LA-UR-14-20901
Approved for public release; distribution is unlimited.

Title: Ultrafast optical microscopy on single semiconductor nanowires

Author(s): Seo, Minah
Yoo, Jinkyoung
Dayeh, Shadi A
Picraux, Samuel T.
Taylor, Antoinette
Prasankumar, Rohit P.

Intended for: SPIE Photonics West 2014, 2014-02-01/2014-02-07 (San Francisco, California, United States)

Issued: 2014-02-13

Ultrafast Optical Microscopy on Single Semiconductor Nanowires

Minah Seo*, Jinkyoung Yoo, Shadi A. Dayeh, Samuel T. Picraux, Antoinette J. Taylor, Rohit P. Prasankumar
Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, NM, 87545, USA
*Current affiliation: Sensor System Research Center, Korea Institute of Science and Technology, Seoul, Republic of Korea

ABSTRACT

Ultrafast optical microscopy (UOM) combines a typical optical microscope and femtosecond (fs) lasers that produce high intensity, ultrashort pulses at high repetition rates over a broad wavelength range. This enables new types of imaging modalities, including scanning optical pump-probe microscopy, which varies the relative pump and probe positions on the sample, and ultrafast optical wide field microscopy, which is capable of rapidly acquiring wide field images at different time delays, that can measure nearly any sample in a non-contact manner with simultaneously high spatial and temporal resolution. We directly tracked carriers in space and time throughout a semiconductor nanowire (NW) by varying the focused position of a strong optical "pump" pulse along the axis of a Si core-shell NW while probing the resulting changes in carrier density with a weaker "probe" pulse at one end of the NW. The resulting time-dependent dynamics reveals the influence of oxide layer encapsulation on surface state passivation in core-shell NWs, as well as the presence of strong acoustic phonon oscillations, observed here for the first time in single NWs. Time-resolved wide field images of the photoinduced changes in transmission for a patterned semiconductor thin film and a single silicon nanowire after optical excitation are also captured in real time using a two-dimensional smart pixel array detector. Our experiments enable us to extract several fundamental parameters in these samples, including the diffusion current, surface recombination velocity, diffusion coefficients, and diffusion velocities, without the influence of contacts.

Keywords: Ultrafast spectroscopy, semiconductor nanowire, ultrafast optical microscopy, carrier dynamics, diffusion current, surface recombination velocity, nanophotonics

1. INTRODUCTION

Silicon nanowires (SiNWs) have attracted much attention because of their great potential for nanophotonic and nanoelectronic applications [1-3]. However, to fully realize this promise, an understanding of non-equilibrium carrier dynamics in these quasi-one-dimensional (1D) systems, especially on an ultrashort time scale, is critical. In this respect, there remains a lack of basic understanding on how light interacts with individual NWs on an ultrashort time scale. To date, inhomogeneities in NW ensembles have made it difficult to unambiguously extract their underlying physics. To study the optical properties of NWs without any complications from the broad size and alignment distribution in nanowire ensembles, we isolate the NW directly and measure ultrafast carrier dynamics on a single NW using ultrafast optical microscopy (UOM). Time- and space-resolved measurements demonstrate the influence of surface-mediated mechanisms on carrier dynamics in a single heterostructured NW. The results suggest the possibility of tailoring carrier relaxation in a single nanowire for a desired application.

Semiconductor nanowire heterostructures can be grown either axially or radially, where the additional layers typically have different material composition (e.g., Si/Ge NWs) or doping (e.g., p-doped Si/n-doped Si). This has greatly extended NW functionality, leading to energy harvesting systems [4] and NW LEDs [5, 6]. For instance, Si NW arrays with radial p-n junctions are explored for photovoltaic applications [4], which allow high solar-energy-conversion efficiencies by using a radial collection geometry. To achieve competitive conversion efficiencies, it is essential to find an optimal NW size and characterize the radial junction properties for efficient carrier collection. From a more applied perspective, interest in NW-based solar cells has increased due to their ability to separate electron-hole pairs through the intrinsic band alignment of a Ge core/Si shell structure [7]. Their viability, however, will depend on the speed of both charge separation across the core/shell interface and limiting interface recombination. In addition, enhanced thermoelectric performance has been reported by using various NW sizes and impurity doping levels [8], along with rough Si NW

arrays to greatly reduce the thermal conductivity without significantly affecting the thermoelectric power and electrical resistivity [9]. In these heterostructured NWs designed for thermoelectric applications, the figure of merit, ZT, is proportional to the electrical conductivity, which is affected by the interface properties.

The examples described above underline the importance of understanding charge transport through separate layers and across interfaces in NW heterostructures. Heterostructured semiconductor nanowires (NWs) have been demonstrated as promising functional units for photovoltaics, in which charge separation is achieved through radial heterostructuring, and NW-based transistors, in which axially heterostructured NWs can be used as the operating p-n junction, due to their unique electrical and optical properties. The interfaces between different layers in NW heterostructures strongly influence their properties and in turn device performance. However, a basic understanding of how these interfaces affect charge transport is lacking, as previous studies have provided little information due to their technical limitations.

Here we use UOM to measure carrier dynamics and charge transport velocities in single NW heterostructures with high temporal and spatial resolution in a non-contact, non-invasive manner. Our implementation of UOM is based on the well-known technique of optical pump-probe spectroscopy, which uses an intense femtosecond "pump" pulse to excite carriers into a non-equilibrium state [10]. The resulting dynamics can be measured by observing the pump-induced changes in the transmission or reflection ($\Delta T/T$) of a weaker "probe" pulse as a function of the time delay, t, between the two pulses. Since there is no external electric field across the semiconductor in our experimental configuration, diffusion takes place due to the change in concentration of the carriers. Then the charge carriers will move from a place of higher concentration to a place of lower concentration, producing a current that is known as the diffusion current. This flow of carriers can be detected by a weaker 'probe' pulse at a given position as a function of a time delay and separate space between two pulses, once the direction of the diffusion current is determined by the change in the carrier concentrations. Therefore, by measuring the time-resolved photoinduced change in transmission ($\Delta T/T$) at a specific position and varying the relative pump and probe positions, we can measure carrier relaxation and track the diffusion current along the NW at ultrashort time scales. A striking difference was observed in the carrier dynamics and diffusion current for Si NWs with or without SiO_2, due to carrier trapping in unpassivated surface states. This observation of different diffusion velocities revealed the role of oxide layer encapsulation in SiNWs, which will impact their use in highly efficient solar cells, tunnel FETs, and NW based LEDs. Finally, we also observed strong acoustic phonon oscillations in both Si and Si/SiO_2 NWs, independent of the probe position, which has not been measured in single SiNWs, to the best of our knowledge.

2. EXPERIMENTAL SETUP FOR ULTRAFAST OPTICAL MICROSCOPY

Our UOM system and a conceptual illustration of UOM with spatially overlapped and separated pump and probe beams, respectively, are shown in Figures 1(a), (b), and (c). A femtosecond Ti:sapphire laser oscillator centered at 840 nm is divided into pump and probe beams, with the probe power < 10% of the pump power. The pump beam is then frequency-doubled in a BBO crystal to generate femtosecond pulses at 420 nm. Our initial experiments, focusing on polarization-dependent dynamics, imaged the sample position as well as the pump (~25 μm diameter) and probe (~20 μm diameter) spots onto a CCD camera though a 50X microscope objective lens at the back side of the sample (Fig. 1(b)) [11]. Real time monitoring of both pump and probe spots allows us to control their positions on the NW. These experiments used vapor-liquid-solid (VLS) grown SiNWs that were dry transferred onto a sapphire substrate with diameters of d = 50~240 nm, and lengths of l ~ 80 μm. Subsequently, to measure carrier diffusion, we used a 20X objective to focus the pump and probe beams to 5 μm and 2 μm spots, respectively, and slightly tilted the pump beam to spatially overlap or separate the two spots along the NW (Fig. 1(c)); this enabled us to measure carrier dynamics and track charge carriers as they propagate along the NW axis [12]. The carrier diffusion experiments used Si and Si/SiO_2 core/shell NWs fabricated by a combination of e-beam lithography and Si deep reactive ion etching, followed by thermal oxidation and stripping steps to form pristine NW surfaces, which were then transferred onto a transparent sapphire substrate.

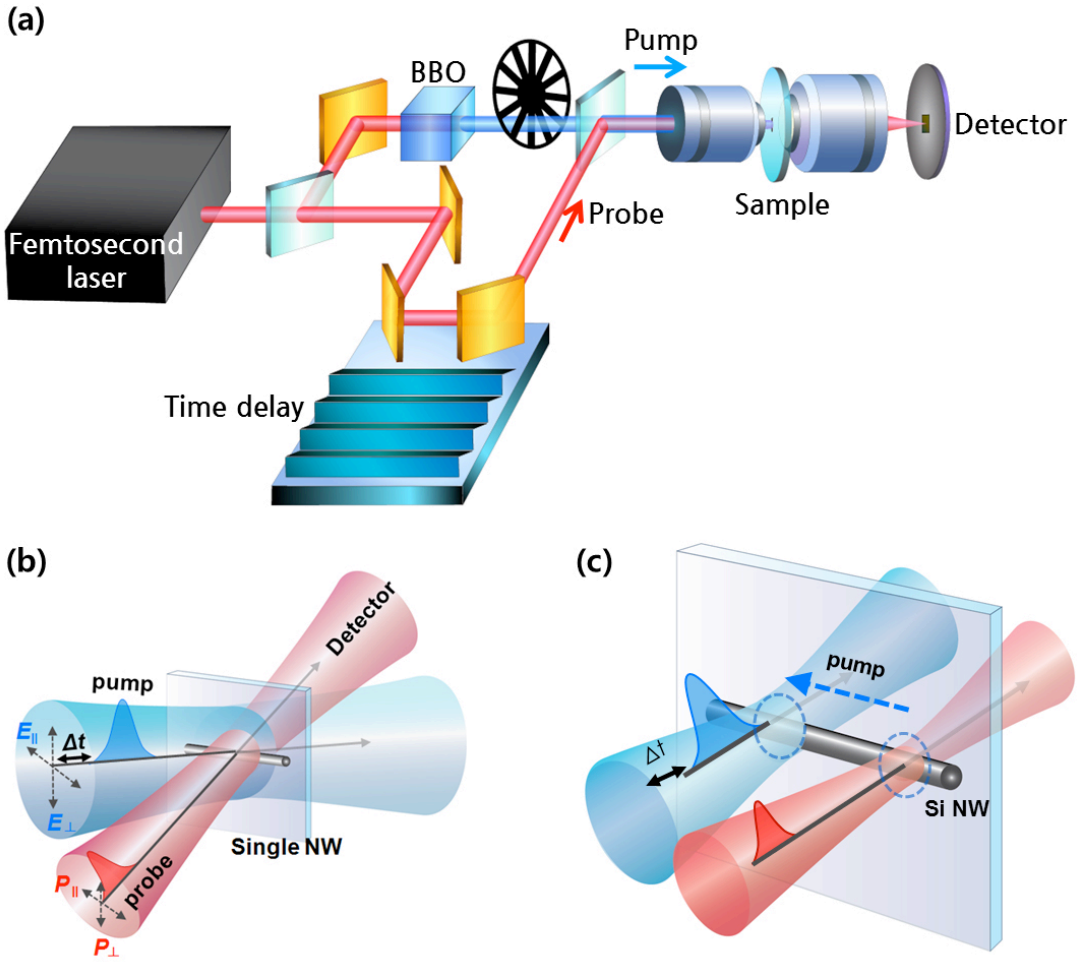

Figure 1. (a) Schematic of our UOM system. (b) Conceptual illustration of UOM with overlapped pump and probe beams. (c) Conceptual illustration of UOM with separated pump and probe beams.

3. POLARIZATION DEPENDENCE OF CARRIER DYNAMICS IN SINGLE SI NWS

Polarization sensitive pump-probe excitation and detection show the different magnitudes of the photoinduced change in NW ensembles for four different sets of pump and probe polarizations (Fig. 2(a)), without significant anisotropy in the relaxation times (Fig. 2(a), inset). In contrast, the first observed ultrafast dynamics in a *single* Si NW reveals a much faster decay constant in comparison with bulk Si and ensemble NWs (Fig. 2(b)). Furthermore, in stark contrast to NW ensembles, there is a clear anisotropy in the ultrafast dynamics measured for parallel and perpendicular polarizations to the long axis of a single NW, as shown in Fig 2(c). We find that this is due to density-dependent Auger recombination, originating from differences in the photoinduced carrier density due to differences in the absorption (i.e., light polarized parallel to the NW axis is absorbed more strongly than perpendicularly polarized light) [11].

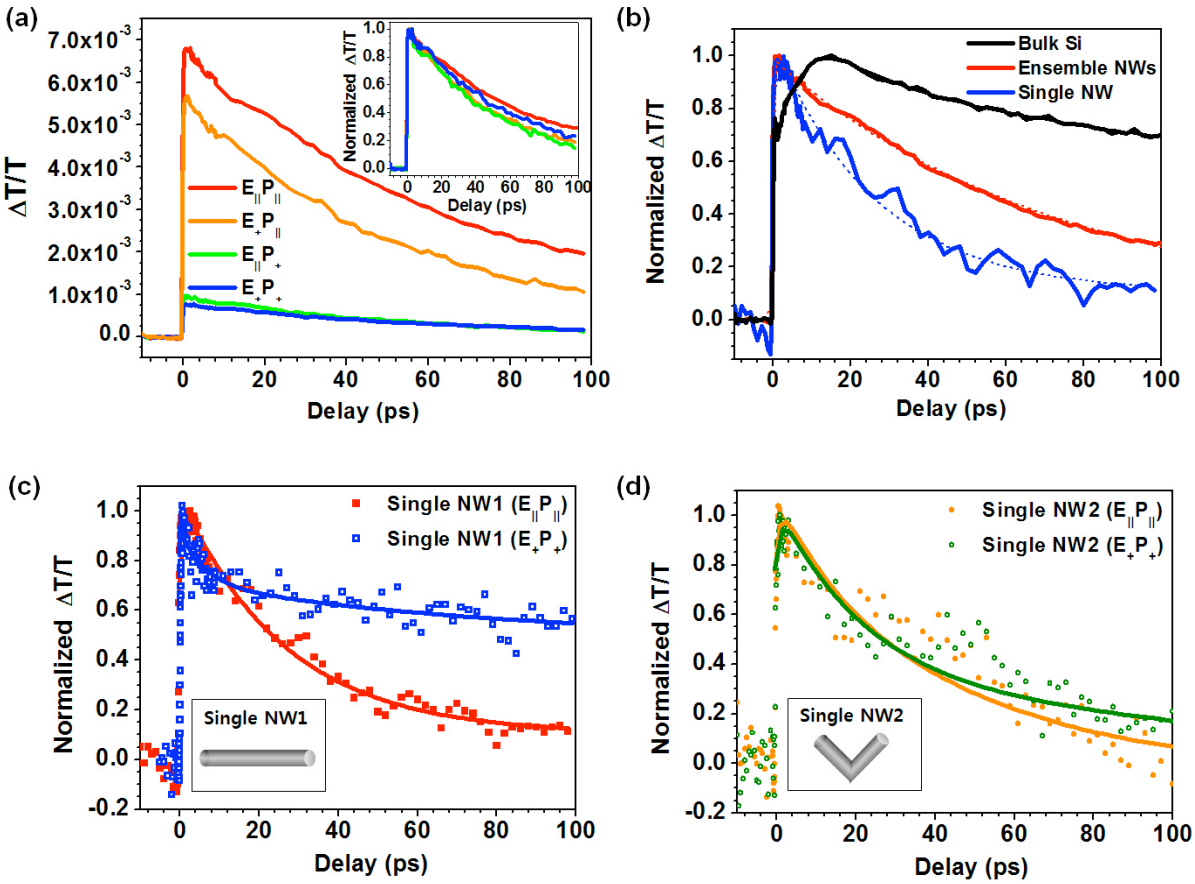

Figure 2. (a) Polarization-dependent ultrafast transmission measurement with 420 *nm* pump and 840 *nm* probe on Si ensemble NWs. (b) Comparison of normalized transmission on bulk Si, ensemble-NWs, and a single Si NW. The inset in (a) shows the normalized transmission in Si NW ensembles for different pump and probe polarization combinations. . Polarization dependent transmission on a straight NW (c) and on a bent NW (d).

The comparison of carrier dynamics between ensemble and single nanowires provides great insight into the influence of incident light polarization on different absorption and interaction mechanisms. The observed anisotropy in single NWs could enable advanced applications, such as optical switching and polarization sensitive photodetection, on the nanoscale, where directional control and high spatial resolution are much desired.

4. MAPPING CARRIER DIFFUSION IN SINGLE SILICON CORE-SHELL NANOWIRES

Subsequently, UOM experiments with spatially separated pump and probe beams were performed on single Si NWs grown with and without a SiO_2 shell layer (Fig. 3(a) and (b)). Since our single Si NWs have very small variation in their diameter (less than 10 nm) along the axis and are perfectly crystalline, they can serve as excellent systems to investigate quasi-1D carrier diffusion. With the probe fixed on one end of the NW, we varied the pump-probe separation from 0 to 5 μm. This revealed strongly position-dependent carrier dynamics due to carrier diffusion. The magnitude of the ΔT/T signal from the core/shell Si NW is about twice that of the bare Si NW, and the decay time is slower in the core/shell NW (~121 ps) than in the bare Si NW (~90 ps). This can be explained by the fact that surface passivation by SiO_2 reduces the surface trap density as well as the surface recombination velocity. These experiments thus reveal a significant influence of SiO_2 passivation on the carrier dynamics, while demonstrating our ability to track carrier diffusion through a single NW. The rise time increases with the pump-probe separation for both the bare Si NW and the Si/SiO_2 NW, revealing strong acoustic phonon oscillations in both cases (Fig. 3(a) and (b)). The difference in carrier diffusion between the two NWs are dramatically visualized in the insets, which show plots of the normalized *ΔT/T* signal

as a function of pump-probe separation and delay time. The slope of the maximum $\Delta T/T$ signal, with accompanying acoustic phonon oscillations, directly denotes the carrier diffusion velocity.

In our experiments, the pump photoinduces a carrier density at one end of the NW (Δn_{pump}), and the probe then observes the resulting non-equilibrium carrier density (Δn_{probe}), even in the absence of an applied external field. The carriers will diffuse from the pump position (x_{pump}) to the probe position (x_{probe}), allowing us to track the transient diffusion current as a function of the probe position. The diffusion current for electrons, J_n, can be expressed as [13]:

$$J_{total}(x,t) = J_n(x,t) + J_p(x,t) \approx q \cdot D \cdot \frac{(\Delta n^{tot}_{pump} - \Delta n^{tot}_{probe})}{(x_{pump} - x_{probe})} \approx q \cdot D \cdot \frac{(\Delta T/T_{overlap} - \Delta T/T_{separation})}{(x_{pump} - x_{probe})} \quad (1)$$

Since the measured $\Delta T/T$ signal is proportional to $\Delta n_{probe}/n_{probe}$, a larger $\Delta T/T$ signal for the Si/SiO_2 NW reflects a higher Δn_{probe} as compared to the core-only SiNW. Therefore a higher concentration gradient, dn, in the core-only SiNW is extracted than that in the Si/SiO_2 core-shell NW, since Δn_{pump} should be the same for both NWs and the diffusion coefficient D_n is also constant, leading to a higher diffusion current for the core-only SiNW. The time-dependent concentration gradient, dn/dt, is also larger in the core-only SiNW than in the Si/SiO_2 core-shell NW, which indicates that the diffusion velocity is larger for the core-only SiNW. The diffusion velocity for the core-only SiNW, extracted by measuring the pump-probe separation and the rise time of the $\Delta T/T$ signal, is ~ 5×10^6 cm/s, while the diffusion velocity for the Si/SiO_2 core/shell NW is ~ 2×10^6 cm/s (Fig. 3(c)). This difference in diffusion velocities gives deep insight into the role of the SiO_2 layer in surface passivation.

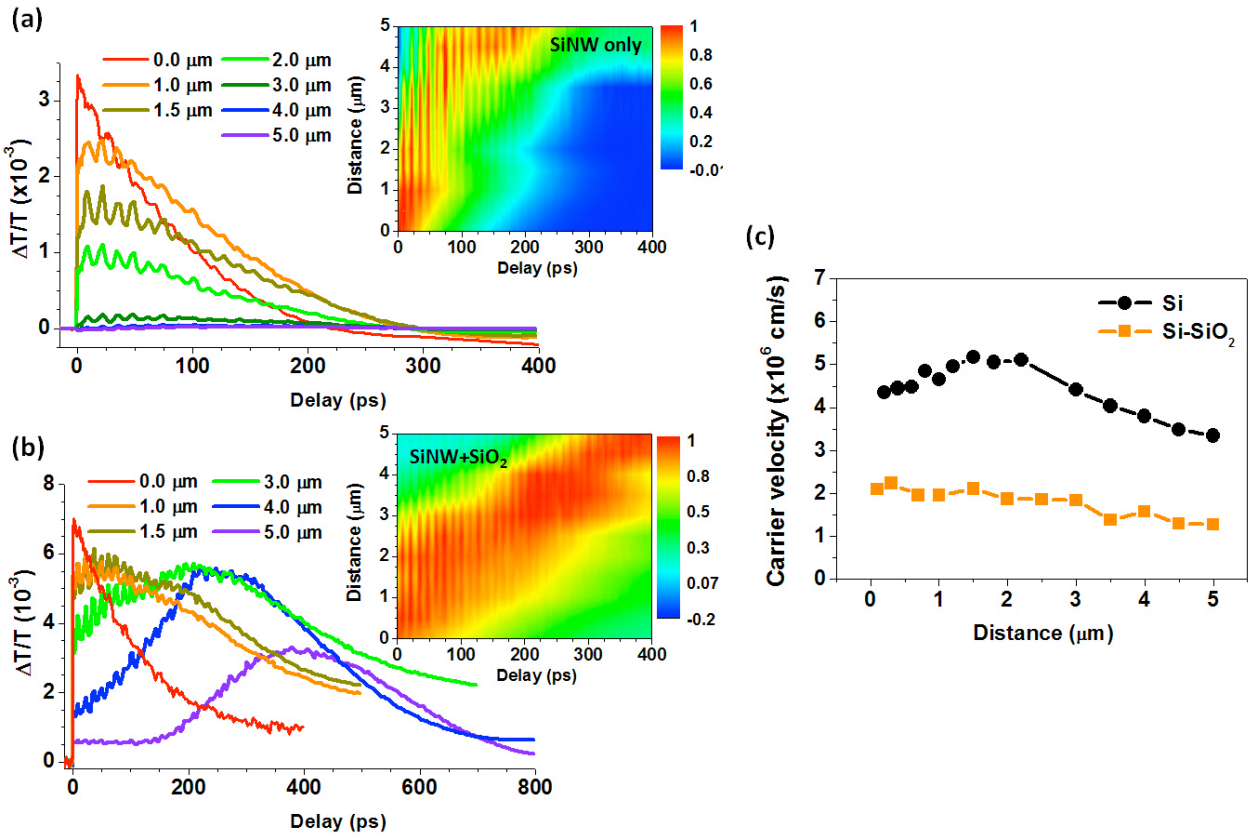

Figure 3. Photoinduced transmission changes for various pump-probe separations for (a) the bare Si NW and (b) the SiO_2 encapsulated SiNW. The insets present two-dimensional maps of the normalized ΔT/T signals as functions of separation and time delay. (c) Carrier velocities of the bare Si NW and the SiO_2 encapsulated SiNW, which are extracted from the data in (a) and (b).

5. CONCLUSION

In conclusion, ultrafast optical microscopy opens new pathways for directly studying carrier dynamics and carrier diffusion in quasi-1D nanosystems. We directly measured polarization-dependent carrier dynamics and diffusion, as well as acoustic phonon oscillations, in single Si and Si/SiO_2 NWs, for the first time by tracking carriers through space and time after femtosecond photoexcitation in a non-contact manner. Ultrafast optical microscopy will thus be useful in further investigations of radially and axially heterostructured NWs for applications in photovoltaic and thermoelectric devices. In general, this research has potential application to NW-based devices and optoelectronics by combining measurements at both micrometer distance and femtosecond time scales to reveal the intrinsic properties of these quasi-one-dimensional nanosystems.

REFERENCES

[1] X. Duan, Y. Huang, R. Agarwal, and C. M. Lieber, "Single-nanowire electrically driven lasers," Nature 421, 241 (2003).

[2] C. Thelander, P. Agarwal, S. Brongersma, J. Eymery, L. F. Feiner, A. Forchel, M. Scheffler, W. Riess, B. J. Ohlsson, U. Gosele et al., "Nanowire-based one-dimensional electronics," Mater. Today 9, 28 (2006).

[3] P. J. Pauzauskie and P. Yang, "Nanowire photonics," Mater. Today 9, 36 (2006).

[4] M. D. Kelzenberg, S. W. Boettcher, J. A. Petykiewicz, D. B. Turner-Evans, M. C. Putnam, E. L. Warren, J. M. Spurgeon, R. M. Briggs, N. S. Lewis and H. A. Atwater, "Enhanced absorption and carrier collection in Si wire arrays for photovoltaic applications," Nature Mater. 9, 239-244 (2010).

[5] M. S. Gudiksen, L. J. Lauhon, J. Wang, D. C. Smith and C. M. Lieber, "Growth of nanowire superlattice structures for nanoscale photonics and electronics," Nature 415, 617-620 (2002).

[6] R. Yan, D. Gargas and P. D. Yang, "Nanowire photonics," Nature Photonics 3, 569-576 (2009).

[7] W. Lu and C. M. Lieber, "Semiconductor nanowires," J. Phys. D: Appl. Phys. 39, R387-R406 (2006).

[8] A. I. Boukai, Y. Bunimovich, J. Tahir-Kheli, J.-K. Yu, W. A. Goddard III and J. R. Heath, "Silicon nanowires as efficient thermoelectric materials," Nature 451, 168 (2008).

[9] A. I. Hochbaum, R. Chen, R. D. Delgado, W. Liang, E. C. Garnett, M. Najarian, A. Majumdar and P. Yang, "Enhanced thermoelectric efficiency of rough silicon nanowires," Nature 451, 163 (2007).

[10] R. P. Prasankumar, P. C. Upadhya and A. J. Taylor, "Ultrafast Dynamics in Semiconductor Nanowires," Physica Status Solidi(b) 246, 1973 (2009).

[11] M. A. Seo, S. A. Dayeh, P. C. Upadhya, J. A. Martinez, B. S. Swartzentruber, S. T. Picraux, A. J. Taylor, and R. P. Prasankumar, "Understanding ultrafast carrier dynamics in single quasi-one-dimensional Si nanowires," Appl. Phys. Lett. 100, 071104 (2012).

[12] M. A. Seo, J. Yoo, S. A. Dayeh, S. T. Picraux, A. J. Taylor, and R. P. Prasankumar, "Mapping carrier diffusion in single silicon core−shell nanowires with ultrafast optical microscopy," Nano Lett., 12, 6334 (2012).

[13] B. G. Streetman, S. Banarjee and S. K. Banerjee, Solid State Electronic Devices (Prentice Hall, 2005).