Dynamics and second-order nonlinear optical susceptibility of photoexcited carriers at Si(111) interfaces

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An interface specific investigation, by time-resolved second-harmonic generation, shows that photoexcited carrier dynamics at Si(111) interfaces depend strongly on surface termination. Oxide- and H-terminated surfaces show distinct transient behavior, with a surface recombination velocity $<10^3$ cm/s. Incompletely H-terminated Si(111) shows faster dynamics, correlating with less interface passivation. A simple model reveals that the second-order nonlinear optical susceptibility of photoexcited carriers is two orders of magnitude greater than that of the valence band electrons. © *2003 American Institute of Physics.*
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Carrier relaxation at semiconductor interfaces is important to surface photochemistry,[1,2] solar energy photoconversion,[3] the modeling of the operation of semiconductor devices,[4] and the degradation of semiconductor transistors.[5] Under ideal situations, carrier recombination, the principal fate of excited carriers, is determined by the rate of radiative decay, which occurs on a nanosecond time scale.[6] However, "trapping centers" exist in the bulk and at interfaces, which accelerate the recombination.[7–9]

There has been controversy regarding the effect of surface chemistry on recombination dynamics. Experiments suggested that recombination at oxygen-induced defects was four times greater than on ordered reconstructed Si surfaces in vacuum.[1] This was surprising as oxidation reportedly reduces the density of midgap states,[10] the very states deemed most efficient at inducing surface recombination.[8,11]

Ultrafast transient optical reflectivity experiments on oxidized Si have been employed to investigate recombination.[12,13] These bulk techniques are sensitive to the interface inasmuch as the surface can provide recombination centers that affect the bulk dynamics.[12] Nominally oxidized Si samples show subnanosecond recovery, consistent with surface recombination velocity (SRV) $>10^4$ cm/s.[12] H-terminated Si displayed sub-20-ps recovery times, corresponding to SRV$\sim 10^6$ cm/s.[12] In order to enhance surface sensitivity, carrier dynamics have been investigated in Si using time resolved transient grating techniques.[14–16] However, this principally probes diffusion and hot carrier energy relaxation. To our knowledge, there has been no surface-specific investigation of carrier relaxation dynamics at the buried Si–SiO$_2$ interface.

In this work, we report the direct investigation of carrier dynamics at buried interfaces by time-resolved second-harmonic generation (TRSHG), a versatile, *in situ*, real-time interface specific probe.[17] The SHG dynamics depend strongly on the surface chemistry. Si(111)–SiO$_2$ and

Si(111)–H interfaces are characterized by SRVs of $<10^3$ cm/s. Incompletely H-terminated Si(111) samples show faster SHG dynamics, reflecting a lesser degree of interface passivation. Defect sites, localized at the Si(111)–H surface, deplete the conduction band carrier population by trapping or recombination. These experiments also provide experimental determination of the second-order nonlinear optical susceptibility of photoexcited carriers.

TRSHG measurements were carried out a with 1 kHz Ti:sapphire regenerative amplifier.[18] The 800-nm pump fluence was typically 7.2 mJ/cm^2, generating 2.4×10^{19} excited electron–hole pairs/cm^3.[12,14] The carrier dynamics were probed by a time-delayed, probe beam incident at a slightly different angle to facilitate spatial discrimination of probe SHG. The fundamental and the SHG were *p*-polarized. Oxide-covered samples were cleaned by degreasing. H-terminated samples were prepared by standard procedures.[19] Experiments on H-terminated Si were carried out in a dry N$_2$ atmosphere to reduce ambient and photo-oxidation effects.[20] The *n*-type Si(111) (P-doped, $\sim$30-Ω cm resistivity, Motorola Phoenix, $\sim$300-μm-thick), samples were oriented to maximize SH signal, that is, at an azimuthal angle ($\phi=0$) defined with respect to the $[2\bar{1}\bar{1}]$ direction.

TRSHG from native-oxide-covered Si exhibits an initial, prompt increase in the SHG response, followed by a recovery on a time scale of nanoseconds (Fig. 1). Absorption of 800 nm (1.55 eV) photons, whose energy is greater than the band gap E_g of Si (1.1 eV), occurs via indirect single photon absorption, creating excited electrons in the X valley and holes near Γ.[16] Two-photon absorption can be neglected.[16]

H-terminated surfaces, on the contrary, show a rapid initial decrease of the SHG with a nanosecond time-scale recovery. The magnitude of the initial pump-induced increase/decrease in SHG depends significantly on interface termination; typically, a 3%–4% increase for native-oxide-Si(111) and a 20% decrease for H–Si(111). The characteristic decay time (3 ± 1 ns) obtained from the exponential fit is the same for Si(111)–H and Si(111)–SiO$_2$ within experimental error. We attribute the similar recovery time of SHG

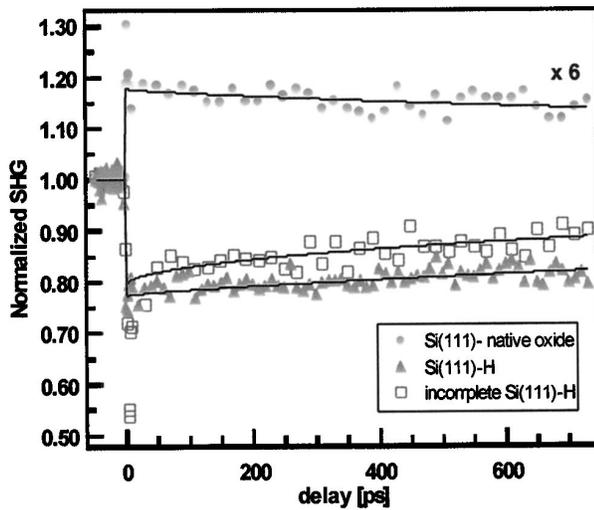[a]Author to whom correspondence should be addressed; electronic mail: borguet@pitt.edu

FIG. 1. Pump-probe SHG from $n\text{-}Si(111)\text{-}SiO_2$, $n\text{-}Si(111)\text{-}H$, and incompletely H-terminated $n\text{-}Si(111)$. The characteristic decay times from exponential fit are 3 ± 1, 3 ± 1, and 1 ns, respectively. The solid lines are calculated curves taking account diffusion, Auger recombination, and surface recombination. The surface recombination velocities are $<10^3$, $<10^3$, and 3×10^4 cm/s for the natively oxidized, H-terminated, and the incompletely H-terminated Si(111), respectively.

on H–Si(111) and Si(111)–SiO$_2$ to similar degree of passivation and number of recombination centers at the interface.

The SHG time dependence can be obscured by changes in the linear optical properties hidden in the Fresnel coefficients.[21] We incorporated the change in the refractive index due to excited carriers in the phenomenological model of SHG developed by Sipe *et al.*[22] Our calculations showed that a significant part $(>\frac{2}{3})$ of the observed carrier-induced SHG response must be due to the pump-induced change in the second-order nonlinear optical properties of the Si–SiO$_2$ interface. In the case of the H–Si(111) dynamics, the linear response contributes less than $\frac{1}{20}$ of the overall transient SHG.

The modulation of second-order response due to excited carriers can be understood, in the simplest approximation, by assuming the second-order nonlinear susceptibility $\chi_s^{(2)}$ to be dependent on the carrier density in the following manner:

$$\chi_s^{(2)} = N\chi^{(2)} + N_*\chi_*^{(2)}, \qquad (1)$$

where N is the valence band electron density of the unperturbed semiconductor and N_* is the photoexcited carrier (electron–hole pair) density. $\chi^{(2)}$ and $\chi_*^{(2)}$ are the nonlinear susceptibilities of the valence band electrons and the excited carriers, respectively. At present, our experiments do not distinguish between photoexcited holes and carriers. The probe pulse creates a carrier density N_*^{probe} at $t<0$. When the pump and the probe are temporally and spatially overlapped ($t=0$), the excited carrier density is the sum of the carrier density created by each pulse, N_*^{all} [Eq. (1)]. The change in SHG signal can be written as

$$\frac{I(t=0)}{I(t<0)} = \frac{|N_*^{\text{all}}\chi_*^{(2)} + N\chi^{(2)}|^2}{|N_*^{\text{probe}}\chi_*^{(2)} + N\chi^{(2)}|^2}, \qquad (2)$$

where $I(t=0)$ is the SHG from the surface at the time of excitation and $I(t<0)$ is the SHG intensity from the unexcited surface.
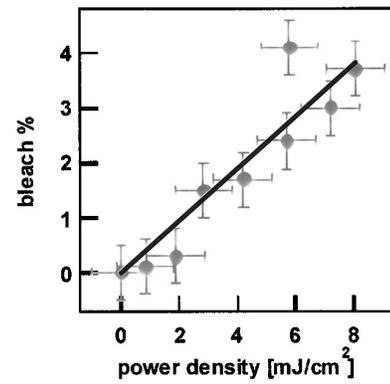

FIG. 2. The dependence of SHG bleach $[I(t=0)/I(t<0)-1]$ on pump power density. The calculated values of the bleach (solid line) were obtained using Eq. (2) taking into account that 70% of the bleach is due to the change in the nonlinear optical properties, and the remainder is due to the change in the linear optical response.

The carrier density N_*^{probe}, created by the probe (5.3 mJ/cm^2 in this experiment) was taken to be 1.7×10^{19} cm^{-3} and $N=2\times10^{23}$ cm^{-3}.[23] We also took into account that only 70% of the bleach comes from the change of the nonlinear optical properties. The fit (Fig. 2) resulted in $\chi_*^{(2)}/\chi^{(2)}=94\pm10$ (the only fit parameter). The observed linear dependence of the bleach on pump power (Fig. 2) further supports the proposed simple model of $\chi_s^{(2)}$.

Actually, it is not surprising to find that the nonlinear response of photoexcited carriers is greater than the nonlinear response of valence band electrons. Photoexcited carriers can, in a first approximation, be considered to be metallic-like, free carriers. Likewise, valence band electrons can be thought of as behaving like those of a dielectric. In a dielectric the electrons are bound but the charge distribution can still adjust in response to the electric field and become polarized, albeit to a lesser extent than the charge distribution of a conductor. Hence, the two order-of-magnitude increase in nonlinear susceptibility for photoexcited carriers. Furthermore, the increase in SHG observed for Si(111)–SiO$_2$ and the decrease observed for Si(111)–H suggests that the photoexcited carrier susceptibilities are in phase for an oxide-terminated surface but out of phase for H-terminated surfaces. We are presently investigating the origin of this phase difference.

The pump-induced SHG signal for Si(111)–SiO$_2$ and Si(111)–H interfaces is consistent with the increased nonlinearity of the photoexcited carriers. Therefore, SHG recovery is attributed to decay of electrons back to the valence band through various relaxation processes. Our model, consisting of one-dimensional coupled diffusion equations for the excited carrier density, included three processes that can result in depletion of conduction electrons at the Si(111)–SiO$_2$ interface: diffusion of carriers toward the bulk, Auger recombination, and surface recombination.[12,14]

The large optical penetration depth ($\sim10\,000$ nm) results in negligible diffusion into the bulk as the gradient in the initial carrier concentration is very small. Thus, TRSHG is sensitive to Auger and surface recombination alone. At high carrier density Auger recombination becomes the dominating relaxation process.[24] The Auger recombination time constant can be estimated by $\tau_{\text{Auger}} = (\gamma_3 N_0^2)^{-1}$, where the Auger re-

combination coefficient γ_3 is 4×10^{-31} cm^6/s.[14] According to Tanaka *et al.*, Auger recombination near the surface occurs two orders of magnitude faster than in the bulk and gives rise to decay on the tens of picosecond time scale.[14] Our modeling of the carrier relaxation dynamics included the Auger recombination process because at our electron–hole pair densities, 2.4×10^{19} cm^{-3}, τ_{Auger} is 4.3 ns, close to the observed decay time, 3 ns. Our results, however, do not support an enhanced Auger recombination rate at the interface.[14]

The SRV is given by $\sigma\cdot v_{th}\cdot N_s$, where $v_{th}\sim10^7$ cm/s is the carrier thermal velocity, $\sigma\sim10^{-15}$ cm^2 is a typical recombination cross section, and N_s is the number of recombination centers.[25] When the SRV is sufficiently high ($\sim10^5$ cm/s), it depletes the conduction band electrons at the surface faster than diffusion or Auger recombination. On the other hand, when the SRV is slow ($\sim10^3$ cm/s), the excited carrier density decay is primarily determined by Auger recombination. The nanosecond time scale (~3 ns) at the Si(111)–SiO$_2$ and Si(111)–H interfaces (Fig. 1) as well as the slower recovery observed at lower pump fluence, are consistent with Auger recombination as the dominant pathway.

The importance of surface recombination is highlighted by the sensitivity of carrier relaxation to Si(111)–H surface preparation. The electronic properties of the Si(111)–H interface, for example the density of surface states, depend strongly on surface preparation.[27] Oxidation of Si(111)–H was observed to increase the density of surface states, formed in the band gap of silicon and attributed to dangling bond defects.[27]

To investigate the influence of defect states on the carrier dynamics, we carried out experiments on an imperfectly H-terminated Si(111) surface. The faster recovery (time constant 1 ns, Fig. 1), corresponding to a SRV$\sim3\times10^4$ cm/s, determined from the best fit to the data, suggests the accelerated removal of photogenerated electrons/holes through surface recombination.[25,26] SHG-RA measurements, carried out under dry N$_2$ atmosphere (RH$<1\%$) to prevent photo or ambient oxidation,[25] confirmed that limited oxidation, <0.01-monolayer oxide formed, takes place. Instead, we suggest that the increased density of surface states is responsible for the observed increase in SRV.[28] The more perfectly H-terminated Si(111) surface has a longer decay time (Fig. 1), consistent with reduced number of defect states, confirming that surface recombination plays an important role in the relaxation of the photoexcited carriers.

Sabbah *et al.* observed transient reflectivity recovery in ~20 ps, corresponding to a SRV of 1.15×10^6 cm/s, at the *n*-type HF-treated Si(100), about two orders of magnitude faster than reported here.[12] The high SRV corresponds to $\sim10^{14}$ recombination centers/cm^2, close to the surface atomic density (6.8×10^{14} atoms/cm^2).[27] It was hypothesized that HF etching, as well as removing the oxide layer, creates defects that accelerate recombination.[12] The H-terminated Si surface is not stable in air, especially under laser irradiation.[26] Gap states can be formed during the oxidation of the Si–H surface, contributing to faster surface recombination.[27] We attribute the faster recovery to the high density of surface/defect states resulting from the HF treatment and subsequent photo and ambient oxidation of the Si(100) surface.

Photoexcited carrier dynamics at Si(111) interfaces have been investigated directly by ultrafast pump-probe SHG. The observed photoinduced SHG response is dominated by the carrier-induced change in the second-order nonlinear optical properties at the Si(111)–SiO$_2$ and Si(111)–H interfaces. A simple model is proposed for the nonlinear susceptibility that predicts a linear dependence of the bleach on the pump fluence, consistent with the data. The second-order susceptibility of photoexcited carriers is determined to be 94 ± 10 times greater that that of valence band electrons. The dynamics of properly passivated interfaces are consistent with surface recombination velocities less than 10^3 cm/s. Carrier relaxation is sensitive to the ''quality'' of the H-termination, and the degree of passivation. The more complete the H termination, the slower the recombination dynamics.

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