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6. AUTHORS John Papanikolas, James K. Parker			5d. PROJECT NUMBER		
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14. ABSTRACT This project involved the investigation of the photoluminescence properties of individual ZnO nano-rods, characterization of charge carrier dynamics at different locations within a single ZnO rod, and strain-induced electron-hole recombination in silicon nanowires, all using femtosecond pump-probe microscopy techniques developed in this laboratory. It was found that charge carrier dynamics are a function of location within a nano-wire (near the end or the middle), and that strain within a silicon nanowire significantly reduces the lifetime of charge carriers, with the results suggesting that development of strain enabled optoelectronic devices with indirect					
15. SUBJECT TERMS ultrafast imaging, strained nanomaterials, electron-hole plasma dynamics, microscopy, whispering gallery modes, nanowires,					
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Report Title

Final Report for Ultrafast Nonlinear Microscopy in III-V Semiconductor Nanostructures

ABSTRACT

This project involved the investigation of the photoluminescence properties of individual ZnO nano-rods, characterization of charge carrier dynamics at different locations within a single ZnO rod, and strain-induced electron-hole recombination in silicon nanowires, all using femtosecond pump-probe microscopy techniques developed in this laboratory. It was found that charge carrier dynamics are a function of location within a nano-wire (near the end or the middle), and that strain within a silicon nanowire significantly reduces the lifetime of charge carriers, with the results suggesting that development of strain-enabled optoelectronic devices with indirect-bandgap materials should be possible.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
10/06/2014	3.00 Ralph L. House, Justin R. Kirschbrown, Brian P. Mehl, Michelle M. Gabriel, Joseph A. Puccio, James K. Parker, John M. Papanikolas. Characterizing Electron–Hole Plasma Dynamics at Different Points in Individual ZnO Rods, The Journal of Physical Chemistry C, (11 2011): 0. doi: 10.1021/jp207830h
10/10/2014	4.00 Erik M. Grumstrup, Michelle M. Gabriel, Christopher W. Pinion, James K. Parker, James F. Cahoon, John M. Papanikolas. Reversible Strain-Induced Electron–Hole Recombination in Silicon Nanowires Observed with Femtosecond Pump–Probe Microscopy, Nano Letters, (10 2014): 0. doi: 10.1021/nl5026166
10/11/2013	2.00 Justin R. Kirschbrown, Ralph L. House, Brian P. Mehl, James K. Parker, John M. Papanikolas. 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, Journal of Physical Chemistry C, (04 2013): 10653. doi:
TOTAL:	3

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

"Using Ultrafast Pump-Probe Microscopy to Image Carrier Migration and Carrier Recombination in Si and ZnO Nanowires", Eastern Analytical Symposium and Exposition, Sommerset, NJ, 2013.

"Spatially Resolved Carrier Dynamics in ZnO Rods Observed Through Ultrafast Pump-Probe Microscopy", Joint School of Nanoscience and Nanoengineering, North Carolina A&T University, Greensboro, NC, 2012.

"Ultrafast Dynamics with Spacial Specificity: Application of Femtosecond Microscopy to the Study of Carrier Dynamics in Photoexcited ZnO Nanorods", Department of Chemistry, Lehigh University, Bethlehem, PA, 2012.

"Ultrafast Spatially Resolved Carrier Dynamics in Individual ZnO Rods", Department of Chemistry, University of Colorado at Boulder, Boulder, CO, 2012.

"Ultrafast Spatially Resolved Carrier Dynamics in Individual ZnO Rods", Department of Chemistry, Colorado State University, Fort Collins, CO, 2012.

"Ultrafast Pump-Probe Microscopy in Individual ZnO Rods", Department of Chemistry, Notre Dame University, South Bend IN, 2012.

"Ultrafast Carrier Dynamics in Individual ZnO Rods", UNC-SERC Solar Energy Research Symposium, Durham NC, 2012.

"Ultrafast Spatially Resolved Carrier Dynamics in Individual ZnO Rods", Department of Chemistry, Duke University, Durham, NC, 2011.

"Ultrafast Spatially Resolved Carrier Dynamics in Individual ZnO Rods", Department of Chemistry, University of Maryland, College Park, MD, 2011.

"Ultrafast Pump-Probe Microscopy in Individual ZnO Rods", Department of Chemistry, University of Central Florida, Orlando, FL, 2011.

"Ultrafast Pump-Probe Microscopy in Individual ZnO Rods", Department of Chemistry, University of Florida, Gainesville, FL, 2011.

"Ultrafast Pump-Probe Microscopy in Individual ZnO Rods", Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC, 2011.

Number of Presentations: 12.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received

Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received

Paper

12/15/2011 1.00 Justin R. Kirschbrown, Brian P. Mehl, Ralph L. House, Michelle M. Gabriel, Joseph A. Puccio, James K. Parker , John M. Papanikolas. Characterizing electron-hole plasma dynamics at different points in individual ZnO rods, Journal of Physical Chemistry C (12 2011)

TOTAL: 1

Number of Manuscripts:

Books

Received

Book

TOTAL:

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Michelle Gabriel	0.33	
Justin Kirschbrown	0.67	
FTE Equivalent:	1.00	
Total Number:	2	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
Erik Grumstrup	0.33
David Zigler	0.33
FTE Equivalent:	0.66
Total Number:	2

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields: 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Justin Kirschbrown

Total Number:

1

Names of other research staff

NAME

PERCENT SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

This project investigated three related phenomena: photoluminescence properties of ZnO nanorods, charge carrier dynamics within ZnO nanorods, and charge-carrier recombination dynamics in silicon nanowires.

Two-photon emission microscopy was used to investigate the photoluminescence properties of individual ZnO rods. The rods are 10–20 micrometers in length with a tapered cross section that varies from 1 to 2 micrometers at the midpoint to several hundred nanometers at the ends. The tapered shape and hexagonal cross section result in complex optical resonator modes that lead to periodic patterns in the two-photon emission image. Finite-difference frequency domain methods using a series of excitation sources, including focused Gaussian, point dipole, and plane wave, suggest that resonator modes have both standing wave (Fabry-Pérot) and whispering gallery mode character, whose relative contributions vary along the rod axis.

Two-photon emission microscopy was used to characterize the charge carrier dynamics at different locations within a single ZnO rod. Photoexcitation by a focused laser produces carriers (electrons and holes) in a localized region. Emission is detected using both time-integrated and time-resolved methods. Results show that the electron-hole plasma (EHP) state plays a larger role at the end of the rod compared to other points within the structure, where electron-hole recombination proceeds through an excitonic state. The origin of this spatial dependence is attributed to the physical confinement at the end of the structure that prevents an expansion of the photoexcited electron-hole cloud through processes such as carrier diffusion. Whispering gallery modes are identified as contributing to a periodic emission pattern along the length of the structure.

Pump-probe microscopy was used with femtosecond temporal resolution and submicron spatial resolution to characterize charge-carrier recombination and transport dynamics in silicon nanowires locally strained by bending deformation. The electron-hole recombination rate increases with strain for values above a threshold of about 1% and, in highly strained (~5%) regions of the nanowire, increases 6-fold. The changes in recombination rate are independent of nanowire diameter and reversible upon reduction of the applied strain, indicating the effect originates from alterations to the nanowire 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 it is likely that the results will assist the development of strain-enabled optoelectronic devices with indirect-bandgap materials such as silicon.

Technology Transfer

N/A

Ultrafast Nonlinear Microscopy in III-V Semiconductor Nanostructures
Army Research Office, Contract Number: W911NF-04-D-0004
John M. Papanikolas and James K. Parker

Final Project Report

Efforts during the reporting period centered on the spatially resolved photophysics of needle-shaped ZnO and contributed to our understanding of the photoluminescence properties of these individual structures on experimental and theoretical level.

1.) Spatially-resolved Electronic Dynamics

The scanning electron microscopy (SEM) image of a typical structure is shown in the top right of Figure 1. The rods are crystalline structures that are 10 and 20 μm in length with hexagonal cross-sections that taper from $\sim 1\text{-}2\ \mu\text{m}$ at their widest point to $\sim 300\text{-}500\ \text{nm}$ at their ends. The optical properties were studied using two-photon emission microscopy. Here, individual ZnO rods were excited by 730 nm a femtosecond laser pulse focused to a diffraction limited spot by a microscope objective (0.8 NA, 50x), resulting in a simultaneous absorption of two photons that promotes electrons from the valence band to the conduction band. Since the two-photon excitation region is small (380 nm) compared to the rod's size, only a localized region is excited. The free carriers that are created can relax into excitonic states that lie just below the conduction band, giving rise to a UV-blue emission centered at $\sim 390\ \text{nm}$, or into trap states associated with defects in the crystal lattice, resulting in a broad visible band extending from 500-650 nm. Two-photon emission images (Figure 1, inset) are obtained by raster scanning the sample stage while monitoring either band-edge (390 nm) or trap (550 nm) emission channels.

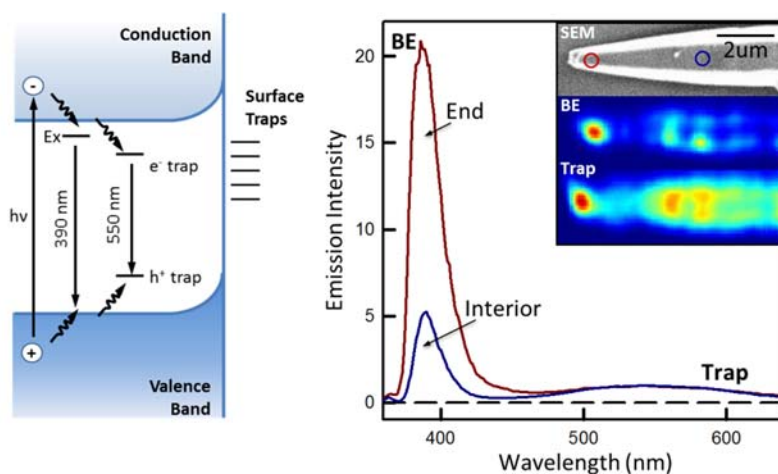


Figure 1: (Left) Illustration of the ZnO band diagram. Two-photon excitation produces free carriers that can either relax into excitonic states or become trapped at defect sites. (Right, Inset) Scanning electron microscopy (SEM) image of typical needle shaped rod, along with the emission images obtained by monitoring either the band-edge (BE) or trap emission channels. Emission spectra collected by positioning the excitation spot at the end (red) or interior (blue) of the structure. The exact locations are indicated by the colored circles in the SEM image. Note that in this particular image, only the left end of the structure is shown.

Both emission images show significant variation in the emission intensity across the structure. The increased area of intensity at the end is a particularly prominent feature in both images; however, close comparison of the images shows that the bright spots are slightly offset, with the trap image showing its most intense emission slightly to the left of the band edge. We are able to obtain both emission and SEM images from the *same* structure. This enables us to correlate spectroscopic observations with structural features, a capability that is critical to forging the connection between object shape and dynamical behavior. Examination of the SEM image for this

structure suggests that this shift is likely a consequence of the roughness observed at the tip of this rod, which would result in a greater defect density and brighter trap emission.

Positioning the excitation spot over a specific part of the structure (e.g. middle or end) enables emission spectra and lifetimes to be measured in a spatially resolved manner. The photoluminescence spectra shown in Figure 1 were collected from the end of the rod and at a point located between the end and middle, denoted “interior”. Both spectra show a narrow transition centered at ~ 390 nm that corresponds to electron hole recombination from the band-edge (BE) and a broad trap emission band at ~ 550 nm (T). While the spectra have the same basic form, the intensity of the band-edge emission relative to the trap depends on the location in the structure, with the spectrum obtained from the end exhibiting a greater BE/T intensity ratio than the interior ($\sim 20:1$ vs $\sim 5:1$). The spatial variation in the BE/T ratio is one indicator that the photophysics at the end of the structure differ markedly from those in the interior.

Time-resolved emission microscopy revealed a time-dependent redshift in the photoluminescence at higher excitation intensities. This red shift is consistent with the formation of an electron-hole plasma (EHP) at higher excitation intensities. At low excitation intensity the band-edge (BE) emission arises predominantly from exciton recombination. As the carrier density increases, Coulombic screening weakens the exciton binding energy, resulting in the dissociation of the electron-hole pairs and the transition to the EHP state. This work was published in *J. Phys. Chem. C* **2011**, 115, (43), 21436-21442.

2.) Optical Resonator Modes: Spatial Variation in the Photoluminescence Images

In addition to the bright ends, the emission from the interior of the rod is periodically modulated and coincides with the hexagonal facets. Not every rod exhibits a pattern of this nature, but most do. A particularly striking example is shown in Figure 2. This spatial variation results from optical cavity modes supported by the rod's hexagonal cross section, which become visible when structure's dimensions are comparable to the wavelength of light. Generally, there are two types of modes: standing wave (Fabry-Perot, FP) resonances that are supported between two parallel facets, and whispering gallery (WG) modes that correspond to propagation of light around the periphery of the rod through total internal reflection off each facet. Both modes have resonance conditions that depend upon the excitation wavelength and the cross-sectional diameter of the rod. Due to the needle shaped structure, the diameter changes along the length of the rod, causing the excitation to go in and out of resonance, giving rise to the pattern.

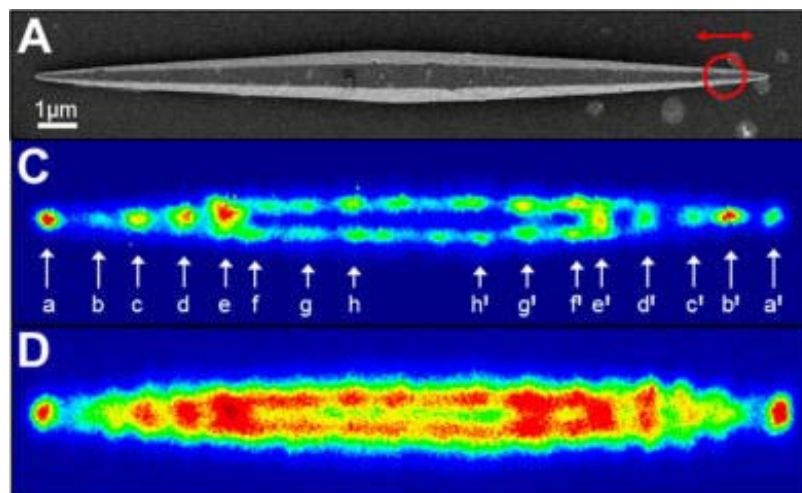


Figure 2: (A) SEM image and (B) emission spectrum of a tapered zinc oxide nanorod. The red circle and double-headed arrow indicate the location at which the spectrum was acquired and the direction of the excitation polarization vector, respectively. (C, D) Photoluminescence images taken at 390 and 550 nm, respectively, show a modulated emission pattern along the structure.

We used finite-difference frequency-domain (FDFD) methods to simulate the distribution of the optical intensity within the structure. Shown in the center of Figure 3 is the simulated emission image for the rod depicted in Figure 2. On either side of the image, are the optical mode patterns observed at different points within the image. When excited on either side of the rod, particularly at larger diameters, the pattern has clear WG mode characteristics, with much of the optical intensity being located near the surface of the rod. However, as the diameter is decreased to a size consistent with the tip, the distribution starts to take on more FP character with greater intensity appearing in the core of the structure. These observations help to explain the spatial variation in the electronic dynamics observed using pump-probe microscopy. The FDTD simulations were published in *J. Phys. Chem. C* **2013**, 117, (20), 10653-10660.

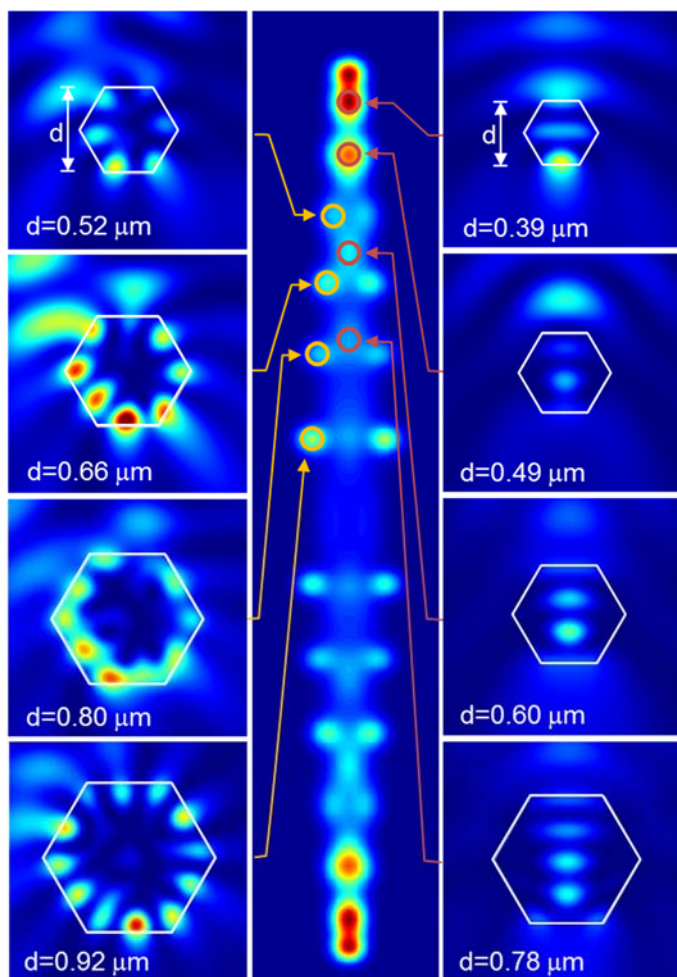


Figure 3: FDTD simulations of the two-photon photoluminescence from a needle-shaped ZnO rod. (Center) Simulated image for the structure depicted in Figure 2. (Left and Right) Images showing the optical field in the hexagonal cross-section of the rod. As the position in the rod changes, the size of the hexagonal resonator also changes, resulting in the different mode patterns.