Coupled Electron-Hole Dynamics at the Si/SiO_2 Interface

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We report a new and surprising enhancement of the electric field at the Si/SiO_2 interface following the cessation of intense pulsed near-infrared radiation. The phenomenon, measured by optical second-harmonic generation, occurs only for photon energies and oxide film thickness that exceed respective thresholds. We attribute the new effect to multiphoton hole injection into the oxide and to an asymmetry in electron and hole dynamics, in particular to distinctly different trapping and detrapping processes. [S0031-9007(98)07589-9]

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In this Letter, we present the first measurements of a pronounced electric field enhancement at the Si/SiO_2 interface, which develops unexpectedly after multiphoton excitation with ultrashort laser pulses is switched off, i.e., dark conditions. We attribute this increase in the interface electric field, in the absence of external radiation, to distinctly different dynamical behavior of holes and electrons at and near the interface. Previous second harmonic generation (SHG) studies by van Driel's group [1–3] on photoexcitation at Si/SiO_2 interfaces have elucidated the unique contribution of electrons in the development of interface electric fields.

The present work establishes for the first time the important role of holes in the dynamical processes leading to charge separation and subsequent quasistatic electric field enhancement both during multiphoton excitation and also under nonperturbative conditions. Wavelength-dependent studies of this new effect show that hole injection occurs for photon energies above 1.52 eV. The subsequent field enhancement is readily observable for oxides that exceed a critical threshold thickness (approximately 30 to 40 Å). For thinner oxides hole dynamics is more complicated due to detrapping of electrons. We propose that the effect is mediated by four-photon excitation of holes across the valence-band offset, charge trapping and detrapping, and subsequent relaxation at the interface. This work bears directly on fundamental physics issues involving carrier dynamics at semiconductor interfaces, charge breakdown mechanisms, and hot carrier injection. In addition, the dependence of the new phenomenon on oxide thickness may have significant consequences on device physics as gate oxide thickness shrinks below 40 Å.

For our studies, we used the optical second-harmonic generation technique, which has proved to be a sensitive probe of semiconductor interfaces [1–11]. The experimental setup is standard for surface SHG measurements. Briefly, a Ti:sapphire laser provides 150 fs pulses, a wavelength range tunable from 7100 to 9100 Å, and an average power of 300 mW at a repetition rate of 80 MHz. The beam is focused to approximately 10 μm in diameter on the sample, and the reflected SHG signal is measured with 0.5 s temporal resolution by a photomultiplier and photon counter. The new phenomenon was observed systematically in a variety of different oxides. A matrix of samples was prepared from lightly boron-doped (10^{15} cm^{-3}) Si(001) wafers covered with thermal oxides of different thicknesses, 40, 50, and 65 Å. Some of these samples were annealed in hydrogen or deuterium containing atmospheres. Thinner oxides were prepared by etching back the oxide in a dilute HF solution to a thickness of about 10 Å.

For all thermal oxide samples studied, a rapid increase in the SHG signal was observed for the first few hundred seconds of irradiation (Fig. 1). It then gradually reached a saturation level defined as Δ_1. The time-dependent SHG (TDSHG) from the Si/SiO_2 interface can be described in general by $I^{2\omega}(t) = |\chi^{(2)} + \chi^{(3)}\mathcal{E}(t)|^2(I^{\omega})^2$, where I^{ω} and $I^{2\omega}(t)$ are the intensities of the fundamental beam and the TDSHG signal, $\chi^{(3)}$ is the third-order nonlinear susceptibility of silicon, $\chi^{(2)}$ is the effective SHG susceptibility from all other sources, and $\mathcal{E}(t)$ is a quasistatic electric field in the silicon space charge region at the Si/SiO_2 interface. $\mathcal{E}(t)$ arises from the charge separation at the interface causing a field perpendicular to the surface. Thus

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the TDSHG technique is a direct contactless method of probing electric fields at the Si/SiO_2 interface.

The initial rise in the TDSHG signal observed in Fig. 1 is similar to results obtained by other groups [1–3,12]. In the work done in van Driel's group [1–3], it was shown that the TDSHG signal increases rapidly when the Si/SiO_2 interface is irradiated by a fundamental beam ($\lambda = 7700$ Å, 110 fs pulses, 1 GW/cm^2 peak intensity, and 76 MHz repetition rate), and then it gradually saturates. van Driel and co-workers attributed this phenomenon to multiphoton excitation of electrons into the SiO_2 conduction band and the subsequent electron transfer and trapping at the oxide/ambient interface [1,2]. This interpretation is consistent with our results. When electrons are excited from the silicon valence band into the oxide conduction band and eventually become trapped primarily on the oxide outer surface, a charge separation occurs. This charge separation alters $\mathcal{E}(t)$ at the interface, which in turn leads to changes in the TDSHG signal [2].

Our results show a new and scientifically revealing phenomenon for all oxides with thicknesses exceeding 40 Å, i.e., a pronounced increase in the TDSHG signal after the excitation beam ($\lambda = 7900$ Å, 10 GW/cm^2 peak intensity) has been blocked for several seconds and then unblocked, as shown in Fig. 1. The magnitude of this dark field enhancement is referred to as Δ_2. After 600 sec of irradiation the excitation beam was blocked. Then 100 sec later the fundamental beam was again switched on. Surprisingly, the initial reading of the TDSHG signal was observed to be much higher than before the beam was blocked. The enhanced signal was seen to decrease in a matter of a few tens of seconds to the former saturation level and followed that saturation trend thereafter. In contrast, the inset of Fig. 1 shows the TDSHG response for a thinner oxide (~10 Å) which does not show the dark related field enhancement, Δ_2. In fact, in this case the field is drastically lowered. van Driel's group monitored the time dependence of the SHG signal after the excitation beam was switched off for a thin oxide (~30 Å) grown in steam [Fig. 1(a) in Ref. [2]]. They observed a decrease in the TDSHG signal, which is identical to the observed TDSHG behavior of our etched sample. Therefore we conclude that as a general feature the newly observed dark electric field enhancement is pronounced for oxide films that exceed a critical threshold thickness in the range 30 to 40 Å. For thinner oxide films, the hole related effect is less apparent due to fast electron detrapping from the surface which neutralizes the holes trapped in the oxide and at the interface.

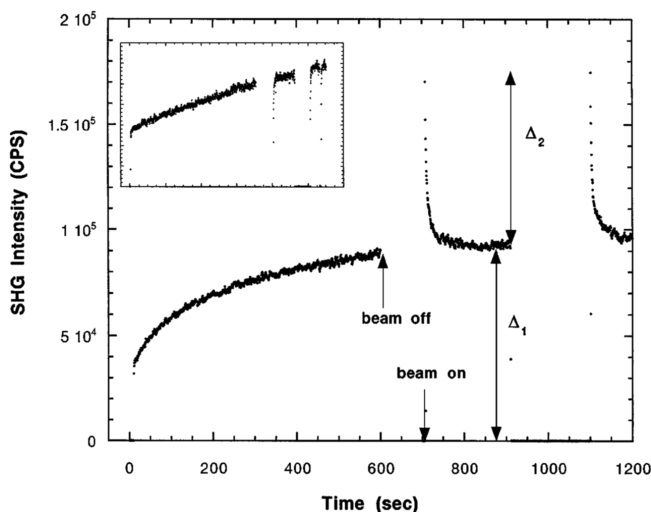

FIG. 1. Time-dependent SHG signal from a 40 Å thermal oxide grown on a p-type Si(001) substrate. Δ_1 represents the beam-on saturated SHG signal while Δ_2 represents the dark field enhanced SHG signal. The inset shows the TDSHG signal from the same wafer after the oxide has been etched down to 10 Å thickness.

Note that for pulsed laser excitation, several pathways exist for promoting electrons and holes to the continuum states of the oxide. In Ref. [1] it was shown that the trapping rate for photoinjected electrons (reciprocal TDSHG rise time) follows approximately an $(I^{\omega})^3$ dependence using a fundamental beam consisting of 110 fs pulses at $\lambda = 7700$ Å. This suggests that three-photon processes including cascaded one- and two-photon processes, or direct three-photon processes occur. We performed power dependent TDSHG measurements similar to the one shown in Fig. 1 on a 40 Å thermal oxide. Figure 2 reveals an approximately $(I^{\omega})^{2.4}$ dependence for the saturated TDSHG signal (Δ_1). In contrast, the dark field enhancement (Δ_2) scales with approximately $(I^{\omega})^{3.5}$. Hence multiphoton absorption processes are likely to account for this novel effect.

To further elucidate the nature of the newly observed phenomenon, we performed TDSHG measurements of Δ_1 and Δ_2 as a function of incident photon energy. Figure 3(a) shows TDSHG results obtained from a 40 Å thermally grown and deuterated oxide at three different photon energies. The three data sets clearly show that Δ_1 decreases with increasing photon energy. In marked contrast, Δ_2 increases with increasing photon energy. We note that the sum, $\Delta_1 + \Delta_2$, remains largely constant

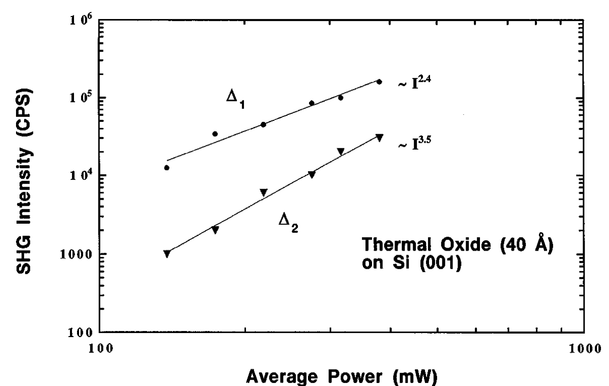

FIG. 2. Power dependence of Δ_1 and Δ_2.

over the range of measured photon energies consistent with charge conservation and our hole-injection model described below. Figure 3(b) summarizes the photon energy dependence of Δ_1 and Δ_2 for all measurements obtained. The data clearly show that Δ_2 occurs only for photon energies above a critical photon energy threshold of approximately 1.52 eV. Moreover, below this threshold, Δ_1, which may be attributed totally to electron injection behavior, is almost at a maximum. van Driel's energy threshold is 1.43 eV (4.3 eV divided by 3). Hence the electron and hole thresholds are at very different energies.

The above observations can be interpreted in a consistent way as follows. Previous measurements using x-ray photoelectron spectroscopy (XPS) gave valence band offsets for both wet and dry oxides varying from 4.35 to 4.9 eV [13,14]. A schematic of the band offsets at the Si/SiO_2 interface is shown in Fig. 4. Taking into account that the band gap of silicon is 1.1 eV and the SiO_2 band gap is approximately 9 eV at room temperature and that the fundamental beam must have a photon energy larger than 1.52 eV, we conclude that it requires four photons (6.08 eV) to create a hole in the oxide valence band, while three photons of greater than 1.36 eV (4.1 eV) are needed to excite an electron from the silicon valence band to the oxide conduction band [1,2].

Because of the significant difference in transition probability between a three-photon and a four-photon process, the excitation of electrons is strongly favored. Therefore the initial feature of TDSHG is dominated by photoinjection of hot electrons, even though there are holes excited into the oxide as well, and some of them may, of course, recombine. When the photon energy is below 1.52 eV, holes are not injected in the oxide and the dynamical behavior is determined solely by electrons. This explains why above 1.52 eV, Δ_1 decreases *since the total field at the interface is lessened due to the injection of holes into the oxide*.

During the injection of electrons and holes into the oxide, several things happen. The density of electron traps in thermally grown bulk silicon dioxide is quite small; considerably less than 1% of the electrons injected at room temperature will therefore be trapped in the insulator [15]. Since electrons have a normal mobility of about 0.002 $m^2/V\,s$ [15], they will leave the oxide very fast (within picoseconds) either to the silicon or to the outer oxide surface. Previous studies have shown that due to the oxygen ambient, hot electrons will eventually travel to the surface where some of them become trapped [2]. For thick oxides, the trapped electrons remain on the oxide-ambient interface after the excitation beam is switched off. For oxides below a critical thickness (~30 Å) the electrons tunnel back and combine with the holes. Our experiments on the thin oxide films (~10 Å) confirm this explanation. The inset of Fig. 1 shows that the TDSHG signal from these samples behaves differently and strongly increases from a very low level after blocking and unblocking the fundamental beam. In this case, a fraction of the electrons was able to move back to the oxide. We note that, after unblocking the excitation beam, the TDSHG intensity from both the etch back and the 40 Å oxide quickly returns to the saturation level reached before blocking the beam. This "memory effect" results from the large dispersion in the electron

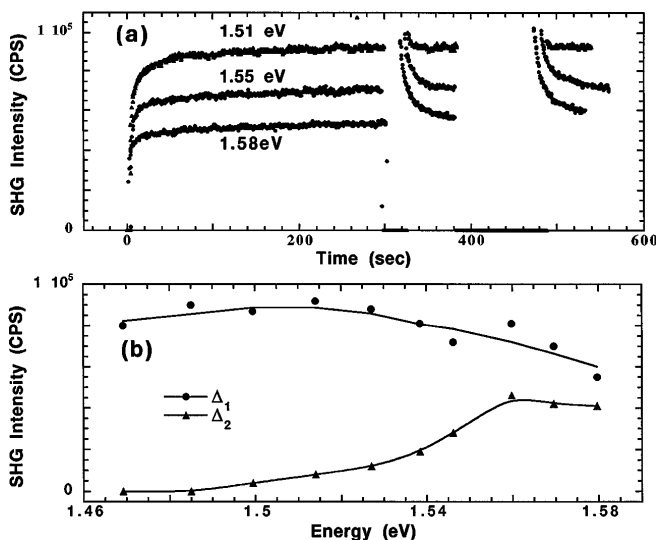

FIG. 3. (a) Time-dependent SHG signal from a 40 Å thermally grown and deuterated oxide for three different photon energies. (b) Photon energy dependence of Δ_1 and Δ_2. The solid curves are guides to the eye.

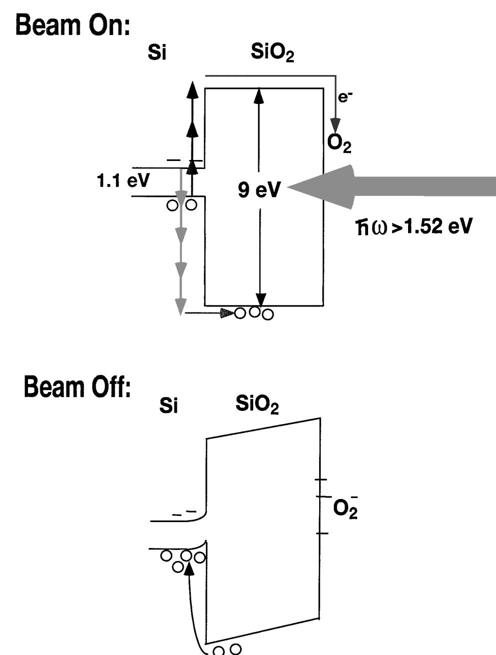

FIG. 4. Schematic diagrams of a three-photon electron and a four-photon hole transfer process from silicon into an ultrathin oxide. For simplicity only the flat-band condition is shown in the top diagram.

detrapping time constants which can be several hundreds of seconds and longer [1,3].

In contrast to electrons, holes in silicon dioxide behave quite differently. The hole transport is highly variable, with a very low apparent mobility, of order 10^{-10} $m^2/V\,s$ [15]. Models explaining this type of charge transport assume a large density of shallow hole traps [15]. The holes are assumed to move either by tunneling between localized states (hole traps) or they become trapped and then reemitted into the valence band with a large time constant dispersion due to the distribution in trap depths. Hole traps are more abundant in thermally grown silicon dioxide than electron traps, and since they also have larger cross sections, a substantial fraction of the injected holes may be captured. It has been reported that as many as 10% of injected holes can become trapped in the oxide close to the Si/SiO_2 interface [16].

As a result of these considerations, we suggest that in the presence of the excitation beam with photon energies greater than 1.52 eV, a substantial proportion of injected holes, having surmounted the valence band offset and crossed the interface into the oxide, remain close to the interface. Consequently, these holes can readily move back to the silicon when the beam is switched off. This movement of holes back to the silicon, under dark conditions, is responsible for the observed enhanced electric field $\mathcal{E}(t)$, as monitored by TDSHG, Δ_2, arising from the increased charge separation at the interface (Fig. 4). Figure 1 verifies this. After again turning on the excitation beam, hot holes move across the interface into the SiO_2. On the other hand, relatively few electrons will move from the silicon to the SiO_2, when the beam is switched on, because they have to drift against an already strong space charge field created by the electrons trapped at the SiO_2 outer surface. Consequently, there are more holes than electrons moving into SiO_2 with the excitation beam on. These two effects combined reduce the charge separation. Therefore the field $\mathcal{E}(t)$ and the TDSHG signal will decrease to near the previous beam-on level, Δ_1, when the excitation beam again illuminates the Si/SiO_2 interface.

This new dark field enhancement effect, which is crucially dependent on oxide thickness and on photon energy, provides significant insight into the role of hole trapping, detrapping, and relaxation at the Si/SiO_2 interface, which critically impacts next-generation microelectronics. In the future, by applying intense tunable infra-red radiation from the Vanderbilt Free-Electron Laser we plan to selectively modify local vibrational modes and simultaneously monitor the changing electronic properties of the Si/SiO_2 interface with this new contactless SHG technique. In particular, this approach will shed light on the observed dramatic lifetime differences between hydrogenated and deuterated interfaces of CMOS devices [17].

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