Raman Antenna Effect in Semiconducting Nanowires*

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Semiconducting Nanowire (NW) Electronic Devices

p-n junctions of InP nanowires

Bipolar-transistors of InP nanowires

Optoelectronic NW Lasers

CdS NW Laser

CdS NW Fabry-Perot Cavity
PL emission @ 300 K

Motivation and Background

• Raman scattering from phonons is sensitive to the symmetry of a crystal and its phonons.

• What can Raman scattering tell us about Semiconducting Nanowires (NWs)?

• Can a polarized Raman experiment be successful on a single nanowire (NW)?

• A Raman antenna effect was reported for a ~ 1 nm diameter carbon nanotube (Resonant Scattering associated with van Hove 1D)
  – What will we see for semiconducting NWs in the diameter range 20<d<200 nm? Will bulk physics or “nano” scale phenomena dominate?

• Can Raman scattering be used to determine the orientation of a single semiconducting NW supported on a substrate?
Pulsed Laser Vaporization NW Growth

GaP Nanowire Growth Conditions:

- **Target composition:** \((\text{GaP})_{0.95}\text{Au}_{0.05}\)
- **Temperature:** 880-920 °C
- **Gas flow rate:** 100 sccm Argon
- **Pressure:** 200 Torr

- VLS growth in a quartz tube
- Catalyst (Au) in target or supported on substrate
GaP NWs: SAD and TEM

Phonon Confinement in small Si NWs
Low Laser Power and Small Wires

- Low Laser power excitation
- Solid line due to Richter Model with diameter distribution
- Bulk dispersion
- Measured nanowire diameter distribution
- Scale Factor $\alpha$ is the fitting parameter
- Universal Value found: $\alpha = 6.3 \pm 0.3$

K Adu, H. Gutierrez, U.Kim, P.C. Eklund, Nano Letters, 5, 409, 2005
SO Modes in Cylindrical GaP NWs

- Raman spectra taken with sample in various dielectric media
- Surface modes frequency depends on dielectric medium (EM field “leaks” out of sample)


\( \lambda_{\text{ex}} = 514.5 \text{ nm} \)
TEM images of Diameter Modulation

GaP NWs

D = 40 nm = mean diameter
λ ~ 35 nm = period of diameter modulation

D = 65 nm
λ ~ 70 nm

D = 48 nm
λ ~ 24 nm

D = 60 nm
λ ~ 50 nm

Diameter modulation (λ) activates SO modes with wavevector

\[ q_{SO} = \frac{2\pi}{\lambda} \]

Raman Scattering from “One” Nanowire (NW)

**Geometrical and Optical Considerations:**

- **NW axis known** (e.g., <111>; orientation of NW axis on TEM grid is known)
- **Orientation of <112> about the NW axis is unknown**
- **Fixed Optical Parameters**
- **Rotate Nanowire in the plane of incidence**
- **Collect Spectrum vs. (θ)**
Control Experiment: G-Band Polar Plot
GaP Nanowires (NWs) on a TEM Grid

- NWs transferred to TEM Grid
- NWs chosen and SAD pattern is taken
- TEM Grid then placed in MicroRaman Spectrometer

Growth direction [11\bar{1}]
GaP Nanowires grown by Laser-Assisted CVD

Growth direction [33\bar{1}]

Growth direction [11\bar{1}]

Growth direction [220]

Random crystalline growth direction in the same batch
Predicted $I(\theta)$ for LO Phonons (GaP)

Based on Bulk GaP Raman Tensor

Incident Radiation

$\beta = 0^\circ$

$\beta = 90^\circ$

$\beta = 135^\circ$

$\beta = 180^\circ$
GaP:

\(d=105 \text{ nm}, \ L=72 \ \mu\text{m}, \ \lambda_{\text{laser}}=488 \text{ nm}\)
Experimental Data (GaP)

$\lambda = 488$ nm

d = 160 nm; L: 22.0 mm, aspect ratio $\sim 168$;
What is the data telling us?

• The NW diameter, not the Raman tensor, seems to control the symmetry of the polar scattering plots

• Consider a classical calculation of the internal Electric Field $E$ in the Nanowire
  – Raman scattering intensity $\sim E^2$ (inside the NW!)
  – We should consider the Mie Scattering problem for a dielectric cylinder
  – Use optical dielectric function of bulk GaP
  – Use analytic formulae or numerical Discrete Dipole Approximation (DDA)
Calculated E-Field Distribution (DDA) (GaP; d=50nm)

\[ I_{Raman} \propto |E|^2 \]

\[ \lambda_{Laser} = 488 \text{nm} \]

\[ E_0 \parallel <111> \]

\[ E_0 \perp <111> \]
Calculated E Field Distribution (DDA) (d=200nm)

\[ I_{\text{Raman}} \propto |E|^2 \]

\[ \lambda_{\text{Laser}} = 488\text{nm} \]

\[ E_0 \parallel <111> \]

\[ E_0 \perp <111> \]
Calculated (DDA) $\int E^2 \, dv$ Polar Plot

(GaP; $\lambda=488$ nm)

D=50 nm; L=1000 nm

D=200 nm; L=1000 nm
Mie Theory vs LO (TO) Intensity Ratio

\[ \frac{I_{//}}{I_{\perp}} \]
Calculated TO Polar Plots: (Mie)x(Raman Tensor)

GaP $<$111$>$; $d=50$ nm; $\lambda=488$ nm

$\beta = 0^\circ$

$\beta = 90^\circ$

$\beta = 135^\circ$

$\beta = 180^\circ$
Summary and Conclusions

- We can routinely measure the Raman spectrum of a single semiconducting nanowire (NW) using MicroRaman backscattering techniques.

- The polarization dependence of the Raman scattering from the LO and TO phonons does not agree with predictions based on the bulk Raman tensor.

- Polarized scattering from the TO and LO phonons mimics the radiation from a “nano-dipole” antenna for small diameter $d$.
  - In agreement with Mie theory for a dielectric cylinder.

- $d/\lambda$ decides the nature of the physics that dominates:
  - $d/\lambda < 1/4$ (small $d$): Mie scattering dominates.
  - $1/4 < d/\lambda < 1/2$ (intermediate $d$): Mie & Raman tensor needed.
  - $d/\lambda > 1/2$ (large $d$): Raman tensor begins to dominate.

- The shape of the polar plot for the TO and LO phonons will determine the absolute orientation of the NW on the substrate (once we have a complete theory).
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Questions??
Discrete Dipole Approximation (DDA)

- An approximation to calculate the scattering and absorption properties of arbitrary objects
- The object is represented with polarizable discrete dipoles
- Assumption: inter-dipole spacing is small compared to any structural lengths in the target, and the wavelength \( \lambda \)
- Specification of the dipole array:
  - Geometry
  - Effective dipole polarizabilities:

\[
\alpha^{\text{DIPR}} = \frac{\alpha^{\text{CM}}} {1 + (\alpha^{\text{CM}}/d^3)[(b_1 + m^2 b_2 + m^2 b_3 S)(kd)^2 - (2/3)i(kd)^3]}
\]

Where, \( \alpha^{\text{CM}} = \frac{3d^3}{4\pi} \frac{\epsilon_i - 1}{\epsilon_i + 2} \) is Clausius-Mossotti polarizabilities, \( b_1, b_2, \) and \( b_3 \) are constants, \( S = \sum_{j=1}^{3} \beta_i \beta_j \).

Antenna Effect in Nanotubes


Jorio, A., ... and Dresselhaus, M.S., Phys. Rev. B, 65, 121402, 2002
Finite Length Effects (DDA) 
\(d=100\text{nm}, L=1\mu\text{m}, \lambda_{\text{light}}=488\text{nm}\)
Electric Field of GaP Cylinder
(Diameter=10nm, Aspect ratio=10, $\lambda_{\text{light}}=488\text{nm}$)

Parallel

Perpendicular
Electric Field of GaP Cylinder
(Diameter=50nm, Aspect ratio=10, $\lambda_{\text{light}}=488\text{nm}$)

Parallel

Perpendicular
Electric Field of GaP Cylinder
(Diameter=100nm, Aspect ratio=10, λ_{light}=488nm)