NANO LETTERS

Reversible Strain-Induced Electron–Hole Recombination in Silicon Nanowires Observed with Femtosecond Pump–Probe Microscopy

Erik M. Grumstrup,^{*,†,‡} Michelle M. Gabriel,[†] Christopher W. Pinion,[†] James K. Parker,[‡] James F. Cahoon,^{*,†} and John M. Papanikolas^{*,†}

[†]Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599, United States [‡]Chemical Sciences Division, US Army Research Office, P.O. Box 12211, Research Triangle Park, North Carolina 27709, United States

Supporting Information

ABSTRACT: Strain-induced changes to the electronic structure of nanoscale materials provide a promising avenue for expanding the optoelectronic functionality of semiconductor nanostructures in device applications. Here we use pump-probe microscopy with femtosecond temporal resolution and submicron spatial resolution to characterize charge-carrier recombination and transport dynamics in silicon nanowires (NWs) locally strained by bending deformation. The electron-hole recombination rate increases with strain for values above a threshold of $\sim 1\%$ and, in highly strained (\sim 5%) regions of the NW, increases 6-fold. The changes in recombination rate are independent of NW



diameter and reversible upon reduction of the applied strain, indicating the effect originates from alterations to the NW bulk electronic structure rather than introduction of defects. The results highlight the strong relationship between strain, electronic structure, and charge-carrier dynamics in low-dimensional semiconductor systems, and we anticipate the results will assist the development of strain-enabled optoelectronic devices with indirect-bandgap materials such as silicon.

KEYWORDS: Ultrafast imaging, strained nanomaterials, spectroscopy

attice strain produced by bending deformation can ✓ significantly alter material properties, such as band energies, symmetry, and carrier mobility, providing the potential means to develop novel functionalities in nanoscale devices.¹⁻⁵ In Si nanowires (NWs), for example, strain may offer a route toward Si lasers and light-emitting diodes (LEDs),⁶ enhanced carrier transport in nanoscale electronics,^{7–9} and junctionless charge separation in Si NW-based photovoltaics.¹⁰ The potential for accessing such unique functionalities has prompted both experimental¹¹⁻¹⁶ and theoretical^{4,6-10,17,18} studies of materials under high levels (>2%) of both homogeneous and inhomogeneous strain. Spectroscopic methods provide direct insight into the influence of lattice strain on the electronic structure. For example, straininduced redshifts in the emission spectra of bent ZnO^{11-14} and CdSe¹⁵ NWs observed using fluorescence microscopy indicate that lattice strain can significantly reduce the band gap, and cathodoluminescence measurements of ZnO NWs suggest excitons tend to drift from regions of compressive strain (with larger bandgap) toward regions of tensile strain (with smaller bandgap) at cryogenic temperatures.¹⁶ While strain has a clear impact on the electronic structure of nanomaterials, its influence on the carrier dynamics (e.g., carrier lifetime and mobility) remains largely unexplored, particularly in indirectbandgap materials such as Si and Ge that cannot be studied using luminescent techniques.

Here we present time-resolved pump-probe microscopy¹⁹⁻²³ measurements of the photoexcited charge carrier dynamics in individual Si NWs that are inhomogeneously strained through bending deformation. The combination of submicron spatial resolution and femtosecond temporal resolution, as well as the ability to control the position of the probe beam relative to the pump beam, enables direct measurement of both charge carrier diffusion constants and electron-hole recombination rates at localized points along straight and bent regions of individual NWs. Decay kinetics collected at 144 discrete locations within 14 different NWs show a clear correlation between the electron-hole recombination rate and the degree of lattice strain, with NWs exhibiting up to a 6-fold increase of the carrier recombination rate in regions experiencing the highest strain (~5%). By studying NWs on flexible polydimethylsiloxane (PDMS) substrates, we further show the changes in the recombination rate are reversible, indicating that the intrinsic electronic structure of

Received: July 10, 2014 Revised: September 2, 2014

low dimensional semiconductor systems can be manipulated by straining the lattice without introducing defects.

In these experiments, photoexcited carriers are created in a localized region of a single NW by a femtosecond laser pulse (pump: 425 nm, 0.4 pJ/pulse, 300 μ J/cm²) that is focused to a near diffraction-limited spot by a microscope objective (100×, NA = 0.8). The spatial and temporal evolution of the photogenerated carriers are followed by a second laser pulse (probe: 850 nm, 150 μ J/cm²) that is also focused by the objective. Pump-induced changes in the intensity of probe pulses are monitored by collecting the probe light transmitted through the sample and directing it onto a two-channel balanced photodetector coupled to a digital lock-in amplifier. The probe beam can be laterally positioned relative to the pump spot by adjusting the angle of incidence at the back aperture of the microscope objective using a pair of computercontrolled mirrors. The spatial evolution of the photoexcited carrier density is monitored by scanning the probe position on a pixel-by-pixel basis relative to the pump at a fixed pumpprobe temporal delay time, Δt . The microscope is capable of measuring the carrier dynamics in a localized region of a single structure with spatial resolution of ~700 nm and a temporal resolution of ~ 500 fs.^{21–23}

Intrinsic Si NW samples were synthesized by the vapor– liquid–solid (VLS) mechanism at 420 °C using Au catalysts for VLS growth in a low-pressure chemical vapor deposition system under conditions identical to those described previously.²⁴ NWs were thermally oxidized at 1000 °C for 60 s in 100 Torr flowing oxygen to form a 5–10 nm-thick thermal oxide and were mechanically transferred from the growth substrates to microscopy slides for imaging. The scanning electron microscopy (SEM) image of a typical ~100 nm diameter Si NW (denoted NW1) that was bent during the transfer from the growth substrate to a microscope slide is shown in Figure 1A. Although the lattice in the straight segments of the NW is under little external stress, the bent region experiences compression and tension on the inner and outer edges, respectively.

Microscopy measurements performed with spatially overlapped pump and probe pulses show distinct decay kinetics in the straight segments compared to the bent segments. The decay kinetics obtained at the seven different locations along NW1 (indicated by the corresponding circles in panel A) are displayed in Figure 1B. At all seven locations, there is an initial increase in probe transmittance that reflects the population of free carriers produced by photoexcitation.^{22,25} The decay of the signal reflects recombination of electrons and holes, which under low-strain conditions (blue traces) occurs primarily at the surface. In the regions of high curvature (red and green traces), the electron-hole recombination is faster, with the higher-curvature points in red decaying more quickly than the lower-curvature point in green.

Spatial variation in carrier recombination can be visualized in pump-probe images (Figure 1C). Here, the pump-probe delay is fixed, and the focused pump and probe beams are scanned over the structure to produce a spatial map of the transient signal at a specific delay time. The raw ("as collected") images obtained in this manner generally show a spatial variation in the signal intensity that stems from a dependence of the absorption and scattering cross sections on the laser beam polarizations. Even though the magnitude of the transient signal is diminished in regions where the wire is oriented orthogonal to the polarization axis, the kinetics are not



Figure 1. Charge carrier recombination in a Si NW locally strained by a bending deformation (A) SEM image of a bent Si nanowire ~100 nm in diameter (NW1). Colored circles denote regions where transient kinetics were acquired; scale bar, 2 μ m. (B) Normalized kinetic traces of carrier recombination dynamics collected at multiple locations on NW1. Red, green, and blue data points correspond to the locations denoted by red, green, and blue circles in panel A, respectively. Solid lines correspond to a fit of each kinetic trace to eq 1. (C) Sequence of spatially overlapped pump–probe images from NW1 in panel A, showing faster carrier recombination near the bent, high-strain region. The upper image depicts the raw ("as collected") data, whereas the bottom four images are normalized relative to the data at $\Delta t = 0$ ps; scale bar, 2 μ m.

affected.²² The images in the lower portion of Figure 1C have been normalized to remove this spatial variation, resulting in a constant signal intensity along the NW at $\Delta t = 0$ ps. As the delay between pump and probe pulses is increased, the signal in the bent region of the NW fades quickly compared to the straight segments, consistent with faster electron-hole recombination. Closer inspection of the images indicates that the increase in the recombination rate varies continuously along the bend, with the region of highest curvature showing the fastest recombination. The discussion below expands upon this qualitative observation by providing a quantitative correlation between the recombination rate and degree of NW curvature.

Electron-hole recombination rates were determined by fitting kinetic traces, such as those depicted in Figure 1B, to a previously developed model of diffusion and recombination²² consisting of a single-exponential function modified to account for the size of the pump and probe beams as well as carrier diffusion out of the probe volume:

$$I(\Delta t, \Delta x) = \frac{a_0}{\beta(\Delta t)} \exp\left(\frac{-4\ln(2)\Delta x^2}{\beta(\Delta t)^2}\right) \exp(-k_{\rm obs}\Delta t)$$
(1)

with

$$\beta(\Delta t)^2 = \gamma_1^2 + \gamma_2^2 + 16\ln(2)D\Delta t$$
 (2)

In eq 1, Δx defines the spatial separation between pump and probe spots along the wire ($\Delta x = 0$ for these spatially overlapped kinetics traces), a_0 is a normalization constant, and $k_{\rm obs}$ is the electron-hole recombination rate. In eq 2, $\gamma_1 = 430$ nm and $\gamma_2 = 860$ nm are the full-width at half-maximums (FWHMs) of the pump and probe spots, and *D* is the effective ambipolar diffusion constant of the material.



Figure 2. Charge carrier diffusion in a Si NW locally strained by a bending deformation (A) SEM image of a bent Si nanowire ~100 nm in diameter (NW2); scale bar, 5 μ m. (B) Spatially separated pump-probe images of carrier diffusion at the location indicated by the black circle in panel A. Dashed white lines denote the location of the NW; scale bar, 1 μ m. (C) Normalized carrier profiles obtained by integrating the spatially separated images shown in panel B in the direction orthogonal to carrier diffusion. Data are shown as symbols, and solid lines represent fits of the data to eq 3. (D) Change in the square of the carrier profile fwhm, $\beta(\Delta t)^2 - \beta(0)^2$, as a function of pump-probe delay for bent (red square) and straight (black triangle) locations indicated by the red and black circles, respectively, in panel A. The blue shaded region shows the range of diffusion constants (6.0 cm²/s < D < 10.0 cm²/s) found for four additional NWs characterized.

The diffusion constant is determined using the spatially separated pump-probe microscopy configuration that allows direct and contactless characterization of the transport properties. Figure 2A shows an SEM image of a single bent Si NW (NW2) with black and red circles indicating straight and bent regions, respectively, where carrier transport was characterized. In Figure 2B, spatially separated pump-probe images obtained from the straight region at $\Delta t = 0$, 78, and 145 ps show progressive broadening of the photogenerated charge cloud as a result of carrier diffusion.

Normalized carrier profiles, generated by integrating the images along the direction normal to the NW axis, are shown in Figure 2C. These profiles are fit to the spatially dependent terms of eq 1:

$$I'(\Delta t, \Delta x) = \frac{a_0}{\beta(\Delta t)} \exp\left(\frac{-4\ln(2)\Delta x^2}{\beta(\Delta t)^2}\right)$$
(3)

to extract the fwhm of the distribution, $\beta(\Delta t)$. A plot of $\beta(\Delta t)^2$ as a function of pump-probe delay yields a linear relationship with a slope that is proportional to the diffusion constant, D, and a y-intercept, $\beta(0)$, that reflects the pump and probe spot sizes (see eq 2 for $\Delta t = 0$ ps). Figure 2D shows the timedependent component of the fwhm, $(\beta(\Delta t)^2 - \beta(0)^2)$, for the bent and straight regions of NW2. Analysis of this data yielded diffusion constants of 7.5 \pm 0.2 cm²/s and 7.8 \pm 0.1 cm²/s, respectively, for the two regions. Characterization of carrier transport in four additional NWs yielded diffusion constants that ranged from 6 cm²/s and 10 cm²/s with no apparent correlation between the local curvature and the diffusion constant. The average diffusion constant found for these NWs $(\sim 8 \text{ cm}^2/\text{s})$ is significantly lower than the bulk ambipolar diffusion constant of 18 cm²/s,²⁶ which is most likely a consequence of the high photoexcited carrier density ($\sim 4 \times$

10¹⁹ cm⁻³) dominating transport through carrier–carrier scattering.²⁷

Although lattice strain is anticipated to affect charge carrier mobility,^{7-9,17} the lack of a strain dependence in our measurements may be a consequence of several factors. First, in Si, the electron mobility (μ_e) is typically increased in regions under tensile strain and decreased under compression, with the opposite behavior expected for the hole mobility ($\mu_{\rm h}$). Since the ambipolar diffusion constant depends upon both (i.e., D = $(2k_{\rm B}T/q)(\mu_{\rm e}\mu_{\rm h}/\mu_{\rm e} + \mu_{\rm h})$, where $k_{\rm B}$ is the Boltzmann constant, T is temperature, and q is elementary charge), an increase in the electron mobility could be partially offset by a decrease in hole mobility, resulting in very little difference in the measured ambipolar diffusion constant. In addition, a strain dependence may be masked by the diffraction-limited spatial averaging that samples both compressive (at the inside edge) and tensile (at the outside edge) strain of the bent NW (see Figure 4 and discussion below). In this case, minimal impact on the transport properties arising from strain would be apparent.

Electron-hole recombination times were determined by fitting the kinetic traces shown in Figure 1B to eq 1 with D = 8 cm²/s. This analysis yielded recombination times of ~150 ps in the straight segments (blue circles) and 72 and 33 ps at the bent regions indicated by the green and red circles, respectively, in Figure 1A. Although we used an average carrier diffusion constant of 8 cm²/s for fitting the kinetic traces, fits conducted with values of *D* from 6 to 10 cm²/s changed the extracted rates by less than 15%.

The simplest explanation for the increase in the recombination rate in the regions of higher curvature is an increase in the trap density due to bond breaking or dislocation effects in the crystal lattice or at the surface.^{18,19} The creation of defect sites would likely be irreversible, causing rapid recombination to persist even after release of the deformation. To test this idea,

Figure 3. Reversibility of the strain-dependent carrier recombination rate. (A) Pump-probe images at $\Delta t = 0$ for NW3 ($d \sim 100$ nm) deposited on a flexible PDMS substrate in initial stretched (1), relaxed (2), and restretched (3) configurations; scale bars, 5 μ m. (B) Transient kinetic traces collected from the same position (indicated by circles in panel A) along the length of NW3 in its initial straight (1), bent (2), and straightened (3) configurations.

we investigated carrier recombination dynamics in NWs transferred to a stretched poly(dimethylsiloxane) (PDMS) substrate. The pump-probe image taken at $\Delta t = 0$ ps for a single Si nanowire (NW3) in its initial straight configuration is shown in panel 1 of Figure 3A. The electron-hole recombination time (Figure 3B) observed at the point indicated by the black circle is similar to those observed in the low curvature regions of NW1. The substrate was then allowed to relax, and NW3 adopted a bent configuration (panel 2). The rate of recombination at a corresponding position along NW3 (red circle) increases, commensurate with the higher-curvature regions of NW1. Finally, the substrate was restretched (panel 3), and NW3 returned to its initial straight configuration. Once the deformation was released, recombination slowed, returning to its prebent character. This reversible behavior suggests that the changes in the recombination kinetics observed in regions of higher curvature are not the result of an increase in defect density but rather stem from an intrinsic change in the energetics or symmetry of NW band structure due to elastic deformation of the lattice.

The strain induced by elastic deformation of a NW from bending can be analytically determined from the local radius of curvature, R (Figure 4A). The strain in this configuration consists of a gradual shift from lattice compression at the inner edge to lattice tension at the outer edge and has a maximum magnitude, $|\varepsilon|$, that can be expressed in terms of *R* and the NW diameter, d, as $|\varepsilon| = d/2R$ (see Figure 4B). For the locations indicated by the blue circles in NW1 (Figure 1A), the calculated strain is less than 1%, and the observed electronhole recombination rate, k_{obs} , is between 6 and 8 ns⁻¹. The regions of higher curvature (green and red circles in Figure 1A) on the NW have $|\varepsilon| = 1.9\%$ ($k_{obs} = 13.8 \text{ ns}^{-1}$) and $|\varepsilon| = 2.7\%$ $(k_{\rm obs} = 30.3 \text{ ns}^{-1})$, respectively. This corresponds to enhancement factors of \sim 2 at 2% strain and 4–5 at 3% strain. Given the lateral resolution of the microscope, k_{obs} is a spatial average of the carrier recombination dynamics that encompasses regions experiencing both tension and compression. As a result of this spatial averaging, the observed rate reflects the average of the carrier recombination dynamics throughout the NW.

Multiple electron-hole recombination mechanisms are potentially present in NWs, producing an observed recombination rate that is the sum of bulk and surface processes:

$$k_{\rm obs} = k_{\rm s} + k_{\rm r} + k_{\rm SRH} + k_{\rm A} \tag{4}$$

Figure 4. Correlation between carrier recombination rate and lattice strain. (A) SEM image of a bent Si NW (~100 nm in diameter) illustrating the local radius of curvature, *R*. The scale bar is 1 μ m. (B) Schematic showing the regions of compression (shaded blue) and tension (shaded red) predicted in a bent NW. (C) Combined strain dependence of the carrier recombination rate for 14 individual NWs. *R* was determined for each measurement through analysis of the NW transmission images, and the diameter was determined from SEM images. NWs grown with 100 nm Au catalysts (gray circles) and 50 nm Au catalysts (red squares) show the same trend. The black solid line is a quadratic trend line fit to the 100 nm rates. Red dashed line shows behavior predicted for 50 nm NWs if strain-dependent rate contributions were a surface effect. Inset: illustration of surface and bulk contributions to the overall electron—hole recombination rate as a function of strain.

where k_s , k_r , k_{SRH} , and k_A represent the rates associated with surface, radiative, Shockley–Read–Hall (SRH), and Auger recombination, respectively. Previous work in our lab showed that recombination in straight NW segments takes place at the surface and is well-described by $k_s = 4S/d$, where the surface recombination velocity (*S*) parametrizes the surface quality.^{21,22,25} The inverse diameter dependence in this expression reflects the geometrical localization of recombination events to the surface. In these low-dimensional NWs, radiative and SRH recombination mechanisms do not compete with surface recombination, which is orders of magnitude faster at room temperature.^{25,28,29} Auger recombination can also contribute to the observed rate; however, the pump–probe decays are independent of the pump pulse energies below 0.4 pJ/pulse, in both bent and straight regions of individual NWs (Figure S1), indicating that at the excitation energies of these experiments, Auger processes are not a major contributor (i.e., $k_A \approx 0$).

The increase in recombination rate upon bending deformation could arise from a strain-induced enhancement of one or more of these mechanisms. Thus, the observed electron-hole recombination rate can be expressed as a sum of strain-independent (k_0) and strain-dependent $(k(\varepsilon))$ contributions:

$$k_{\rm obs} = k_0 + k(\varepsilon) \tag{5}$$

The strain-dependent component, $k(\varepsilon) = k_{obs} - k_0$, is plotted in Figure 4C for 144 measurements across 14 different wires. Due to differences in surface quality and diameter, we determined k_0 on a NW-by-NW basis by averaging the low strain (<0.5%) recombination rates found for each individual NW. It appears that the carrier recombination rate is independent of strain up to a value of ~0.7%, at which point the strain-dependent contribution begins to influence the overall recombination dynamics.

Although the reversibility of the strain-dependent recombination suggests an intrinsic change to the band structure, the reversibility alone is insufficient to determine if the change in recombination results from a process in the core of the NW or at the surface, due, for example, to changes in the coupling between the bulk bands and the surface states. Nevertheless, these two scenarios can be distinguished by examining NWs of different diameters. If surface recombination (k_s) is increased by lattice strain, then the strain dependence should scale inversely with NW diameter (since $k_s = 4S/d$). The black line in Figure 4C is a quadratic trend line fit to the \sim 100 nm NW data. If the strain effect is occurring at the surface, then recombination rates collected from ~50 nm wires should lie along the dashed red line (which shows a 2-fold greater strain variation due to the 2-fold difference in diameter). This is not the case. Strain-dependent recombination rates collected from \sim 50 nm diameter wires (shown as red squares in Figure 4C) follow a similar trend as the \sim 100 nm diameter NWs. Although there is some spread in the data, the strain-dependent rates appear inconsistent with a surface recombination model, suggesting that the strain-induced increase in the rate, $k(\varepsilon)$, is primarily a consequence of recombination events that are occurring throughout the NW volume.

The dependence of the electron—hole recombination rate on strain is illustrated in the inset of Figure 4C. At low strain ($\varepsilon < 0.7\%$), recombination via typical bulk mechanisms (i.e., SRH, Auger, radiative) is slow, and the overall recombination is dominated by the surface (i.e., $k_{obs} \approx k_0 = k_s$). Lattice strain introduced by bending deformation enhances the bulk recombination rate, and at $\varepsilon \sim 0.7\%$, the strain-induced enhancement in the bulk recombination rate has a noticeable impact on the overall rate. By 4–5% strain, it dominates the recombination process. Even though it is unclear which specific bulk mechanism (SRH or, radiative) is affected, in either case, the increase likely arises from strain-induced changes to the Si band structure that include a reduced band gap or, in the case

of the inhomogeneous strain (such as that produced by bending deformation), a change to the symmetry of the lattice.

A number of mechanisms may be at play in determining the carrier recombination kinetics in bent NWs. Calculations performed by other groups on strained Si predict that the bandgap can be reduced by as much as 0.5 eV at 4-5% strain, suggesting that faster recombination may occur through improved energetic overlap of the photogenerated carriers with the manifold of trap states.^{6,7,10,30} However, it is also predicted¹⁰ that the conduction and valence band energies are both stabilized in regions of tensile strain, and they are both increased in energy in regions of compressive strain. Thus, in the neighborhood of a bend, a potential gradient should exist across the NW that would serve to rapidly separate electrons and holes, lengthening the charge carrier lifetime in the region of a bend. The absence of this behavior in the strain-dependent rate constant may stem from the high density of photogenerated carriers, which could screen the effects of the straininduced potential in a manner analogous to recent measurements made by our group of a P-I-N junction.²³ Efforts directed toward reducing the photoexcited carrier density and improving spatial resolution (to possibly image charge separation in a bent NW) are currently underway. In addition to energetic effects, calculations also show dramatic changes to the band symmetry occur with increasing strain, resulting in a loss of the indirect band gap character.^{6,7,10,30} Because electron-hole recombination events in indirect semiconductors (e.g., unstrained Si) typically require the emission of multiple phonons to span the energy and momentum difference between conduction and valence band electrons,³¹ this rearrangement of the electronic structure may mitigate the momentum mismatch and accelerate both SRH and radiative electron-hole recombination.

In summary, we have observed carrier recombination rates in bent Si NWs that are nearly 6-fold higher than straight Si NWs. The enhancement is reversible, with bent wires recovering their unstrained carrier decay kinetics when they are straightened. The observations are consistent with elastic strain-induced changes to the intrinsic electronic structure of NWs, whereby a reduction in the band gap energy and alteration of conduction and valence band symmetry causes faster free carrier recombination. These results have important implications for a broad range of Si-based devices, in which changes to the fundamental material properties of Si make strain a tool for achieving novel functionality in electronic and optoelectronic devices. Although promising, the peripheral effects of strain in Si, particularly the enhanced carrier recombination rate, may be problematic to the efficient operation of these devices, especially optoelectronic devices that rely on long charge carrier lifetimes, such as nanostructured solar cells. Further studies of the effects of strain on the carrier dynamics of silicon (and other material) nanostructures, particularly in architectures amenable to device applications (uniaxial, biaxial strained NWs), will be important indicators for the development of strained NW technologies.

ASSOCIATED CONTENT

Supporting Information

Power-dependent kinetics for both bent and straight regions of a Si NW. This material is available free of charge via the Internet at http://pubs.acs.org.

Ε

AUTHOR INFORMATION

Corresponding Authors

*E-mail: E.M.G. (erik.grumstrup@montana.edu).

*E-mail: J.F.C. (jfcahoon@unc.edu).

*E-mail: J.M.P. (john_papanikolas@unc.edu).

Present Address

E.M.G.: Department of Chemistry and Biochemistry, Montana State University, Bozeman, MT 59717.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This project was supported by the National Science Foundation under grant numbers CHE-1213379 (E.M.G., M.M.G., and J.M.P) and DMR-1308695 (C.W.P. and J.F.C.). E.M.G. was supported by a National Research Council postdoctoral fellowship funded by the Army Research Office.

REFERENCES

(1) Smith, A. M.; Mohs, A. M.; Nie, S. Nat. Nanotechnol. 2009, 4 (1), 56–63.

(2) Sun, Y. T.; Scott, E.; Toshikazu, N. Strain Effect in Semiconductors; Springer: New York, 2010.

(3) Suess, M. J.; Geiger, R.; Minamisawa, R. A.; Schiefler, G.; Frigerio, J.; Chrastina, D.; Isella, G.; Spolenak, R.; Faist, J.; Sigg, H. *Nat. Photonics* **2013**, *7* (6), 467–473.

(4) Li, J.; Shan, Z.; Ma, E. MRS Bull. 2014, 39 (02), 108-114.

(5) Priolo, F.; Gregorkiewicz, T.; Galli, M.; Krauss, T. F. Nat. Nanotechnol. 2014, 9 (1), 19–32.

(6) Shiri, D.; Verma, A.; Selvakumar, C. R.; Anantram, M. P. Sci. Rep. 2012, 2, 461.

(7) Shiri, D.; Kong, Y.; Buin, A.; Anantram, M. P. Appl. Phys. Lett. 2008, 93 (7), 073114.

(8) Niquet, Y. M.; Delerue, C.; Krzeminski, C. Nano Lett. 2012, 12 (7), 3545–50.

(9) Nguyen, V. H.; Triozon, F.; Bonnet, F. D. R.; Niquet, Y. M. IEEE Trans. Electron Devices **2013**, 60 (5), 1506–1513.

(10) Wu, Z.; Neaton, J. B.; Grossman, J. C. Nano Lett. 2009, 9 (6), 2418–22.

(11) Xue, H.; Pan, N.; Li, M.; Wu, Y.; Wang, X.; Hou, J. G. Nanotechnology **2010**, 21 (21), 215701.

(12) Xu, S.; Guo, W.; Du, S.; Loy, M. M.; Wang, N. Nano Lett. 2012, 12 (11), 5802-7.

(13) Wei, B.; Zheng, K.; Ji, Y.; Zhang, Y.; Zhang, Z.; Han, X. Nano Lett. 2012, 12 (9), 4595-9.

(14) Han, X.; Kou, L.; Zhang, Z.; Zhang, Z.; Zhu, X.; Xu, J.; Liao, Z.; Guo, W.; Yu, D. *Adv. Mater.* **2012**, *24* (34), 4707–4711.

(15) Sun, L.; Kim do, H.; Oh, K. H.; Agarwal, R. *Nano Lett.* **2013**, *13* (8), 3836–42.

(16) Fu, X.; Jacopin, G.; Shahmohammadi, M.; Liu, R.; Benameur, M.; Ganiere, J. D.; Feng, J.; Guo, W.; Liao, Z. M.; Deveaud, B.; Yu, D. *ACS Nano* **2014**, *8* (4), 3412–20.

(17) Richard, S.; Aniel, F. d. r.; Fishman, G.; Cavassilas, N. J. Appl. Phys. 2003, 94 (3), 1795.

(18) Yu, D.; Feng, J.; Hone, J. MRS Bull. 2014, 39 (02), 157-162.

(19) Mehl, B. P.; Kirschbrown, J. R.; House, R. L.; Papanikolas, J. M. J. Phys. Chem. Lett. **2011**, 2 (14), 1777–1781.

(20) Mehl, B. P.; Kirschbrown, J. R.; Gabriel, M. M.; House, R. L.; Papanikolas, J. M. J. Phys. Chem. B 2013, 117 (16), 4390-4398.

(21) Gabriel, M. M.; Kirschbrown, J. R.; Christesen, J. D.; Pinion, C. W.; Zigler, D. F.; Grumstrup, E. M.; Mehl, B. P.; Cating, E. E.;

Cahoon, J. F.; Papanikolas, J. M. Nano Lett. **2013**, *13* (3), 1336–40. (22) Grumstrup, E. M.; Gabriel, M. M.; Cating, E. M.; Pinion, C. W.; Christesen, J. D.; Kirschbrown, J. R.; Vallorz, E. L.; Cahoon, J. F.; Papanikolas, J. M. J. Phys. Chem. C **2014**, *118* (16), 8634–8640. (23) Gabriel, M. M.; Grumstrup, E. M.; Kirschbrown, J. R.; Pinion, C. W.; Christesen, J. D.; Zigler, D. F.; Cating, E. E.; Cahoon, J. F.; Papanikolas, J. M. *Nano Lett.* **2014**, *14* (6), 3079–87.

(24) Christesen, J. D.; Pinion, C. W.; Grumstrup, E. M.; Papanikolas, J. M.; Cahoon, J. F. *Nano Lett.* **2013**, *13* (12), 6281–6.

(25) Grumstrup, E. M.; Cating, E. M.; Gabriel, M. M.; Pinion, C. W.; Christesen, J. D.; Kirschbrown, J. R.; Vallorz, E. L.; Cahoon, J. F.;

Papanikolas, J. M. J. Phys. Chem. C 2014, 118 (16), 8626–8633.
(26) Sze, S. M.; Ng, K. K. Physics of Semiconductor Devices; John

Wiley & Sons: New York, 2007. (27) Li, C.-M.; Sjodin, T.; Dai, H.-L. Phys. Rev. B **1997**, 56 (23),

(27) Li, C.-M.; Sjouin, T.; Dai, H.-L. Phys. Rev. B 1997, 30 (23), 15252–15255.

(28) Allen, J. E.; Hemesath, E. R.; Perea, D. E.; Lensch-Falk, J. L.; Li, Z. Y.; Yin, F.; Gass, M. H.; Wang, P.; Bleloch, A. L.; Palmer, R. E.; Lauhon, L. I. *Nat. Nanotechnol.* **2008**, 3 (3), 168–73.

(29) Dan, Y.; Seo, K.; Takei, K.; Meza, J. H.; Javey, A.; Crozier, K. B. *Nano Lett.* **2011**, *11* (6), 2527–32.

(30) Munguía, J.; Bremond, G.; Bluet, J. M.; Hartmann, J. M.; Mermoux, M. Appl. Phys. Lett. **2008**, 93 (10), 102101.

(31) Henry, C.; Lang, D. Phys. Rev. B 1977, 15 (2), 989-1016.

F

Imaging Charge Separation and Carrier Recombination in Nanowire p-i-n Junctions Using Ultrafast Microscopy

Michelle M. Gabriel, Erik M. Grumstrup, Justin R. Kirschbrown, Christopher W. Pinion, Joseph D. Christesen, David F. Zigler, Emma E. M. Cating, James F. Cahoon,* and John M. Papanikolas*

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States

Supporting Information

ABSTRACT: Silicon nanowires incorporating p-type/n-type (p-n) junctions have been introduced as basic building blocks for future nanoscale electronic components. Controlling charge flow through these doped nanostructures is central to their function, yet our understanding of this process is inferred from measurements that average over entire structures or integrate over long times. Here, we have used femtosecond pump-probe microscopy to directly image the dynamics of photogenerated charge carriers in silicon nanowires encoded with p-n junctions along the growth axis. Initially, motion is dictated by carrier-

carrier interactions, resulting in diffusive spreading of the neutral electron—hole cloud. Charge separation occurs at longer times as the carrier distribution reaches the edges of the depletion region, leading to a persistent electron population in the n-type region. Time-resolved visualization of the carrier dynamics yields clear, direct information on fundamental drift, diffusion, and recombination processes in these systems, providing a powerful tool for understanding and improving materials for nanotechnology.

KEYWORDS: Femtosecond microscopy, charge transport, silicon nanowire, ultrafast imaging

detailed understanding of the factors that govern the A motion of mobile charge carriers through nanostructures is critical to the rational design of nanoscale devices.¹⁻⁸ Understanding carrier motion is particularly important for nanowires (NWs) encoded with p-n junctions, which have been widely explored for use in photovoltaic devices based on a range of materials including Si,^{9–16} InP,¹⁷ GaAs,^{18,19} and CdS.^{20,21} Because of the inherently small dimensions, many nanoelectronic components operate at high carrier concentrations resulting from heavy doping or high injection conditions. In this regime, carrier-carrier interactions and other many body effects (e.g., dopant/carrier interactions, electron screening, and electron-hole scattering) must be considered.²²⁻²⁴ Charge carrier dynamics in nanostructures are further complicated by unintentional electric fields created through surface charging^{25,26} or ionized defects. Under conditions of high carrier density and short length scales, our understanding of charge carrier flow through nanostructures draws heavily on experimental observations coupled with sophisticated simulations. Most experimental information of this type is inferred from ultrafast time-resolved measurements that are spatially averaged over entire structures²⁷⁻³⁰ or steadystate observations made on single structures or devices using functional imaging techniques.^{31–35} While such methods are powerful tools for probing nanomaterials and have been applied with great success, the combination of spatial and temporal information provided by ultrafast microscopy³⁶⁻⁴⁴ enables a characterization of carrier dynamics in relation to specific

structural features, and it does so using all optical detection without the need for active electrical connection.

This report describes the use of a femtosecond pump–probe microscopy technique $^{36-39}$ to visualize charge carrier motion across axial p-type/intrinsic/n-type (p-i-n) silicon nanowire (SiNW) junctions. The microscopy results are combined with finite element simulations^{15,45} to yield a detailed picture of the charge separation process. Our results reveal characteristics of these junctions that could not be obtained without the spatiotemporal resolution of the microscope. For instance, we find that the lifetime of charge carriers depends sensitively on position in the junction, changing by more than 1 order of magnitude from the p-type to n-type segments. Significant variation is also observed across the intrinsic segment with faster population loss near the boundaries being consistent with deformation of the built-in electric field predicted by finite element simulations. The ultrafast microscope used in this work is capable of exciting a structure in one location and probing it in another, enabling the direct visualization of the charge carrier motion. Pump-probe images obtained following excitation in the middle of the intrinsic segment show that the evolution of the charge carrier cloud is initially dominated by carrier-carrier interactions, causing it to spread at early times through ambipolar diffusion. It is not until 300-400 ps after excitation,

 Received:
 January 10, 2014

 Revised:
 May 2, 2014

 Published:
 May 27, 2014

Figure 1. Characteristics of silicon NW p-i-n junctions. (a) The p-i-n axial doping profile (left) compared with corresponding SEM images (right) for three silicon NW structures denoted J1, J2, and J3. Horizontal dashed lines represent junction positions estimated from growth parameters. (b) Illustration of charges present within the junction. Mobile holes (circled positive charges) in the p-type region (pink) diffuse into the intrinsic segment leaving behind fixed negatively charged acceptors. On the other side, mobile electrons (circled negative charges) in the n-type region (blue) diffuse into the intrinsic segment leaving behind fixed positively charged donors. Incomplete recombination in the intrinsic segment leads to residual free carriers at the interfaces. (c) Finite element solutions for charge density, ρ , and electric field, *E*, along the axis of a p-i-n junction. The model consists a 100 nm cylindrical wire with a 2 μ m p-type region, a 2 μ m intrinsic region, and a 2 μ m n-type region. To simulate the characteristics of the p-i-n junction, the built-in potential is calculated and applied across contacts placed at either end of the wire. Note the break in the *x*-axis such that only ~150 nm around each interface is displayed.

when the cloud reaches the boundaries of the intrinsic segment and depletion region, that evidence of charge separation is observed. The insights gained from visualization of the carrier dynamics have direct implications for the synthesis, design, and performance of many nanoscale devices.

Nanowire Junctions. The SiNW structures used in this study, which were synthesized by the vapor-liquid-solid (VLS) mechanism, are ~100 nm in diameter and consist of a long (>10 μ m) p-type region followed by a 2 μ m intrinsic segment and 3 μ m n-type region. The p-type and n-type regions are doped with boron and phosphorus, respectively, at a nominal doping level of 3×10^{19} cm⁻³. The location of the p-in junction is determined by its proximity to the ~ 100 nm gold catalyst used for VLS growth, which is easily identified at the tip of each p-i-n junction (J1, J2, and J3) in the three scanning electron microscopy (SEM) images in Figure 1a. The intrinsic layer grown between the p-type and n-type segments increases the length of the depletion region, giving rise to an internal electric field that extends across the intrinsic segment. When the layer is short (<100 nm), this field is nearly constant;⁴⁵ however, as its length increases, the electric field produced by the junction becomes more complicated.⁴⁶ This increased complexity is illustrated by finite element simulations of a p-i-n junction with a 2 μ m intrinsic segment, which show significant variation in both the charge density and electric field near the interfaces. The charge density distribution at the i-n boundary consists of fixed positive charges in the n-type material that are partially counter balanced by the accumulation of free electrons within the intrinsic segment (Figure 1b). At the p-i boundary,

the situation is reversed with the fixed negative charges being offset by the accumulation of mobile holes. Thus, the p-i-n junction behaves more like two separate junctions⁴⁶ (a p-i junction and an i-n junction) that are close enough that partial recombination of the mobile electrons and holes is possible but far enough apart that it is not complete. The close proximity of the positive and negative charge distributions at the interfaces gives rise to a spike in the electric field magnitude (10^7 V/m) with a smaller (10^5 V/m) but relatively constant field in the center of the intrinsic segment (Figure 1c).

Spatially Resolved Population Decay of Photogenerated Carriers. A free carrier population of $\sim 10^5$ electron-hole pairs $(5 \times 10^{19} \text{ carriers/cm}^3)$ is generated in a localized region of the SiNW by photoexcitation with a 425 nm femtosecond laser pulse focused to a diffraction-limited spot by a microscope objective (100×, 0.8 NA). The decay of this photogenerated population is monitored using a delayed 850 nm probe pulse that is also focused to a diffraction limited spot by the objective and spatially overlapped with the pump beam. Pump-probe measurements are performed by positioning the focal point of the two beams at a specific location within a single NW structure using a piezoelectric scanning stage. The pump and probe pulses have equivalent pulse energies (2.5 pJ at a 1.6 MHz repetition rate); however, the absorption coefficient for Si at the 850 nm probe wavelength is \sim 100 times smaller than at the 425 nm pump wavelength. Thus, absorption of the probe beam is negligible compared to the pump, as is customary for transient absorption measurements. After passing through the sample, the probe beam is collected and focused onto a

Figure 2. Time-resolved measurements with spatially overlapped pump-probe microscopy. (a) Normalized decay kinetics in a p-i-n NW (J1) following localized photoexcitation within the n-type region (blue curve), the intrinsic region (green curve), and the p-type region (red). The exact locations of photoexcitation are indicated with colored circles on the SEM image in panel c. All three decays were fit (solid traces) to a sum of two exponentials with a negative offset, $\Delta I(t) = A_1 e^{-t/r^2} + A_2 e^{-t/r^2} - y_0$ in which the average lifetime was determined by $(1/\tau)_{Avg} = [(A_1/\tau_1) + (A_2/\tau_2)]/(A_1 + A_2)$. (b,c) Spatially resolved transient absorption images collected at various pump-probe delays for p-i-n silicon NW junctions, J2 and J1, respectively. Doping profile schematics and corresponding SEM images are shown to the left of the pump-probe images. The same scale is used for SEM and pump-probe images and scale bars are 1 μ m. Dotted lines represent the approximate locations of the junction interfaces, and outlines from the SEM images are superimposed on each pump-probe image to represent approximate location of the wire. Each pump-probe image is depicted using a normalized color scale with the relative amplitudes indicated by the scaling factors at the bottom right of each image.

balanced photodiode detector. Pump-induced changes in the probe intensity (ΔI) are then monitored as a function of pump-probe delay using lock-in detection. The microscope is capable of measuring the transient response of a single NW structure with ~700 nm lateral resolution and a time resolution of ~500 fs.³⁸

Pump-probe measurements obtained at the center of the intrinsic region of a p-i-n SiNW (green curve in Figure 2a) show an initial photoinduced transparency (i.e., bleach) that decays during the first 500 ps after photoexcitation, ultimately becoming a net absorptive signal at long delays. The transient bleach originates from several potential contributions, including changes in the NW absorption that arise from state filling by photoexcited holes in the valence band and electrons in the conduction band or from changes in the NW scattering cross section that arise from a transient modulation of the refractive index due to photoexcited carriers.⁴⁷ With either mechanism, the magnitude of the bleach signal reflects the population of free carriers (electrons and holes). The long-lived absorption is attributed to absorption by carriers that become trapped at defect sites in the lattice and to a thermal modulation of refractive index that results from the ~ 10 °C rise in temperature caused by carrier relaxation.⁴⁷

Changes in the amplitude of the bleach signal can reflect several dynamical processes. Transient absorption experiments performed on undoped Si NWs show an initial increase in the amplitude of the bleach during the first 500 fs that results from the relaxation of carriers to the band edge.⁴⁷ On the picosecond

time scale, the decay of the bleach reflects the decrease in the free carrier population within the localized probe spot due to electron—hole recombination and diffusion away from the point of excitation.³⁸ For indirect band gap semiconductors, electron—hole recombination occurs through a mixture of trap-mediated recombination processes, which take place predominately at the surface in nanostructures. At high doping levels or large photoexcited carrier densities, Auger recombination can also become a dominant process; however, in order to minimize its contribution, pump—probe experiments were performed at excitation intensities in which the time scale for recombination was independent of the pump pulse energy.

Pump-probe microscopy enables direct observation of the carrier lifetime as a function of position in the p-i-n junction. Excitation of the intrinsic and n-type regions exhibit similar decay kinetics (81 and 97 ps, respectively) but differ from the transient response in the p-type region, which occurs much more rapidly (13 ps). The faster decay in this region suggests a characteristically higher surface recombination velocity for the p-type region of the SiNWs. This observation is consistent with passivation of the NW surface by a native oxide layer, which is known to serve as better surface passivation for n-type Si than p-type Si.48 While kinetic measurements at discrete spatial locations can be used to quantify decay rates, spatial variation in the lifetime of the free carrier population is more easily visualized by scanning the pulse pair over the structure at a series of fixed pump-probe delay times to generate timeresolved images. Pump-probe images for several time delays are shown for two p-i-n junctions, J2 and J1, in Figure 2b and 2c, respectively. At early times (0 ps), a positive going (bleach) signal is observed throughout the entire structure. As the pump-probe delay increases, a complex spatial variation in the transient signal emerges in which three distinct regions that coincide with the p-type, intrinsic, and n-type segments of the junction are evident. Within the p-type and n-type regions there is nearly uniform behavior⁴⁹ with the rapid loss of the bleach signal in the p-type region and the slower loss in the n-type segment being consistent with the pump-probe transients collected at single points (Figure 2a). On the other hand, the intrinsic segment shows distinctly different behavior in the center compared to the two ends with regions near the i-n and p-i boundaries decaying faster. While the faster decay observed at the p-i boundary is likely influenced by the rapid loss of the bleach in the p-type region itself, the i-n interface is surrounded by longer lived bleach signals, suggesting that the rapid decay is a consequence of the boundary. This spatial variation in the dynamics may be an indicator of the intense electric field at the interfaces predicted by the finite element simulations (Figure 1c). The electric field could induce charge separation or enhance free carrier tunneling into trap sites,^{50,51} and both processes would appear as a rapid decay of the signal in this region. The results clearly demonstrate that pump-probe microscopy provides far more specific details on the spatial variation of carrier dynamics than can be measured by established methods such as scanning photocurrent microscopy.³¹⁻³⁴

Imaging Charge Carrier Motion. The spatial evolution of the charge carrier cloud along the NW axis is mapped with a spatially separated imaging mode that uses two separate positioning mechanisms for the pump and probe beams. The pump spot is positioned over a particular point in the structure through adjustment of the x-y sample stage. Independent placement of the probe beam is accomplished by directing it through a pair of scanning mirrors that vary the angle of the probe beam relative to the fixed pump beam, enabling the position of the focused probe spot to be displaced from the pump by a distance of up to 20 μ m.

Spatially separated pump-probe (SSPP) images collected with the pump focused on the center of the intrinsic segments in wires J1 and J3 are shown in Figure 3 for several pumpprobe delay times. The image at 0 ps reflects the size of the charge carrier cloud produced by the pump pulse. Initially, this cloud spreads symmetrically in both directions along the wire, reaching the boundaries of the intrinsic segment within 300-400 ps after excitation. As the charge cloud approaches the edges of the intrinsic segment, its evolution becomes asymmetric, and over the next 200 ps a bleach appears in the n-type region that then persists well beyond 1 ns. In the case of J3, free carriers are discernible in the n-type region even at 12.5 ns after excitation. This result is qualitatively different than observations in intrinsic NWs in which the free carrier population disappears within 600-700 ps due to electronhole recombination.³⁸ The persistent signal observed in the ntype region is indicative of the formation of a long-lived charge separated state. The absence of a signal from the holes in the ptype region could be an indication that transient absorption signal arises primarily from the electrons or that the hole population is distributed over a large region of the p-type segment and is simply not detected in this experiment.

The simplest picture of charge carrier motion in a p-n junction would show electrons and holes drifting in opposite

Figure 3. Time-resolved measurements with spatially separated pump-probe microscopy. (a,b) Evolution of photoexcited charge carrier cloud after excitation in the center of the intrinsic region of SiNW p-i-n junctions J1 (panel a) and J3 (panel b). (Top) SEM images of each wire with 1 μ m scale bars. The location of the excitation spot is depicted by the red circle. (Bottom) Series of SSPP images acquired at the pump-probe delay times denoted in lower left of each image. Location of the NW is depicted by black outlines. Each image is displayed using a normalized color scale with the relative amplitudes indicated by the scaling factors at the lower right of each image. Vertical dashed lines mark the positions of dopant transitions in each NW. Animations of the SSPP images for each of the junctions are provided as Supporting Information.

directions with independent, uncorrelated motion as a result of the built-in electric field. Unless the electrons and holes contribute equally to the transient signal, field-driven motion should result in an asymmetric evolution of the photoinduced transparency in the SSPP images. Furthermore, finite element simulations discussed below indicate that when the carrier motion is dictated by the field, the charge cloud should spread rapidly, reaching the boundaries of the intrinsic segment within 20-30 ps. Although the symmetric evolution observed in the SSPP images cannot rule out field-driven motion (the electrons and holes could contribute equally to the transient signal), the time scale for spreading across the intrinsic segment is much longer (300-400 ps) than that predicted for field-driven motion. Instead, the spatial evolution observed in the SSPP images closely resembles carrier diffusion,³⁸ suggesting that the electric field in the middle of the junction is too weak to influence carrier motion at early times. This result is most likely a consequence of a strong electrostatic attraction between the photogenerated charge carriers that opposes separation of the positive (hole) and negative (electron) charge clouds. At low carrier densities, these interactions are negligible and motion is largely governed by the built-in field of the p-n junction. However, at higher carrier concentrations carrier interactions begin to dominate and screen the effects of the built-in electric field. It is because of these carrier-carrier interactions that the neutral electron-hole cloud persists and (ambipolar) diffusion is initially observed. At later times, once the cloud has reached the edges of the intrinsic segment, the built-in field of the junction begins to affect the dynamics, ultimately leading to formation of a long-lived charge-separated state.

Computational Simulations of Charge Carrier Motion at Low and High Injection. The role of carrier-carrier interactions in the motion of the charge carriers is illustrated by a simple time-propagated finite element simulation. The model consists of an intrinsic SiNW 100 nm in diameter and 10 μ m in length with an applied electric field along the NW axis to represent the built-in field of an axial p-i-n junction (Figure 4a). A localized Gaussian distribution (600 nm fwhm) of carriers (electrons and holes) is generated at the center of the wire with a temporal growth profile that corresponds to excitation by an ultrafast laser pulse (500 fs fwhm). The spatial distributions for both the electron and hole populations evolve in time and are subjected to drift and diffusion with differences in electron and hole mobilities taken into account, as well as electron-hole recombination by Auger, surface, and Shockley-Read-Hall mechanisms as described previously.⁴⁵ While the simulations do not account for ballistic motion of the carriers, it is unlikely that ballistic transport is an important factor in these experiments. Pump-probe measurements show that relaxation of the charge carriers to the band edge occurs in less than a picosecond,⁴⁷ suggesting that charge carrier scattering, and the transition from ballistic to diffusive behavior, occurs on time scales much shorter than those monitored here.

The charge carrier distribution exhibits qualitatively different behavior depending upon the initial density of photoinjected carriers. At the lowest injection level ($\sim 10^{15}$ cm⁻³), the electrons and holes are easily separated by the applied field (10^6) V/m) and move rapidly in opposite directions, traversing the first 2 μ m in ~30-50 ps (Figure 4b). The electron and hole populations move with different speeds due to the difference in electron and hole mobilities. The separation of the electron and hole distributions occurs faster than electron-hole recombination; as a result, almost all (97%) of the carriers are extracted by the electrodes. As the carrier density increases to 10^{16} cm⁻³, interactions between electrons and holes become increasingly important (Figure 4c). At this injection level, charge separation is observed at the edges of the distribution where the carrier density is lower and the field is able to strip the electrons from the right-hand side of the distribution and holes from the lefthand side, accelerating the carriers toward the more positive and negative electrodes, respectively. In the center of the distribution, where the carrier density is higher, charge separation is suppressed by strong electron-hole electrostatic attraction. The quasi-neutral charge cloud formed by the

Figure 4. Finite element simulation of charge carrier evolution through a NW under applied bias. (a) Diagram of the intrinsic NW finite element simulation. Metal contacts are placed at the ends of a 10 μ m long NW with 100 nm diameter. A bias is applied across the wire to induce an electric field with a magnitude of 10⁶ V/m. A Gaussian distribution of carriers is generated at the center of the NW (corresponding to an axial position of 0 μ m). (b–d) Charge carrier evolution along the wire axis under (b) low injection (~10¹⁵ cm⁻³) electrons and holes), (c) intermediate injection (~10¹⁶ cm⁻³), and (d) high injection (~10¹⁷ cm⁻³). Hole distributions are shaded in red and electron distributions in blue with shading getting lighter at longer times. Areas where the distributions overlap appear purple.

overlapping electron and hole populations (indicated by purple shading) spreads through ambipolar diffusion while simultaneously decaying in amplitude due to electron-hole recombination. Because electron-hole recombination competes with charge separation, only 70% of the carriers are extracted through the electrodes. At the highest densities simulated (10^{17}) cm⁻³), charge separation occurs only in the wings of the distribution (Figure 4d), and as a result, only 40% of the carriers are collected by the electrodes. The quasi-neutral charge cloud that remains exhibits a net flow toward the positive electrode as it broadens and decays in amplitude. This directional motion is a consequence of the applied electric field and mobility difference between electrons and holes. The carrier-carrier interactions cause the less mobile carriers (holes) to be dragged along with the higher mobility carriers (electrons). While the carriers move quickly at low carrier

Figure 5. Finite element simulation of the spatially separated pump-probe images. (a) Illustration of the finite element simulation model, which consists of a cylindrical intrinsic NW. Metal contacts with applied bias provide the internal electric field. The surface recombination velocity (*S*) varies along the length of the NW to mimic the spatial variation in the recombination time and enhanced recombination in the p-type region. A Gaussian distribution of carriers $(3 \times 10^{19} \text{ cm}^{-3})$ is generated at the center of the NW at an axial position of 0 μ m. (b) Charge carrier evolution along the wire axis. Hole distributions are shaded in red and electron distributions in blue with lighter shading at longer times. Areas where the distributions overlap appear purple. Inset shows the 200 ps time slice with an expanded vertical scale to show the charge separation that occurs in the wings of the distribution. Lower panel shows time slice at 800 ps. (c) Construction of simulated image. Upper image depicts the bleach contribution arising from the free carrier (electron and hole) population. Middle image depicts the absorptive contribution (negative signal). Lower image is the simulated SSPP image that is obtained by summing the bleach and absorptive contributions. (d) Simulated SSPP images at a series of pump-probe delays. Each image is displayed using a normalized color scale with the relative amplitudes indicated by the scaling factors at the lower left of each image.

density, the time scale associated with the evolution of the quasi-neutral charge cloud observed at high density is significantly slower, occurring over hundreds of picoseconds. This time scale is similar to that observed in the evolution of the SSPP images, implying the spatial evolution observed in the SSPP images corresponds largely to evolution of the quasineutral charge cloud.

Although the simulations confirm that charge carrier evolution within the p-i-n junctions is largely governed by carrier–carrier interactions, they also indicate that the junction can separate electrons and holes only when the carrier density drops below $10^{16}-10^{17}$ cm⁻³. This regime is ~2–3 orders of magnitude lower than the injection level estimated for the SSPP experiment.

Simulation of SSPP Images. While the model depicted in Figure 4 is valuable for illustrating the dependence of the carrier motion on photogenerated carrier density, it does not account for the spatial variation in the electron-hole recombination

(Figure 2). In addition, the photogenerated carrier density in the simulation is significantly smaller than the density created experimentally by the pump pulse, preventing a direct comparison between the simulations and the transient absorption images.

The model illustrated in Figure 5a expands upon the previous simulation by including a surface recombination rate that varies along the length of the NW. In order to account for the faster electron—hole recombination observed in the p-type segment, the surface recombination velocity for the left-most 4 μ m of the NW is 10 times greater ($S = 10^5$ cm/s) than the rest of the wire ($S = 10^4$ cm/s). Furthermore, the initial peak carrier density is set to 3×10^{19} cm⁻³, which is comparable to the photogenerated carrier density in the SSPP experiment but is about 500 times greater than highest carrier density depicted in Figure 4. As a result of the strong carrier—carrier interactions, the charge cloud spreads as a quasi-neutral packet, exhibiting a net flow toward the positive electrode (Figure 5b). While this

Letter

Figure 6. Mechanism for charge separation in a p-i-n NW junction under high photogenerated carrier densities. (i) Carriers are generated at the center of the intrinsic region by an ultrafast laser pulse focused to a diffraction-limited spot. Photoexcited carriers are depicted as solid circles (blue for electrons and light orange for holes). Because of the high photoexcited charge carrier density, carrier–carrier interactions dominate, screening the influence of the electric field that results from the presence of fixed negative charges in the p-type region (pink) and fixed positive charges in the n-type region (blue), as well as mobile carriers that accumulate near the boundaries. (ii) Carrier density is reduced by electron–hole recombination as the photogenerated carrier cloud spreads across the intrinsic region. (iii) Further reduction in the photogenerated carrier density occurs as the photogenerated holes reach the n-type boundary and recombine with free electrons (open blue circles). On the opposite side, photogenerated electrons recombine with free holes (open light pink circles) from the p-type region. (iv) Rapid surface recombination in p-type with slower recombination in n-type regions. (v) The reduced carrier density and large field at the boundary leads to the formation of a long-lived charge-separated state.

net shift arises in part from the difference in carrier mobilities, the faster surface recombination in the left-most section of the wire also contributes to the asymmetry of the carrier packet evolution. Charge separation is also observed but only in the wings of the distribution where the carrier density is low enough that the electric field can overcome the carrier–carrier interactions (Figure 5b, insets). Approximately 1% of the electrons and holes are separated in this manner with the remaining carriers recombining within the first nanosecond after excitation.

To facilitate direct comparison of the experiment and computational model, simulated SSPP images are constructed as illustrated in Figure 5c for the 800 ps time frame. The bleach signal (red) resulting from free carriers is obtained by convolving the density profile obtained from the simulations with a Gaussian (650 nm fwhm) transverse to the NW axis. The long-lived absorptive signal (blue) is represented in an adhoc fashion by a fixed, two-dimensional Gaussian with an amplitude and width determined from SSPP images at long times. The full simulated image is formed from a linear addition of these two contributions. The simulated images (Figure 5d) show a strong resemblance to the SSPP images, reproducing both the time scale and asymmetry of the evolution. Because the separated charges are extracted by the electrodes, the positive-going amplitude depicted in the simulated images represents a quasi-neutral charge cloud consisting of both electrons and holes with nearly equal carrier densities. The similarity between the simulated images and the SSPP images

Nano Letters

suggests that much of the asymmetric evolution observed in the pump-probe images arises from a combination of two factors: (i) differences in the electron and hole mobilities, which causes the quasi-neutral charge cloud to drift toward the positive electrode, and (ii) faster electron-hole recombination in the ptype segment compared to the intrinsic and n-type regions.

Although the simulations are intended to mimic the p-i-n junctions, there is a notable difference between the model and the experimental measurements. The SSPP experiments are performed on isolated wires under open-circuit conditions whereas the simulations model the junction as a wire connected to an external circuit, which is needed to mimic the built-in electric field. A long-lived charge-separated state can be produced in the experiment but would not be expected in the simulations because separated charges are extracted by the electrodes. Thus, the simulations recover many of the qualitative features of the SSPP images but do not reproduce the long-lived signals that are observed on the nanosecond time scale (e.g., 12.5 ns frame in Figure 3b) and are attributed to charge separation.

This analysis leads to the description of carrier migration and separation illustrated in Figure 6. Photoexcitation produces a neutral electron-hole cloud consisting of free electrons and holes in the middle of the intrinsic segment (Figure 6i). Because of the high photogenerated carrier density, carriercarrier interactions result in a significant energy penalty for charge separation, and as a consequence the neutral distribution spreads across the intrinsic segment with little influence from the built-in electric field (Figure 6ii). As it spreads, electronhole recombination reduces the carrier density by a factor 10-20. Once the charge cloud reaches the depletion region boundaries (200-400 ps), photogenerated carriers near the ntype region encounter the free electrons that have accumulated near the i-n boundary, resulting in enhanced recombination, with a similar process occurring at the p-i boundary. Recombination may also be assisted by the larger field^{50,51} predicted to be at the boundary by the finite element simulations (Figure 6iii). Together, these processes further decrease the overall carrier density, and the reduced carrier density, combined with the larger field, facilitates charge separation. At 400-500 ps after photoexcitation, the edge of the charge cloud that is enriched with electrons (holes) passes into the n-type (p-type) region through a combination of both diffusion and field-induced drift (Figure 6iv). As the cloud enters the p-type region, rapid electron-hole surface recombination occurs, leaving behind the excess holes. The analogous process occurs in the n-type region but on a longer time scale. By 500-1000 ps only the excess electrons and holes remain, giving rise to the long-lived charge-separated state that is observed experimentally (Figure 6v).

Visualization of charge carrier motion with ultrafast microscopy provides a window through which the physical factors that influence carriers as they navigate through individual nanostructures can be viewed. The combined spatial and temporal resolution of pump—probe microscopy makes it well-suited to capture the complexities of the charge carrier behavior. A detailed understanding of how charges move through individual nanostructures will only become increasingly important as materials with greater complexity are targeted for sophisticated nanoscale electronic and optoelectronic applications.

ASSOCIATED CONTENT

S Supporting Information

Video file animations of the spatially separated pump-probe images for J1 (si_001.avi) and J3 (si_002.avi). This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: (J.F.C.) jfcahoon@unc.edu.

*E-mail: (J.M.P.) john_papanikolas@unc.edu.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This project was supported by the National Science Foundation under Grants CHE-1213379 (M.M.G, E.M.G., E.E.M.C, D.F.Z., and J.M.P) and DMR-1308695 (C.W.P., J.D.C., and J.F.C).

REFERENCES

(1) Lieber, C. M. MRS Bull. 2011, 36 (12), 1052-1063.

(2) Yang, P. D.; Yan, R. X.; Fardy, M. Nano Lett. **2010**, *10* (5), 1529–1536.

(3) Garnett, E. C.; Brongersma, M. L.; Cui, Y.; McGehee, M. D. Annu. Rev. Mater. Res. 2011, 41, 269–295.

(4) Peng, K. Q.; Lee, S. T. Adv. Mater. 2011, 23 (2), 198-215.

(5) Cui, Y.; Lieber, C. M. Science 2001, 291 (5505), 851-853.

(6) Cui, Y.; Zhong, Z.; Wang, D.; Wang, W. U.; Lieber, C. M. Nano Lett. 2003, 3 (2), 149–152.

(7) Lu, W.; Lieber, C. M. J. Phys. D: Appl. Phys. 2006, 39 (21), R387-R406.

(8) Goldberger, J.; Hochbaum, A. I.; Fan, R.; Yang, P. Nano Lett. 2006, 6 (5), 973–977.

(9) Kempa, T. J.; Tian, B. Z.; Kim, D. R.; Hu, J. S.; Zheng, X. L.; Lieber, C. M. Nano Lett. **2008**, 8 (10), 3456–3460.

(10) Kempa, T. J.; Day, R. W.; Kim, S. K.; Park, H. G.; Lieber, C. M. *Energy Environ. Sci.* **2013**, *6* (3), 719–733.

(11) Tian, B. Z.; Zheng, X. L.; Kempa, T. J.; Fang, Y.; Yu, N. F.; Yu, G. H.; Huang, J. L.; Lieber, C. M. *Nature* **2007**, 449 (7164), 885–890.

(12) Kempa, T. J.; Cahoon, J. F.; Kim, S. K.; Day, R. W.; Bell, D. C.; Park, H. G.; Lieber, C. M. Proc. Nat. Acad. Sci. U.S.A. **2012**, 109 (5), 1407–1412.

(13) Kim, S.-K.; Day, R. W.; Cahoon, J. F.; Kempa, T. J.; Song, K.-D.; Park, H.-G.; Lieber, C. M. *Nano Lett.* **2012**, *12* (9), 4971–4976.

(14) Kelzenberg, M. D.; Turner-Evans, D. B.; Putnam, M. C.; Boettcher, S. W.; Briggs, R. M.; Baek, J. Y.; Lewis, N. S.; Atwater, H. A. *Energy Environ. Sci.* **2011**, *4* (3), 866–871.

(15) Zhang, X.; Pinion, C. W.; Christesen, J. D.; Flynn, C. J.; Celano, T. A.; Cahoon, J. F. J. Phys. Chem. Lett. **2013**, 4 (12), 2002–2009.

(16) Mohite, A. D.; Perea, D. E.; Singh, S.; Dayeh, S. A.; Campbell, I. H.; Picraux, S. T.; Htoon, H. *Nano Lett.* **2012**, *12* (4), 1965–71.

(17) Wallentin, J.; Anttu, N.; Asoli, D.; Huffman, M.; Aberg, I.; Magnusson, M. H.; Siefer, G.; Fuss-Kailuweit, P.; Dimroth, F.; Witzigmann, B.; Xu, H. Q.; Samuelson, L.; Deppert, K.; Borgstrom, M. T. Science **2013**, 339 (6123), 1057–1060.

(18) Krogstrup, P.; Jorgensen, H. I.; Heiss, M.; Demichel, O.; Holm, J. V.; Aagesen, M.; Nygard, J.; Morral, A. F. I. *Nat. Photonics* **2013**, 7 (4), 306–310.

(19) Colombo, C.; Heiss, M.; Gratzel, M.; Morral, A. F. I. Appl. Phys. Lett. 2009, 94 (17), 173108.

(20) Tang, J. Y.; Huo, Z. Y.; Brittman, S.; Gao, H. W.; Yang, P. D. Nat. Nanotechnol. 2011, 6 (9), 568–572.

(21) Fan, Z. Y.; Razavi, H.; Do, J. W.; Moriwaki, A.; Ergen, O.; Chueh, Y. L.; Leu, P. W.; Ho, J. C.; Takahashi, T.; Reichertz, L. A.;

Neale, S.; Yu, K.; Wu, M.; Ager, J. W.; Javey, A. Nat. Mater. 2009, 8 (8), 648-653.

(22) Mnatsakanov, T. T.; Rostovtsev, I. L.; Philatov, N. I. Solid-State Electron. 1987, 30 (6), 579–585.

(23) Mnatsakanov, T. T.; Shuman, V. B.; Pomortseva, L. I.; Schröder, D.; Schlögl, A. Solid-State Electron. 2000, 44 (3), 383–392.

(24) Kerr, M. J.; Cuevas, A. J. Appl. Phys. 2002, 91 (4), 2473.

(25) Schmidt, V.; Senz, S.; Gösele, U. Appl. Phys. A 2007, 86 (2), 187–191.

(26) Schmidt, V.; Wittemann, J. V.; Senz, S.; Gösele, U. Adv. Mater. **2009**, 21 (25–26), 2681–2702.

(27) Kar, A.; Upadhya, P. C.; Dayeh, S. A.; Picraux, S. T.; Taylor, A. J.; Prasankumar, R. P. *IEEE J. Sel. Top. Quantum Electron.* **2011**, *17* (4), 889–895.

(28) Prasankumar, R. P.; Upadhya, P. C.; Taylor, A. J. Phys. Status Solidi B 2009, 246 (9), 1973-1995.

(29) Song, J. K.; Willer, U.; Szarko, J. M.; Leone, S. R.; Li, S.; Zhao, Y. J. Phys. Chem. C 2008, 112 (5), 1679–1684.

(30) Styers-Barnett, D. J.; Ellison, S. P.; Mehl, B. P.; Westlake, B. C.; House, R. L.; Park, C.; Wise, K. E.; Papanikolas, J. M. J. Phys. Chem. C 2008, 112 (12), 4507–4516.

(31) Ahn, Y.; Dunning, J.; Park, J. Nano Lett. 2005, 5 (7), 1367–1370.

(32) Howell, S. L.; Padalkar, S.; Yoon, K.; Li, Q.; Koleske, D. D.; Wierer, J. J.; Wang, G. T.; Lauhon, L. J. *Nano Lett.* **2013**, *13* (11), 5123-8.

(33) Gu, Y.; Romankiewicz, J. P.; David, J. K.; Lensch, J. L.; Lauhon, L. J.; Kwak, E. S.; Odom, T. W. J. Vac. Sci. Technol., B 2006, 24 (4), 2172.

(34) Allen, J. E.; Hemesath, E. R.; Lauhon, L. J. Nano Lett. 2009, 9 (5), 1903–1908.

(35) Gutsche, C.; Niepelt, R.; Gnauck, M.; Lysov, A.; Prost, W.; Ronning, C.; Tegude, F. J. *Nano Lett.* **2012**, *12* (3), 1453–1458.

(36) Mehl, B. P.; Kirschbrown, J. R.; Gabriel, M. M.; House, R. L.; Papanikolas, J. M. J. Phys. Chem. B 2013, 117 (16), 4390–4398.

(37) Mehl, B. P.; Kirschbrown, J. R.; House, R. L.; Papanikolas, J. M. J. Phys. Chem. Lett. **2011**, 2 (14), 1777–1781.

(38) Gabriel, M. M.; Kirschbrown, J. R.; Christesen, J. D.; Pinion, C. W.; Zigler, D. F.; Grumstrup, E. M.; Mehl, B. P.; Cating, E. E. M.;

Cahoon, J. F.; Papanikolas, J. M. Nano Lett. 2013, 13 (3), 1336–1340.

(39) Grumstrup, E. M.; Gabriel, M. M.; Cating, E. M.; Pinion, C. W.; Christesen, J. D.; Kirschbrown, J. R.; Vallorz, E. L.; Cahoon, J. F.;

Papanikolas, J. M. J. Phys. Chem. C 2014, 118 (16), 8634-8640.

(40) Berweger, S.; Atkin, J. M.; Olmon, R. L.; Raschke, M. B. J. Phys. Chem. Lett. 2012, 3 (7), 945–952.

(41) Schumacher, T.; Giessen, H.; Lippitz, M. Nano Lett. 2013, 13 (4), 1706–1710.

(42) Gao, B.; Hartland, G. V.; Huang, L. B. ACS Nano 2012, 6 (6), 5083–5090.

(43) Carey, C. R.; Yu, Y.; Kuno, M.; Hartland, G. V. J. Phys. Chem. C 2009, 113 (44), 19077–19081.

(44) Seo, M. A.; Yoo, J.; Dayeh, S. A.; Picraux, S. T.; Taylor, A. J.; Prasankumar, R. P. Nano Lett. **2012**, *12* (12), 6334–8.

(45) Christesen, J. D.; Zhang, X.; Pinion, C. W.; Celano, T. A.; Flynn, C. J.; Cahoon, J. F. *Nano Lett.* **2012**, *12* (11), 6024–9.

(46) Shah, A. *Thin-Film Silicon Solar Cells*; EPFL Press: Lausanne, Switzerland, 2010.

(47) Grumstrup, E. M.; Cating, E. M.; Gabriel, M. M.; Pinion, C. W.;

Christesen, J. D.; Kirschbrown, J. R.; Vallorz, E. L.; Cahoon, J. F.; Papanikolas, J. M. J. Phys. Chem. C 2014, 118 (16), 8626-8633.

(48) Aberle, A. G. Prog. Photovoltaics 2000, 8, 473-487.

(49) Also apparent at the tip of the wire is a transient response from the catalyst, which shows an initial bleach that quickly decays, becoming a long-lived absorption.

(50) Schenk, A. Solid-State Electron. 1992, 35 (11), 1585-1596.

(51) Hurkx, G. A. M.; Klaassen, D. B. M.; Knuvers, M. P. G. IEEE Trans. Electron Devices **1992**, 39 (2), 331–338.

Direct Imaging of Free Carrier and Trap Carrier Motion in Silicon Nanowires by Spatially-Separated Femtosecond Pump–Probe Microscopy

Michelle M. Gabriel, Justin R. Kirschbrown, Joseph D. Christesen, Christopher W. Pinion, David F. Zigler, Erik M. Grumstrup, Brian P. Mehl, Emma E. M. Cating, James F. Cahoon,* and John M. Papanikolas*

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States

ABSTRACT: We have developed a pump–probe microscope capable of exciting a single semiconductor nanostructure in one location and probing it in another with both high spatial and temporal resolution. Experiments performed on Si nanowires enable a direct visualization of the charge cloud produced by photoexcitation at a localized spot as it spreads along the nanowire axis. The time-resolved images show clear evidence of rapid diffusional spreading and recombination of the free carriers, which is consistent with ambipolar diffusion and a surface recombination velocity of ~10⁴ cm/s. The free carrier dynamics are followed by trap carrier migration on slower time scales.

KEYWORDS: Ultrafast microscopy, silicon nanowire, carrier diffusion, pump-probe spectroscopy

he motion of charge carriers through nanoscale structures is of central importance to many emerging technologies in nanoscale electronics, optoelectronics, and solar energy conversion.¹⁻⁴ The interaction of charge carriers with the surfaces, localized defects, and electrical contacts in nanostructured devices can have a profound influence on the migration of electrons and holes through a semiconductor structure. These effects have generally been inferred through optical and electrical measurements that average over an entire structure, or an ensemble of structures, and do not directly measure the local carrier motion. To acquire this information, methods with submicrometer spatial resolution and picosecond temporal resolution are needed. The pursuit of such methods is not new, and time-resolved optical microscopies have been applied to a broad range of problems.⁵⁻¹⁸ The most common approaches are emission-based but are limited to the picosecond time range and require fluorescent samples. Pump-probe methods provide access to faster time scales but are more difficult to implement. Nevertheless, several recent reports from our group,^{5,6} and others,^{10–18} describe their extension to microscopy, particularly in far-field configurations.

Here, direct imaging of carrier motion in Si nanowires is accomplished using a pump-probe microscope that can excite a structure in one location and monitor the arrival of photoexcited carriers in another. Similar examples¹⁹⁻²² have appeared in the literature. In this work, we present results with diffraction-limited pump-probe beams that provide a high (submicrometer) lateral resolution. This unique configuration permits the collection of spatially separated pump-probe (SSPP) *images*, allowing direct visualization of the carrier population over time. This capability permits us to distinguish between rapid free carrier motion and the slower migration of trapped carriers, as discussed below.

Intrinsic Si nanowires (i-Si) were grown by a vapor-liquidsolid (VLS) mechanism²³ using a home-built, hot-wall chemical vapor deposition (CVD) system.³ For a typical growth run, Au nanoparticles with diameters of ~250 nm were dispersed on Si (100) wafers coated with 600 nm thermal oxide, and these wafers were inserted into the center of a quartz-tube furnace. Nanowires were grown with a total reactor pressure of 40 Torr using a gas flow of 2.00 standard cubic centimeters per minute (sccm) silane and 200 sccm hydrogen as carrier gas. The reactor was held at 600 °C for 2 min to nucleate wire growth and then cooled (10 °C/min) to 450 °C for continued wire growth over two hours. For n-type Si nanowires (n-Si), an additional flow of 10.00 sccm phosphine (1000 ppm in hydrogen) was used to provide a source of phosphorus dopant at a relative concentration of ~200:1 Si:P. After completion of wire growth, nanowires were thermally oxidized at 1000 °C for 60 s in 100 Torr flowing oxygen to form a 5-10 nm-thick thermal oxide. Nanowires were then mechanically transferred onto quartz substrates for microscopy imaging.

The transient absorption microscope is illustrated in Figure 1. The 850 nm output of a mode-locked Ti:Sapphire oscillator is split by a 10/90 beam splitter. The higher power beam is frequency doubled to 425 nm and used as the pump, while the other is used as the probe. Two synchronized acousto-optic modulator (AOM) pulse pickers reduce the repetition rates of the pump and probe beams to 1.6 MHz, thus ensuring complete relaxation before the next pump–probe pulse pair arrives at the sample. A motorized linear stage controls the time delay between excitation and probe pulses. Both the pump and probe beams are attenuated to 20 pJ per pulse, recombined

Received:January 21, 2013Published:February 19, 2013

Nano Letters

Figure 1. Overview of the experimental system. (A) Illustration of the spatially separated pump-probe (SSPP) microscope. An x-y scanning stage positions the structure under the 425 nm pump spot; the 850 nm probe spot is positioned relative to the pump with a scanning mirror assembly. (B) Schematic illustration of spatially separated scanning. (C) SEM image of the UNC logo defined in Au by electron-beam lithography; scale bar, 2 μ m. (D) Left, optical transmission images obtained with the pump (I) and probe (II) beams scanned over a lower-center portion of the Au structure, as denoted by the inset box in panel C, that contains an ~400 nm gap; scale bars, 1 μ m. Red indicates maximum transmission images acquired by raster-scanning the probe beam over the entire Au structure shown in panel C using either the x-y stage (III) or the mirror assembly (IV); scale bars, 4 μ m.

using a dichroic beam splitter, and then directed onto the back aperture of a $50 \times (0.8 \text{ NA})$ objective that focuses them to diffraction limited spots within a single structure. Diffraction limited spatial resolution in our instrument has been confirmed in two-photon emission images.⁵ Images of the UNC logo defined in Au on a quartz substrate (Figure 1C) obtained using the pump and probe beams (Figure 1D) are consistent with diffraction-limited focusing of the two spots, with the pump spot being smaller than the probe. The probe beam is collected by a condenser lens, filtered to remove residual pump light, and directed onto a balanced photodiode. The pump beam is modulated at 10 kHz using the AOM, and pump-induced changes in the intensity of the probe pulse are monitored by a digital lock-in amplifier, producing the measured change in intensity, ΔI , plotted in the figures discussed below. The timeresolution of the instrument is \sim 500 fs.^{5,6}

Initial experiments were performed by measuring kinetics from spatially overlapped pump and probe beams positioned $3-5 \ \mu m$ from the end of three nanowire samples (Figure 2). We estimate that photoexcitation by the pump pulse produced $\sim 10^{19}-10^{20}$ carriers/cm³ assuming an absorption efficiency of 10-100% at the excitation wavelength of 425 nm.^{1,2} Pumpprobe transient signals are shown for two i-Si wires, NW1 and

Figure 2. Normalized pump-probe microscopy decay kinetics following photoexcitation of a localized region in three different Si nanowires; NW1 (red) and NW2 (green) are intrinsic, and NW3 (blue) is n-type. All three were fit to a triexponential decay (solid lines, see Table 1 for fitting parameters). Inset: SEM images of the three wires showing the location of pump excitation as a red circle; scale bars, 2 μ m.

NW2, and an n-Si wire, NW3, with diameters of 160, 210, and 330 nm, respectively. Exact locations of excitation are indicated on the respective SEM images in Figure 2. The two i-Si NW transient signals exhibit an intense positive going (bleach) feature that becomes weakly negative (absorptive) at several hundred ps before returning to zero signal. These transient signals are similar to pump—probe measurements performed on ensembles of Si nanowires.²⁴ The signals include contributions from the free carrier (electron and hole) and trap carrier populations and can arise from changes in absorptivity and/or reflectivity upon photoexcitation as well as carrier lensing effects due to the spatially localized excitation.^{5,6}

All three transient signals can be well fit to a superposition of a positive going signal that decays with biexponential kinetics (τ_1, τ_2) , and a smaller negative going signal with a much slower decay time, τ_3 (see Table 1).²⁵ The two i-Si wires exhibit different decay kinetics, with NW1 showing a faster initial decay $(\tau_{avg} = 67 \text{ ps})$ than NW2 $(\tau_{avg} = 112 \text{ ps})$, but with a slower recovery time back to zero signal, $\tau_3 = 2300 \text{ ps}$ (NW1) versus 551 ps (NW2). We attribute the initial decay to free carrier recombination and diffusion and the slower, negative amplitude component to trapped carrier recombination. For semiconductor nanowires, surface recombination is often the predominant recombination mechanism, and the surface recombination velocity, S, can be calculated from the carrier lifetime, τ , as $S = d/4\tau$, where *d* is the nanowire diameter.^{3,4,26,27} The values derived from this analysis using the measured τ_{avg} are 6.0×10^4 cm/s and 4.7×10^4 cm/s for NW1 and NW2, respectively. These values are upper limits to the actual surface recombination velocities because Auger recombination and carrier diffusion (discussed below) also contribute to the decay. Nevertheless, the similarity between the S values for these two wires suggests that the initial decay is dominated by a surface recombination mechanism.

The n-Si wire (NW3) shows a much faster initial decay (τ_{avg} = 11 ps) and recovers with τ_3 = 1146 ps. The origin of the much faster decay in the n-Si wire is possibly a result of

Letter

Table 1. Parameters	Used To Fit Kinetics	Derived from Pump-Probe	Microscopy to a Sum o	f Three Exponentials,
$\Delta I(t) = A_1 \mathrm{e}^{-t/\tau 1} + A_2$	$e^{-t/\tau^2} + A_3 e^{-t/\tau^3}$	-		•

	$ au_1$ (A ₁)	$ au_2$ ((A ₂)	$ au_3$	(A_3)	$ au_{ m avg}^{a}$
NW1	29.8 ps	(0.34)	144 ps	(0.78)	2300 ps	(-0.12)	67 ps
NW2	46.8 ps	(0.34)	248 ps	(0.87)	551 ps	(-0.23)	112 ps
NW3	1.75 ps	(0.06)	15 ps	(1.01)	1146 ps	(-0.07)	11 ps
^a Average decay time for the two fast components, i.e., $(1/\tau_{Avg}) = [(A_1/\tau_1) + (A_2/\tau_2)]/(A_1 + A_2).$							

Figure 3. Time-resolved SSPP microscopy images. (A) NW1, (B) NW2, and (C) NW3. Left, SEM images of 5 μ m sections of each wire centered around the pump laser excitation spot; (image sizes, 2 μ m × 5 μ m; scale bars, 1 μ m). The location of the excitation spot is depicted by the red circle. For each sample, the tip of the wire lies beyond the top of the image. Right, series of SSPP images acquired at the pump–probe delay times denoted above each image. Location of the nanowire is depicted by the faint lines. Each image is 2 μ m × 5 μ m and is depicted using a normalized color scale with the relative amplitudes indicated by the scaling factors in the bottom-right corner of each image.

increased Auger recombination due to the high electron majority-carrier concentration. A second possibility is the presence of an amorphous Si shell surrounding the crystalline core, as suggested by the rougher surface and larger diameter observed in the SEM image. Regardless of the exact origin, the electron—hole recombination rate in this n-Si wire is substantially greater than the i-Si wires.

To characterize the diffusion process in the Si nanowires, we have directly imaged charge carrier motion using SSPP microscopy, in which the structure is excited in one location and probed in another. This experiment is accomplished by incorporating two separate positioning mechanisms for the pump and probe beams. The pump spot is positioned over a particular point in the structure through adjustment of the x-ysample stage. Independent placement of the probe beam is accomplished by directing it through a pair of mirrors with computer-controlled actuators, which vary the angle of the probe beam relative to the fixed pump beam (Figure 1A). The use of two (master/slave) mirrors allows adjustment of this angle while keeping the beam centered on the objective aperture. By scanning this angle, the position of the focused probe spot can be displaced from the pump by a distance (Δ_{pp}) of 10–20 μ m while still remaining within the objective's field of view. Figure 1D compares transmission images taken using the scanning mirror assembly and the scanning stage. Both transmission images reproduce not only the general shape, but also the finer details of the structure, and the similarity of these two images to the SEM image demonstrates the distortion-free imaging capability of this scanning mechanism.

The SSPP microscope can be operated in two different modes. In one operational mode, the delay time between the pump and probe beams is held fixed, and the spatial displacement of the pump and probe is scanned, resulting in an image of the spatial variation in the transient absorption signal at a particular time after photoexcitation. SSPP images are shown for three different nanowires (NW1, NW2, and NW3) in Figure 3. At early pump-probe delays (near $\Delta t = 0$ ps), the images show an intense positive (red) transient absorption feature, with a spatial extent commensurate with the size of the pump spot. For the i-Si wires (NW1 and NW2), this spot spreads rapidly along the long axis of the nanowire, growing $4-5 \ \mu m$ in length during the first 300–500 ps. At the pump-probe delay time in which the transient signal crosses zero (refer to Figure 2), a trough appears at the location of the excitation spot that eventually becomes a net negative signal. The final images show the positive features disappearing altogether, leaving behind a negative (blue) region that broadens on a slow time scale. We attribute the rapid evolution of the intense positive signal to the diffusion of free carriers (electrons and holes) out of the excitation volume and the negative signal at long times to trap carrier motion. Rapid electron-hole recombination in the n-Si wire (NW3), on the other hand, limits the extent of spatial diffusion, and the initial feature shows no substantial broadening.

Figure 4. Spatially separated pump-probe (SSPP) transient signals. (A) SSPP image obtained at $\Delta t = 0$ overlaid with the spatial locations, a-e, of the displaced probe beam, which correspond to separations of $\Delta_{\rm pp} = 0$, 1.02, 1.45, 1.83, and 2.32 μ m, respectively; scale bar, 1 μ m. (B) Transient signals obtained from NW2 by fixing the spatial separation, $\Delta_{\rm pp}$, between the pump and probe spots and scanning the pump-probe delay. The curves labeled a-e correspond to the positions indicated in panel A. Also shown is the transient signal, labeled Σ , obtained by summation of the individual SSPP signals. Individual data points are denoted by open yellow circles, and the solid line is a fit to $\Delta I(t) = A_1 e^{-t/\tau 1} + A_2 e^{-t/\tau^2}$ with $\tau_1 = 380$ ps ($A_1 = 3.21$) and $\tau_2 = 900$ ps ($A_2 = -1.02$).

The second operational mode of the SSPP microscope fixes the displacement between the pump and probe laser spots and scans the delay time between them. Figure 4 shows decay traces for five different separations, $\Delta_{\rm pp}$, along the NW2 nanowire axis. When the pump and probe are spatially coincident (Δ_{pp} = 0), the maximum signal intensity is observed at $\Delta t = 0$ ps. A delayed rise in the signal is observed when the probe pulse is positioned away from the excitation spot ($\Delta_{pp} > 0$), reflecting the time needed for carriers to migrate from the pump region to the probe region. There is also an overall decrease in the intensity of the signal as the pump-probe separation is increased. At $\Delta_{pp} = 2.32 \ \mu m$, the overall intensity of the signal makes it difficult to discern the arrival of carriers when depicted on an absolute scale (Figure 4); however, when the transients are displayed normalized to their respective maxima (Figure 5A), it is clear that free carriers are migrating as far as 2.7 μ m from the excitation region. These time-resolved data indicate that the spatially coincident pump-probe transient signals shown in Figure 2 are influenced by the diffusional motion of charge carriers away from the excitation region. In principal, the summation of transient signals obtained at different pumpprobe separations (shown as the curve \sum in Figure 4) should reflect the total free carrier population and remove effects from diffusional motion. This curve is well fit to a superposition of decays with positive and negative amplitudes; however, unlike the $\Delta_{pp} = 0 \ \mu m$ signal, the decay of the positive signal in the superposition is reproduced by a single exponential with time constant of τ = 380 ps, providing a more accurate measure of the free carrier lifetime. This value for τ gives a revised surface

Figure 5. Experimental and simulated transient signals. (A) Normalized SSPP transient signals obtained from NW2. The curves labeled a–f correspond to separations $\Delta_{\rm pp} = 0$, 1.02, 1.45, 1.83, 2.32, and 2.76 μ m, respectively. (B) Analogous set of SSPP curves predicted by eq 1 using $D = 18 \text{ cm}^2/\text{s}$ and $\tau = 380 \text{ ps}$. The pump and probe laser profiles have full width at half maximum values of 350 and 700 nm, respectively, and are included in the simulation curves.

recombination velocity for NW2 of 1.4×10^4 cm/s, which is comparable to the value, $S = 7 \times 10^3$ cm/s, determined for wires grown under similar growth conditions.³

To quantitatively interpret the charge carrier motion observed with SSPP microscopy, we have developed a simple model that includes ambipolar diffusion of the free carrier population, a recombination process with a single first-order rate constant $(1/\tau)$, and Gaussian profiles that represent the pump and probe laser beams centered at x = 0 and $x = \Delta_{pp}$, respectively. In this model, the number of carriers interacting with the displaced probe beam can be written as:

$$N(\Delta_{\rm pp}, t) = \int_{-\infty}^{\infty} I(x - \Delta_{\rm pp}) \eta(x, t) \mathrm{d}x \tag{1}$$

where $I(x - \Delta_{pp})$ is a normalized Gaussian centered at $x = \Delta_{pp}$ that describes the intensity profile of the probe beam, and $\eta(x,t)$ is the carrier distribution created by the pump pulse. At t = 0 this distribution will mirror the intensity profile of the pump beam and spread with increasing time. It can be written as:

$$\eta(x, t) = \int_{-\infty}^{\infty} I(x') p(x - x', t) dx'$$
(2)

where I(x) is the optical intensity profile of the focused pump laser beam used in the experiment (represented by a normalized Gaussian) and $p(\xi,t)$ describes the diffusional spreading of N carriers from an initial point located at $\xi = 0$, i.e.:

$$p(\xi, t) = \frac{N}{\sqrt{4\pi Dt}} \exp\left(-\frac{t}{\tau}\right) \exp\left(-\frac{\xi^2}{4Dt}\right)$$
(3)

Nano Letters

In this expression τ is the free carrier lifetime and D is the ambipolar diffusion constant.²⁸

Figure 5 compares this diffusional model (eq 1) with the experimentally observed SSPP transient signals from NW2. The experimental data shows a steady increase in the spreading of the carrier cloud, reaching several micrometers in a few hundred picoseconds. The calculated curves (Figure 5B) were obtained using the ambipolar diffusion constant for bulk Si (D ~ 18 cm²/s) and a carrier lifetime τ = 380 ps. The calculated curves qualitatively resemble those observed in the SSPP experiment, indicating that diffusional processes in Si nanowires grown by a VLS mechanism are remarkably similar to those in single-crystalline bulk Si materials. There are differences, however, particularly at smaller pump-probe displacements and shorter time delays. In this regime, the model predicts a greater extent of diffusion than observed experimentally, a difference which could be the result of changes in the diffusion constant because of carrier scattering within the nanowires. The exact reasons are currently under investigation.

We have developed a pump-probe microscope capable of photoexciting a single nanostructure in one location and probing it in another. Experiments performed on Si nanowires enable a direct visualization of the charge cloud produced by photoexcitation of a localized spot and spreading of this cloud along the nanowire axis. The time-resolved images show clear evidence of rapid diffusion and recombination of the free carriers followed by trap carrier migration on slower time scales.

AUTHOR INFORMATION

Corresponding Author

*E-mail: john_papanikolas@unc.edu, jfcahoon@unc.edu.

Author Contributions

M.M.G. and J.R.K. contributed equally.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by a grant from the National Science Foundation (CHE-1213379). J.D.C., C.W.P., and J.F.C. acknowledge support from UNC-Chapel Hill start-up funding.

REFERENCES

(1) Kempa, T. J.; Cahoon, J. F.; Kim, S. K.; Day, R. W.; Bell, D. C.; Park, H. G.; Lieber, C. M. Proc. Natl. Acad. Sci. **2012**, 109, 1407.

(2) Kim, S. K.; Day, R. W.; Cahoon, J. F.; Kempa, T. J.; Song, K. D.; Park, H. G.; Lieber, C. M. *Nano Lett.* **2012**, *12*, 4971.

(3) Christesen, J. D.; Zhang, X.; Pinion, C. W.; Celano, T. A.; Flynn, C. J.; Cahoon, J. F. *Nano Lett.* **2012**, *12*, 6024.

(4) Kelzenberg, M. D.; Turner-Evans, D. B.; Putnam, M. C.; Boettcher, S. W.; Briggs, R. M.; Baek, J. Y.; Lewis, N. S.; Atwater, H. A. *Energy Environ. Sci.* **2011**, *4*, 866.

(5) Mehl, B. P.; Kirschbrown, J. R.; Gabriel, M. M.; House, R. L.; Papanikolas, J. M. J. Phys. Chem. B **2013**, DOI: 10.1021/jp307089h.

(6) Mehl, B. P.; Kirschbrown, J. R.; House, R. L.; Papanikolas, J. M. J. Phys. Chem. Lett. 2011, 2, 1777.

(7) House, R. L.; Mehl, B. P.; Kirschbrown, J. R.; Barnes, S. C.; Papanikolas, J. M. J. Phys. Chem. C 2011, 115, 10806.

(8) House, R. L.; Kirschbrown, J. R.; Mehl, B. P.; Gabriel, M. M.; Puccio, J. A.; Parker, J. K.; Papanikolas, J. M. *J. Phys. Chem. C* **2011**, *115*, 21436.

- (9) House, R. L.; Mehl, B. P.; Zhang, C.; Kirschbrown, J. R.; Barnes, S. C.; Papanikolas, J. M. *Proc. SPIE* **2009**, 7396, 73960G.
- (10) Gundlach, L.; Piotrowiak, P. Opt. Lett. 2008, 33, 992.

- (12) Song, J. K.; Willer, U.; Szarko, J. M.; Leone, S. R.; Li, S.; Zhao, Y. J. Phys. Chem. C 2008, 112, 1679.
- (13) Johnson, J. C.; Knutsen, K. P.; Yan, H. Q.; Law, M.; Zhang, Y. F.; Yang, P. D.; Saykally, R. J. Nano Lett. **2004**, *4*, 197.
- (14) Huang, L. B.; Hartland, G. V.; Chu, L. Q.; Luxmi; Feenstra, R. M.; Lian, C. X.; Tahy, K.; Xing, H. L. Nano Lett. **2010**, *10*, 1308.

(15) Carey, C. R.; Yu, Y. H.; Kuno, M.; Hartland, G. V. J. Phys. Chem. C 2009, 113, 19077.

(16) Fujino, T.; Fujima, T.; Tahara, T. J. Phys. Chem. B 2005, 109, 15327.

(17) Fu, D.; Ye, T.; Matthews, T. E.; Grichnik, J.; Hong, L.; Simon, J. D.; Warren, W. S. J. Biomed. Opt. **2008**, *13*, 054036.

(18) Polli, D.; Grancini, G.; Clark, J.; Celebrano, M.; Virgili, T.; Cerullo, G.; Lanzani, G. Adv. Mater. **2010**, *22*, 3048.

(19) Seo, M. A.; Yoo, J.; Dayeh, S. A.; Picraux, S. T.; Taylor, A. J.; Prasankumar, R. P. *Nano Lett.* **2012**, *12*, 6334.

(20) Seo, M. A.; Dayeh, S. A.; Upadhya, P. C.; Martinez, J. A.; Swartzentruber, B. S.; Picraux, S. T.; Taylor, A. J.; Prasankumar, R. P. *Appl. Phys. Lett.* **2012**, *100*, 071104.

(21) Ruzicka, B. A.; Zhao, H. J. Opt. Soc. Am. B 2012, 29, A43.

(22) Kumar, N.; Ruzicka, B. A.; Butch, N. P.; Syers, P.; Kirshenbaum, K.; Paglione, J.; Zhao, H. *Phys. Rev. B* **2011**, *83*, 235306.

(23) Schmidt, V.; Wittemann, J. V.; Gosele, U. Chem. Rev. 2010, 110, 361.

(24) Kar, A.; Upadhya, P. C.; Dayeh, S. A.; Picraux, S. T.; Taylor, A. J.; Prasankumar, R. P. *IEEE J. Sel. Top. Quant.* **2011**, *17*, 889.

(25) The n-Si wire transient depicted in Figure 2 has been inverted (i.e., multiplied by -1). The reason this wire shows an initial absorption rather than a bleach is not entirely clear; however, in other experiments on ZnO we observed (ref 5) similar sign-changes that stemmed from a Kerr lensing contribution (in addition to absorptive features) to the overall signal. This contribution could either be positive or negative, depending upon the details of the pump-probe overlap. This process could be at play in this wire.

(26) Mohite, A. D.; Perea, D. E.; Singh, S.; Dayeh, S. A.; Campbell, I. H.; Picraux, S. T.; Htoon, H. *Nano Lett.* **2012**, *12*, 1965.

(27) Allen, J. E.; Hemesath, E. R.; Perea, D. E.; Lensch-Falk, J. L.; Li, Z. Y.; Yin, F.; Gass, M. H.; Wang, P.; Bleloch, A. L.; Palmer, R. E.; Lauhon, L. J. *Nat. Nanotechnol.* **2008**, *3*, 168.

(28) Sze, S. M.; Ng, K. K. In *Physics of Semiconductor Devices*; 3rd ed.; Wiley-Interscience: New York, 2007; p 566.

Ultrafast Carrier Dynamics in Individual Silicon Nanowires: Characterization of Diameter-Dependent Carrier Lifetime and Surface Recombination with Pump–Probe Microscopy

Erik M. Grumstrup, Michelle M. Gabriel, Emma M. Cating, Christopher W. Pinion, Joseph D. Christesen, Justin R. Kirschbrown, Ernest L. Vallorz, III, James F. Cahoon,* and John M. Papanikolas*

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States

ABSTRACT: Ultrafast charge carrier dynamics in silicon nanowires (NWs) grown by a vapor-liquid-solid mechanism were interrogated with optical pump-probe microscopy. The high time and spatial resolutions achieved by the experiments provide insight into the charge carrier dynamics of single nanostructures. Individual NWs were excited by a femtosecond pump pulse focused to a diffraction-limited spot, producing photogenerated carriers (electrons and holes) in a localized region of the structure. Photoexcited carriers undergo both electron-hole recombination and diffusional migration away from the excitation spot on similar time scales. The evolution of the carrier population is monitored by a delayed probe pulse that is also focused to a diffraction-limited spot. When the pump and probe are spatially overlapped, the transient signal reflects both recombination and carrier migration. Diffusional motion is directly observed by spatially separating the pump and probe beams, enabling carriers to be generated in one location and detected in another.

Quantitative analysis of the signals yields a statistical distribution of carrier lifetimes from a large number of individual NWs. On average, the lifetime was found to be linearly proportional to the diameter, consistent with a surface-mediated recombination mechanism. These results highlight the capability of pump-probe microscopy to quantitatively evaluate key recombination characteristics in semiconductor nanostructures, which are important for their implementation in nanotechnologies.

he optical and electronic properties of semiconductor I nanomaterials are strongly influenced by their shape and composition, making them a promising platform on which to develop a variety of nanotechnologies.^{1,2} While the strong structure-function relationship allows great flexibility in tuning these materials for specific device applications, $^{3-8}$ it also poses a great challenge for quantitatively characterizing and understanding dynamical phenomena. For example, surface recombination of photogenerated carriers is central to the performance of many active devices, and it becomes the dominant mechanism of carrier recombination as the sizes of these devices approach the nanoscale.^{7,9,10} Direct measurement of the recombination rate can be obtained using common spectroscopic tools such as femtosecond transient absorption spec-troscopy.^{11,12} The difficulty with these spectroscopic methods is that they average over a large ensemble of nanostructures where there is frequently considerable variation in size and shape from one structure to the next. Furthermore, high-aspectratio materials (e.g., nanowires) often contain a distribution of secondary structures (i.e., local curvature in bent wires). The extensive averaging over the distribution of sizes, shapes, and secondary structures, as well as extraneous materials (residual reactants, catalysts, etc.) that may be present within the sample, makes it difficult to interpret transient signals obtained from ensembles in terms of fundamental dynamical processes. An alternative strategy involves performing measurements on single objects using time-resolved optical microscopy,13-17

allowing the carrier dynamics to be correlated with shape, orientation, and morphology. Moreover, these methods can reveal spatially dependent phenomena, such as carrier diffusion and dynamical heterogeneity, at the single-structure level, which are inaccessible by conventional spectroscopic techniques.

In a previous paper, our group demonstrated the use of ultrafast microscopy to examine charge carrier recombination dynamics of silicon nanowires (NWs) on a wire-to-wire basis.¹⁵ The high spatial resolution achieved by the optical microscope provides insight into the electron-hole recombination and carrier migration dynamics of a single nanostructure. In these experiments, an individual NW is excited by a femtosecond pump pulse that has been focused to a diffraction-limited spot by a microscope objective, producing photogenerated carriers (electrons and holes) in a localized region of the structure. After a well-defined delay, the excitation is probed by a second femtosecond laser pulse that is spatially overlapped with the pump pulse, and pump-induced changes to the transmission of the probe beam are detected. In this spatially overlapped pump-probe (SOPP) configuration, the decay of the signal reflects both electron-hole recombination and migration of carriers away from the excitation spot and out of the probe beam. Motion of the carriers is observed directly using a spatially separated pump-probe (SSPP) configuration, in

Received:March 19, 2014Published:March 21, 2014

The Journal of Physical Chemistry C

Figure 1. SEM characterization of NW samples. (A) SEM image of sample d50 in a region where NW density is high. TA measurements in ref 18 were performed in these higher density regions to maximize optical absorption. The scale bar is 10 μ m. (B) SEM image of sample d50 in a region where NW density is lower. Microscopy measurements were performed in these lower density regions to isolate the spectroscopic signals from individual wires. The small yellow circle above the scale bar is 500 nm in diameter to illustrate the approximate size of the focused laser beams. The scale bar is 10 μ m. (C) Diameter distributions for samples d100, d60, d50, and d40 measured by SEM (adapted from ref 18).

which carriers are created in one location and detected in another, thereby enabling the direct imaging of carrier diffusion.

In this paper, we expand on this previous work and characterize numerous wires to reveal a broad distribution of carrier lifetimes that is largely determined by wire-to-wire variations in diameter. Quantitative analysis of the data allows carrier diffusion along the length of the wire to be decoupled from the measured kinetics and shows that carrier recombination is consistent with a surface-mediated mechanism in which the lifetime (τ) is proportional to the NW diameter (d), i.e., τ = d/4S. The surface recombination velocity (S) provides a measure of surface quality and has both fundamental and technological significance. It offers a quantitative means of studying the interaction of carriers with the surface and for comparing different surface passivation strategies. It can also be related to the density of surface states, which governs the behavior of many active electronic components, making it of interest to many nanotechnologies. Pump-probe microscopy enables the measurement of carrier lifetimes at specific points within an individual structure, which can then be used, with the nanowire diameter, to extract a value for S. We compare the microscopy results to those obtained on the same set of samples using femtosecond transient absorption (TA) spectroscopy, which measures the ensemble-averaged lifetimes.¹⁸ The TA-measured lifetimes are 2-3 times shorter than those observed by microscopy, a discrepancy that may arise from differences in the distribution of secondary structures accessed in the two experiments. The combined set of results demonstrates that the two methods, ensemble TA and pump-probe microscopy, provide complementary views of the carrier dynamics in semiconductor nanostructures.

EXPERIMENTAL SECTION

Intrinsic Si NWs were grown by a vapor-liquid-solid mechanism¹ using a home-built, hot-wall chemical vapor deposition (CVD) system.⁶ For a typical growth run, Au nanoparticles with diameters of ~30, 50, 60, and 100 nm were dispersed on quartz substrates. NWs were grown with a total reactor pressure of 40 Torr using a gas flow of 2.00 standard cubic centimeters per minute (sccm) of silane and 200 sccm of hydrogen as carrier gas. The reactor was held at 450 °C for 2

min to nucleate wire growth and then cooled (12 °C/min) to 410 °C for continued wire growth over 2 h. After completion of wire growth, NWs were thermally oxidized at 1000 °C for 60 s in 100 Torr of flowing oxygen to form a 5–10 nm thick thermal oxide. The samples were then immersed in 2-propanol, which upon evaporation collapses the NWs onto the plane of the quartz substrate, forming the dense mat of randomly oriented, overlapping NWs shown in Figure 1A. Scanning electron microscopy (SEM) images reveal a large number of high-quality NWs that remain largely unbroken upon collapse (Figure 1A).

The pump-probe microscope has been described in detail elsewhere.¹⁵ Briefly, a portion of the output beam comprised of 100 fs fwhm (full width at half-maximum) pulses centered at 850 nm is split, and each arm is passed through a pair of synchronized acousto-optic modulators (AOMs; Gooch and Housego), which reduce the pulse repetition rate to 1.6 MHz. The pump beam is frequency doubled by a β -barium borate (BBO) crystal, attenuated to 2.5 pJ/pulse, and modulated at a 50% duty cycle by the AOM. It was verified that further reduction of the pump power did not change the transient kinetics. The probe beam (630 fJ/pulse) is passed onto a mechanical delay stage and a pair of computer-controlled mirrors before being collinearly coupled onto the pump beam path with a dichroic mirror. Despite the comparable fluence of pump and probe beams, the probe beam only weakly interacts with the Si NW sample due to a 100-fold lower extinction coefficient at 850 nm compared to 425 nm.¹⁹ Pump and probe beams are focused onto the sample with a 0.8 NA 100 \times ultralong working distance objective. The transmitted probe beam is collected with a condenser, passed through a filter to attenuate transmitted pump light, and detected on one channel of a balanced photodetector. The other channel is balanced with a portion of the probe beam picked off before the microscope. The change in transmittance is detected by lock-in detection (SR810, Stanford Research) and processed with home-written Matlab software. All measurements were performed at room temperature in an ambient atmosphere.

RESULTS AND DISCUSSION

Nanowire Samples. Microscopy measurements were performed at the edges of the densest regions so that individual NWs could be resolved without multiple overlapping wires contributing to the measured signal (Figure 1B). These experiments focus on four samples denoted d40, d50, d60, and d100 with average diameters of 38, 52, 59, and 101 nm, respectively (Figure 1C).¹⁸

Pump–Probe Microscopy. Carrier recombination dynamics were monitored with a pump–probe microscope that possesses femtosecond temporal resolution and near-diffraction-limited spatial resolution. The microscope, which uses an objective to focus the 425 nm pump and 850 nm probe beams to near-diffraction-limited spots within a single structure, can be operated in two modes, SOPP and SSPP, as discussed above. A comparison of conventional bright-field and SOPP images for the d50 sample is displayed in Figure 2. The bright-field image

Figure 2. Comparison of conventional bright-field and transient SOPP imaging of NW samples. (A) Conventional bright-field optical image of a ~40 μ m × 40 μ m region of the d50 sample containing 50 nm diameter NWs. (B) SOPP image of the sample region shown in panel A and collected at a pump-probe delay of $\Delta t = 0$ ps. (C) Higher resolution image of the boxed region in panel B. The spatial resolution of SOPP images is ~500 nm fwhm and is comparable to the resolution of the bright-field image.

(Figure 2A) shows a number of individual NWs in the field of view. The pump-probe images (Figure 2B,C), which map the spatial variation in the transient absorption signal,^{20,21} were obtained by holding the delay fixed at $\Delta t = 0$ ps and raster scanning the sample underneath the spatially overlapped pulses. At early times, photoexcitation by the pump pulse causes an increase in the detected intensity of the probe beam, i.e., $\Delta I =$ $I_{\text{pump on}} - I_{\text{pump off}} > 0$, which is represented by warmer colors in the color map. This photoinduced transparency is partially attributed to changes in NW absorption resulting from band filling by photoexcited free carriers that occupy low-energy states in the conduction and valence bands of Si. The intensity of the probe beam is also affected by changes in NW scattering arising from shifts in the index of refraction brought on by photoexcitation. While it is difficult to disentangle the relative contributions of absorption and scattering, in either case the associated increase in probe transmittance (the bleach signal) is proportional to the free carrier density, and thus provides a means to monitor changes in the electron and hole populations. In addition to this positive-going bleach, photoinduced absorption of free carriers and trapped carriers may also contribute to the overall transient spectra as a negative-going signal. However, consistent with previous studies of silicon, the overall signal is positive at early times, suggesting that carrier absorption (free or trapped) is a minor component relative to band filling. 11,16,22,23

The variation in signal magnitude observed between and within individual NWs across the SOPP image is not the result of spatial heterogeneity in the intrinsic properties of the NW (e.g., crystallinity, defect density, surface passivation), but rather stems from a combination of extrinsic factors. For example, overlapping wires result in greater signal size compared with other NW sections. NWs located at the focal plane experience the highest pump intensity, generating a greater carrier density and larger transient signals. There is also a polarization effect. The images in Figure 2B,C were collected with the pump and probe polarization vectors directed along the horizontal axis of the image. While the decay kinetics are polarization independent, the magnitude of the pump-probe signal is larger when the probe polarization is directed parallel to the NW axis. Thus, NWs with significant curvature exhibit substantial variation along the growth axis, with segments aligned along the probe polarization appearing brighter. Indeed, SOPP images obtained from straight isolated NWs show very little variation in signal intensity along the wire axis, indicative of the production of highly uniform structures by the VLS growth process. Thus, the spatial variation observed in the collapsed NW films is most likely a reflection of extrinsic experimental factors and does not indicate a lack of material uniformity.

Distribution of Decay Kinetics. The decay kinetics of 25-50 individual NWs were collected with spatially overlapped pump and probe beams (SOPP configuration) in each of the four samples. The kinetic traces measured from each point are shown in blue in Figure 3 and reveal that a single sample possesses a wide distribution of decay rates. While there is significant variation from one trace to the next, they share a common decay profile in which the transient bleach (positive ΔI) decays over several hundred picoseconds as result of electron-hole recombination, eventually changing sign to yield a low-amplitude absorptive component that persists beyond 1 ns. The negative-going component has characteristics that are consistent with a combination of thermal effects resulting from localized heating by the pump pulse²⁴ and trap carrier absorption.

To facilitate a direct comparison with TA results, the 25–50 kinetic traces from each sample were averaged, producing the single kinetic trace shown in black in each panel of Figure 3. A comparable decay curve collected by TA at $\lambda_{\text{probe}} = 650$ nm is depicted by the gray squares.¹⁸ While qualitatively similar, the average decay collected with SOPP microscopy (black curve) is generally slower than the corresponding TA measurement (gray squares). This discrepancy is not caused by probing different regions of the spectrum as the photoinduced bleach is a spectrally broad feature that shows identical decay kinetics at $\lambda_{\text{probe}} = 650$ nm and $\lambda_{\text{probe}} = 850$ nm.¹⁸ Rather, as we will discuss in more detail below, the shorter TA-measured lifetimes likely stem from greater contributions from both bent NWs and non-NW structures.

Contribution of Charge Carrier Diffusion. The decay of the transient absorption signal obtained in the SOPP measurement reflects the loss of free carrier population in the probe region resulting from electron—hole recombination and diffusional migration of charge carriers out of the excitation volume. Motion of the charge carriers is directly observed in SSPP images (Figure 4B). In this configuration, the pump probe delay time is fixed and the probe beam is raster scanned with respect to the stationary pump beam by means of a scanning mirror assembly. The photoinduced transmission change is measured on a pixel-by-pixel basis, resulting in an image of the spatial distribution of carriers.

Article

Figure 3. Comparison of diameter-dependent recombination kinetics from SOPP microscopy and TA spectroscopy for samples (A) d100, (B) d60, (C) d50, and (D) d40. SOPP measurements acquired at multiple spatial positions within each sample are shown in light blue. The average and standard deviation of these SOPP measurements are shown as a solid black curve and shaded blue region, respectively. Transient kinetics measured with TA at $\lambda_{\text{probe}} = 650$ nm are shown as gray squares.

Figure 4. Imaging of charge carrier diffusion. (A) SOPP image of an NW within the d50 sample. The scale bar is 1 μ m. The orange circle indicates the position of the pump beam for measurements in panel B. (B) SSPP images collected at the delay time denoted in the upper left corner of each image. The scale bar is 1 μ m. The dashed black lines are visual guides indicating the location of the NW. The line thickness reflects the average diameter of the sample (52 nm). Each image is depicted using a normalized color table with the normalization factor denoted in the lower right corner of each image.

The SSPP image at $\Delta t = 0$ ps shows a circular, positive-going signal that reflects the photoinduced transparency resulting from the localized distribution of free carriers produced by the pump pulse. This image is well described as a two-dimensional Gaussian with an fwhm of \sim 700 nm, providing a measure of the lateral resolution of the SSPP method.²⁵ At longer time delays, the carrier cloud elongates along the NW axis, providing a direct observation of the free-carrier diffusional motion away from the excitation spot. As the free carriers recombine and diffuse away from the excitation spot, a low-amplitude absorptive component (blue, negative signal in Figure 4B) emerges that, unlike the free carrier signal, remains largely localized at the point of excitation. This static size is consistent with the assignment of the negative-going signal to a combination of trap carrier absorption and localized heating,¹⁸ both of which should exhibit little spatial expansion compared to the free carriers. Trapped carriers move slower than free carriers because they are confined to localized states within the

lattice, and thermal diffusion in silicon ($\alpha = 0.8 \text{ cm}^2/\text{s}$) is more than an order of magnitude slower than the ambipolar carrier diffusion constant ($D_{\rm B} = 18 \text{ cm}^2/\text{s}$).²⁶

While the SSPP images in Figure 4B provide a valuable visualization of the carrier motion, acquisition of images at a sufficient number of time delays to permit a quantitative kinetic analysis is not experimentally feasible. Instead, we have monitored the decay of the transient absorption signal as a function of time with the spatial separation (Δx) between the pump and probe spots along the NW held fixed, as shown in Figure 5. Panel A shows an SOPP image of an NW from sample d50 at $\Delta t = 0$ ps. The four different kinetic traces in Figure 5B are produced by positioning the pump beam at the location marked by the arrow in Figure 5A with the probe beam located at the black, red, green, and blue circles. The decay obtained with $\Delta x = 0$, which is identical to that of the SOPP configuration described above, exhibits its maximum signal at $\Delta t = 0$. When the probe is separated from the pump (i.e., $\Delta x >$

Figure 5. Kinetics of charge carrier diffusion. (A) SOPP image of a single NW in the d50 sample collected at a pump-probe delay of $\Delta t = 0$ ps. The wire is excited at the location indicated by the arrow, and colored circles denote the position of the probe beam for the kinetics displayed in panel B. The scale bar is 1 μ m. (B) SSPP transient kinetics collected at pump-probe separations $\Delta x = 0.0$ (black squares), 0.56 (red circles), 0.87 (green triangles), and 1.18 (blue inverted triangles) μ m indicated by the corresponding colored circles in panel A. Solid lines show a global fit of the experimental data to eq 3.

0), the maximum free carrier signal occurs at $\Delta t > 0$ ps, reflecting the time necessary for the photoexcited carriers to diffuse from the excitation region and arrive at the probe location.

The carrier diffusion and electron-hole recombination contributions to the transient absorption signal in the SSPP experiment, $I_{\Delta x}(t)$, are described by

$$I_{\Delta x}(t) = A_{\Delta x}(t) \exp(-t/\tau_{\rm r}) + a_{\infty}$$
(1)

where τ_r is the carrier lifetime, Δx is the displacement between the pump and probe, and a_{∞} is an offset to account for the long-lived absorptive component. The impact of carrier motion on the transient absorption signal is contained in the timedependent pre-exponential factor, $A_{\Delta x}(t)$, which is given by the double convolution over the spatial coordinates of pump and probe beams with the linear diffusion equation. Assuming Gaussian beam profiles, this function can be expressed as

$$A_{\Delta x}(t) = \frac{a_0}{\gamma_2 \gamma_2 \sqrt{D_B t}} \int_{\infty}^{-\infty} dx' \exp\left(\frac{-4(x' - \Delta x)^2 \ln(2)}{\gamma_2^2}\right) \\ \int_{\infty}^{-\infty} dx'' \exp\left(\frac{-4(x'')^2 \ln(2)}{\gamma_1^2}\right) \\ \exp\left(\frac{-(x' - x'')^2}{4\pi D_B t}\right)$$
(2)

where γ_1 and γ_2 are the pump and probe spatial fwhms, respectively, $D_{\rm B}$ is the ambipolar bulk diffusion constant for silicon (18 cm²/s), and a_0 is a time-independent intensity

scaling factor. The integrals in eq 2 can be solved analytically and substituted into eq 1 to give

$$I_{\Delta x}(t) = \frac{a_0}{\beta(t)} \exp\left(\frac{(-4\ln(2)\Delta x^2)}{\beta(t)^2}\right) \exp(-t/\tau_r) + a_{\infty}$$
(3)

where $\beta(t) = (\gamma_1^2 + \gamma_2^2 + 16D_Bt \ln(2))^{1/2}$. Implicit in this expression is the assumption that both pump and probe absorption events are linear; that is, the photogenerated carrier population is proportional to the intensity of the pump beam, and the change in probe intensity is proportional to the pump-induced carrier population. In ref 15, we demonstrated qualitative agreement between the model and observed carrier dynamics in Si NWs. The analytical form expressed by eq 3 allows a quantitative evaluation of both diffusion and recombination dynamics of the photogenerated carriers.

The solid lines in Figure 5B show results from a global fit of the four transients to eq 3. The pump and probe spot sizes (γ_1 = 310 nm and γ_2 = 620) were determined by deconvolution of the $\Delta t = 0$ ps SSPP image (first panel in Figure 4B) assuming the pump is half the diameter of the probe. The offset used to account for the long-lived absorptive contribution was fixed at $a_{\infty} = -0.68$ in the $\Delta x = 0$ data but set to zero for the others. All four kinetic traces are well fit by the model using only the shared parameters, a_0 and τ_r , suggesting the relevant diffusion and carrier recombination processes are adequately described by eq 3. The carrier lifetime determined by this global fit is $\tau_r =$ 218 \pm 3 ps. Note that a fit of the $\Delta x = 0$ transient in Figure 5B to a single-exponential function yields a carrier lifetime of 107 ps, which is nearly 2-fold shorter than the value determined from the fit to eq 3. This result highlights the substantial underestimation of the carrier lifetime that can result from an analysis that does not properly account for carrier diffusion.

Electron-Hole Recombination Kinetics. Ideally, SSPP kinetics like those in Figure 5 would be collected for each NW, allowing a global fit of carrier diffusion and recombination dynamics, but current experimental limitations make this impractical. However, with knowledge of pump and probe spot sizes, a single fit to the spatially overlapped decay ($\Delta x = 0$) using eq 3 should recover the correct carrier lifetime. To test this hypothesis, we fit the $\Delta x = 0$ kinetic trace in Figure 5B using eq 3 and recovered a lifetime of $\tau_{\rm S}$ = 217 ± 6 ps. This value compares favorably with the lifetime determined by the global fit to the set of spatially separated kinetic traces. Similar agreement between the lifetimes obtained by the two methods was found across multiple data sets, indicating that eq 3 can disentangle the recombination and diffusion contributions and enable extraction of the carrier recombination lifetime from spatially overlapped kinetic traces.

The distribution of lifetimes in the NW samples was determined by fitting eq 3 to each of the 25-50 SOPP transient kinetic traces collected for the four samples (light blue curves in Figure 3). The distribution is plotted with green bars (which indicate the centers of 35 ps wide bins) in Figure 6, and a fit to the histogram with a Weibull model is shown as a solid black curve.

Because of their high surface to volume ratio, electron-hole recombination in NWs is expected to be dominated by surface traps.^{7,9,18} The increase in average lifetime that is observed with increasing NW diameter is consistent with surface recombination as the primary decay mechanism. In this limit, bulk

Figure 6. Comparison of lifetime distributions determined by pumpprobe microscopy (green bars) and TA (blue shaded curve) for samples (A) d40, (B) d50, (C) d60, and (D) d100. The microscopy distribution is generated by fitting eq 3 to each of the spatially overlapped transients shown in Figure 3 to extract a carrier lifetime. The bin width is 35 ps for the lifetime histogram. The black solid line shows the fit of the microscopy data to a Weibull distribution. The TA lifetime distribution is determined by the SEM-measured diameters together with the spectroscopically measured surface recombination velocity. For each sample, the lifetime with maximum probability from TA and microscopy is noted next to each distribution.

recombination processes are negligible, and the carrier lifetime scales linearly with the NW diameter (d):

$$\tau_{\rm r} = \frac{a}{4S} \tag{4}$$

where *S* is the surface recombination velocity, which reflects surface quality.²⁷⁻²⁹ The values of *S* calculated from the average diameters and lifetimes measured for each sample (Table 1) are

Table 1. Summary of Surface Recombination Velocities Determined by Microscopy and TA

			$S (10^4 \text{ cm/s})$	
sample ID	d (nm)	lifetime, $\tau_{\rm r}~({\rm ps})$	microscopy ^b	TA^{a}
d40	38	87	1.09 (0.08)	2.05 (0.09)
d50	52	161	0.81 (0.05)	1.87 (0.07)
d60	59	168	0.88 (0.02)	1.71 (0.06)
d100	101	420	0.60 (0.03)	2.96 (0.22)

^aErrors shown in parentheses are 1 standard deviation in the fitted parameter, *S.* ^bErrors shown in parentheses are determined from 1 standard deviation uncertainty in the center of the fit (black solid lines, Figure 6) to the lifetimes.

comparable to recombination velocities observed in bulk materials³⁰ and single NWs.^{6,18} Interestingly, the smaller diameter wires exhibit large recombination velocities, which could be a manifestation of the higher radius of curvature at their surface, which would presumably give rise to a greater defect density. While such a result is intriguing, variations from sample to sample make it difficult to draw definitive conclusions without additional experiments dedicated to resolving this effect.

Lifetimes obtained from pump-probe microscopy of individual NWs are $\sim 2-5$ times longer than those obtained with TA (Figure 6).¹⁸ The exact origin of this difference is unclear; however, because both experiments were performed on the same samples, it must arise from differences in the

structures probed in the two studies. Unlike the microscopy experiment, which samples select regions of individual NWs, the TA experiment samples the full distribution of nanostructures as well as extraneous material, including side products, residual reactants, catalysts, etc., that still remain in the sample. Contributions from these undesired materials to the TA signal will skew the decay to shorter times, causing the recombination to appear faster than it actually is in NWs themselves. While SEM images of the samples suggest the volume of non-NW materials is too small to substantially influence the measured TA signal (Figure 1A), the larger absorption cross section of these materials (amorphous silicon has an extinction coefficient that is over an order of magnitude greater than that of crystalline silicon, for example) could cause them to contribute disproportionately to the total signal. While this makes it difficult to rule these structures out, it is unlikely that they are the primary source of the difference between the microscopy and TA results.

A second possibility stems from the fact that, although the TA and microscopy experiments were performed on the same sample, the two experiments probed different regions of the film. Femtosecond TA spectra were collected in areas of high NW density, where the optical absorption was greater. In these regions, the individual NWs are constrained in their orientation and adopt conformations with significant local curvature (Figure 1A). Microscopy measurements, on the other hand, were performed at the edge of the samples where there were fewer overlapping wires. While the lower density makes it possible to isolate individual NWs, it also results in wires with less curvature (Figure 1B). The difference between the microscopy and TA results may reflect this difference in NW secondary structure. In ZnO and CdS NWs, for example, curvature is known to strongly influence the electronic structure of the bulk lattice, 31,32 and the strain induced by bending could increase the defect density.²⁹ We anticipate that both would shorten the carrier lifetime, and could largely account for the differences observed between the two techniques. A quantitative analysis of the influence of secondary structure on the charge carrier lifetime is currently under way.

In summary, we have studied carrier recombination and diffusion in individual silicon NWs. SSPP microscopy was used to directly image carrier spatial evolution on ultrafast time scales. We have developed a model that allows carrier diffusion to be decoupled from the recombination dynamics in SOPP measurements, which should allow rapid characterization of many individual nanostructures within an ensemble. A survey of individual NWs grown with catalysts of various diameters shows a distribution of carrier recombination rates, which can be attributed to the distribution of NW diameters within each sample. On average, measurements of individual NWs exhibit longer lifetimes than ensemble measurements of the same NWs, highlighting the important role sample heterogeneity plays in determining the spectroscopic observables and functionality of nanostructures.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: john_papanikolas@unc.edu. *E-mail: jfcahoon@unc.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grants CHE-1213379 and DMR-1308695 (C.W.P., J.D.C., and J.F.C.).

REFERENCES

(1) Schmidt, V.; Wittemann, J. V.; Senz, S.; Gösele, U. Silicon Nanowires: A Review on Aspects of Their Growth and Their Electrical Properties. *Adv. Mater.* **2009**, *21*, 2681–2702.

(2) Rurali, R. Colloquium: Structural, Electronic, and Transport Properties of Silicon Nanowires. *Rev. Mod. Phys.* 2010, 82, 427–449.

(3) Cui, Y.; Lieber, C. M. Functional Nanoscale Electronic Devices Assembled Using Silicon Nanowire Building Blocks. *Science* **2001**, *291*, 851–3.

(4) Cui, Y.; Zhong, Z.; Wang, D.; Wang, W. U.; Lieber, C. M. High Performance Silicon Nanowire Field Effect Transistors. *Nano Lett.* **2003**, *3*, 149–152.

(5) Goldberger, J.; Hochbaum, A. I.; Fan, R.; Yang, P. Silicon Vertically Integrated Nanowire Field Effect Transistors. *Nano Lett.* **2006**, *6*, 973–977.

(6) Christesen, J. D.; Zhang, X.; Pinion, C. W.; Celano, T. A.; Flynn, C. J.; Cahoon, J. F. Design Principles for Photovoltaic Devices Based on Si Nanowires with Axial or Radial P-N Junctions. *Nano Lett.* **2012**, *12*, 6024–9.

(7) Mohite, A. D.; Perea, D. E.; Singh, S.; Dayeh, S. A.; Campbell, I. H.; Picraux, S. T.; Htoon, H. Highly Efficient Charge Separation and Collection across in Situ Doped Axial Vls-Grown Si Nanowire P-N Junctions. *Nano Lett.* **2012**, *12*, 1965–71.

(8) Korkin, A. Nanoscale Applications for Information and Energy Systems; Springer: New York, 2013.

(9) Allen, J. E.; Hemesath, E. R.; Perea, D. E.; Lensch-Falk, J. L.; Li, Z. Y.; Yin, F.; Gass, M. H.; Wang, P.; Bleloch, A. L.; Palmer, R. E.; Lauhon, L. J. High-Resolution Detection of Au Catalyst Atoms in Si Nanowires. *Nat. Nanotechnol.* **2008**, *3*, 168–73.

(10) Dan, Y.; Seo, K.; Takei, K.; Meza, J. H.; Javey, A.; Crozier, K. B. Dramatic Reduction of Surface Recombination by in Situ Surface Passivation of Silicon Nanowires. *Nano Lett.* **2011**, *11*, 2527–32.

(11) Wheeler, D. A.; Huang, J.-A.; Newhouse, R. J.; Zhang, W.-F.; Lee, S.-T.; Zhang, J. Z. Ultrafast Exciton Dynamics in Silicon Nanowires. J. Phys. Chem. Lett. **2012**, *3*, 766–771.

(12) Seo, M. A.; Dayeh, S. A.; Upadhya, P. C.; Martinez, J. A.; Swartzentruber, B. S.; Picraux, S. T.; Taylor, A. J.; Prasankumar, R. P. Understanding Ultrafast Carrier Dynamics in Single Quasi-One-Dimensional Si Nanowires. *Appl. Phys. Lett.* **2012**, *100*, 071104.

(13) Gao, B.; Hartland, G. V.; Huang, L. B. Transient Absorption Spectroscopy and Imaging of Individual Chirality-Assigned Single-Walled Carbon Nanotubes. *ACS Nano* **2012**, *6*, 5083–5090.

(14) Mehl, B. P.; House, R. L.; Uppal, A.; Reams, A. J.; Zhang, C.; Kirschbrown, J. R.; Papanikolas, J. M. Direct Imaging of Optical Cavity Modes in ZnO Rods Using Second Harmonic Generation Microscopy. *J. Phys. Chem. A* **2010**, *114*, 1241–1246.

(15) Gabriel, M. M.; Kirschbrown, J. R.; Christesen, J. D.; Pinion, C. W.; Zigler, D. F.; Grumstrup, E. M.; Mehl, B. P.; Cating, E. E.; Cahoon, J. F.; Papanikolas, J. M. Direct Imaging of Free Carrier and Trap Carrier Motion in Silicon Nanowires by Spatially-Separated Femtosecond Pump-Probe Microscopy. *Nano Lett.* **2013**, *13*, 1336–40.

(16) Seo, M. A.; Yoo, J.; Dayeh, S. A.; Picraux, S. T.; Taylor, A. J.; Prasankumar, R. P. Mapping Carrier Diffusion in Single Silicon Core-Shell Nanowires with Ultrafast Optical Microscopy. *Nano Lett.* **2012**, *12*, 6334–8.

(17) Qi, J.; Belcher, A. M.; White, J. M. Spectroscopy of Individual Silicon Nanowires. *Appl. Phys. Lett.* **2003**, *82*, 2616.

(18) Grumstrup, E. M.; Cating, E. E.; Gabriel, M. M.; Pinion, C. W.; Christesen, J. D.; Kirschbrown, J. R.; Vallorz, E. L. I.; Cahoon, J. F.; Papanikolas, J. M. Ultrafast Carrier Dynamics of Silicon Nanowire Ensembles: The Impact of Geometrical Heterogeneity on Charge Carrier Lifetime. J. Phys. Chem. C 2014, DOI: 10.1021/jp501079b. Article

(20) Mehl, B. P.; Kirschbrown, J. R.; Gabriel, M. M.; House, R. L.; Papanikolas, J. M. Pump-Probe Microscopy: Spatially Resolved Carrier Dynamics in ZnO Rods and the Influence of Optical Cavity Resonator Modes. J. Phys. Chem. B **2013**, 117, 4390–4398.

(21) Mehl, B. P.; Kirschbrown, J. R.; House, R. L.; Papanikolas, J. M. The End Is Different Than the Middle: Spatially Dependent Dynamics in ZnO Rods Observed by Femtosecond Pump-Probe Microscopy. *J. Phys. Chem. Lett.* **2011**, *2*, 1777–1781.

(22) Myers, K.; Wang, Q.; Dexheimer, S. Ultrafast Carrier Dynamics in Nanocrystalline Silicon. *Phys. Rev. B* 2001, 64.

(23) Sjodin, T.; Petek, H.; Dai, H. L. Ultrafast Carrier Dynamics in Silicon: A Two-Color Transient Reflection Grating Study on a (111)Surface. *Phys. Rev. Lett.* **1998**, *81*, 5664–5667.

(24) On the basis of the density of carriers generated by the excitation pulse and the heat capacity of bulk silicon, we estimate that the lattice temperature rises by almost 10 $^{\circ}$ C with each pump pulse.

(25) In SOPP images, where the pump and probe pulses are scanned together, the resolution is given by the product of the spatial modes of the two beams. In the spatially separated mode, the probe is scanned relative to the pump beam, and the spatial resolution is a convolution of the two spatial modes.

(26) Sze, S. M.; Ng, K. K. Physics of Semiconductor Devices; John Wiley & Sons: Hoboken, NJ, 2007.

(27) Fitzgerald, E. A.; Grove, A. S. Surface Recombination in Semiconductors. *Surf. Sci.* **1968**, *9*, 347–369.

(28) Lannoo, M. Electron-States and Recombination Velocities at Semiconductor Surfaces and Interfaces. *Rev. Phys. Appl.* **1987**, *22*, 789–795.

(29) Aspnes, D. E. Recombination at Semiconductor Surfaces and Interfaces. *Surf. Sci.* **1983**, *132*, 406–421.

(30) Sabbah, A.; Riffe, D. Femtosecond Pump-Probe Reflectivity Study of Silicon Carrier Dynamics. *Phys. Rev. B* 2002, 66.

(31) Xue, H.; Pan, N.; Li, M.; Wu, Y.; Wang, X.; Hou, J. G. Probing the Strain Effect on near Band Edge Emission of a Curved ZnO Nanowire Via Spatially Resolved Cathodoluminescence. *Nanotechnol*ogy **2010**, *21*, 215701.

(32) Sun, L.; Kim do, H.; Oh, K. H.; Agarwal, R. Strain-Induced Large Exciton Energy Shifts in Buckled CdS Nanowires. *Nano Lett.* **2013**, *13*, 3836–42.

Ultrafast Carrier Dynamics of Silicon Nanowire Ensembles: The Impact of Geometrical Heterogeneity on Charge Carrier Lifetime

Erik M. Grumstrup, Emma M. Cating, Michelle M. Gabriel, Christopher W. Pinion, Joseph D. Christesen, Justin R. Kirschbrown, Ernest L. Vallorz, III, James F. Cahoon,* and John M. Papanikolas*

Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, North Carolina 27599-3290, United States

Supporting Information

ABSTRACT: Ultrafast carrier dynamics in silicon nanowires with average diameters of 40, 50, 60, and 100 nm were studied with transient absorption spectroscopy. After 388 nm photoexcitation near the direct band gap of silicon, broadband spectra from 400 to 800 nm were collected between 200 fs and 1.3 ns. The transient spectra exhibited both absorptive and bleach features that evolved on multiple time scales, reflecting contributions from carrier thermalization and recombination as well as transient shifts of the ground-state absorption spectrum. The initially formed "hot" carriers relaxed to the band edge within the first ~300 fs, followed by recombination over several hundreds of picoseconds. The charge carrier lifetime progressively decreased with decreasing diameter, a result consistent with

a surface-mediated recombination process. Recombination dynamics were quantitatively modeled using the diameter distribution measured from each sample, and this analysis yielded a consistent surface recombination velocity of $\sim 2 \times 10^4$ cm/s across all samples. The results indicate that transient absorption spectroscopy, which interrogates thousands of individual nanostructures simultaneously, can be an accurate probe of material parameters in inhomogeneous semiconductor samples when geometrical differences within the ensemble are properly analyzed.

INTRODUCTION

Methods for the bottom-up synthesis of complex semiconductor nanomaterials have advanced rapidly over the past two decades. Despite efforts to develop uniform and reproducible growth processes, heterogeneity in semiconductor nanostructures is a recurring problem.^{1,2} The variation from structure-to-structure and synthesis-to-synthesis poses a major challenge for characterization efforts and ultimately to technologies that rely on the identical operation of individual nanoscale objects. For example, small changes in size or morphology of subwavelength or quantum-confined objects can cause pronounced changes in absorption or emission properties.^{3–8} Similarly, high surface-to-volume ratios cause minor changes in size to strongly influence charge carrier transport and recombination processes.^{9–11} As a consequence, spectroscopic measurements performed on nanomaterials are fundamentally influenced by structure-to-structure differences and other sources of sample heterogeneity.

Techniques that probe ensembles of nanostructures, such as femtosecond transient absorption (TA) spectroscopy, are complicated by experimental observables that reflect the full distribution of nanostructure sizes and shapes as well as extraneous material, including side products, residual reactants, catalysts, etc., that may still remain in the sample. In nanostructures with high aspect ratios, the electronic structure can also be affected by differences in secondary structure (i.e., local curvature in bent wires).^{12,13} All of these structures, not just the ideal nanostructures, contribute to the signal, producing

nonexponential kinetics that reflect a multitude of dynamical processes. As a result, interpretation of the transient response in terms of simple physical models is often not possible or straightforward. While sample heterogeneity can be partially overcome using ultrafast microscopy methods that interrogate single nanostructures,^{14–19} they require that data be collected on many individual objects to draw statistically meaningful conclusions. Compared to pump–probe microscopy, TA is easily implemented with a broadband probe, providing a full transient spectrum. The ability to monitor spectral evolution facilitates a detailed analysis, making TA an important tool for characterizing dynamical processes such as carrier relaxation and recombination.^{12,13}

In this paper, we describe the application of TA spectroscopy to the study of carrier dynamics in ensembles of silicon nanowires (NWs). Transient spectra obtained throughout the visible and near-IR (400-800 nm) are composed of a broad photobleach on which narrower features arising from NW absorption and scattering modes appear. The evolution of the spectra with time indicates that the photoexcited carrier population undergoes intraband relaxation to the band edge in several hundred femtoseconds followed by electron-hole recombination in several hundred picoseconds. Examination of NWs of different diameters shows that the recombination

Received:January 30, 2014Revised:March 15, 2014Published:March 21, 2014

Figure 1. SEM images of NW substrates. (A) Sample grown with 50 nm Au nanoparticles (d50). The dotted circle with a 100 μ m diameter illustrates the spatial extent of the pump beam (100 μ m fwhm). (B) Magnified image showing a high density of individual NWs. (C) Image showing individual NWs and regions of suboptimal NW growth denoted by arrows.

process is dominated by a surface-mediated mechanism, in which the average carrier lifetime (τ) is related to the NW diameter (d) and surface recombination velocity (S), i.e., $\tau = d/4S$.^{9,11}

The surface recombination velocity provides a measure of surface quality, which is of interest for both fundamental and technological reasons. From a fundamental standpoint, S provides a quantitative means of studying the interaction of carriers with the surface and for comparing different surface passivation strategies. From a technological perspective, S can be related to the density of surface states, which in turn governs the behavior of many active electronic components. Recombination velocities in NWs are often determined using photo-current methods,^{5,9,11,20} which require the fabrication of functioning single-NW devices, effectively limiting characterization to a few isolated structures. As an alternative, here we use pump-probe methods to directly time-resolve the carrier lifetime. Using a kinetic model that accounts for the diameter distribution, we extract a value of S for each sample. The recombination velocities are within a factor of 2 of each other across an array of samples with diameters ranging from 30 to 100 nm that were prepared in a similar manner but are generally 2- or 3-fold greater than those obtained at specific points within individual NWs using femtosecond pump-probe microscopy.²¹ This difference may arise from a number of factors related to the material and structural heterogeneity of the ensemble, underscoring the complexity of interpreting ensemble measurements that probe all materials, desired and undesired, within a sample.

EXPERIMENTAL SECTION

Intrinsic Si NW samples were synthesized by a vapor-liquidsolid (VLS) mechanism using Au nanoparticle catalysts.^{5,17} The reactor was held at 450 °C for 2 min to nucleate wire growth and then cooled (12 °C/min) to 410 °C for continued wire growth over 2 h using 2 sccm SiH₄ and 200 sccm H₂ at 40 Torr.⁵ Immersion of the substrate in isopropanol and slow evaporation of the solvent from the surface collapsed the NWs into the dense, randomly oriented mat shown in Figure 1A. The NWs were collapsed to reduce optical scattering and to enhance pump-probe spatial overlap by placing all NWs within the same focal plane. After collapsing the nanowires onto the substrate, they were thermally oxidized at 1000 °C for 1 min under 100 Torr of O₂.

Transient absorption measurements were performed using pulses centered at 775 nm (150 fs fwhm) derived from a Ti:sapphire regenerative amplifier (Clark-MXR 2210) operating at 1 kHz. The pump beam was generated by frequency doubling 35 μ J of the fundamental in a BBO crystal, and the

white light continuum used for the probe beam was generated by focusing ~3 μ J into a translating CaF₂ crystal. The pump was coupled onto a mechanical delay stage, attenuated, and focused onto the sample using a 300 mm lens to achieve a spot size of 100 μ m fwhm. The probe was focused onto the sample with a 250 mm aluminum spherical mirror (90 μ m fwhm spot size), coupled into a 0.15 m spectrometer dispersed on a 1200 grooves/mm grating, and detected on a high-speed diode array. The pump beam was mechanically chopped at half the repetition rate of the laser (500 Hz), and interleaved pump on and pump off spectra were collected.

RESULTS AND DISCUSSION

Nanowire Samples. These experiments focus on four samples of NWs, denoted d40, d50, d60, and d100, which were grown using Au catalysts with average diameters of 30, 50, 60, and 100 nm, respectively. Scanning electron microscopy (SEM) images reveal that the NWs remained largely unbroken upon collapse (Figure 1A,B). Imaging of individual structures shows that while the majority of the NWs are smooth (Figure 1C), there are regions of nonuniform growth, as highlighted by the arrows in Figure 1C. These regions result from a number of processes, including the incubation period needed to supersaturate Au catalysts prior to VLS growth²² and from nucleation of multiple NWs from single Au nanoparticles.²³ The polydispersity in the NW diameters present in each sample was characterized by measuring the diameters of 150-200 individual NWs in a SEM, resulting in the histogram depicted in Figure 2. The experimental histogram was fit to a Weibull distribution:

$$g'(d) = B\left(\frac{d}{\Gamma}\right)^{k-1} e^{-(d/\Gamma)^k}$$
(1)

Here *B* is a scaling parameter and *k* and Γ are parameters that reflect the symmetry and width of the distribution, respectively. A Weibull distribution was used as it is both asymmetric which produces a more accurate representation of the measured diameter distribution and because it has no amplitude at zero diameter. The distributions for the four samples have maxima at 38 nm (d40), 52 nm (d50), 59 nm (d60), and 101 nm (d100) and widths that range from 20 to 40 nm, which presumably arise from a combination of polydispersity in the catalyst diameter and nonuniform NW growth as noted above. While a perfectly uniform diameter along the length of the NW is not expected, no effort was made to measure the diameter of each NW at the same relative position. Thus, the histograms should accurately reflect the distribution of diameters sampled by the TA measurement.

Figure 2. Distribution of NW diameters measured by SEM. Histograms were generated by binning the measured diameters in 3 nm increments. Uncertainty in an individual diameter measurement is estimated to be ± 5 nm based on making repeated measurements of the same NW. The experimental histogram is fit to a Weibull distribution (eq 1) as shown by the black solid line in each panel.

Ground-State Spectroscopy. Figure 3A shows the UV– vis extinction spectra of the four samples, which are measured in transmission mode and therefore reflect a combination of both absorption and scattering by the NWs. The spectra consist of a broad absorption band that increases toward shorter wavelengths, similar to bulk silicon, superimposed with several

Figure 3. (A) Measured ground-state extinction spectra $(1 - I/I_0)$ of the four diameter NW samples: d40 (black), d50 (red), d60 (blue), and d100 (green). (B) Spectra showing simulated absorption efficiency for an ensemble of NWs weighted by the fits to the distributions shown in Figure 2.

narrower features that result from optical resonator modes supported within the cross section of the NW.^{6,7,15,24} While all the samples possess these resonances, the most prominent is observed in the d100 spectrum near 520 nm. Finite-element simulations of the NW absorption spectrum (Figure 3B), obtained by a weighted average of spectra from NWs with diameters ranging from 50 to 150 nm, qualitatively reproduce the absorption profile of the d100 sample. Details of the procedure to generate the simulated spectra are in the Supporting Information.

Transient Spectroscopy. Transient absorption (TA) spectra for the four samples are shown in Figure 4 (black solid curves). The spectra were collected at a pump-probe delay of 250 fs using a white light continuum probe that extends from 400 to 800 nm and a pump wavelength of 388 nm $(255 \,\mu\text{J/cm}^2)$. Pump and probe spot sizes were 100 and 90 μm fwhm, respectively, so the field sampled in these experiments encompassed thousands of wires and was approximately equivalent in size to the circle shown in Figure 1A. Excitation at 388 nm produces carriers with energy near the direct band gap, and given the extinction coefficient of bulk Si (0.02 nm^{-1}),²⁵ we estimate the initial photoexcited carrier density at this fluence to be $\sim 5 \times 10^{19}$ cm⁻³. Because the diameters of the NWs studied are much larger than the Bohr radius $(2.2 \text{ nm})^2$ photoexcitation produces free carriers (i.e., bulk-like behavior). The transient spectra for the three smallest diameters are qualitatively similar; each exhibits a broad positive band that spans much of the visible spectrum. For the 100 nm NWs, the broad positive band is accompanied by a narrower derivativelike feature that coincides with the optical resonator mode at \sim 520 nm in the ground-state spectrum (Figure 3A).

The positive-going signals correspond to a pump-induced increase in the probe intensity (i.e., a photoinduced bleach) that has several potential contributions. The first stems from changes in the absorptive properties of the NW due to band filling by photoexcited free carriers that occupy low-energy states in the conduction and valence bands of Si. Photoinduced absorption by free carriers and trapped carriers may also contribute to the overall transient spectra as a negative-going signal; however, consistent with previous studies of silicon, the overall signal is positive at early times, suggesting that carrier absorption (free or trapped) is a minor component.^{26–29} In addition, photogenerated carriers decrease the index of refraction, which in turn can reduce the NW scattering and lead to an increase in the probe intensity.^{20,24}

While both optically induced changes in absorption and refractive index have analogous processes in bulk semiconductors, the subwavelength dimensions of the NW give rise to optical resonator modes that can also influence both NW absorption and scattering. For example, photoinduced changes to the refractive index resulting from the presence of free carriers will also shift the position of the NW's optical resonator modes, which could be the origin of the derivativelike feature seen in the transient spectrum of d100 (Figure 4D). In this scenario, the transient spectrum can be modeled simply by calculating difference spectra, $J_{\Delta}(\lambda)$, according to

$$J_{\Delta}(\lambda) = \frac{T^{\rm GS}(\lambda + \Delta\lambda) - T^{\rm GS}(\lambda)}{T^{\rm GS}(\lambda)}$$
(2)

where $T^{GS}(\lambda)$ is the ground-state transmission spectrum and $\Delta \lambda$ is a spectral shift. In microcavities, the wavelength supported by an optical resonator mode is proportional to

Figure 4. Early time ($\Delta t = 275$ fs) transient absorption spectra for samples (A) d40, (B) d50, (C) d60, and (D) d100 nm. Black solid lines represent experimental data, and blue dashed lines represent the difference spectra, J_{Δ} , obtained by shifting the ground-state transmission spectrum according to eqs 2 and 3. The agreement between the difference spectrum and the transient spectrum is good in the case of d100 (panel D), especially between 450 and 600 nm. The agreement is not as good at wavelengths longer than 600 nm in any of the samples, consistent with the assignment of this broad feature to band filling and scattering.

the index of refraction,⁷ suggesting that $\Delta \lambda = c_0 \Delta n$, where c_0 is a constant scaling factor that is related to the size of the resonator and the mode number. The change in the index of refraction (Δn) depends upon the density of photogenerated carriers (N) and is given by^{20,22}

$$\Delta n(\lambda) = -\frac{\lambda^2 e^2 N}{2\pi n_0(\lambda) c^2 m^*}$$
(3)

where *e* is the fundamental charge, $n_0(\lambda)$ is the refractive index in the absence of photoexcited carriers, *c* is the speed of light, and m^* is the reduced mass of the electron and hole $(0.2m_e)$.

The difference spectrum, $J_{\Delta}(\lambda)$, calculated using eqs 2 and 3 is depicted for d100 in Figure 4D (blue dashed curve) and corresponds to a 0.8 nm blue-shift of the ground-state transmission spectrum at 400 nm and a 4.9 nm blue-shift at 800 nm. This spectrum is in qualitative agreement with the transient absorption spectrum observed at 275 fs, largely reproducing the derivative feature, suggesting that the derivative line shape and its subsequent evolution can be understood as a transient spectral shift of the NW ground-state absorption spectrum in response to the photoexcited carrier population.

The optical resonator mode in the 100 nm NWs leads to an especially dramatic modulation of the transient spectrum. On the other hand, the smaller diameter NWs do not show distinct optical modes nor the clear derivative-like spectral features in their transient spectra. While the difference spectra, $J_{\Delta m}$, calculated for the other three samples (with the same scaling factor, c_0) (Figure 4A–C) share some of the features observed in the transient spectra, the overall agreement is not as good as for d100. These results suggests that the early time transient spectra are composed of features from both band filling/ scattering as well as from a transient shifts of the optical resonator modes. It further suggests that the contribution from spectral shifting is largely restricted to the shorter wavelengths (<600 nm) where optical resonator modes are supported, while

at longer wavelengths the transient spectra are likely dominated by band filling and scattering.

Although it is difficult to disentangle the relative magnitudes of the contributions due to band-filling, scattering, and changes in the resonator modes, they all scale with the density of photoexcited carriers. Thus, the transient absorption signal reflects the free carrier population and can be used to monitor its decay.

Spectral Evolution and Carrier Recombination. The spectral evolution of the 50 nm sample obtained with low pump pulse energies (255 μ J/cm²) is shown in Figure 5. The set of transient spectra show a broad positive-going bleach at early times. The majority of the bleach (\sim 70%) appears within the instrument response, while the remaining 30% grows in during the first 1 ps with a rise time of 300 ± 40 fs (Figure 5B). We attribute this increase in bleach amplitude to intraband relaxation of the carriers. Photoexcitation at 388 nm (3.2 eV) produces free carriers with ~ 2 eV of excess energy relative to the Si band gap (1.12 eV). As the carriers undergo intraband relaxation through phonon scattering, they fill states near the band edges, reducing absorption at visible and near-IR wavelengths. The 300 fs time constant is consistent with previously reported time scales for carrier thermalization in bulk²⁶ and nanocrystalline silicon.³⁰ After the initial growth in the first 1 ps, the amplitude of the broad signal from \sim 500-800 nm decays and changes sign around 200 ps, switching from a positive-going bleach signal to a negative-going absorptive signal that persists for more than a nanosecond (see Figure 5A,C). We attribute the decay of the bleach to a reduction in the free carrier population as a result of electron-hole recombination.

Multiple recombination mechanisms are potentially present in these NWs, resulting in an apparent recombination rate (k)that is a sum of the rates of all processes, i.e.

$$k = k_{\rm r} + k_{\rm SRH} + k_{\rm a} + k_{\rm s} \tag{4}$$

0.1

Figure 5. Transient photophysics of the 50 nm NW sample (d50). (A) Transient spectra at pump-probe delay times from 275 fs to 1.3 ns. The free carrier signal grows in magnitude between 275 fs and 1 ps and then decays to a low-amplitude negative band. (B) Early time dynamics at $\lambda_{\text{probe}} = 650$ nm (gray squares). The blue curve represents the instrument response function. A fit of the data to a single-exponential rise convolved with the instrument response is shown as the solid black curve. The time constant ($\tau = 300$ fs) determined from the fit is consistent with carrier cooling to the band edge. (C) Kinetics at $\lambda_{\text{probe}} = 650$ nm showing carrier recombination in the first 200 ps followed by a long-lived absorptive component.

10

∆t (ps)

100

1000

where k_r , k_{SRH} , k_a , and k_s represent the rates of direct, Shockley–Read–Hall (SRH), Auger, and surface recombination, respectively. Direct recombination is negligible in Si because it is an indirect band gap semiconductor. For bulk Si at low excitation intensities, recombination occurs primarily through midband gap trap states associated with impurities or defect states and is modeled as SRH recombination. Auger recombination becomes increasingly important at the high freecarrier concentrations present in degenerately doped materials or under high-injection conditions. In addition, trap states at the surface also serve as recombination sites, giving rise to surface recombination that is parametrized by the surface recombination velocity, S.

In silicon NWs with large surface-to-volume ratios, surface recombination is often the dominant recombination process.^{9,10,17,20} Neglecting the bulk recombination mechanisms $(k_r, k_{\rm srh}, {\rm and } k_{\rm a})$, the observed recombination rate is given by $k = k_{\rm s} = (\tau_{\rm s}^{-1})$, where the surface recombination time can be written in terms of the surface recombination velocity (*S*), which accounts for both electron and hole trapping probabilities,³¹ and the NW diameter (*d*) as $\tau_{\rm s} = d/4S$. The diameter dependence in this expression is a geometrical factor and is valid in the limit that diffusion to the surface is rapid compared to recombination,³² a condition satisfied for the diameters of NWs studied here.

Because the TA experiment samples thousands of NWs with a range of diameters, the electron-hole recombination is not described by a single lifetime but rather a distribution of lifetimes, $g(\tau_s)$. The observed time-dependent signal, I(t), can be expressed as a superposition of single-exponential components weighted by this distribution function:

$$I(t) = I_0 \int_0^\infty g(\tau_s) e^{-t/\tau_s} d\tau_s + I_\infty$$
(5)

where the first term reflects the contribution of each surface recombination lifetime and second term, I_{∞} , accounts for the long-lived absorption that persists for longer than 1 ns.

The surface recombination velocity for each sample was determined by fitting the decay of the photoinduced bleach to eq 5. The functional form of $g(\tau_s)$ is constructed from the diameter distribution for each sample (eq 1) and the relationship $\tau_s = d/4S$, i.e., $g(\tau_s) = g'(4S\tau_s)$. The use of this expression assumes that the section of the NW sampled by the photogenerated carriers has a uniform diameter. Analysis of the SEM images showed that points along the NW separated by 20 μ m (or more) showed no measurable difference in diameter. Since carriers diffuse only a few micrometers in their lifetime,¹⁷ this assumption holds. Incorporation of $g(\tau_s)$ into eq 5 results in an expression with three adjustable parameters: I_{0} , I_{∞} and S. Fits to the single wavelength decays for each of the four samples are shown as solid lines in Figure 6 (left panels), along with the corresponding lifetime distributions (right panels). The data are well-described by a surface-dominated mechanism, yielding surface recombination velocities of S_{\rm d100} = (2.96 \pm $(0.22) \times 10^4 \text{ cm/s}, S_{d60} = (1.71 \pm 0.06) \times 10^4 \text{ cm/s}, S_{d50} = (1.87)^{-10} \text{ cm/s}$ \pm 0.07) × 10⁴ cm/s, and S_{d40} = (2.05 \pm 0.09) × 10⁴ cm/s.

Figure 6. Single-wavelength decay kinetics at $\lambda_{\text{probe}} = 650$ nm and distribution functions, $g(\tau_s)$, for the (A) 40, (B) 50, (C) 60, and (D) 100 nm diameter samples. Left panels: experimental kinetic data (gray squares) and the best fits to the data using eq 5 (black curves). Right panels: lifetime distributions, $g(\tau_s)$, determined from the fit to eq 5. The maximum of each distribution is labeled and denoted by the dashed gray line.

While these values are comparable to recombination velocities observed in bulk materials²⁶ and single NWs, 5,17,27 describing each sample with a single (average) surface recombination velocity is most likely an oversimplification; variation in *S* is likely from wire to wire or even at different points along the same NW due to variation in trap density.

Fits of the transient kinetics to eq 5 using other functional forms of the diameter distribution (Gaussian, sum of two Gaussians) produced surface recombination velocities for the larger NWs that were within 10% of those found using a Weibull distribution. For the smaller diameter NWs, the fits using these distributions were unstable because the wings of the Gaussian functions resulted in nonzero probability at d = 0. The Weibull distribution was ultimately chosen as it can have asymmetric character and because it is well-behaved near d = 0.

Because all four samples were prepared in the same manner, we expect them to share similar surface properties and hence have similar surface recombination velocities. For the three smallest diameters, this is qualitatively the case. On the other hand, the recombination velocity for the 100 nm wires is about 1.5 times larger. It is difficult to draw conclusions from this observation, however, because pump-probe microscopy measurements performed on individual wires within the same set of samples²¹ yield carrier lifetimes that are ~2-5 times longer than those obtained from TA, suggesting that the carrier lifetimes obtained from TA are skewed toward smaller values for all of the samples.

The appearance of shorter recombination times in the TA measurement compared with ultrafast microscopy²¹ could arise from several factors. One possibility is that the TA signal is influenced by the many smaller structures resulting from uncontrolled growth and by the catalyst particles and other debris that exhibit faster decays than the NWs themselves. While SEM images (Figure 1) of the samples suggest the volume of non-NW materials is too small to substantially influence the TA signal, differences in absorption cross sections (amorphous silicon has an extinction coefficient that is ten times greater than crystalline silicon,²⁵ for example) may cause these materials to contribute disproportionately to the total signal, making it difficult to rule them out completely. The difference in the results of the two experiments could also arise from NW curvature, which is anticipated to alter electronic structure of the bulk lattice^{12,13,33} and increase defect density.³¹ We anticipate that both would shorten the carrier lifetime, suggesting that NW secondary structure may substantially influence the TA measurement. In either case, the differences observed from sample-to-sample in the TA experiment underscore the need to be cautious when extracting quantitative information from methods that measure the ensemble.

Surface recombination is not the only mechanism contributing to the decay of the free carrier population, especially at higher excitation intensities where there is a greater density of photogenerated carriers. Figure 7 shows the bleach decay kinetics for the 50 nm sample at five pulse energies ranging from 76 to 1020 μ J/cm². The three lowest pulse energies in this series exhibit identical kinetics within the error of the experiment, indicating that the recombination process is independent of the pulse energy and well attributed to a surface-mediated process as discussed above. A shorter charge carrier lifetime is observed at the two highest pulse energies, consistent with Auger recombination, which arises from a threecarrier interaction. The total rate associated with the loss of the

Figure 7. Power-dependent recombination kinetics at $\lambda_{\text{probe}} = 650 \text{ nm}$ for the 50 nm diameter sample (d50). The hollow squares show transient kinetics collected for powers ranging from 76 μ J/cm² to 1.02 mJ/cm². Solid lines show a global fit to the five kinetic traces using eq 6. The fit-determined photoexcited carrier density is 4 × 10¹⁹ cm⁻³ at the lowest power and 5 × 10²⁰ cm⁻³ at the highest power.

At (ps)

free carrier population can be expressed as the sum of Auger and surface recombination processes

$$k = \frac{\mathrm{d}\rho}{\mathrm{d}t} \approx k_{\mathrm{a}} + k_{\mathrm{s}} = -\left(A_{\mathrm{x}}\rho^{3} + \frac{1}{\langle\tau_{\mathrm{s}}\rangle}\rho\right) \tag{6}$$

where ρ is the charge carrier density, A_r is the ambipolar Auger recombination constant, which for Si is $\sim 3.79 \times 10^{-31}$ cm⁶/s³ and $\langle \tau_s \rangle$ is the average recombination time determined from the analysis of the single-wavelength kinetics. For a given $\langle \tau_s \rangle$, ρ is determined as a function of time through direct integration of eq 6 subject to an initial photogenerated carrier population, ρ_0 . The solid lines in Figure 7 are the result of a global fit to the five kinetics traces at different pulse energies, using ρ_0 at the lowest power as the only adjustable parameter with ρ_0 at higher powers scaled by the relative pulse energy. The best global fit was obtained with a photoexcited carrier density of 1.3×10^{20} cm^{-3} when the excitation intensity is 255 μ J/cm², which is in good agreement with the 5×10^{19} cm⁻³ carrier density that was estimated based on the bulk absorption coefficient. Overall, the power-dependent kinetics are in good agreement with this model, confirming that Auger recombination is the most likely origin of the intensity-dependent lifetime.

Contributions to the Transient Signal at Long Times. The transient spectra of all samples at $\Delta t = 1.3$ ns, a sufficiently long time for all free carriers to have recombined, are shown in Figure 8. The spectra show positive- and negative-going features that are approximately 10-fold lower in amplitude than the features at $\Delta t = 275$ fs shown in Figure 4. One possible contribution to the spectra is absorption by a population of trapped carriers. Trapped carriers may not be the only contributor, however. The $\Delta t = 1.3$ ns transient spectrum of d100 (Figure 8D), like the $\Delta t = 275$ fs transient spectrum (Figure 4D), shows a derivative-like feature that is again suggestive of a shift in the ground-state spectrum. This feature is inverted, however, relative to the early time spectrum (Figure 4D), suggesting a red-shift rather than blue-shift in the ground-state spectrum. The red dashed curves in each panel of Figure 8 show difference spectra calculated using eq 2 with a constant red-shift of $\Delta \lambda = 1$ nm. While there are a number of

Figure 8. Transient absorption and calculated difference spectra for the (A) 40, (B) 50, (C) 60, and (D) 100 nm diameter samples. Black solid lines represent the transient absorption spectra at $\Delta t = 1.3$ ns. Dashed red lines represent difference spectra calculated by shifting the ground-state spectrum by $\Delta = 1$ nm.

possible mechanisms that could lead to such a shift, one likely contributor is heating of the lattice from the thermalization and recombination of charge carriers. As the carriers cool the average temperature of the lattice rises, leading to an increase in the index of refraction²⁶ and a corresponding red-shift in the optical resonator modes. On the basis of the density of carriers generated by the excitation pulse and the heat capacity of bulk silicon, we estimate that the lattice temperature rises by almost 10 °C with each pump pulse. A difference spectrum calculated (Figure S2) from ground-state transmission spectra collected at 16 and 30 °C ($J'(T) = (T_{T=30^{\circ}C}^{GS} - T_{T=16^{\circ}C}^{GS})/T_{T=16^{\circ}C}^{GS}$) exhibits the same inverted derivative feature seen in the TA spectra. Overall, these spectra suggest that the long-lived signal is due, at least in part, to lattice heating.

CONCLUSIONS

In summary, we have monitored the carrier recombination kinetics of intrinsic silicon NWs using ultrafast transient absorption spectroscopy. At early pump-probe delay times, NW transient spectra are strongly influenced by optical resonator modes at short wavelengths, 400-600 nm, which can be well-interpreted by carrier-induced shifts of the refractive index. Reduced scattering and band filling by photoexcited free carriers dominate the spectra at longer wavelengths. This region of the spectrum grows in magnitude over the first 300 fs as hot carriers cool to the band edge. The decay of the bleach, which is attributed to electron-hole recombination, occurs over several hundred picoseconds and is found to be dependent on the NW diameter, consistent with surface recombination. Analysis of the transient data using a model that incorporates the diameter distribution measured via SEM yields surface recombination velocities ranging from 1.7 \times 10^4 to 3.0×10^4 cm/s for the different samples. Comparison with femtosecond microscopy measurements performed on the same samples²¹ indicate that decay of the bleach signal in the transient absorption measurement is influenced by NW secondary structure as well as non-NW structures (e.g., catalyst particles, uncontrolled growth structures) that are interspersed

with the wires, resulting in an overestimate of the recombination velocity. The TA experiments underscore that ensemble spectroscopies are powerful methods for characterizing the excited state dynamics of NW samples if heterogeneities present in the sample can be properly accounted for during analysis of the data.

ASSOCIATED CONTENT

S Supporting Information

Detailed description of absorption efficiency calculation; transient spectra for NW samples d40, 450, d60, and d100; difference spectrum calculated from temperature-dependent ground-state spectra of sample d100. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Authors

*E-mail: jfcahoon@unc.edu (J.F.C.). *E-mail: john_papanikolas@unc.edu (J.M.P.).

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation under Grants CHE-1213379 and DMR-1308695 (C.W.P., J.D.C., and J.F.C.).

REFERENCES

(1) Schmidt, V.; Wittemann, J. V.; Senz, S.; Gösele, U. Silicon Nanowires: A Review on Aspects of Their Growth and Their Electrical Properties. *Adv. Mater.* **2009**, *21*, 2681–2702.

(2) Rurali, R. Colloquium: Structural, Electronic, and Transport Properties of Silicon Nanowires. *Rev. Mod. Phys.* 2010, *82*, 427–449.
(3) Lin, C.; Povinelli, M. L. Optical Absorption Enhancement in Silicon Nanowire Arrays with a Large Lattice Constant for Photovoltaic Applications. *Opt. Express* 2009, *17*, 19371–81.

(4) Mehl, B. P.; Kirschbrown, J. R.; House, R. L.; Papanikolas, J. M. The End Is Different Than the Middle: Spatially Dependent Dynamics

The Journal of Physical Chemistry C

(5) Christesen, J. D.; Zhang, X.; Pinion, C. W.; Celano, T. A.; Flynn, C. J.; Cahoon, J. F. Design Principles for Photovoltaic Devices Based on Si Nanowires with Axial or Radial P-N Junctions. *Nano Lett.* **2012**, *12*, 6024–9.

(6) Kim, S. K.; Day, R. W.; Cahoon, J. F.; Kempa, T. J.; Song, K. D.; Park, H. G.; Lieber, C. M. Tuning Light Absorption in Core/Shell Silicon Nanowire Photovoltaic Devices through Morphological Design. *Nano Lett.* **2012**, *12*, 4971–6.

(7) Kirschbrown, J. R.; House, R. L.; Mehl, B. P.; Parker, J. K.; Papanikolas, J. M. Hybrid Standing Wave and Whispering Gallery Modes in Needle-Shaped Zno Rods: Simulation of Emission Microscopy Images Using Finite Difference Frequency Domain Methods with a Focused Gaussian Source. J. Phys. Chem. C 2013, 117, 10653–10660.

(8) Wallentin, J.; Anttu, N.; Asoli, D.; Huffman, M.; Aberg, I.; Magnusson, M. H.; Siefer, G.; Fuss-Kailuweit, P.; Dimroth, F.; Witzigmann, B.; Xu, H. Q.; Samuelson, L.; Deppert, K.; Borgstrom, M. T. Inp Nanowire Array Solar Cells Achieving 13.8% Efficiency by Exceeding the Ray Optics Limit. *Science* **2013**, 339, 1057–1060.

(9) Allen, J. E.; Hemesath, E. R.; Perea, D. E.; Lensch-Falk, J. L.; Li, Z. Y.; Yin, F.; Gass, M. H.; Wang, P.; Bleloch, A. L.; Palmer, R. E.; Lauhon, L. J. High-Resolution Detection of Au Catalyst Atoms in Si Nanowires. *Nat. Nanotechnol.* **2008**, *3*, 168–73.

(10) Dan, Y.; Seo, K.; Takei, K.; Meza, J. H.; Javey, A.; Crozier, K. B. Dramatic Reduction of Surface Recombination by in Situ Surface Passivation of Silicon Nanowires. *Nano Lett.* **2011**, *11*, 2527–32.

(11) Mohite, A. D.; Perea, D. E.; Singh, S.; Dayeh, S. A.; Campbell, I. H.; Picraux, S. T.; Htoon, H. Highly Efficient Charge Separation and Collection across in Situ Doped Axial Vls-Grown Si Nanowire P-N Junctions. *Nano Lett.* **2012**, *12*, 1965–71.

(12) Sun, L.; Kim do, H.; Oh, K. H.; Agarwal, R. Strain-Induced Large Exciton Energy Shifts in Buckled Cds Nanowires. *Nano Lett.* **2013**, *13*, 3836–42.

(13) Signorello, G.; Karg, S.; Bjork, M. T.; Gotsmann, B.; Riel, H. Tuning the Light Emission from GaAs Nanowires over 290 MeV with Uniaxial Strain. *Nano Lett.* **2013**, *13*, 917–24.

(14) Qi, J.; Belcher, A. M.; White, J. M. Spectroscopy of Individual Silicon Nanowires. *Appl. Phys. Lett.* **2003**, *82*, 2616.

(15) Mehl, B. P.; House, R. L.; Uppal, A.; Reams, A. J.; Zhang, C.; Kirschbrown, J. R.; Papanikolas, J. M. Direct Imaging of Optical Cavity Modes in Zno Rods Using Second Harmonic Generation Microscopy. *J. Phys. Chem. A* **2010**, *114*, 1241–1246.

(16) Gao, B.; Hartland, G. V.; Huang, L. B. Transient Absorption Spectroscopy and Imaging of Individual Chirality-Assigned Single-Walled Carbon Nanotubes. *ACS Nano* **2012**, *6*, 5083–5090.

(17) Gabriel, M. M.; Kirschbrown, J. R.; Christesen, J. D.; Pinion, C. W.; Zigler, D. F.; Grumstrup, E. M.; Mehl, B. P.; Cating, E. E.; Cahoon, J. F.; Papanikolas, J. M. Direct Imaging of Free Carrier and Trap Carrier Motion in Silicon Nanowires by Spatially-Separated Femtosecond Pump-Probe Microscopy. *Nano Lett.* **2013**, *13*, 1336–40.

(18) Seo, M. A.; Yoo, J.; Dayeh, S. A.; Picraux, S. T.; Taylor, A. J.; Prasankumar, R. P. Mapping Carrier Diffusion in Single Silicon Core-Shell Nanowires with Ultrafast Optical Microscopy. *Nano Lett.* **2012**, *12*, 6334–8.

(19) Wong, C. Y.; Penwell, S. B.; Cotts, B. L.; Noriega, R.; Wu, H.; Ginsberg, N. S. Revealing Exciton Dynamics in a Small-Molecule Organic Semiconducting Film with Subdomain Transient Absorption Microscopy. *J. Phys. Chem. C* **2013**, *117*, 22111–22122.

(20) Jung, Y.; Vacic, A.; Perea, D. E.; Picraux, S. T.; Reed, M. A. Minority Carrier Lifetimes and Surface Effects in Vls-Grown Axial P-N Junction Silicon Nanowires. *Adv. Mater.* **2011**, *23*, 4306–4311.

(21) Grumstrup, E. M.; Gabriel, M. M.; Cating, E. E.; Pinion, C. W.; Christesen, J. D.; Vallorz, E. L. I.; Cahoon, J. F.; Papanikolas, J. M. Ultrafast Carrier Dynamics in Individual Silicon Nanowires: Characterization of Diameter-Dependent Carrier Lifetime and Surface Recombination with Pump-Probe Microscopy. J. Phys. Chem. C 2014, DOI: 10.1021/jp502737e.

(22) Kalache, B.; Cabarrocas, P. R. i.; Morral, A. F. i. Observation of Incubation Times in the Nucleation of Silicon Nanowires Obtained by the Vapor-Liquid-Solid Method. *Jpn. J. Appl. Phys.* **2006**, *45*, L190–L193.

(23) Wang, D.; Tu, R.; Zhang, L.; Dai, H. Deterministic One-to-One Synthesis of Germanium Nanowires and Individual Gold Nanoseed Patterning for Aligned Nanowire Arrays. *Angew. Chem., Int. Ed.* **2005**, 44, 2925–2929.

(24) Zhang, X.; Pinion, C. W.; Christesen, J. D.; Flynn, C. J.; Celano, T. A.; Cahoon, J. F. Horizontal Silicon Nanowires with Radial P–N Junctions: A Platform for Unconventional Solar Cells. *J. Phys. Chem. Lett.* **2013**, *4*, 2002–2009.

(25) Palik, E. D. Handbook of Optical Constants of Solids; Springer-Verlag: Berlin, 1985.

(26) Sabbah, A.; Riffe, D. Femtosecond Pump-Probe Reflectivity Study of Silicon Carrier Dynamics. *Phys. Rev. B* 2002, 66.

(27) Seo, M. A.; Dayeh, S. A.; Upadhya, P. C.; Martinez, J. A.; Swartzentruber, B. S.; Picraux, S. T.; Taylor, A. J.; Prasankumar, R. P. Understanding Ultrafast Carrier Dynamics in Single Quasi-One-Dimensional Si Nanowires. *Appl. Phys. Lett.* **2012**, *100*, 071104.

(28) Sjodin, T.; Petek, H.; Dai, H. L. Ultrafast Carrier Dynamics in Silicon: A Two-Color Transient Reflection Grating Study on a (111) Surface. *Phys. Rev. Lett.* **1998**, *81*, 5664–5667.

(29) Wheeler, D. A.; Huang, J.-A.; Newhouse, R. J.; Zhang, W.-F.; Lee, S.-T.; Zhang, J. Z. Ultrafast Exciton Dynamics in Silicon Nanowires. J. Phys. Chem. Lett. **2012**, *3*, 766–771.

(30) Myers, K.; Wang, Q.; Dexheimer, S. Ultrafast Carrier Dynamics in Nanocrystalline Silicon. *Phys. Rev. B* 2001, 64.

(31) Aspnes, D. E. Recombination at Semiconductor Surfaces and Interfaces. *Surf. Sci.* **1983**, *132*, 406–421.

(32) Crank, J. *The Mathematics of Diffusion*; Clarendon Press: Oxford, UK, 1979.

(33) Sun, Y. T., Scott, E.; Toshikazu, N. Strain Effect in Semiconductors; Springer: Berlin, 2010.

(34) Kerr, M. J.; Čuevas, A. General Parameterization of Auger Recombination in Crystalline Silicon. J. Appl. Phys. 2002, 91, 2473.