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Combined electron-hole dynamics at UV-irradiated ultrathin Si-SiO_2 interfaces probed by second harmonic generation

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UV irradiation of ultrathin SiO_2 on Si can lead to injection of both holes and electrons into the oxide. 4.9-eV photons lead to electron injection while 6.7-eV photons open up the hole injection channel. The holes and electrons can trap, generating electric fields of opposite signs. Second harmonic generation (SHG) is sensitive to both the sign and magnitude of the electric field at the buried interface, revealed by opposing electric field induced second harmonic (EFISH) generation contributions. The SHG response of UV-irradiated Si-SiO_2 slowly evolves to the SHG pattern characteristic for unirradiated Si-SiO_2. We attribute the phenomenon to combined dynamics of electrons and holes at the Si-SiO_2 interface.

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The behavior of charge carriers, electrons and holes, at semiconductor/dielectric interfaces dictates the behavior of electronic devices. Complex dynamics of hot carriers may occur in the ultrathin SiO_2 layer that comprises the $\sim 2-3$ nm gate dielectrics in modern devices. At these thicknesses, a number of fundamental problems related to charge transport arise, e.g., dielectric reliability.[1] These problems may have significant consequences for the operation of semiconductor devices in microelectronic and optoelectronic applications.

Charge traps in the Si/SiO_2 system can be characterized by electric methods such as capacitance-voltage and current-voltage measurements.[1,2] The nondestructive and *in situ* character of surface specific optical techniques, such as SHG, can offer temporal, spatial, and spectral resolution providing additional insight into oxide trap characterization and carrier dynamics at any optically accessible interface.[3–7] SHG sensitivity to charge, strain, micro-roughness as well as the progress of chemical reactions on semiconductor interfaces has been demonstrated.[8–19]

Electron transfer, trapping, and detrapping at Si-SiO_2 interfaces was reported by van Driel *et al.* to induce transient, i.e., time-dependent Second Harmonic Generation (TD-SHG).[15,16] TD-SHG was ascribed to electron transfer across the Si-SiO_2 interface and trapping leading to a variation in the interfacial charge and a change in the nonlinear susceptibility.[16,17] Time-dependent SHG has enabled the temporal evolution of interface charging to be followed as electrons are promoted across the Si/SiO_2 interface.[13,16,17] The trapping time constants showed a nonlinear dependence on laser fluence, suggesting a multiphoton-mediated process.[16]

The trapped interfacial charge induces an electric field, E_{DC}, in the near-interface region. The presence of an interfacial electric field results in an electric-field-induced second harmonic (EFISH) source term that adds to the usual $\chi^{(2)}$ term:

$$I(2\omega) = C|\chi^{(2)} + \chi^{(3)}:E_{DC}|^2 I^2(\omega),$$

where E_{DC} depends implicitly on time due to interfacial charge transfer and $\chi^{(3)}$ is a third-order susceptibility that governs the electric-field driven bulk dipole response.[15]

While electron transfer processes at the Si/SiO_2 interface have been studied intensively, the role and characterization of various charge traps in the Si-SiO_2 system is still a subject of intense interest.[7,10–12,18–22] Of particular interest is the behavior of holes. While the multiphoton injection and dynamics of holes was recently reported at the Si/SiO_2 interface,[13] the interpretation has been called into question.[14] In this Rapid Communication, we report the nonlinear optical detection of simultaneous one photon electron and hole injection into SiO_2 and their dynamics at the Si-SiO_2 interface. The dynamics of the electrons and holes are quite different and can be separately probed by TD-SHG. This work has important implications for UV based processes in the fabrication and operation of semiconductor devices, e.g. UV lithography, UV-erase memory,[20,21] and UV cleaning.[2] UV irradiation of SiO_2 surfaces in air is very efficient in the removal organic monolayers from these surfaces through the combined action of photogenerated reactive oxygen species and UV photons.[22]

The SHG experiments, using an optical setup described in detail elsewhere, were carried out at 100 mW average power resulting in 1.3 GW/cm^2 peak power (9.1 kW/cm^2 average irradiance), unless otherwise specified.[23,24] All scans were taken with 800 nm or 730 nm p-polarized input light and p-polarized second-harmonic intensity unless otherwise indicated. The samples were azimuthally oriented to a maximum of the second harmonic rotational anisotropy (SHG-RA) pattern to provide the maximum sensitivity to interfacial charging.[24] SHG-RA patterns were acquired at low power at 800 nm to minimize laser-induced interface charging. 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 recovery by briefly exposing the sample to the beam (''recovery'' stage).[16,24]

Experiments were performed on Czochralski-grown n-type, phosphorus-doped ($>50\ \Omega$*cm), Si(111) samples (Silicon Quest), $\sim 500\ \mu$m thick, polished on both sides. Chemicals for sample treatment were used as received. Samples were degreased by sonicating in organics.[24] The oxide thickness was found by ellipsometry to be 1.8 ± 0.1 nm for Si(111)/SiO_2. After degreasing, samples were cleaned by the SC1 procedure.[24,25]

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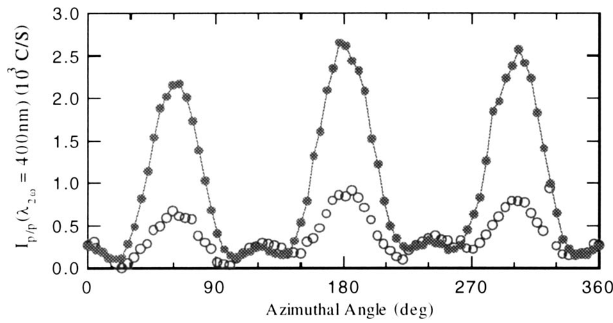

FIG. 1. RA SHG on Si(111)-SiO_2 at 800 nm; 4 kW/cm^2 average power density (0.6 GW/cm^2 peak power density). ○ (degreasing+SC1); ● (degreasing+SC1+all-lines UV).

The UV irradiation was performed on the degreased and SC1-cleaned samples by illuminating the sample by a low-pressure Hg/Ar UV lamp (Oriel Instruments) for 2 hrs in ambient laboratory air (T=25 °C, RH∼50%).[22] The lamp emitted 185-nm and 254-nm light (∼mW/cm^2) with 1:15 vacuum intensity ratio. The other spectral lines >254 nm were comparable in intensity to the 185 nm line. SHG experiments on Si-SiO_2 were started approximately 1 hr after UV irradiation. The UV lamp was kept close to the Si surface (∼3 cm) to minimize the absorption of the 185-nm line in air. To test the influence of the individual spectral lines a filter was used to remove the 185-nm line and transmit the 254-nm UV line. A 1-cm quartz cell (NSG Precision Cells, Inc.) with ethanol (Pharmco Products, Inc. 200 proof, ACS/USP grade) provides close to 100% transmission for the 254 nm line and cuts off the 185 nm line.[26] No detectable increase in oxide thickness was found each step of the surface treatment: degreasing, SC1-treatment, ethanol-filtered or "all-line" UV irradiation.

The nonlinear optical response of the UV-treated Si-SiO_2 surface is dramatically different from that of an unirradiated sample. This is revealed, for example by SHG-RA experiments performed at 800 nm at 4.0 kW/cm^2 average irradiance on UV-irradiated and unirradiated Si-SiO_2 (Fig. 1). These SHG-RA experiments were performed prior to TD-SHG measurements. The enhanced magnitude of the SHG signal on the UV-irradiated sample (Fig. 1), is reminiscent of the increase in SHG magnitude with external DC bias observed in metal-oxide-semiconductor (n-Si(111)-SiO_2-Cr) [MOS] structures attributed to EFISH effects induced by a DC bias.[27–30]

We ascribe the SHG increase to EFISH effects associated with charge buildup at the interface, caused by the UV irradiation. Both our experiments and bias-dependent measurements of SHG from MOS Si(111) structures[28] show that the increase of the SHG signal occurs on major maxima of SHG-RA. This is in line with our previous observation that the EFISH contribution to SHG from Si(111) has both isotropic and anisotropic components of comparable magnitudes that interfere destructively at minor maxima and constructively at major maxima.[24]

Irradiation of the Si-SiO_2 interface with the pulsed laser- or CW UV-lamp light can open various charge transfer routes (Fig. 2).[13,17,31] In particular, both electrons and holes

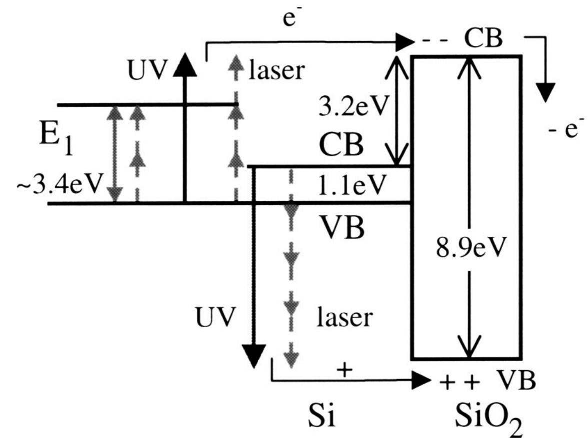

FIG. 2. Energy diagram of the Si-SiO_2 system and paths of charge transfer (Refs. 13, 17, 31).

can be injected into the oxide. Due to the band offsets at the Si-SiO_2 interface, the threshold energies for electron and hole injection are different. The injection of electrons from the Si valence band to the SiO_2 conduction band may occur either through the one-photon UV-light excitation, requiring at least 4.3 eV (288 nm) or through a laser-induced multi-photon excitation (Fig. 2). The process of hole injection into the oxide requires either four-photon excitation with our laser (1.5–1.7 eV, 800–730 nm), or single-photon excitation with UV above 5.7 eV (218 nm).[13] Four-photon injection, earlier reported as a hole injection mechanism,[13] is not efficient at the low, ∼1 GW/cm^2, peak laser irradiances employed here and in study of Wang *et al.*[14] However, the UV lamp can inject electrons and holes into the SiO_2 (CB) by 254-nm (4.9eV) and 185-nm (6.7 eV) photons, respectively.

To understand the dynamics of the UV-induced charging of the interface, TD-SHG experiments were performed on samples immediately after recording the SHG-RA patterns. TD-SHG from n-Si(111)-SiO_2 samples with and without prior UV irradiation (Fig. 3), is characterized by several dramatic differences:

(1) The TD-SHG on the UV-treated n-Si(111)-SiO_2 sample displays an "inverted" shape, i.e. the TD-SHG decreases with time during the "irradiation" stage and in-

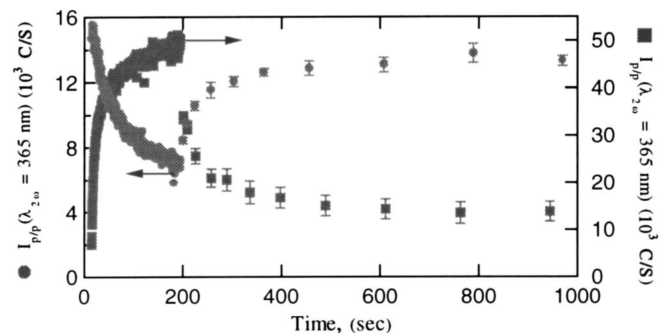

FIG. 3. TD-SHG from n-Si(111)-SiO_2, λ_ω=730 nm. Major maximum of SHG-RA. ■ SC1-cleaned; ● SC1-cleaned+2 hrs of all-line UV, ∼1 hr after UV irradiation.

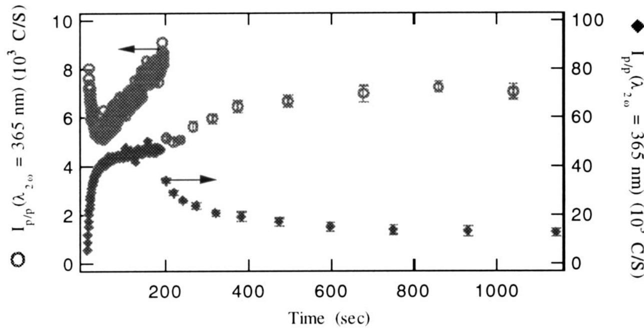

FIG. 4. SHG from Si(111)-SiO_2 λ_ω=730 nm. Major maximum of SHG-RA. ◆ SC1 cleaned+ethanol-filtered UV, ~1 hr after UV irradiation. ○ SC1 cleaned+all-lines UV, ~20 hr after UV irradiation.

creases during the "recovery" stage. Normally, on Si-SiO_2, one would observe the TD-SHG increase during near IR laser irradiation.[16]

(2) The initial (quiescent) SHG signal on the UV-treated n-Si(111)-SiO_2 sample is an order of magnitude higher than on the unirradiated sample.

Some similarities, however, exist:

(i) The presence of a recovery stage in TD-SHG: the SHG signal returns close to the initial value when the laser is blocked/unblocked periodically (Fig. 3).

(ii) The absence of TD-SHG at a minor maximum of SHG-RA, consistent with our previous result that interference between the isotropic and anisotropic EFISH terms results in zero contribution to TD-SHG at a minor maximum of Si(111)-SiO_2 SHG-RA.[24]

(iii) The incomplete recovery of TD-SHG in both cases (Fig. 3).

The effects of UV irradiation are not permanent. For example, the UV-irradiated n-Si(111)-SiO_2 sample, displays a slow conversion of the "inverted" UV-like TD-SHG pattern to the more usual (solid squares in Fig. 3) TD-SHG pattern characteristic of Si surfaces not exposed to UV. 20 hrs after the UV irradiation, TD-SHG on the UV-treated n-Si(111)-SiO_2 showed a lower value of the initial (quiescent) SHG signal as well as a "U-shaped" TD-SHG: an initial decrease of TD-SHG is followed by an increase during the laser irradiation (Fig. 4). We believe that the observed phenomena can be explained in terms of a combined electron-hole dynamics picture.

Laser excitation at 730 nm is two-photon resonant with the E_1 critical point, located at approximately 3.4 eV (365 nm).[32] This wavelength, as opposed to 800 nm, enhances the efficiency of electron injection into the oxide conduction band through a two-photon resonance with E_1 (Fig. 2). Holes can be created in the oxide valence band through a four-photon process.[13] The efficiency of multiphoton injection depends nonlinearly on the input power.[17] Under the present experimental conditions of ~1 GW/cm^2 peak power, due to the asymmetry values of the band offsets in Si-SiO_2, four-photon injection of holes into the silicon oxide is negligible compared to the three-photon electron injection.[14,17,23,33]

Holes and electrons undergo substantially different trapping/detrapping dynamics. Holes are reported to be heavier and much less mobile than electrons in silicon dioxide—electron mobility is about 0.002 m^2/Vs vs approximately 10^{-10} m^2/Vs for holes.[13,34] Hole traps are reported to have a several orders of magnitude greater trapping cross section and to be more abundant in silicon dioxide, particularly in thermally grown SiO_2.[13,35] Therefore, a substantial number of holes can be captured during UV irradiation due to low hole mobility and high trapping cross section. The holes then remain close to the Si-SiO_2 interface and have a much greater time constant for relaxation.[13] We observe the relaxation of holes occurring on a time scale of tens of hours as opposed to a time scale of minutes for electrons. Electrons, much more mobile than holes, travel, upon UV excitation, to the oxide outer interface where they undergo ambient-gas-assisted trapping.[15,17] Electrons photoinjected into SiO_2 undergo relaxation back to the bulk Si on a time scale of minutes.[16,24] Therefore, 1 hr after irradiation, the majority of photoinjected electrons have relaxed away from the oxide.[16,24] The lower-mobility holes, remaining in the oxide, give rise to the EFISH-associated increase of the second harmonic signal seen in Fig 1. When a TD-SHG experiment is performed on such a sample, electrons are injected into the oxide, reducing the electric field associated with the holes and their EFISH contribution. This causes the second harmonic signal to decrease during the laser irradiation (Fig. 3).

When the laser is blocked, laser-excited electrons relax back to the Si. The field associated with the holes is restored causing the increase of the SH signal during the recovery-probing stage of the TD-SHG experiment (solid circles in Fig. 3). Electrons do not permanently quench the holes. The "inverted" TD-SHG behavior was not evident immediately after the UV irradiation indicating that UV-promoted electrons need to relax to yield the "inverted" TD-SHG behavior, characteristic of the EFISH effect of the holes.

Hole relaxation, though slow, takes place. The TD-SHG taken 20 hrs after UV-irradiation of Si-SiO_2 (Fig. 4), shows that the initial SHG signal has reduced and is closer to the initial SHG signal on UV-unirradiated sample. Moreover, since the irradiances, hence electron injection rates, were the same, the U-shape behavior of the SHG signal suggests that 20 hrs after UV irradiation, fewer laser-induced electrons are needed to neutralize the field associated with the holes. The SHG signal decreases to a minimum when presumably the electron- and hole-associated electric fields cancel each other. The signal level at the minimum of the U-shaped TD-SHG is very close to that of the quiescent TD-SHG (initial TD-SHG) of the SC1-treated sample that was not subjected to UV irradiation (Fig. 3), and therefore does not have an EFISH contribution of UV-photoexcited carriers to SHG.

The removal of the 185-nm photons by the ethanol filter during irradiation renders both TD-SHG and SHG-RA similar to those of the SC1-cleaned Si-SiO_2 interface. We attribute this behavior to the removal of the interfacial DC electric field caused by hole injection. Successive TD-SHG scans on Si-SiO_2 irradiated by ethanol filtered UV look very

similar, like the diamond-symbol trace in Fig. 4, suggesting the absence of hole dynamics on samples UV-irradiated through the ethanol filter.

In conclusion, SHG can probe the UV injection of both electrons and holes, and the resultant dynamics and charge-trapping/detrapping properties of the Si(111)-SiO_2 interface. Electrons photoinjected into the oxide relax back to the silicon several orders of magnitude more rapidly than the holes. Evidence of positive charge accumulation is detectable by TD-SHG for tens of hours after UV irradiation. These findings may significantly impact design issues associated with microelectronic devices having ultrathin insulating oxides, particularly for UV lithography and optoelectronic applications.

Note added in proof. Similar results have been observed in our group on samples with thermally grown oxides.

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