

Electron Photoinjection from Silicon to Ultrathin SiO₂ Films via Ambient Oxygen

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Hot electrons are generated in Si(001) at 295 K via linear absorption of >4.3 eV photons or by three-photon processes using 270 fs, 800 nm (1.55 eV) optical pulses. Electron trapping in oxide films is observed via time-dependent optical second harmonic generation induced by the electric field associated with charge transfer. For anodically oxidized samples and constant beam irradiance, the transfer rate decreases to zero with increasing oxide thickness with a characteristic length of 3.5 nm, comparable to the electron scattering length; the rate increases with ambient oxygen pressure (P) as $P^{0.035}$. These results indicate that oxygen is essential to hot electron transfer in ultrathin oxides and serves at least as a trapping catalyst. [S0031-9007(96)00817-4]

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The physical characteristics of the amorphous oxide which forms on crystalline silicon have played a major role in establishing the dominance of silicon in semiconductor technology. Since electrical properties related to charge trapping are especially relevant to the performance of many semiconductor devices, carrier trapping has long been an important field of study. Charge transfer from Si to SiO₂ via thermionic or photoemission apparently is also important in thermal oxidation of Si [1,2]. For thin (<20 nm) oxides [3] and for clean Si [4] there have also been suggestions that electrons from Si may attach to gaseous O₂ in “harpooning” reactions [5] at the surface, although many details are unclear. As dimensions of Si-based devices continue to shrink, it is becoming increasingly important to better understand how thin oxide films influence electron transfer. However, traditional electronic methods for observing trapped charge require metal contacts which prevent oxygen access to the SiO₂/ambient interface and alter the properties of thin oxides through in-diffusion of metal atoms. Noncontact methods such as electron photoemission spectroscopy can only be used *in vacuo*. Since electron activation from the Si valence band into the oxide requires [6] at least $\Delta V = 4.25$ eV, nanosecond ultraviolet (UV) laser pulses [7] are often used to investigate electron transport and even oxide growth. However, since the fluence typically exceeds 10 mJ cm^{-2} and the optical absorption depth in Si is <5 nm [8], transient surface temperature increases of $\gg 100$ K make the separation of photonic and thermal effects difficult. Evidence for electron transfer or trapping is based on *post facto* measurements of irreversible oxide growth.

Optical second harmonic generation (SHG) has proven to be a useful, noninvasive probe of interfaces between centrosymmetric materials [9–18] such as the Si/SiO₂ buried interface which cannot be accessed by other techniques. As an optical technique SHG can be used *in situ*, in the presence of ambient gases. When high repetition rate ~ 100 fs laser pulses are used, high second harmonic (SH) signal sensitivity is obtained with negligible sam-

ple heating [11]. SHG can also detect changes in electric fields [15–18] via a method analogous to electro-optic sampling in noncentrosymmetric media [19]. Earlier we showed [17] that 110 fs pulses with photon energy 1.6 eV ($\lambda = 770$ nm) can generate hot electrons in Si via three-photon processes with subsequent trapping in the oxide; the associated electric field dynamics could be monitored using SHG from the same beam. Using an ultraviolet lamp we herein provide independent confirmation of the hot electron generation process. We also show quantitatively that the electron transfer rate depends on oxide thickness and the pressure of oxygen in the ambient. This definitively shows that ambient oxygen serves at least as a catalyst for electron trapping in ultrathin oxide layers.

Hot electrons were excited in Si using a Hg arc lamp and monochromator providing $>100 \mu\text{W}$ of continuous power between ~ 2 and 5 eV in <0.05 eV bandwidths. The light was focused at normal incidence on Si samples to a diameter of ~ 0.5 cm. This excitation configuration is similar to that used by Yodh and co-workers [20] for studies of SHG from III-V materials. As both an excitation and SH probe beam, we also used output from a regeneratively amplified Ti:sapphire laser producing 270 fs, 800 nm ($\hbar\omega = 1.55$ eV) pulses at 250 kHz repetition rate. This beam was focused at an incidence angle of 80° to a diameter of $\sim 100 \mu\text{m}$ on Si samples, producing average (peak) irradiance up to 1.5 kW cm^{-2} (20 GW cm^{-2}); the steady-state (transient) surface temperature increase is estimated to be <10 K (30 K). The p -polarized SH beam generated in reflection by a p -polarized laser beam was measured with 0.01–1.0 s temporal resolution by a photomultiplier and photon counter gated by a 1 kHz chopper. Samples included p -Si(001) (resistivity 3–7 $\Omega \text{ cm}$), anodically oxidized in 0.1M HCl to produce oxides with thickness between 1 and 11 nm as measured by ellipsometry and x-ray photoelectron spectroscopy [21]; n -Si(001) (resistivity 20–100 $\Omega \text{ cm}$) with ~ 3 nm oxide produced in steam at 850 K, and n -Si(001) (resistivity 20–50 $\Omega \text{ cm}$) with 5–25 nm oxides grown in dry O₂ at 1000 K. The

samples were oriented to maximize the anisotropic SH signal. To observe the influence of ambient gases on charge transfer, samples were placed in a vacuum chamber with UV-transmitting windows. Gases introduced included wet air and research-grade ($<0.01\%$ impurities) dry H_2 , N_2 , Ar, and O_2 . All experiments were carried out at 295 K.

Figure 1(a) shows the time-dependent SH (TDSH) signal during illumination of the n -Si sample with 3 nm thick oxide layer in air; here only the laser is used with an average irradiance of 1.3 kW cm^{-2} . As in Ref. [17] we ascribe the TDSH response to the development of a quasistatic electric field associated with photoinduced electron transport across the Si/SiO₂ interface. The TDSH intensity $I^{(2\omega)}(t)$ can be described by the functional form

$$I^{(2\omega)}(t) = |\chi_0^{(2)} + \chi^{(3)}\mathcal{E}(t)|^2(I^{(\omega)})^2. \quad (1)$$

Here $\chi_0^{(2)}$ represents the quiescent Si/SiO₂ interfacial second-order susceptibility, $\chi^{(3)}$ a third-order susceptibility, and $\mathcal{E}(t)$ the quasistatic electric field. For the data shown in Fig. 1(a) and for $t < 600$ s $\mathcal{E}(t)$ cannot be fit by a single exponential function appropriate for a single trapping process with a constant trapping cross section and detrapping rate [17]. The observed behavior may indicate, for example, multiple traps or a trapping rate dependent on $\mathcal{E}(t)$ [an increase of $\mathcal{E}(t)$ can inhibit electron transport through the oxide]. As Fig. 1(a) shows, an increase in irra-

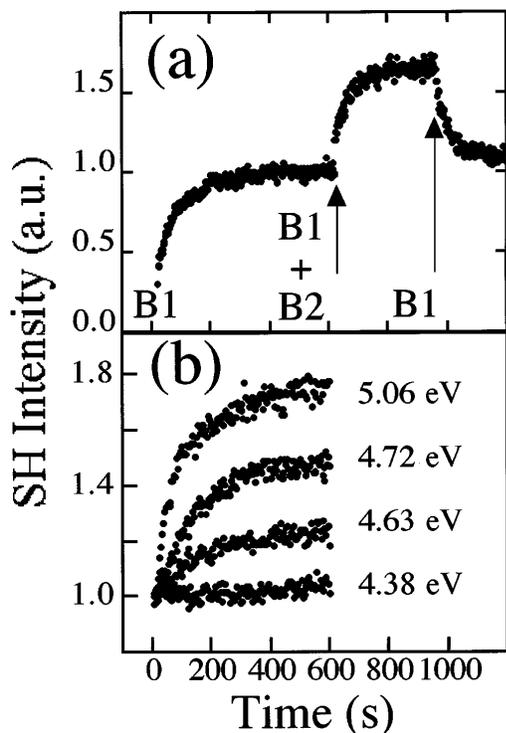


FIG. 1. SHG from an oxidized n -Si(001) sample illuminated by 270 fs, 1.55 eV laser pulses at an angle of incidence of 80° (a) at average irradiance of 1.3 kW cm^{-2} (beam B1), with a second 3.6 kW cm^{-2} (beam B2) at normal incidence; and (b) at average irradiance of 0.5 kW cm^{-2} , with a normal incidence ultraviolet beam at the photon energies indicated.

diance after the steady-state SH level occurs (at $t \sim 600$ s) leads to an additional increase and new steady-state signal. Restoration of the previous irradiance level (at $t \sim 950$ s) causes the SH amplitude to decrease to its previous steady-state value on a time scale of 80 s due to detrapping. These experiments show that a steady-state SH signal does not necessarily imply trap saturation. The detrapping time could be reduced to $\ll 1$ s by electrically grounding the irradiated area of the sample. It is also possible that other types of trapping and detrapping processes may occur, such as trapping of low energy electrons and holes following single photon absorption. However, these processes either are saturated on a much shorter time scale than indicated here or do not involve charge separation contributing to an electric field. Therefore our SHG experiments may not be sensitive to these processes.

As Fig. 1(b) shows, illumination of the sample with photons of energy ≥ 4.38 eV (near $3\hbar\omega$) from a Hg lamp with an average irradiance of $300 \mu\text{W cm}^{-2}$ can induce behavior similar to that observed in Fig. 1(a) (with the laser beam average irradiance at 0.5 kW cm^{-2} , simply used as a SH probe). The threshold photon energy for TDSH behavior has been carefully determined to be 4.3 eV in agreement with ΔV quoted above. For laser excitation alone there are numerous pathways for generating electrons with sufficient energy to overcome ΔV . The approximate $(I^\omega)^3$ dependence of the trapping rate (reciprocal TDSH rise time) we observed earlier [17] suggests that three-photon processes occur. These might include cascaded one- and two-photon absorption, or direct three-photon absorption. Alternatively, SHG or third harmonic generation (THG) processes followed by absorption of fundamental and/or harmonic photons may occur. Earlier we suggested the dominant process for hot electron transfer might be THG followed by reabsorption of $3\hbar\omega$ photons within 5 nm of the Si/SiO₂ interface (absorption depth for 4.8 eV photons [8], also approximately the mean free path of electrons in Si). When the laser is used at 0.5 kW cm^{-2} average irradiance, but the incident polarization is changed from linear to circular, loss of the anisotropic THG contribution reduces the TH signal [22] from $\sim 10^5 \text{ counts s}^{-1}$ ($10^9 \text{ counts s}^{-1} \text{ cm}^{-2}$) to $< 5 \times 10^3 \text{ counts s}^{-1}$. However, the rise time for the SH signal changes by $< 10\%$ where an order of magnitude decrease is expected. Other nonlinear optical processes must therefore be responsible for generating high energy electrons. For example, at a peak irradiance of 10 GW cm^{-2} three-photon absorption (TPA) is estimated to yield an electron flux at the Si/SiO₂ interface of 10^{13} – $10^{15} \text{ cm}^{-2} \text{ s}^{-1}$ [23] for electrons generated within one mean free path of the interface. This flux is more than 3 orders of magnitude higher than that from the THG process. The calculated electron flux related to TPA is comparable to the $10^{14} \text{ cm}^{-2} \text{ s}^{-1}$ photon flux from the Hg lamp required to induce a TDSH response in Fig. 1(b) similar to that shown in Fig. 1(a). Other linear or nonlinear processes may occur as well, or even dominate for samples at different temperature [25], orientation,

doping level, etc. Nevertheless, on the basis of TPA alone, and following hundreds of seconds of illumination, one anticipates transferred electron surface densities $>10^{12} \text{ cm}^{-2}$ and electric fields $>10^4 \text{ V cm}^{-1}$, sufficient to induce measurable changes in the TDSH intensity [15].

To identify the nature of the electron transfer mechanism we measured the TDSH signal for an average irradiance of 0.25 kW cm^{-2} from a family of anodically oxidized *p*-Si samples with different oxide thicknesses. As the SiO_2 thickness increases, the fitted steady-state field decays with a characteristic thickness of $L_c = 3.5 \text{ nm}$ as shown in Fig. 2. This trend was also observed for 5–25 nm thick dry oxides on *n*-Si. By contrast, the tunneling depth is 0.1 nm [26] for electrons facing a 3.2 eV barrier (ΔV minus indirect band gap of Si). Tunneling into the oxide would also give rise to an approximate $\ln(t/t_0)$ variation in $\mathcal{E}(t)$ where t_0 is the characteristic tunneling time. This is not observed. Moreover, the initial (quiescent) value of the SH signal for all samples represented in Fig. 2 is constant, demonstrating that the steady-state TDSH response is strictly photoinduced and is not due to changes in sample properties with oxide thickness. The data displayed in Fig. 2 suggest that electron transfer to the vicinity of the SiO_2 /ambient interface occurs as indicated in the inset.

To confirm this interpretation, we monitored the TDSH signal from the 3 nm oxide *n*-Si sample in the presence of the gases listed above at pressures between 10^{-2} and 760 Torr. For identical illumination conditions and pressures, O_2 gave the largest TDSH response (with air giving a slightly smaller contribution), while the other gases yielded a TDSH response which was at least an order of magnitude smaller. Similar results were obtained using other Si samples. As Fig. 3 shows, when the laser illumi-

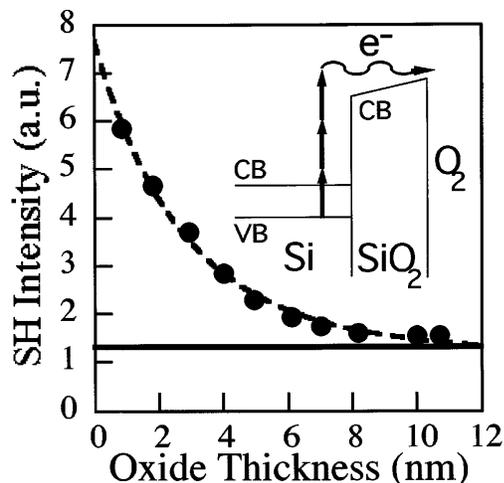


FIG. 2. Oxide thickness dependence of the steady-state SHG from *p*-Si(001) samples for constant irradiance of 0.25 kW cm^{-2} at an angle of incidence of 45° ; the horizontal line indicates the quiescent level observed for all samples. The inset shows a schematic diagram of a possible electron excitation or transfer process (VB = valence band edge; CB = conduction band edge).

nates the sample at a pressure of 10^{-2} Torr and oxygen is introduced to a final pressure of 760 Torr, the SH signal increases dramatically in a time similar to that shown in Fig. 1(a). This rise time is essentially independent of final pressure in the range 10^{-1} –760 Torr. In separate experiments conducted at pressures $<10^{-10}$ Torr no measurable time-dependent SHG was observed. We therefore suggest that ambient oxygen captures electrons (molecular oxygen has an electron affinity of 0.4 eV [27]). The steady-state SH signal varies with oxygen pressure (P) as shown in the inset to Fig. 3; because the TDSH signal changes with P , and time is required before a new steady-state level is reached, successive data points were taken more than 200 s after the pressure was altered. As indicated, the effects of oxygen on the TDSH signal are reversible. The associated $\mathcal{E}(t)$ which monitors trap occupancy varies as $P^{0.035 \pm 0.005}$ for the range of pressures considered. Conventional adsorption as the rate-limiting step for oxygen participation in electron trapping is not consistent with data presented in Fig. 3. If this were the case, the steady-state SH intensity would vary with P according to Henry's law and the TDSH rise time would vary as P^{-1} . An explanation for the observed behavior is that electrons and oxygen attract each other in a harpooning reaction [5] in the vicinity of the SiO_2 /ambient interface and then attach to or penetrate the positively charged solid. When oxygen is pumped from the chamber, the SH signal relaxes to $<5\%$ above its quiescent value in tens of seconds, similar to the time for detrapping observed in Fig. 1(a). The residual signal may be due to the presence of electrons transferred from oxygen to fixed oxide traps, or the generation of new trap sites. The oxygen at the surface or in the oxide at least assists the trapping process in a catalytic role and may even provide the actual trap sites. The weak P dependence of the steady-state SH intensity shown in Fig. 3 suggests that more than enough oxygen is present at all pressures [2] to capture the

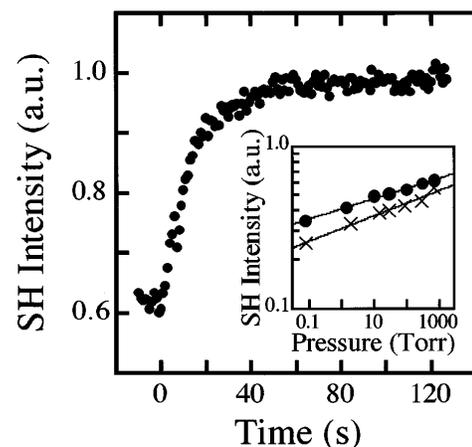


FIG. 3. SHG signal observed from oxidized *n*-Si(001) after the ambient oxygen pressure is increased from 10^{-2} to 760 Torr in 2 s. The inset shows the pressure dependence of the steady-state SHG for increasing (\times) and decreasing (\bullet) pressure. The data sets are offset for clarity.

electrons at the SiO₂/ambient interface. The very weak TDSH response induced by gases other than oxygen and air may be related to impurities with positive electron affinity or residual traps in the oxide. Finally, note that the decay length of the steady-state electric field, $L_c = 3.5$ nm, is comparable to the 3.4 nm scattering length of electrons in the oxide [28]. Scattered electrons would be preferentially redirected back to the positively charged Si before being captured by oxygen. It is also worth noting that the apparent maximum oxide depth of 10 nm for which reversible electron trapping occurs at 295 K is similar to that associated with rapid oxidation of Si at higher temperatures [1].

In conclusion, we have used an *in situ* technique with negligible sample heating to directly and quantitatively demonstrate that ambient oxygen assists the capture of electrons in ultrathin oxide films on silicon. Ambient oxygen is bound weakly to the oxide, rendering the trapping process reversible at room temperature. This is not surprising since significant oxidation occurs only at much higher temperatures, as the activation energy for O₂ diffusion to the Si/SiO₂ interface and oxidation is >1 eV [1,29]. Finally, the techniques presented here may improve our understanding of trapping in Si/oxide systems and, by controlled variation of sample parameters such as temperature, provide information about the onset of irreversible oxidation in the thin oxide regime. Properties such as these will define the physical limitations of the processing and performance of submicron metal-oxide-semiconductor devices.

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