clearly show an enhanced SH response compared to the virgin sample area. Hence, SHG imaging proved to be a sensitive tool for defect imaging.

Discussion

As indicated by the continuous lines in Fig. 2, the temporal evolution of the SH signal can be described by a model involving two exponential functions:

$$I^{(2\omega)}(t) \propto [1 - a_1 \exp(-t/\tau_1) - a_2 \exp(-t/\tau_2)]^2. \quad (4)$$

A fast time constant τ_1 accounts for the ionization of existing electron trap sites in the oxide layer.[3,7] A second, slower time constant τ_2 is attributed to the photo-induced electron trap generation process,[3,7] which is irreversible. The dependence of these time constants on the laser peak intensity follows a power law, $1/\tau_i \propto (I^{(\omega)})^{n_i}$, with $n_1 = 2.9$ and $n_2 = 2.6$ in good agreement with the literature values of $n_1 = 2.8 \pm 0.2$ and $n_2 = 2.5 \pm 0.3$ (ref. 3). Thus, sample areas with a high trap density show an accelerated SH response compared to areas with a low defect density. SHG can therefore be used for defect imaging in Si/SiO_2 interfaces as demonstrated in Fig. 3.

The energy barrier for the injection of hot electrons into the oxide conduction band is 4.3 eV, requiring a 3-photon process.[3,5,6] Clearly, for peak intensities higher than ~45 GW/cm^2 this model is not suitable to describe the observed rise to a maximum and subsequent decline of the SH signal. We suggest that the injection and trapping of holes in the oxide valence band on a time scale of many minutes leads to a decline of the total trapped charge density, yielding a decrease in SH intensity [Equation (3)]. The energy threshold for this process is 5.7 eV, which involves a 4-photon process. It therefore only begins to contribute to the measured SH signal for peak intensities above a threshold of ~45 GW/cm^2. Similar behaviour was observed recently in zirconium-modified Si/$(ZrO)_x(SiO_2)_{1-x}$ interfaces,[8] for which an equivalent interpretation was given. The influence of thermal effects at peak intensities above ~45 GW/cm^2 remains to be investigated. As a first approximation, however, no heat accumulation due to pulsed laser irradiation takes place at an absorption depth in silicon of only few micrometres (laser wavelength 782 nm) and for a time of 12.5 ns between the laser pulses [the heat diffusivity of silicon is 0.85 cm^2/s (ref. 9)].

A more detailed study of charge carrier dynamics and trap generation in native Si/SiO_2 interfaces is in preparation.[10]

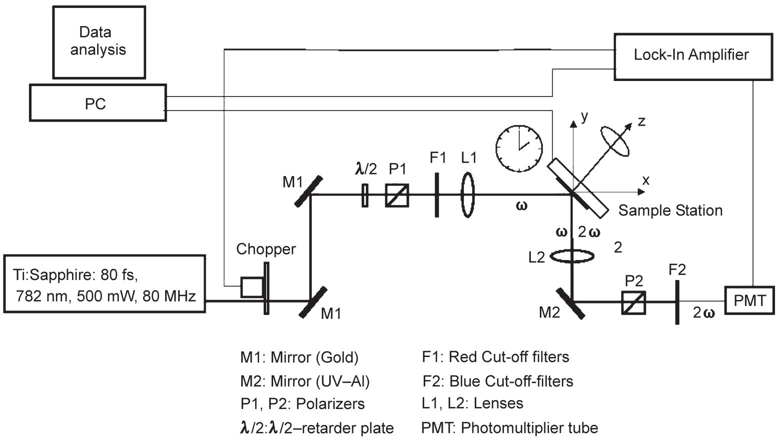

Fig. 1. Schematic illustration of the experimental setup used for SHG measurements. Lock-in technique and computer-automated data acquisition were employed.

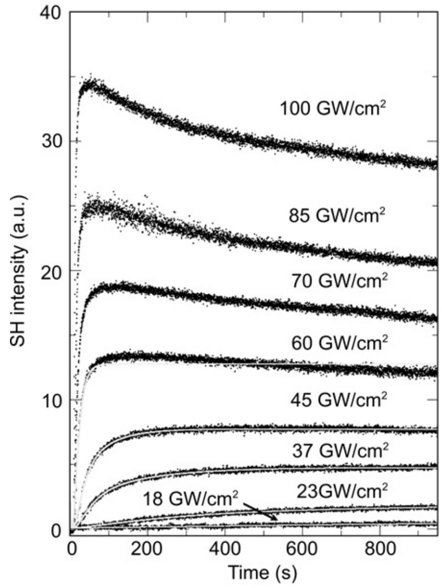

Fig. 2. Temporal evolution of the SH intensity in native Si/SiO_2 interfaces for different laser peak intensities. The continuous lines (18–60 GW/cm^2) are fitted curves using two exponential functions [see Equation (4)].[3,6,7]

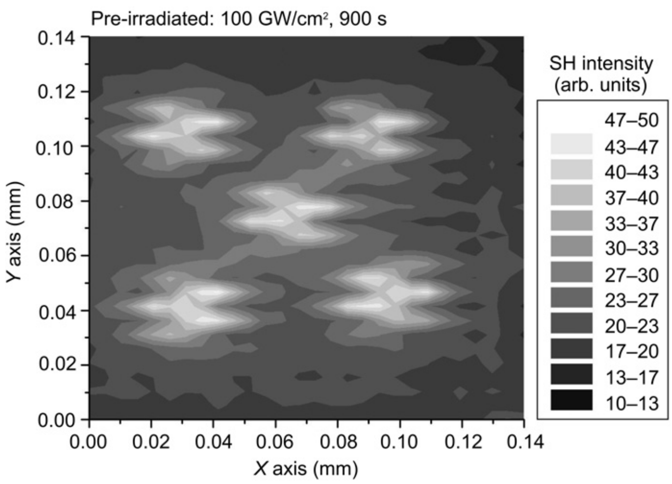

Fig. 3. SHG image of Si/SiO_2 sample pre-irradiated at 5 spots at an intensity of

Summary

We have demonstrated optical second harmonic generation to be a sensitive probe for internal electric fields. Our time-dependent SHG measurements in native Si/SiO_2 confirm earlier findings regarding electron injection and trapping in the ultra-thin SiO_2 layer. For laser peak intensities higher than ~45 GW/cm^2, we found a greatly different temporal evolution of the SH intensity. The observed SH rose to a maximum and the subsequent decline is attributed to the contribution of hole dynamics to the interfacial SH response. We suggest that hole injection and trapping in the SiO_2 valence band on a time scale of many minutes leads to a decline in total trapped charge density and thus in SH intensity. Furthermore, we used SHG imaging to visualize photo-induced defects in the ultra-thin SiO_2 layer.

We thank H. Stafast for his scientific input and also P.E. Walters, T. Stehmann, M. Bartolini and U.G.K. Deutschländer for their support. We gratefully acknowledge the financial support of the Deutsche Akademische Austauschdienst (DAAD), the National Research Foundation and the CSIR National Laser Centre.

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