PennState

Raman Antenna Effect in Semiconducting Nanowires*

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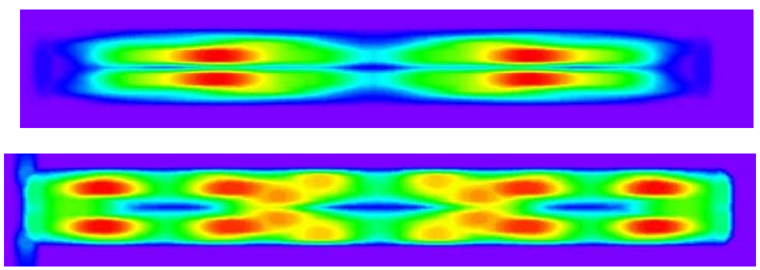
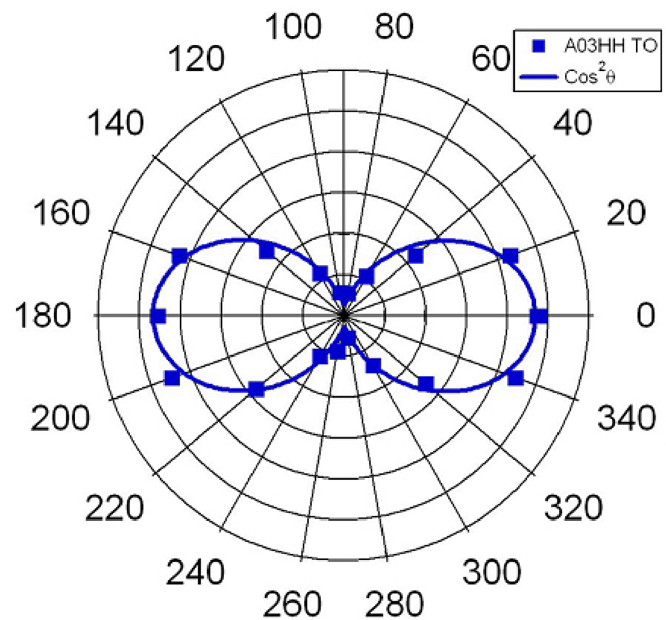
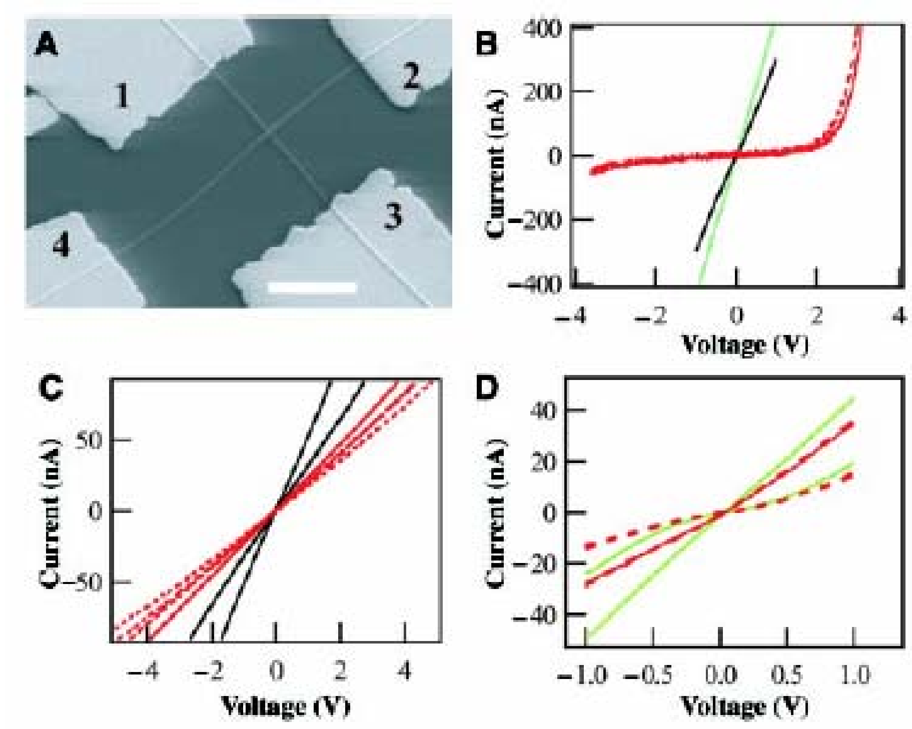
The Pennsylvania State University



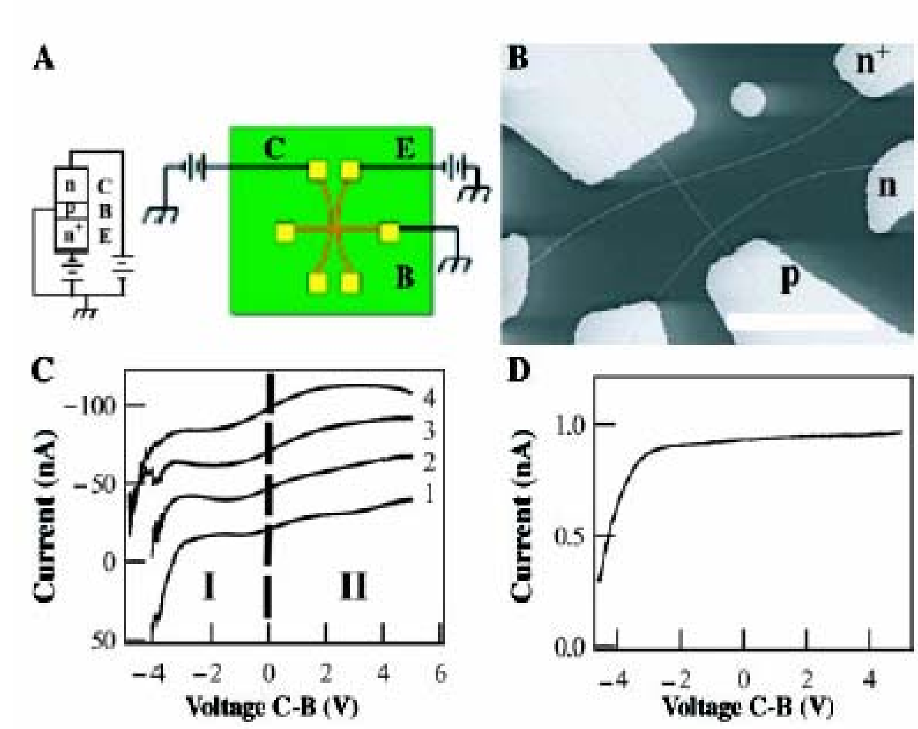
*Supported by NSF-NIRT Program



Semiconducting Nanowire (NW) Electronic Devices



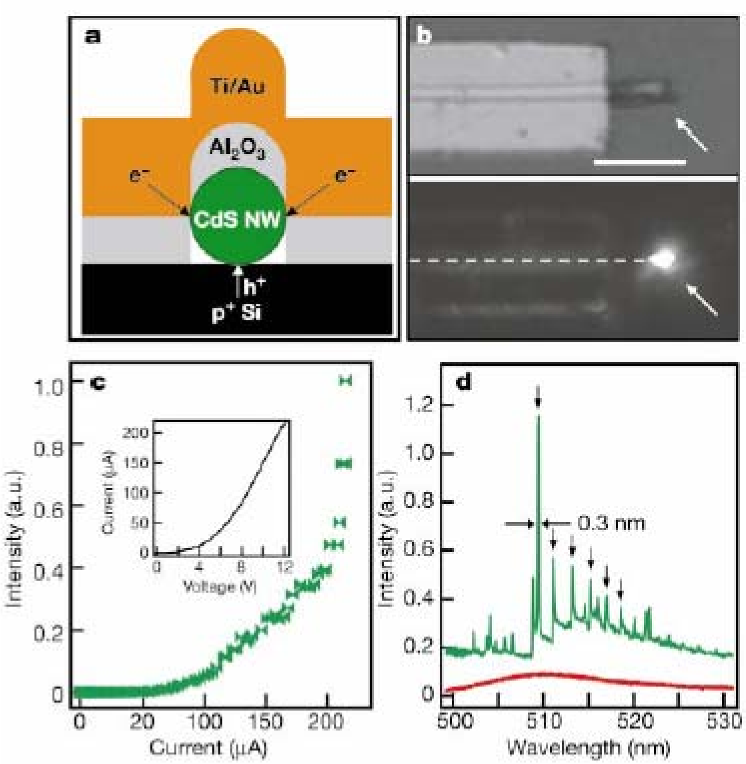
p-n junctions of InP nanowires



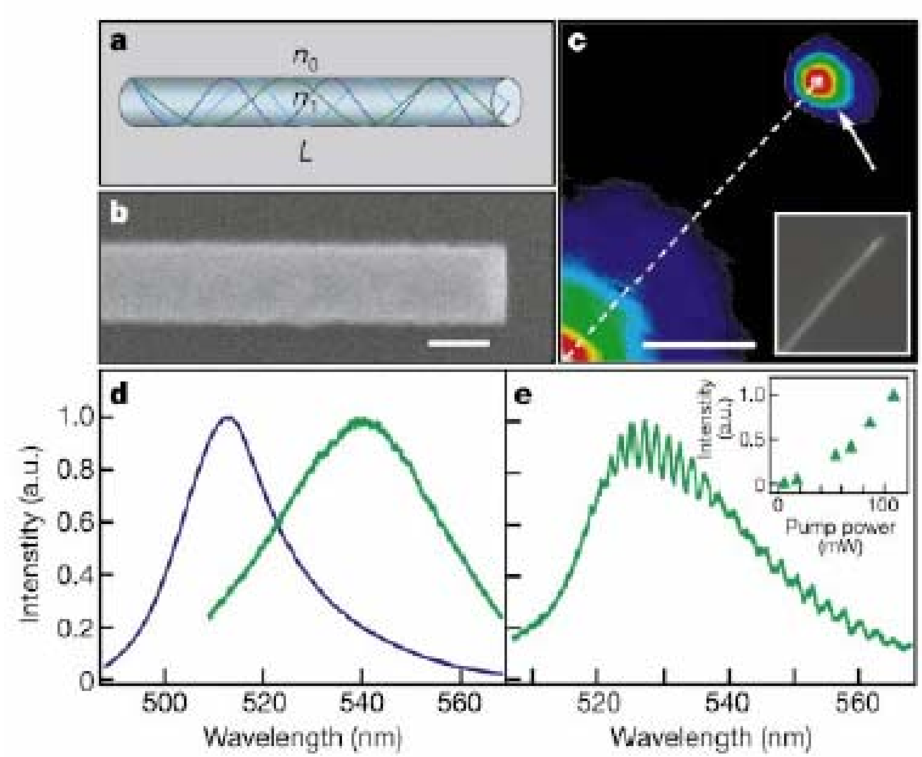
Bipolar-transistors of InP nanowires

Yi Cui and Charles M. Lieber, Science, 291, 851, 2001

Optoelectronic NW Lasers



CdS NW Laser

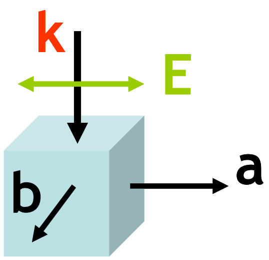


CdS NW Fabry-Perot Cavity
PL emission @ 300 K

X. Duan et. al., Nature, 421, 241, 2003

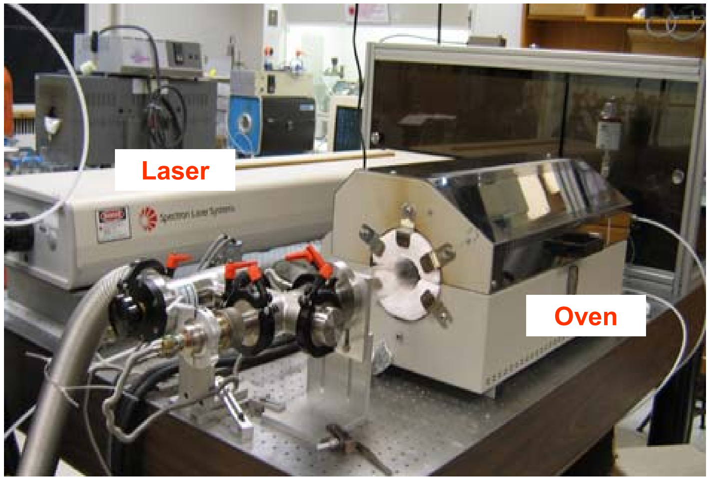
Motivation and Background

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

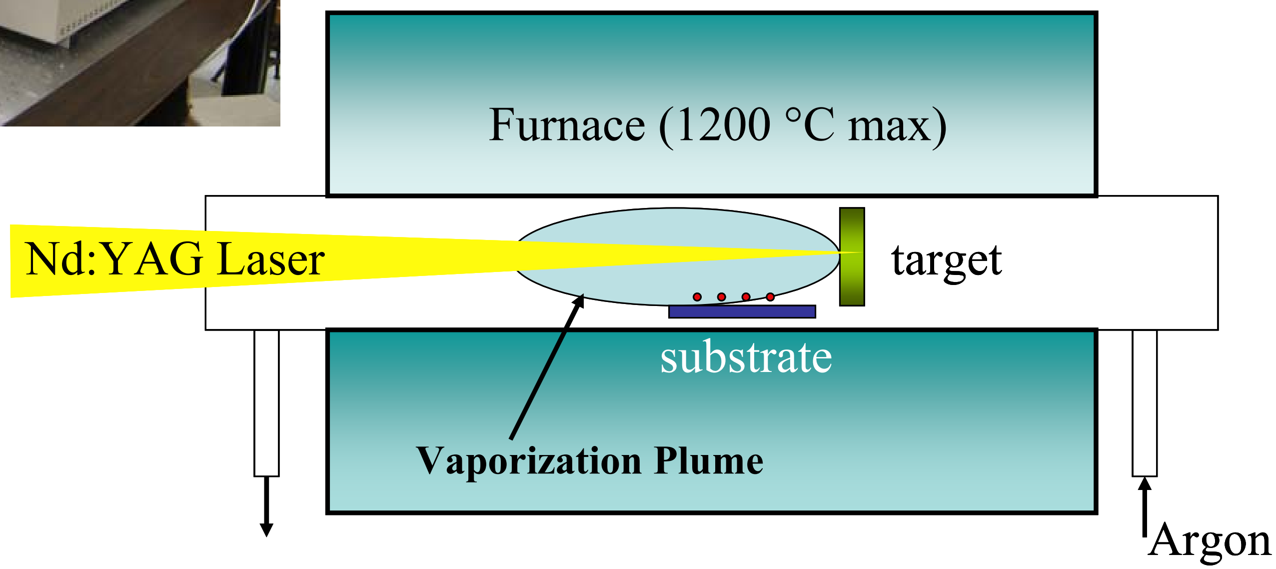


- What can Raman scattering tell us about Semiconducting Nanowires (NWs)?
- Can a polarized Raman experiment be successful on a single nanowire (NW)?
- A Raman antenna effect was reported for a ~ 1 nm diameter carbon nanotube (Resonant Scattering associated with van Hove 1D)
  - What will we see for 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



- •VLS growth in a quartz tube
- •Catalyst (Au) in target or supported on substrate



GaP Nanowire Growth Conditions:

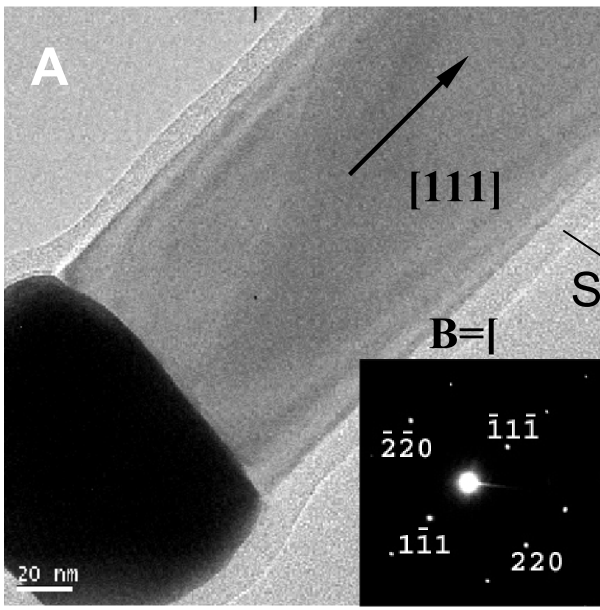
- **Target composition:** $(GaP)_{0.95}Au_{0.05}$
- **Gas flow rate:** 100 sccm Argon

Temperature: 880-920 °C

Pressure: 200 Torr

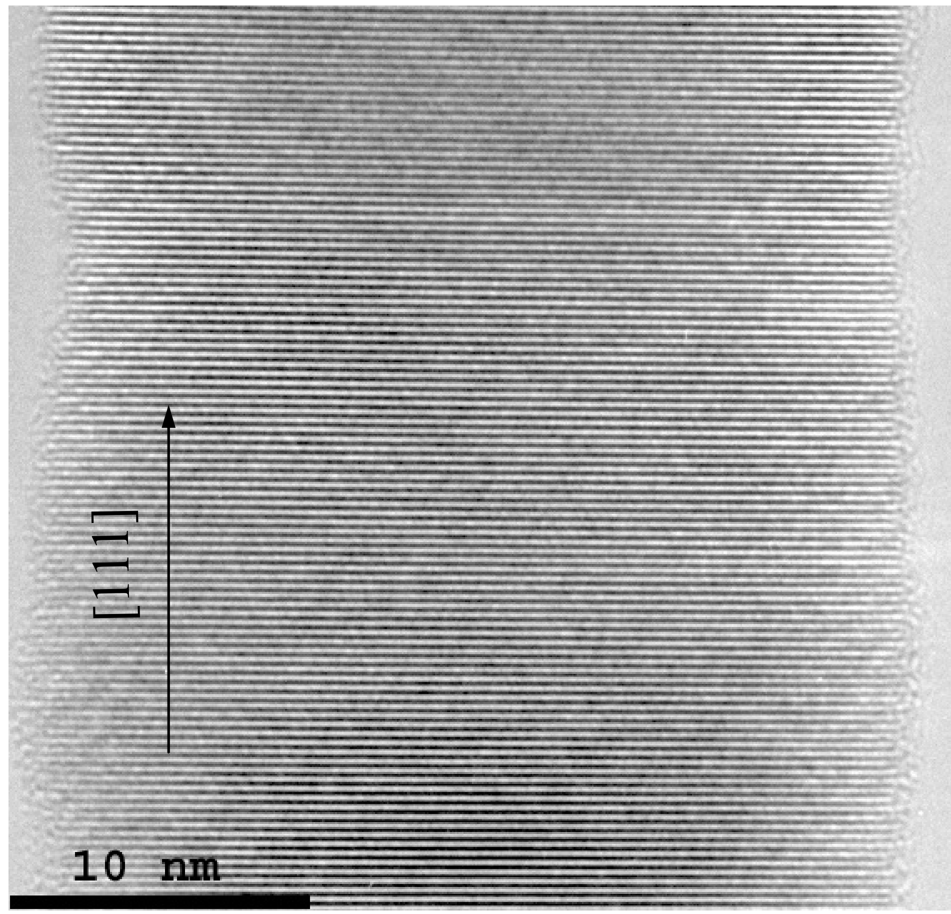
GaP NWs: SAD and TEM

TEM



SAD

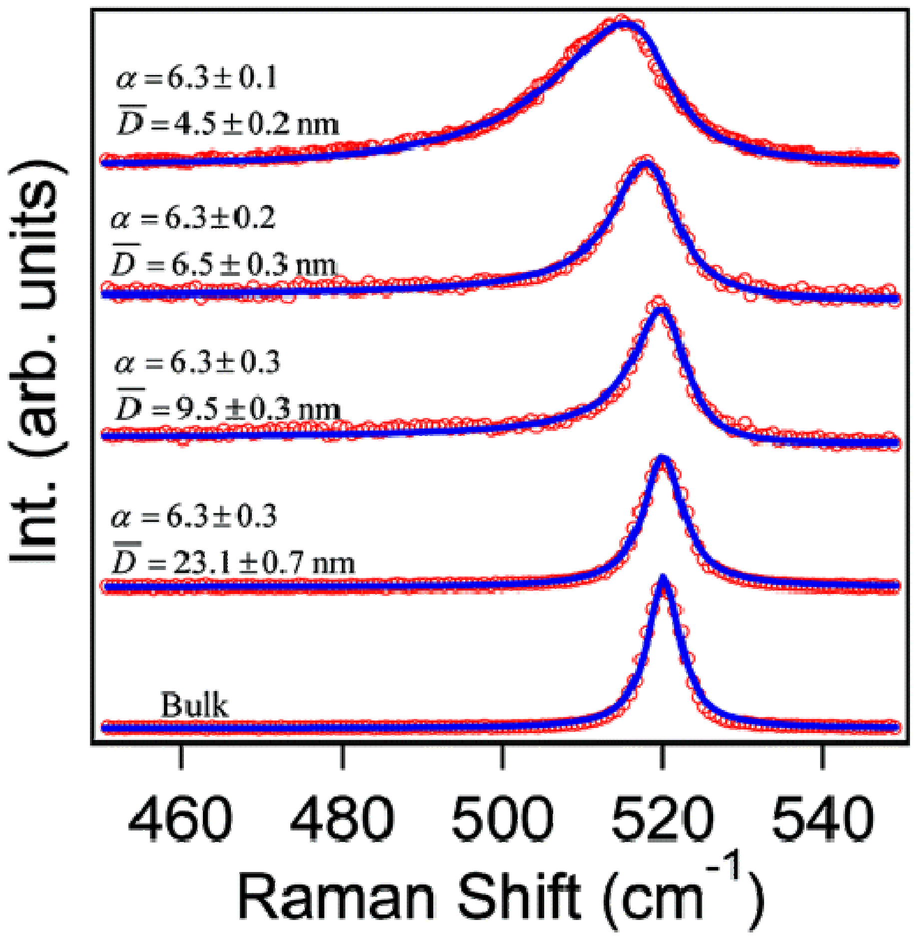
HRTEM



Q. Xiong …P.C.Eklund., J. Nanosci. Nanotech., Vol. 3, No. 4, 335, 2003

Phonon Confinement in small Si NWs

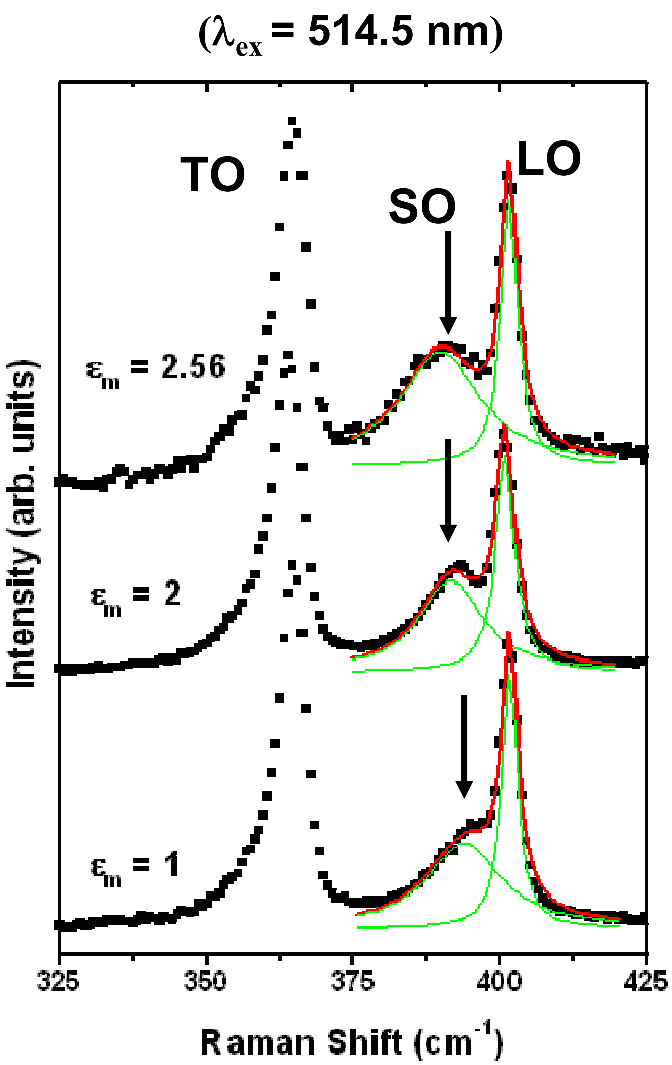
Low Laser Power and Small Wires



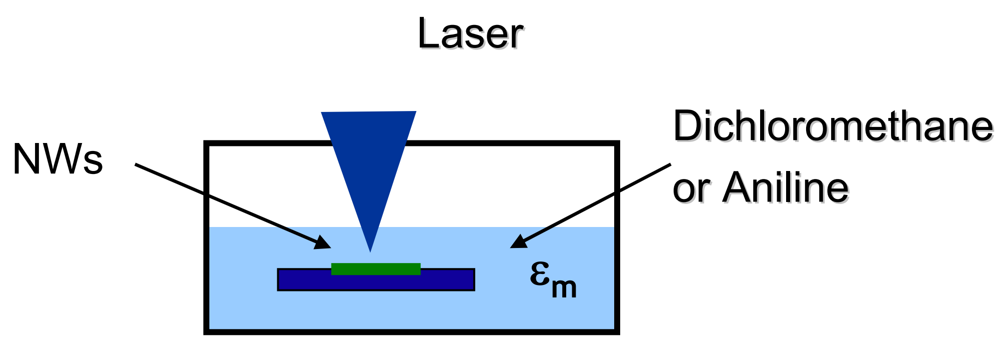
- Low Laser power excitation
- Solid line due to Richter Model with diameter distribution
- Bulk dispersion
- Measured nanowire diameter distribution
- Scale Factor α is the fitting parameter
- Universal Value found: α =6.3 +/- 0.3

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)



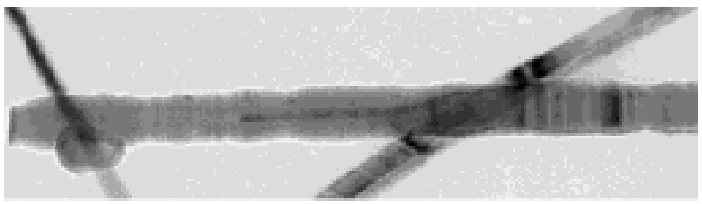
R. Gupta, Q. Xiong, G.D. Mahan, and P.C. Eklund, Nano Lett Vol.3 1745, 2003

TEM images of Diameter Modulation

GaP NWs

D = 40 nm = mean diameter

λ ~ 35 nm = period of diameter modulation

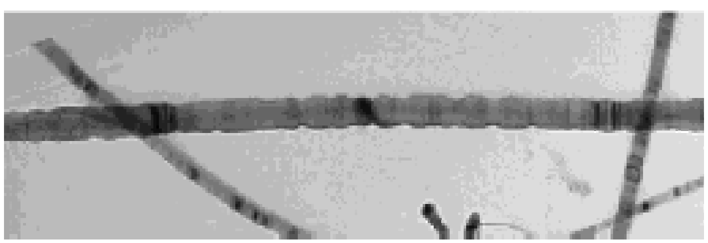


D = 65 nm

λ ~ 70 nm

D = 48 nm

λ ~ 24 nm



D = 60 nm

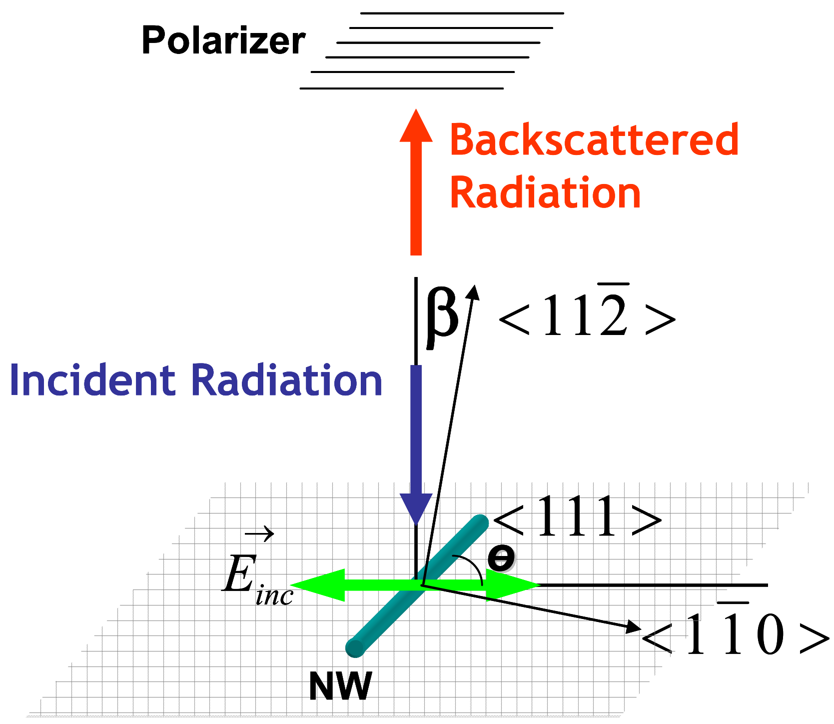
λ ~ 50 nm

Diameter modulation (λ) activates SO modes with wavevector

$q_{SO} = (2\pi/ \lambda)$

R. Gupta, Q. Xiong, G.D. Mahan, and P.C. Eklund, Nano Letters, 3 1745-1750, 2003

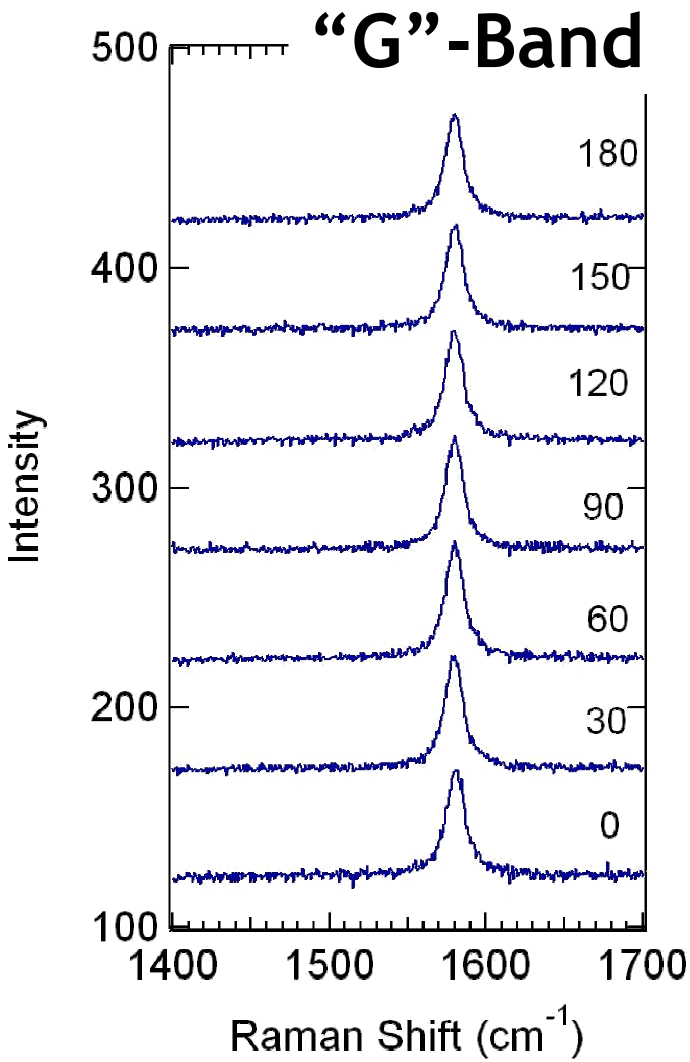
Raman Scattering from “One” Nanowire (NW)

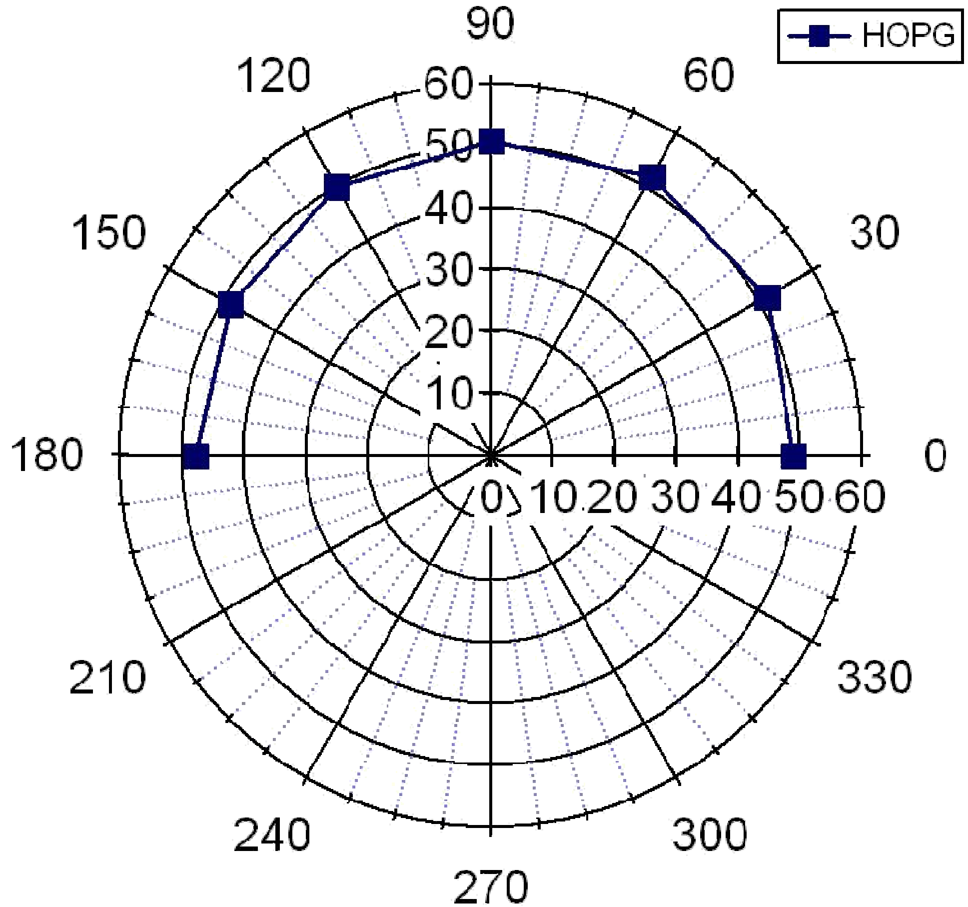


Geometrical and Optical Considerations:

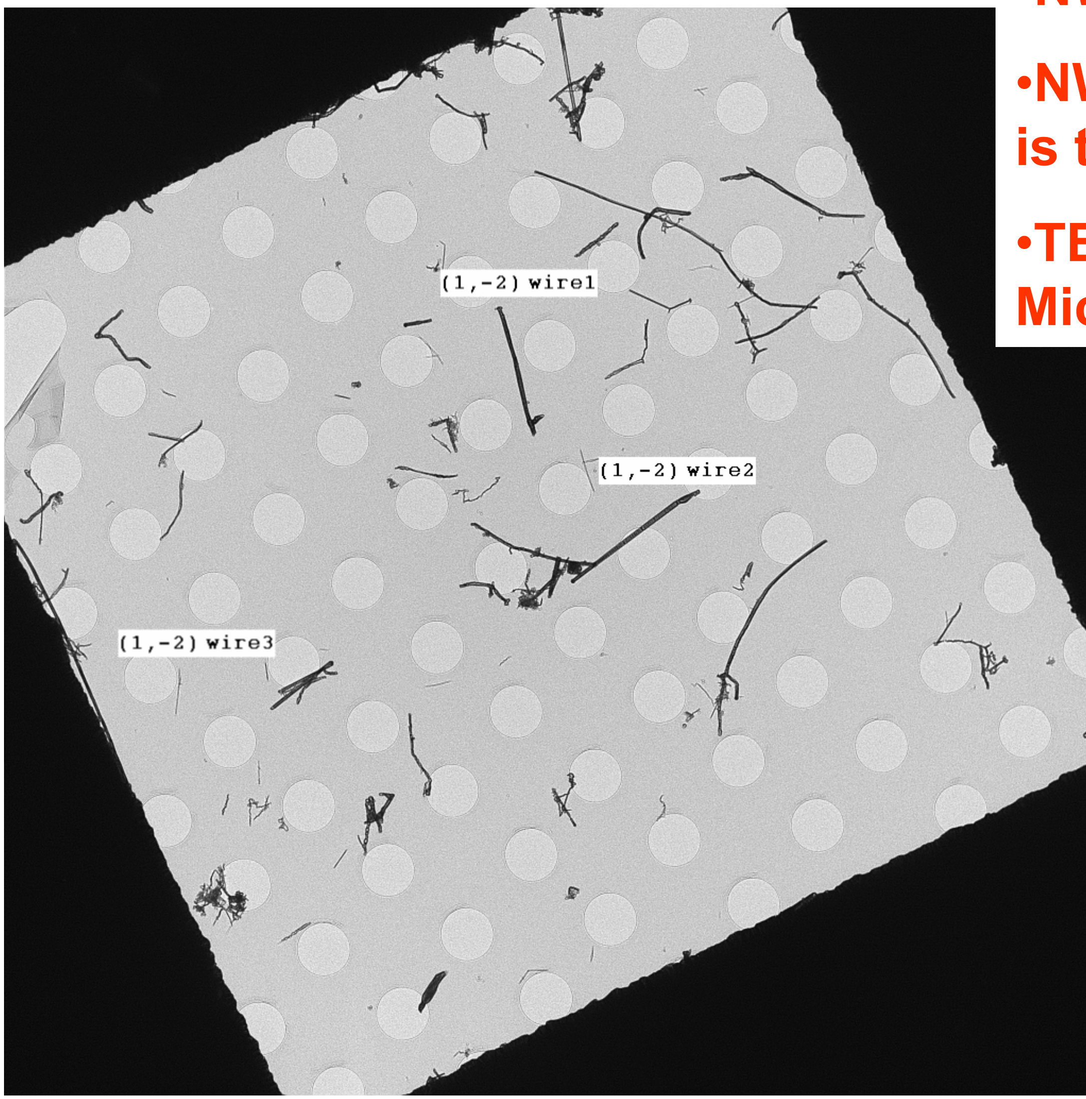
- *NW axis known (e.g., <111>; orientation of NW axis on TEM grid is known*
- *Orientation of <112̄> about the NW axis is unknown*
- *Fixed Optical Parameters*
- *Rotate Nanowire in the plane of incidence*
- *Collect Spectrum vs. (θ)*

Control Experiment: G-Band Polar Plot





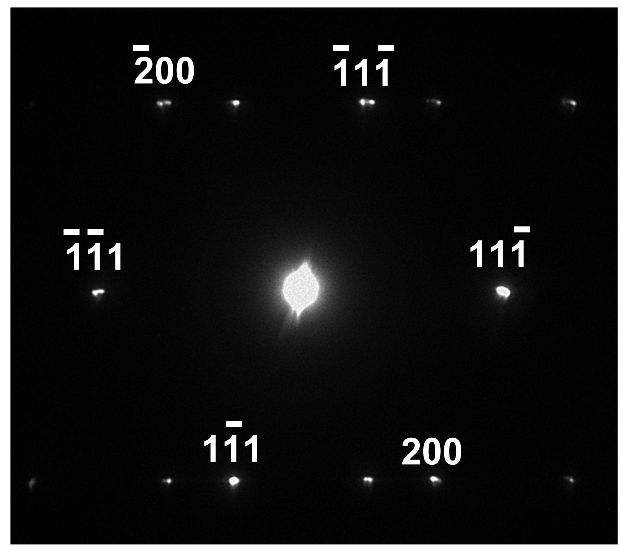
GaP Nanowires (NWs) on a TEM Grid



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

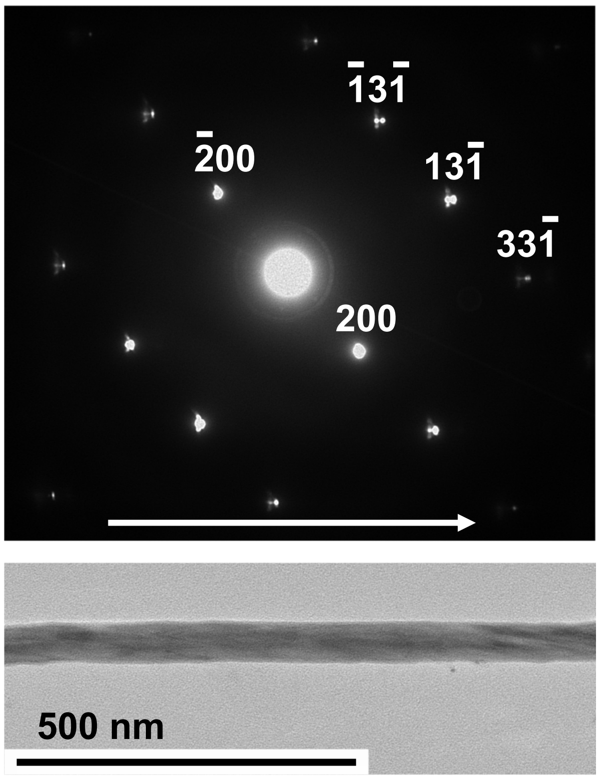
SAD

Growth direction $[11\bar{1}]$

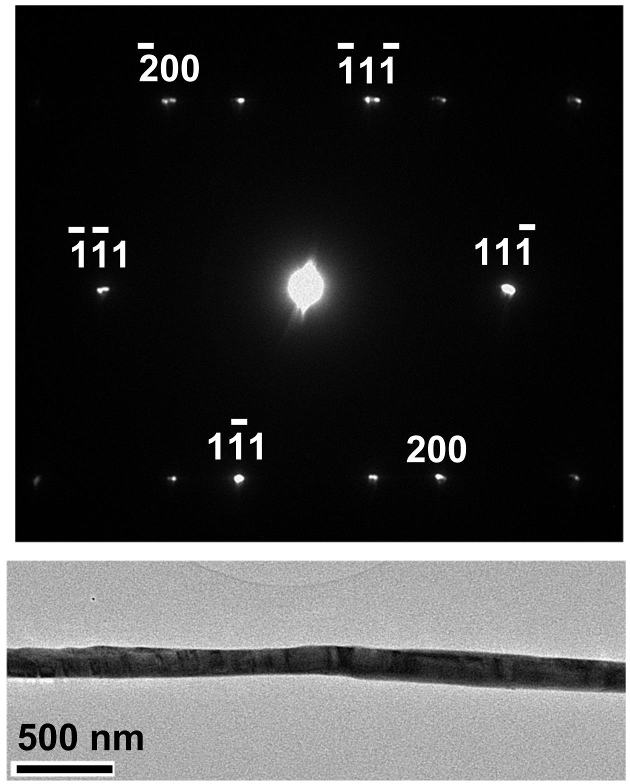


GaP Nanowires grown by Laser-Assisted CVD

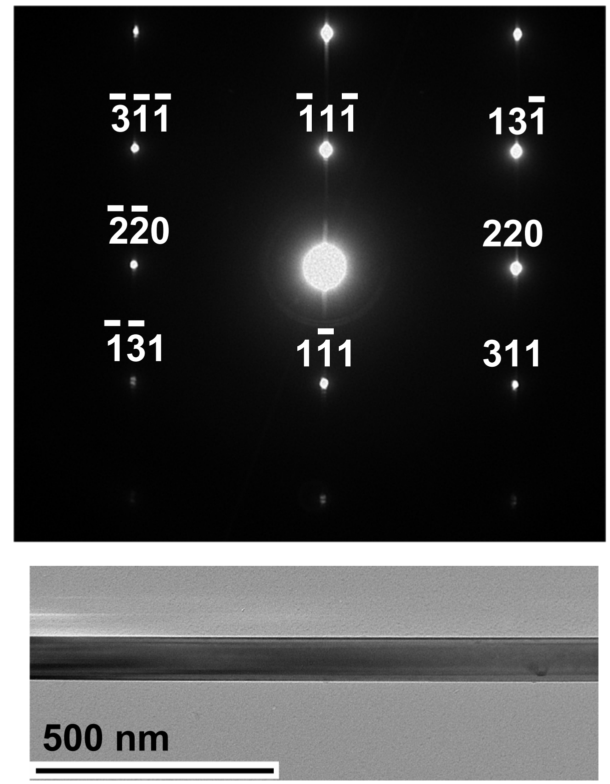
Growth direction [33$\bar{1}$]



Growth direction [11$\bar{1}$]



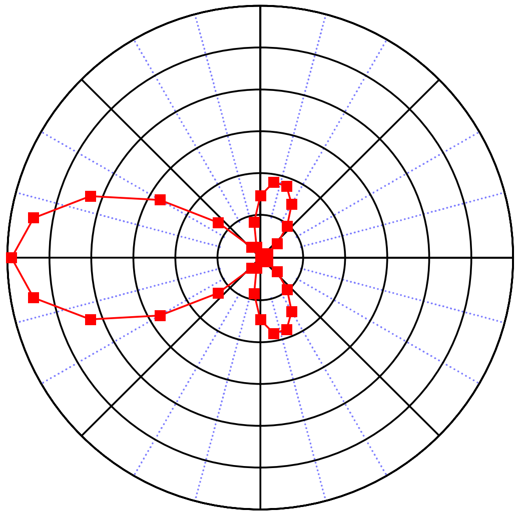
Growth direction [220]



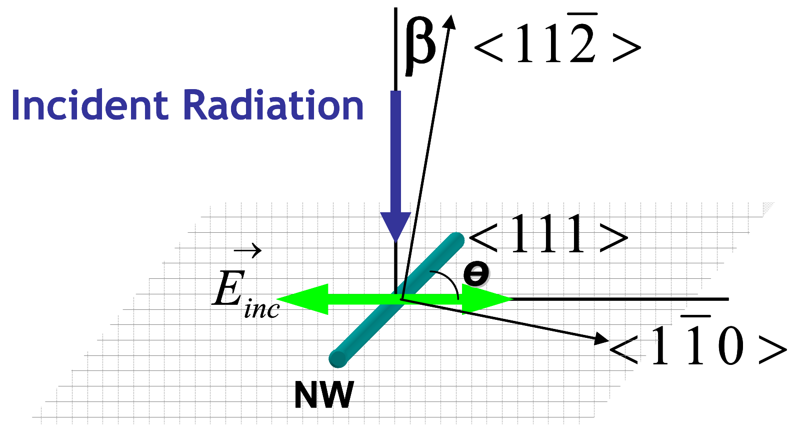
Random crystalline growth direction in the same batch

Predicted I(θ) for LO Phonons (GaP)

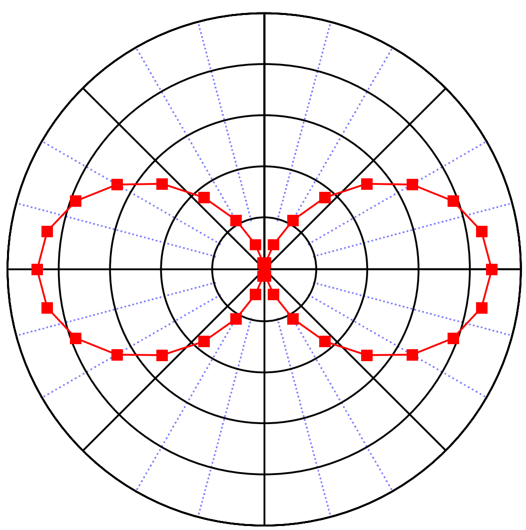
Based on Bulk GaP Raman Tensor



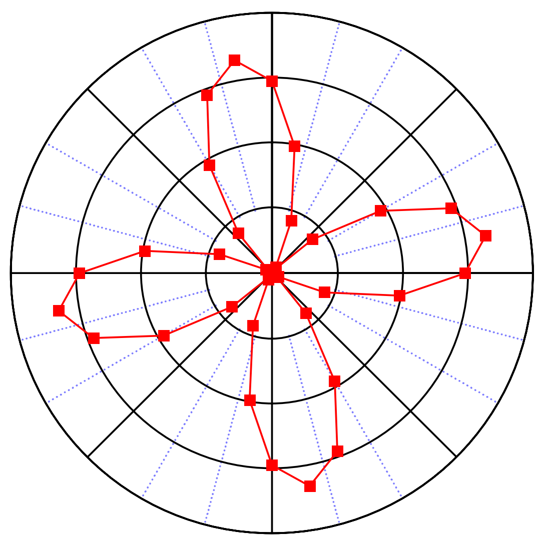
$\beta = 0^\circ$



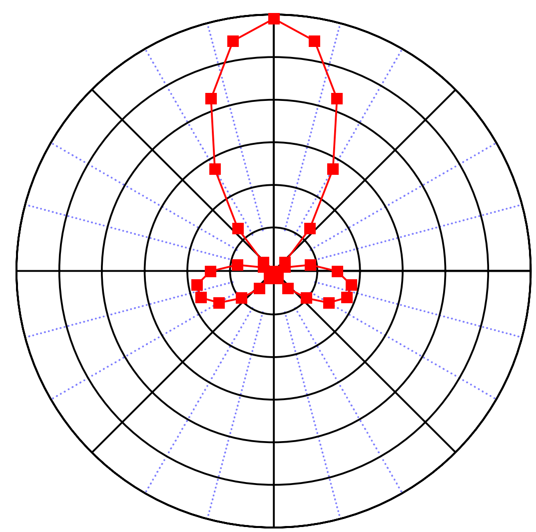
$\beta = 90^\circ$



$\beta = 135^\circ$



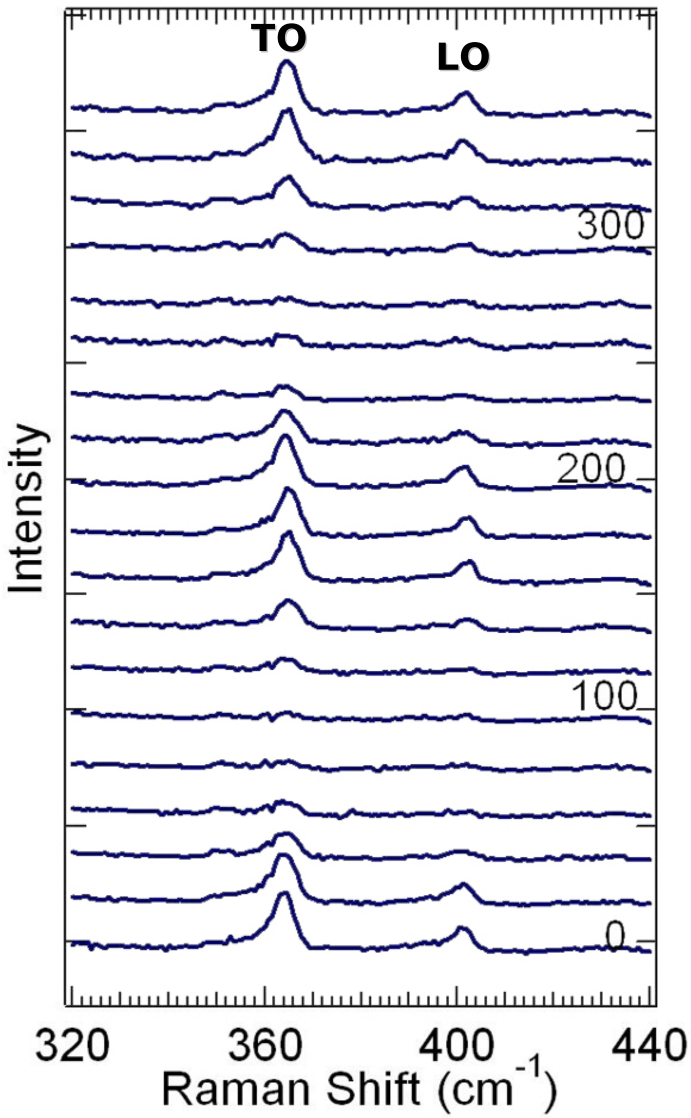
$\beta = 180^\circ$

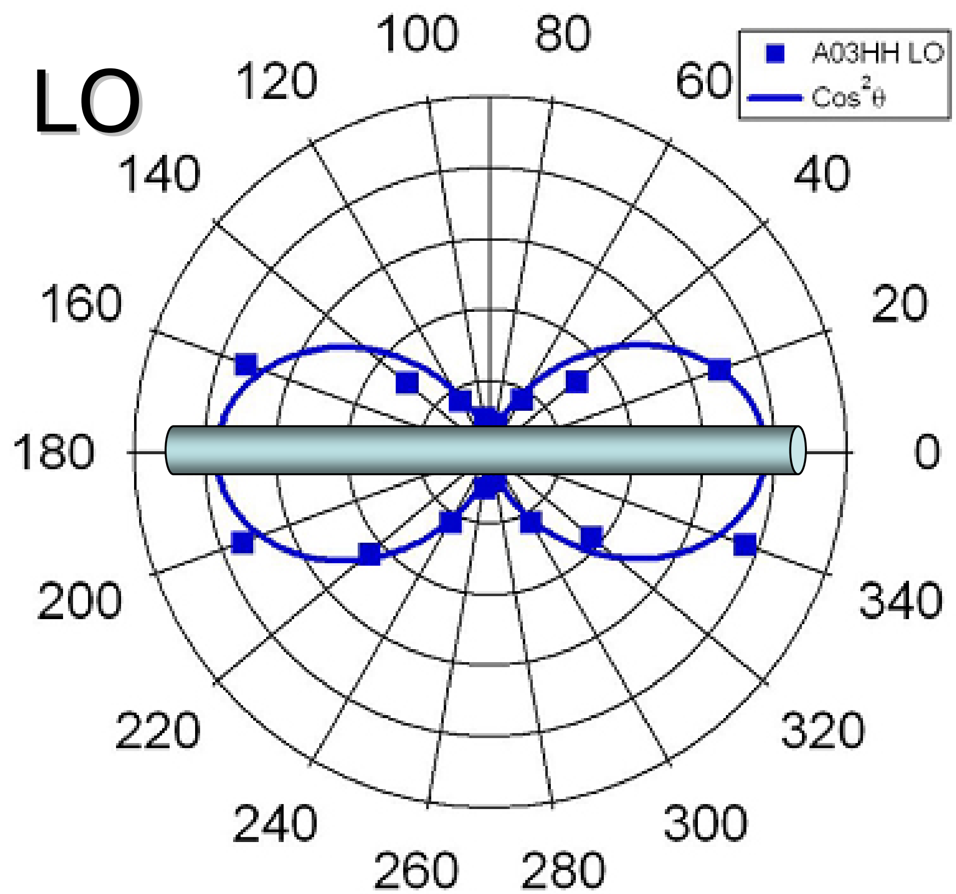


Experimental Data (GaP)

GaP:

d=105 nm, L=72 μm, λ_{laser}=488 nm

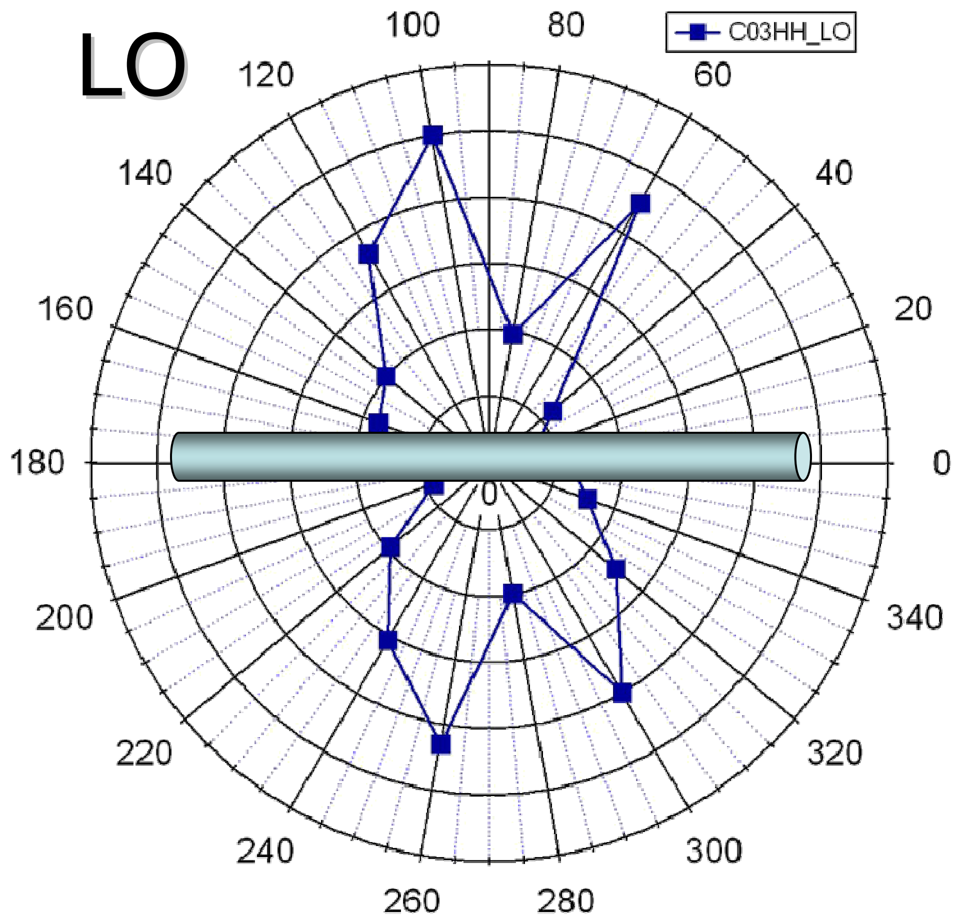


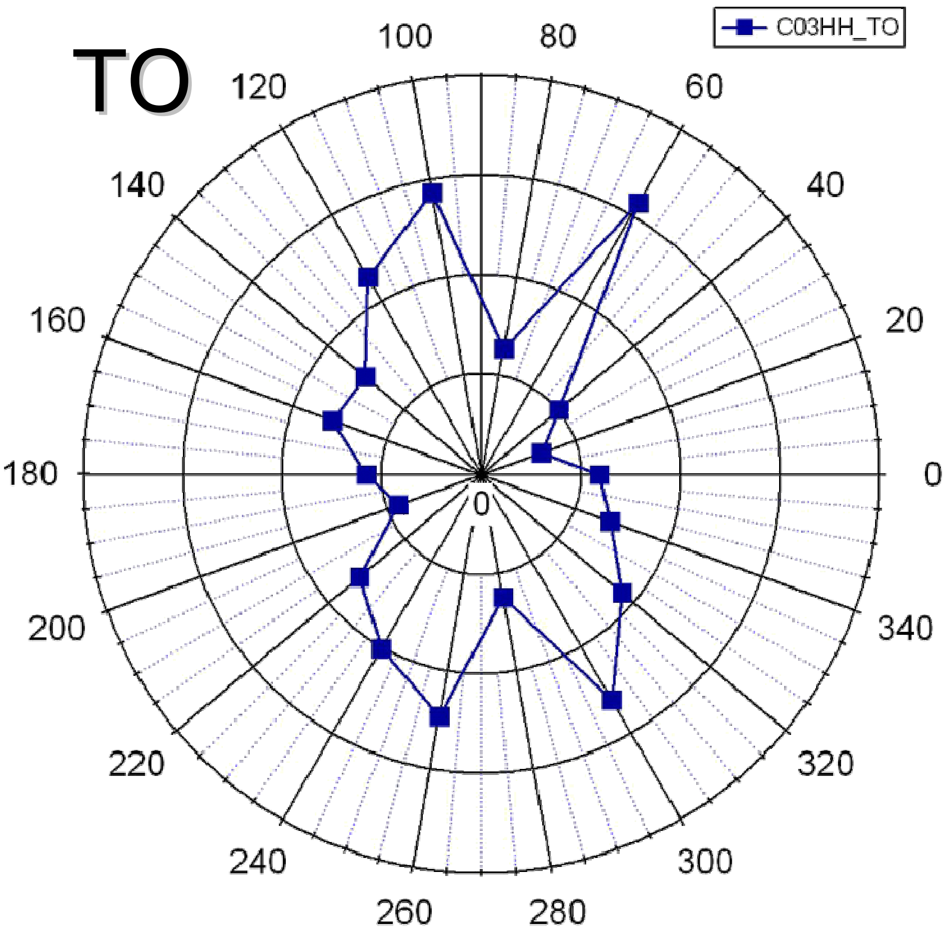


LO and TO Scattering = Dipole Antenna

Experimental Data (GaP)

d = 160 nm; L: 22.0 mm, aspect ratio ~ 168; λ=488 nm





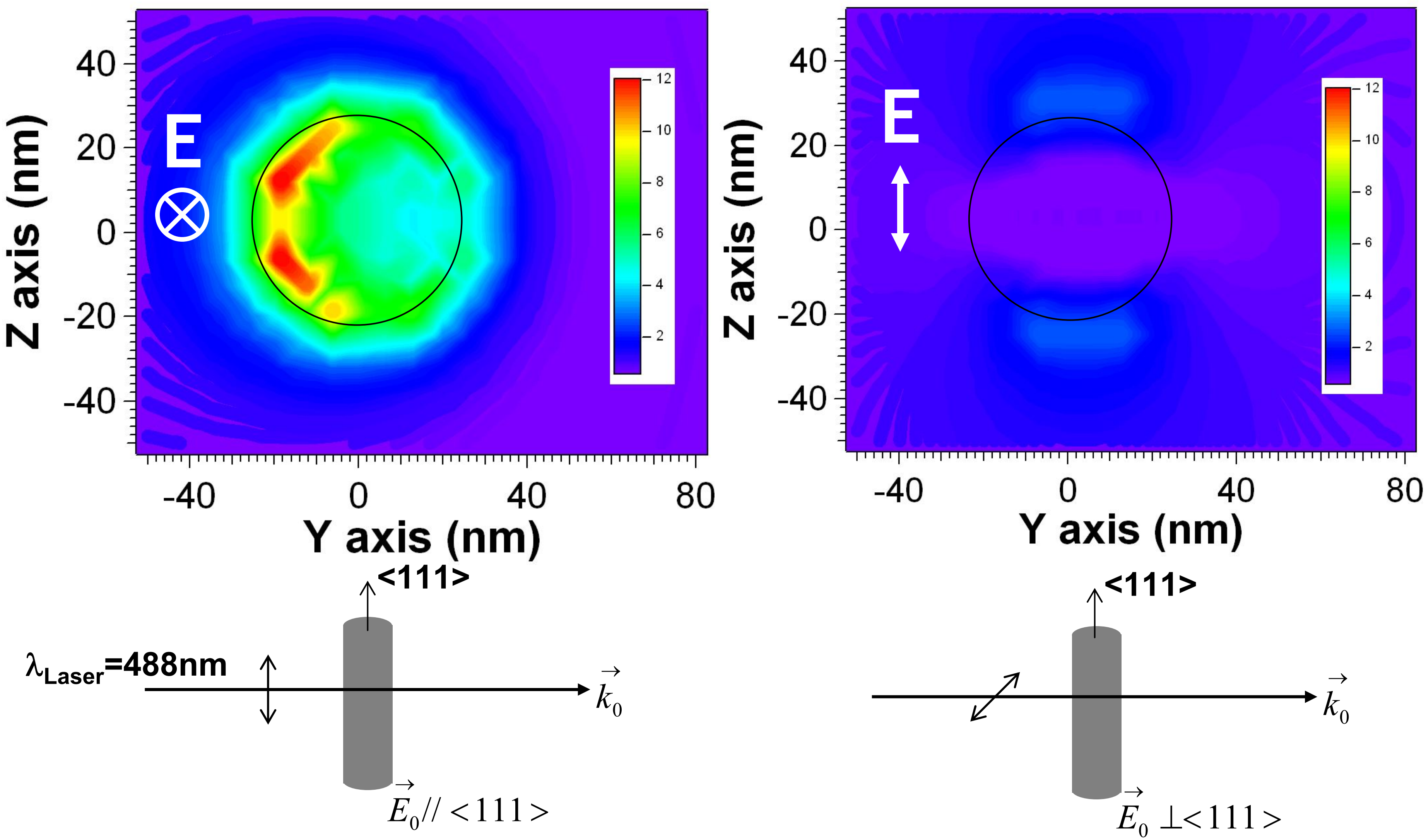
What is the data telling us?

- 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 ~ 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)

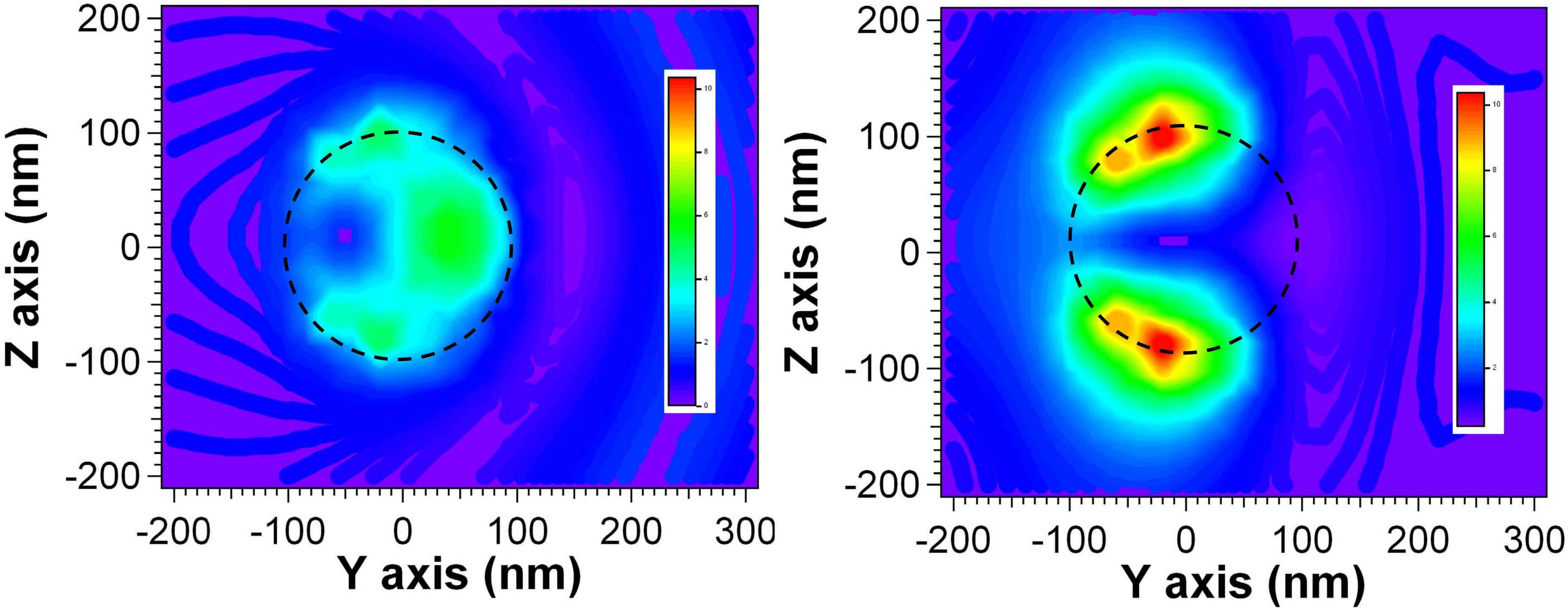
Calculated E-Field Distribution (DDA)

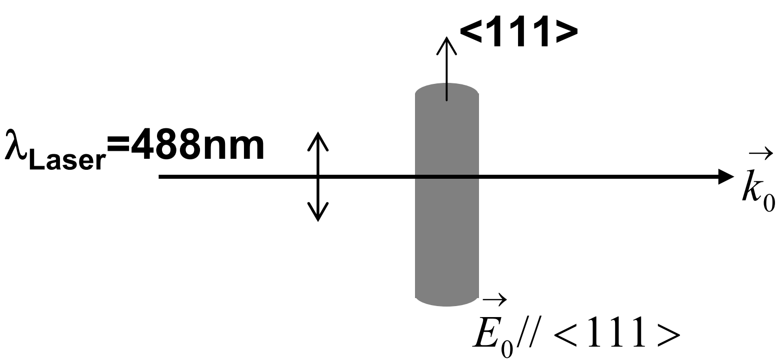
(GaP; d=50nm) $I_{Raman} \propto |E|^2$

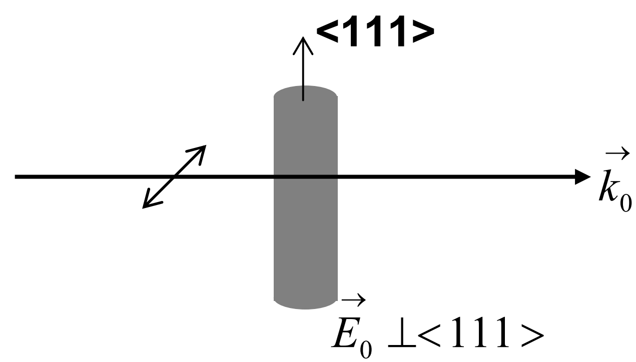


Calculated E Field Distribution (DDA)

(d=200nm) $I_{Raman} \propto |E|^2$

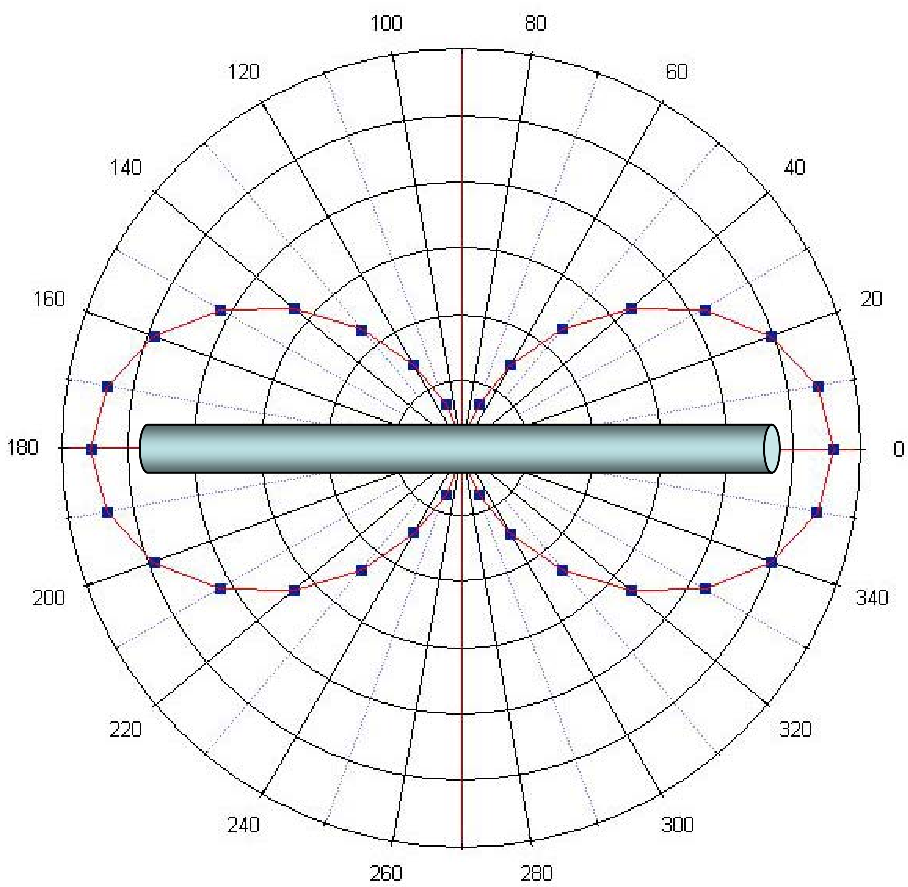




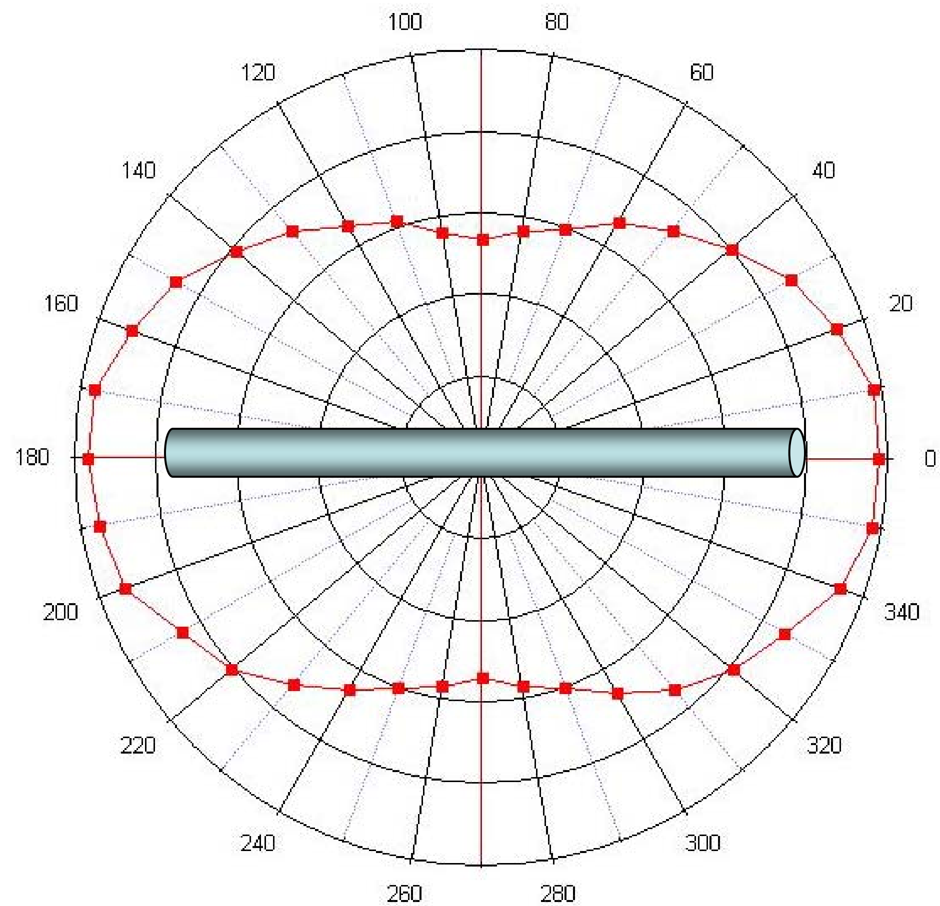


Calculated (DDA) $\int E^2 dv$ Polar Plot

(GaP; λ=488 nm)

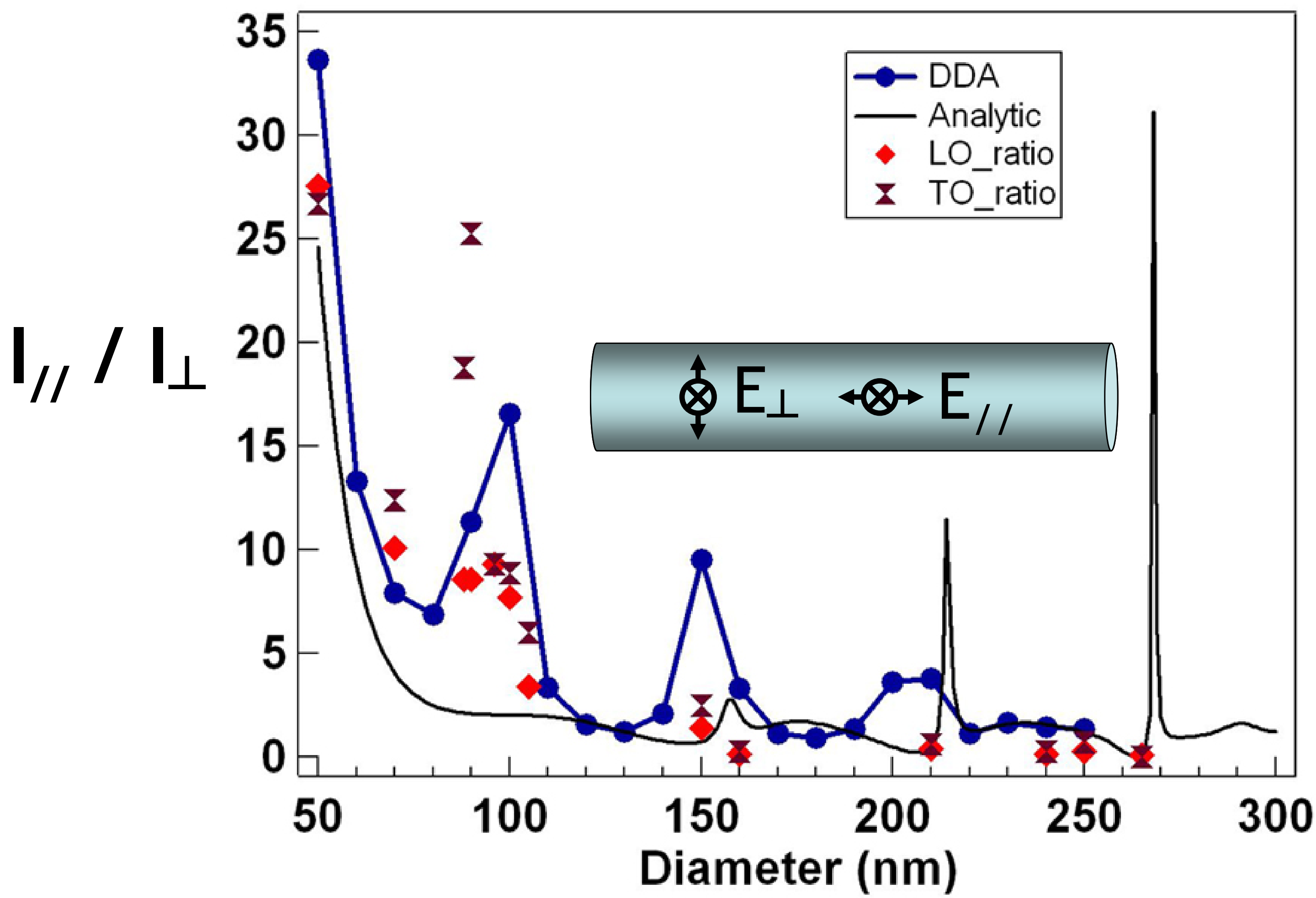


D=50 nm; L=1000 nm

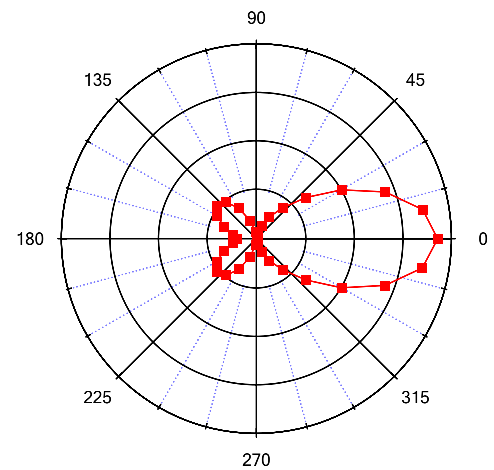


D=200 nm; L=1000 nm

Mie Theory vs LO (TO) Intensity Ratio

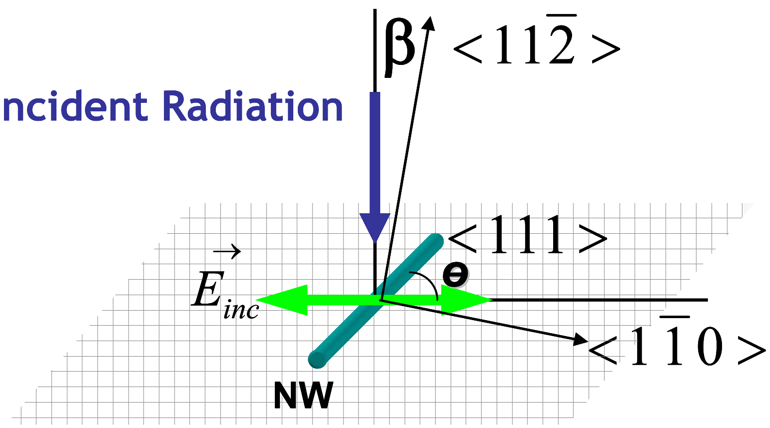


Calculated TO Polar Plots: (Mie)x(Raman Tensor)

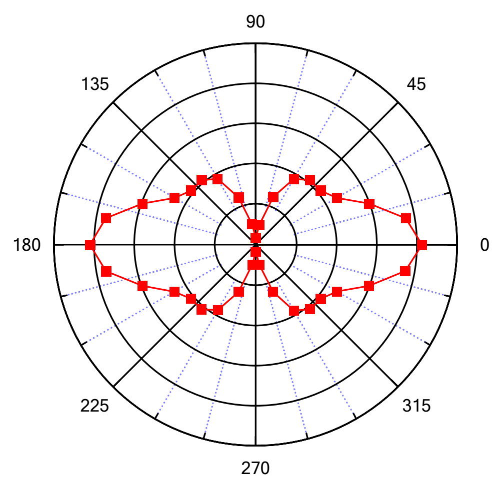


$\beta = 0^\circ$

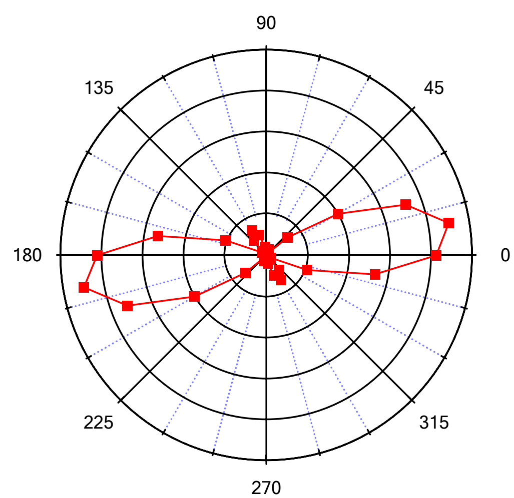
GaP <111>; d=50 nm; λ=488 nm



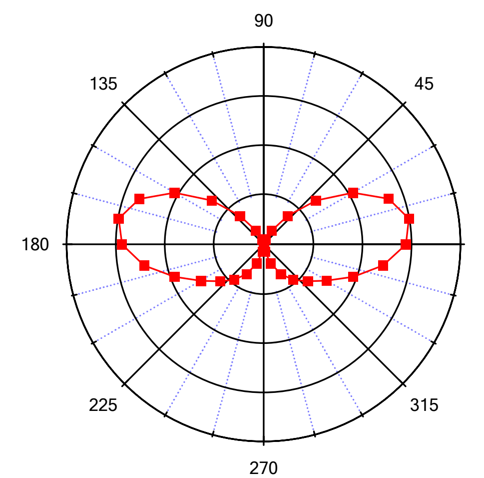
$\beta = 90^\circ$



$\beta = 135^\circ$



$\beta = 180^\circ$



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/λ 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)

Acknowledgements

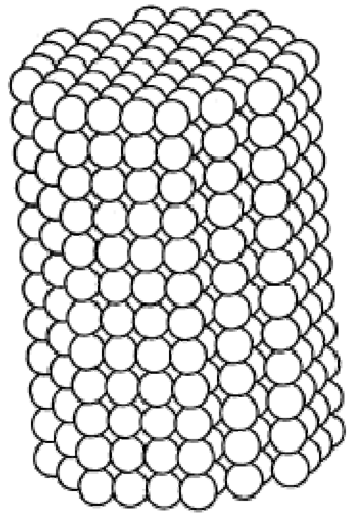
- Dr. Qihua Xiong, Dr. Gugang Chen, Mr. Jian Wu (Physics, Penn State)
- Prof. Doug Werner, Mr. Mike Pellen (EE, Penn State)
- Prof. George Schatz, Dr. Kevin Shuford*
- Support from NSF-NIRT Program (L. Hesse, DMR)

*now at Oak Ridge Nat'l Labs

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 λ
- Specification of the dipole array:
  - Geometry
  - Effective dipole polarizabilities:



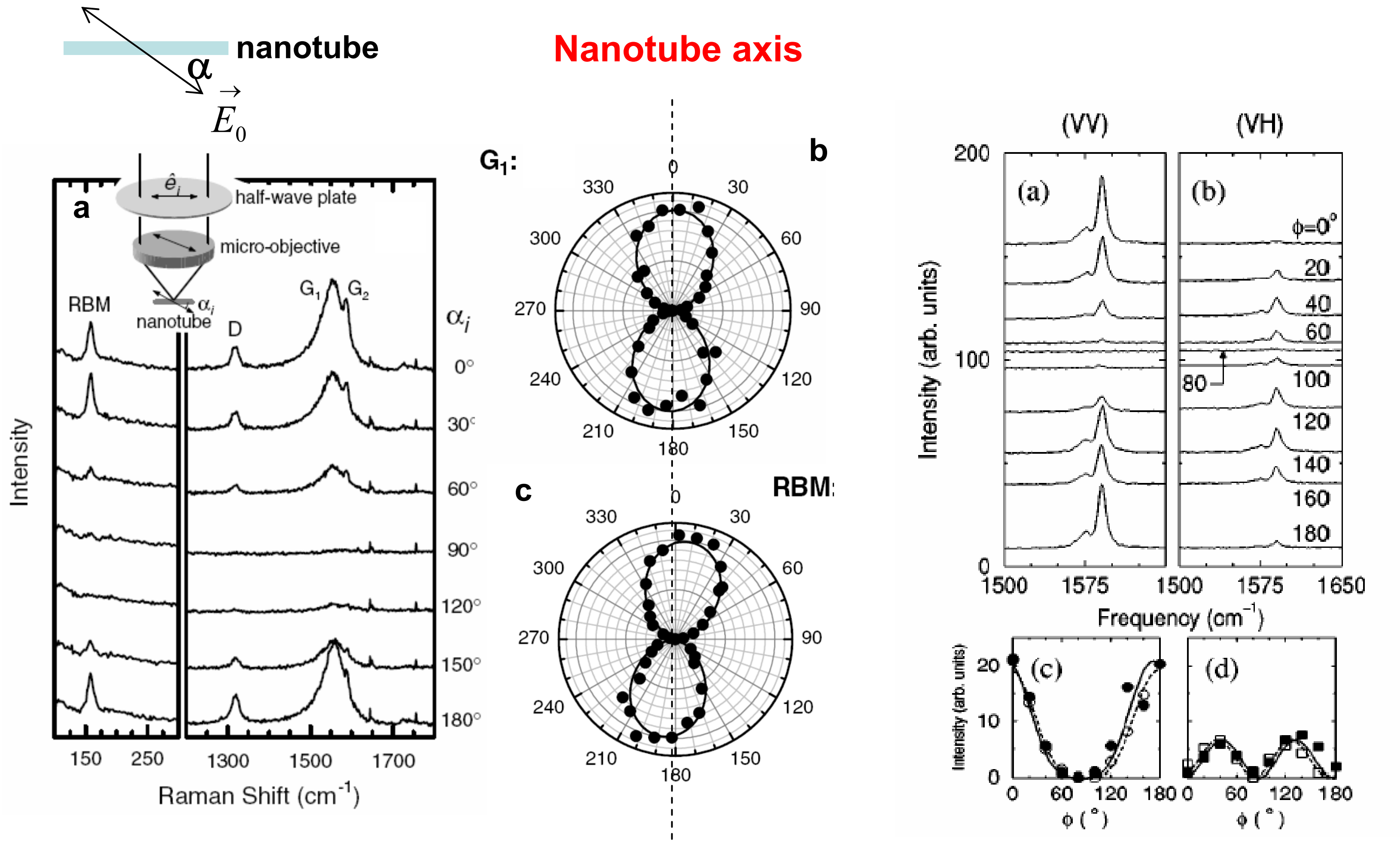
Representation of a "rod" of aspect ratio=1.5

$$\alpha^{\mathrm{LDR}} \approx \frac{\alpha^{CM}}{1 + (\alpha^{CM}/d^3)[(b_1 + m^2 b_2 + m^2 b_3 S)(kd)^2 - (2/3)i(kd)^3]}$$

Where, $\alpha_j^{\mathrm{CM}} = \frac{3d^3}{4\pi}\frac{\epsilon_j - 1}{\epsilon_j + 2}$ is Clausius-Mossotti polarizabilities, b_1, b_2, and b_3 are constants, $S = \sum_{j=1}^{3}(\hat{a}_j \hat{e}_j)^2$

B. T. Draine and P. J. Flatau, J. Opt. Soc. Am. A, 11 (4), 1491, 1994.

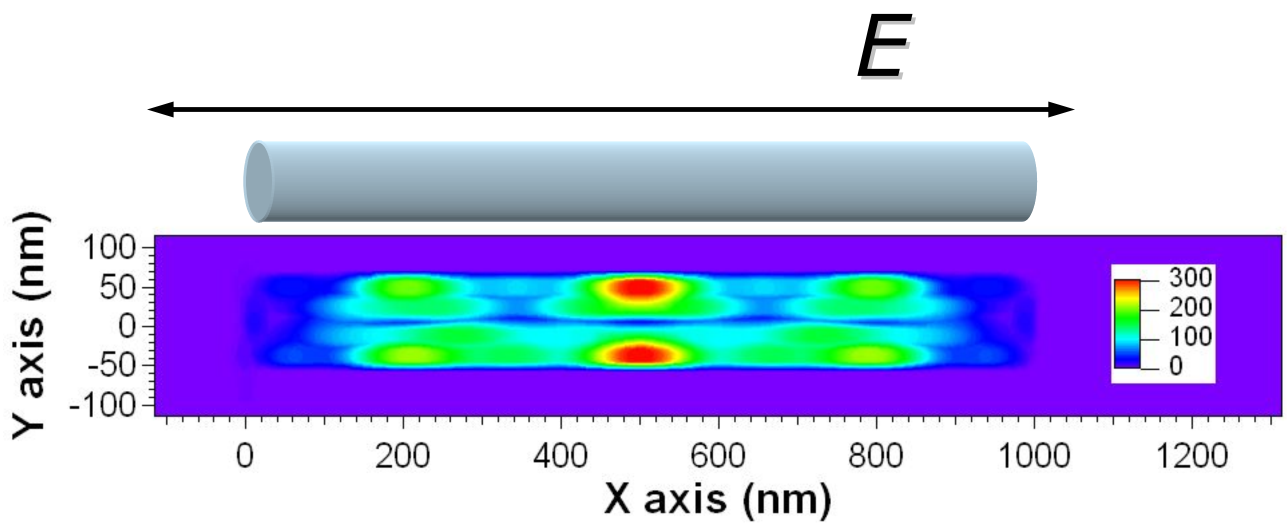
Antenna Effect in Nanotubes

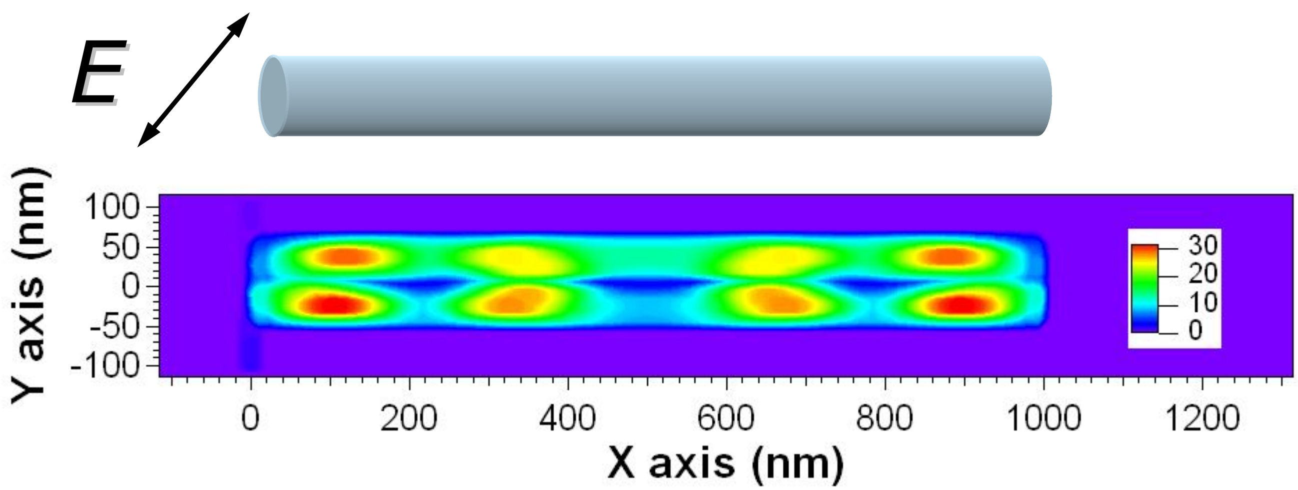


Duesberg, G.S., et al., Phys. Rev. Lett., **85,** 5436, 2000.

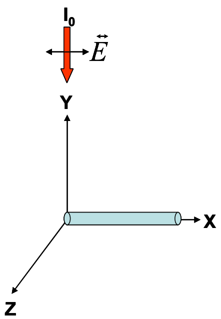
Jorio, A., … and Dresselhaus, M.S., Phys. Rev. B, **65,** 121402, 2002

Finite Length Effects (DDA)
(d=100nm, L=1μm, λ_{light}=488nm)

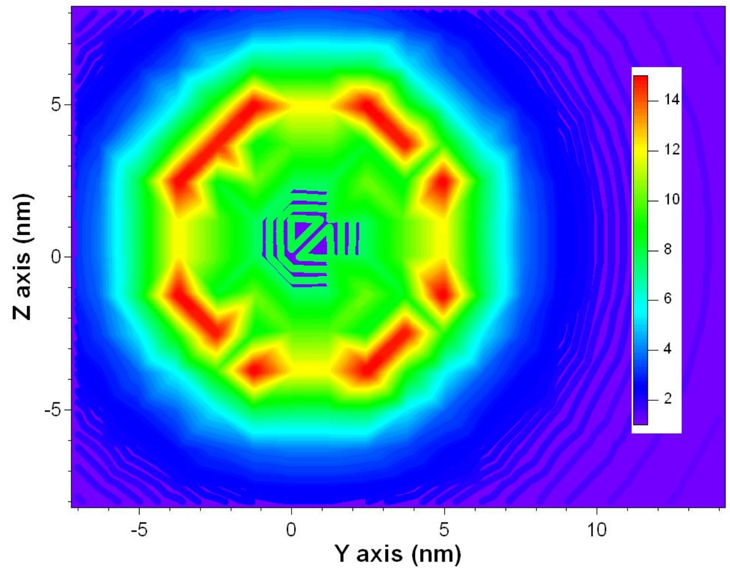


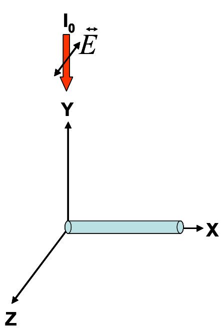


Electric Field of GaP Cylinder
(Diameter=10nm, Aspect ratio=10, λ_{light}=488nm)

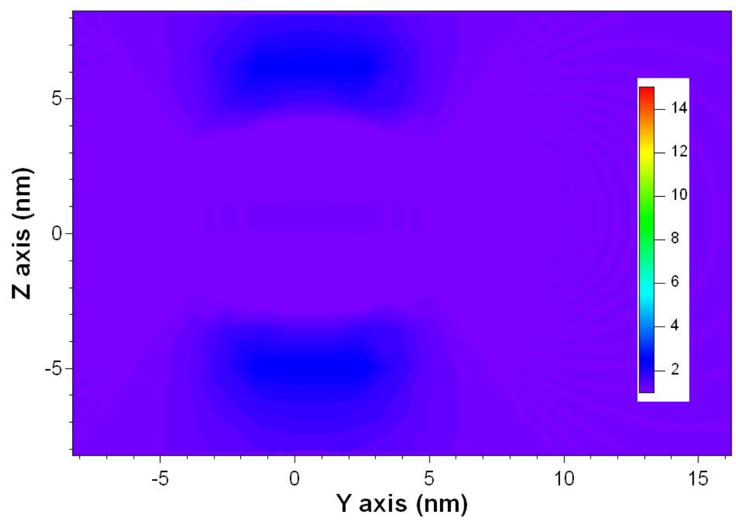


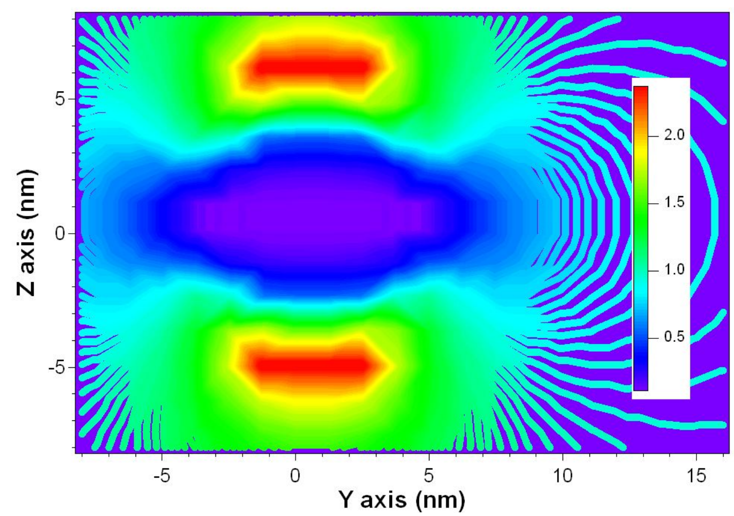
Parallel



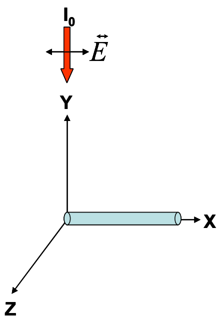


Perpendicular

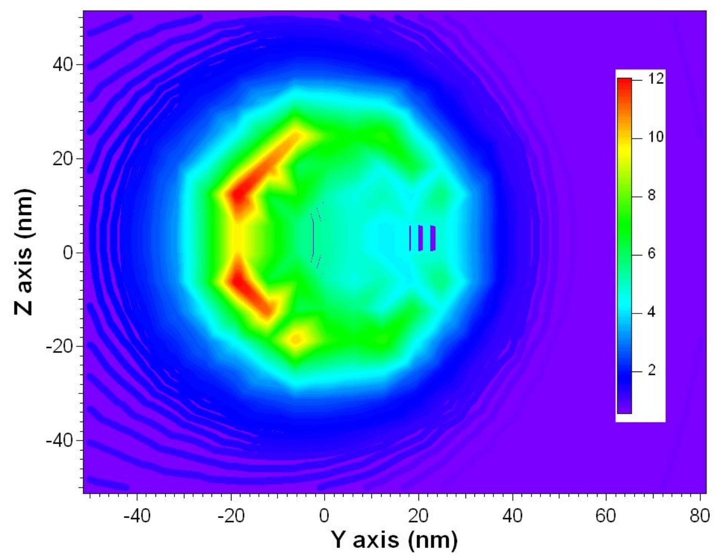


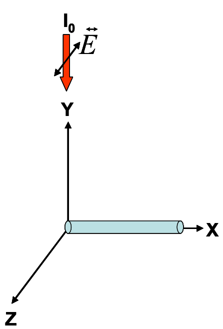


Electric Field of GaP Cylinder
(Diameter=50nm, Aspect ratio=10, λ_{light}=488nm)

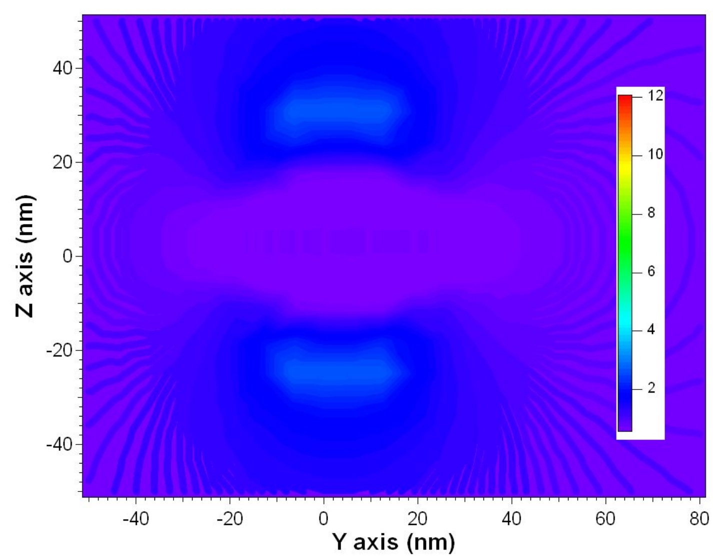


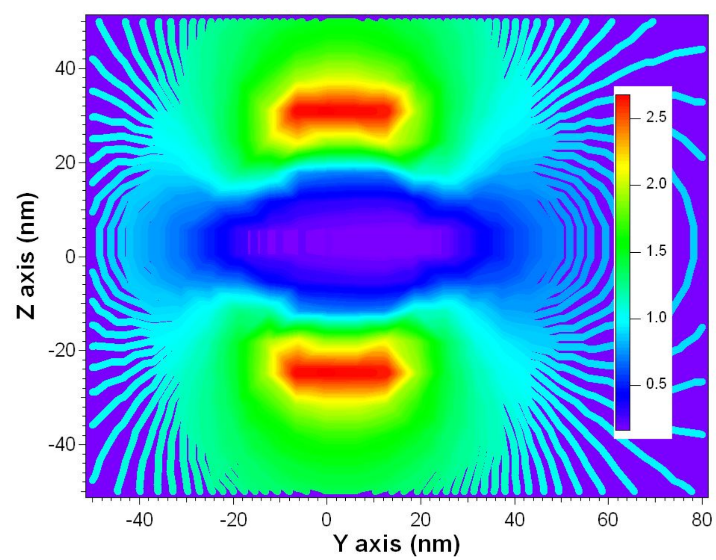
Parallel



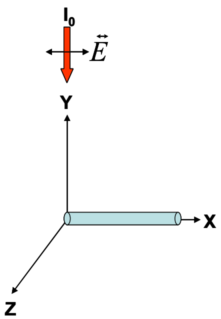


Perpendicular

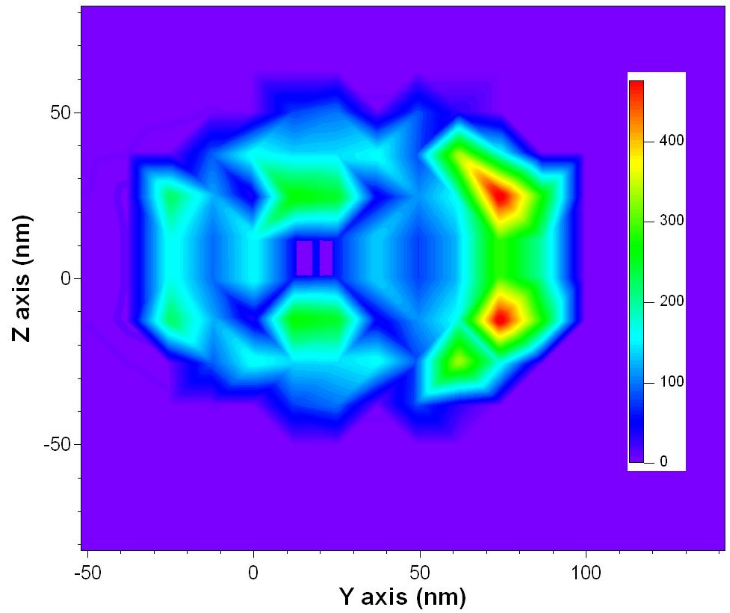


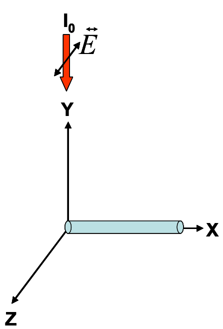


Electric Field of GaP Cylinder
(Diameter=100nm, Aspect ratio=10, λ_{light}=488nm)



Parallel





Perpendicular