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. [DOI: 10.1063/1.1592893]

Carrier relaxation at semiconductor interfaces is important to surface photochemistry, solar energy photoconversion, the modeling of the operation of semiconductor devices, and the degradation of semiconductor transistors. 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. However, “trapping centers” exist in the bulk and at interfaces, which accelerate the recombination.

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. This was surprising as oxidation reportedly reduces the density of midgap states. The very states deemed most efficient at inducing surface recombination have been reported.

Ultras rapid transient optical reflectivity experiments on oxidized Si have been employed to investigate recombination. These bulk techniques are sensitive to the interface inasmuch as the surface can provide recombination centers that affect the bulk dynamics. Nanom with oxidized Si samples show subnanosecond recovery, consistent with surface recombination velocity (SRV) \( > 10^4 \) cm/s. H-terminated Si displayed sub-20-ps recovery times, corresponding to SRV \( \sim 10^5 \) cm/s. In order to enhance surface sensitivity, carrier dynamics have been investigated in Si using time resolved transient grating techniques. 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, \textit{in situ}, real-time interface specific probe. The SHG dynamics depend strongly on the surface chemistry. 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. The 800-nm pump fluence was typically 7.2 mJ/cm\(^2\), generating \( 2.4 \times 10^{19} \) excited electron–hole pairs/cm\(^2\). 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. Experiments on H-terminated Si were carried out in a dry N\(_2\) atmosphere to reduce ambient and photo-oxidation effects. The n-type Si(111) (P-doped, \( \sim 30-\Omega \) cm resistivity, Motorola Phoenix, \( \sim 300-\mu\)m-thick), samples were oriented to maximize SH signal, that is, at an azimuthal angle \( (\phi = 0) \) defined with respect to the \([2\overline{1}T]\) 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 \( \Gamma \). Two-photon absorption can be neglected. 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 (\( 3 \pm 1 \) 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...
The SHG response of photoexcited carriers can be understood, in the simplest approximation, by the change in the refractive index due to excited carriers in the phenomenological model of SHG developed by Sipe et al.\textsuperscript{21} Our calculations showed that a significant part ($>\frac{3}{4}$) 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\textsubscript{2} interface. In the case of the H–Si(111) dynamics, the linear response contributes less than $\frac{1}{3}$ 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 $\chi^{(2)}_s$ to be dependent on the carrier density in the following manner:

$$\chi^{(2)}_s = N \chi^{(2)}_s + N \chi^{(2)}_n,$$

where $N$ is the valence band electron density of the unperturbed semiconductor and $N$ is the photoexcited carrier (electron–hole pair) density. $\chi^{(2)}_s$ and $\chi^{(2)}_n$ 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 $N_{\text{probe}}^{\text{all}}$ 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, $N_{\text{all}}^{\text{all}}$ [Eq. (1)]. The change in SHG signal can be written as

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

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.

The carrier density $N_{\text{probe}}^{\text{all}}$, created by the probe (5.3 mJ/cm\textsuperscript{2} in this experiment) was taken to be $1.7 \times 10^{19}$ cm\textsuperscript{-3} and $N=2 \times 10^{23}$ cm\textsuperscript{-3}.\textsuperscript{22} 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 $\chi^{(2)}_s/\chi^{(2)}_n = 94 \pm 10$ (the only fit parameter). The observed linear dependence of the bleach on pump power (Fig. 2) further supports the proposed simple model of $\chi^{(2)}_s$.

![FIG. 1. Pump-probe SHG from $n$-Si(111)–SiO\textsubscript{2}, $n$-Si(111)–H, and incompletely H-terminated $n$-Si(111). The characteristic decay times from exponential fit are 3 $\pm$ 1, 3 $\pm$ 1, and 1 ns, respectively. The solid lines are calculated curves taking account diffusion, Auger recombination, and surface recombination. The surface recombination velocities are $<10^4$, $<10^3$, and $3 \times 10^4$ cm/s for the natively oxidized, H-terminated, and the incompletely H-terminated Si(111), respectively.](http://apl.aip.org/apl/copyright.jsp)

![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.](http://apl.aip.org/apl/copyright.jsp)
The carrier thermal velocity, \( \tau_{\text{Auger}} \) is 4 x 10^{-31} cm^2/s. 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. Our modeling of the carrier relaxation dynamics included the Auger recombination process because at our electron–hole pair densities, 2.4 x 10^{19} \text{ cm}^{-3}, \tau_{\text{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.

The SRV is given by \( \sigma \cdot v_{\text{th}} \cdot N_s \), where \( v_{\text{th}} \sim 10^5 \text{ cm/s} \) is the carrier thermal velocity, \( \sigma \sim 10^{-15} \text{ cm}^2 \) is a typical recombination cross section, and \( N_s \) is the number of recombination centers. When the SRV is sufficiently high \(( \sim 10^5 \text{ cm/s})\), it depletes the conduction band electrons at the surface faster than diffusion or Auger recombination. On the other hand, when the SRV is slow \(( \sim 10^3 \text{ cm/s})\), the excited carrier density decay is primarily determined by Auger recombination. The nanosecond time scale \(( \sim 3 \text{ ns})\) 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. 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.

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 \(( \sim 3 \times 10^4 \text{ cm/s})\), determined from the best fit to the data, suggests the accelerated removal of photogenerated electrons/holes through surface recombination. SHG-RA measurements, carried out under dry N_2 atmosphere \(( \text{RH} < 1 \%)\) to prevent photo or ambient oxidation, 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. 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 x 10^18 cm/s, at the n-type HF-treated Si(100), about two orders of magnitude faster than reported here. The high SRV corresponds to ~10^14 recombination centers/cm^2, close to the surface atomic density \(( 6.8 \times 10^{14} \text{ atoms/cm}^2)\). It was hypothesized that HF etching, as well as removing the oxide layer, creates defects that accelerate recombination. The H-terminated Si surface is not stable in air, especially under laser irradiation. Gap states can be formed during the oxidation of the Si–H surface, contributing to faster surface recombination. 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 10^5 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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