RF/Microwave Properties of Nanotubes and Nanowires

LABORATORY DIRECTED RESEARCH & DEVELOPMENT

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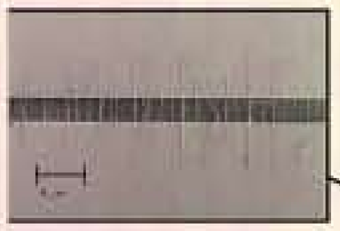
Problem

- Nanowires and nanotubes are expected to have novel electrodynamic properties relevant to:
  - basic nanomaterial physics
  - high-speed / high-frequency electronics and sensor applications
- Limited knowledge of nanostructure microwave electrodynamics exists
- Objective: measure the microwave electrodynamic properties of nanostructures, particularly the frequency dependence of the conductivity
- The experimental challenges were dictated by the scattering nature of the experiment and the physical scale of the nanostructures
  - Addressing nanostructures with microwave equipment
  - Small interaction cross section → small microwave signal
  - Separation of coupling from intrinsic response
  - Obtaining physical parameters from scattering data
- Required a novel microwave waveguide spectroscopy technique

Approach



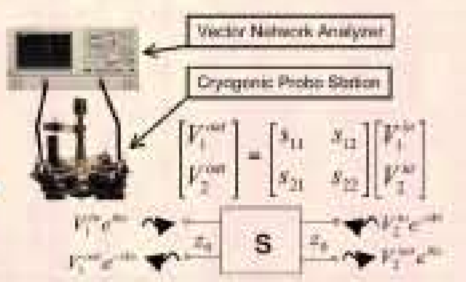
Nanostructure Assembly

- AC dielectrophoretic assembly of ~ parallel nanostructure arrays
- Arrays → Interaction length (signal)
- Coplanar Waveguide (CPW) Structure → Field Confinement

Silicon nanowire ACDEP assembly on CPW

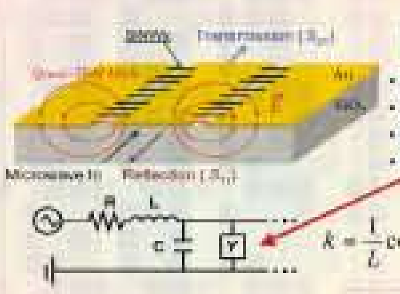
S Parameter Measurement

- 295 K in atmosphere
- 4 K to 295 K (10^{-6} Torr)
- 0.1 to 50 GHz
- "S parameters" (Voltage scattering coefficients)
- Highly accurate calibration technique developed



$$\begin{bmatrix} V_1^{out} \\ V_2^{out} \end{bmatrix} = \begin{bmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{bmatrix} \begin{bmatrix} V_1^{in} \\ V_2^{in} \end{bmatrix}$$

Results



Nanostructure Array Admittance

- SiNWs shunt signal to ground gaps
- CPW Prop. Const. k from S parameters
- Measure with SiNWs and without (ctrl)
- Array admittance Y from change in k

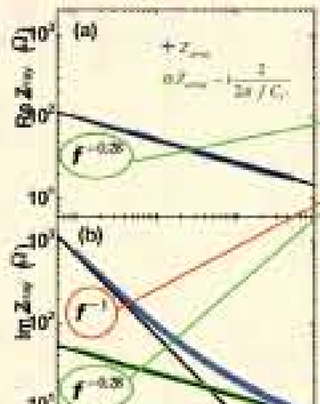
$$k = \frac{1}{L}\cos^{-1}\left(\frac{1 - DetS}{2S_{21}}\right) \qquad Y = -i\omega C\left[\frac{k_{SiNW}^2}{k_{ctrl}^2} - 1\right]$$

Silicon Nanowires

- VLS growth (Penn State[1])
- Primarily single crystal or bi-crystalline
- Native oxide layer (SiO_x)
- n-type (phosphorus)
- p-type (boron)
- undoped (no intentional doping)
- R_{DC} 1-2 orders higher than expected (bulk)
- ACDEP → Arrays ~ 10^4 SiNWs

[1] Y. Wang et al., Nano Lett. 5, 2139 (2005).

Capacitive Coupling and Sublinear Power-Law Conductance



Impedance of ~10^4 n-type SiNW array

- Array Impedance: $Z = Y^{-1}$
- Low frequency Z → capacitive coupling

$$Z_{array} = \frac{1}{Y_{array}} = \frac{1}{G_{array}} + i\frac{2}{2\pi f C_c}$$

- Result is sublinear array conductance

$$G \sim f^{0.26}$$

- Kramers-Kronig Relation satisfied

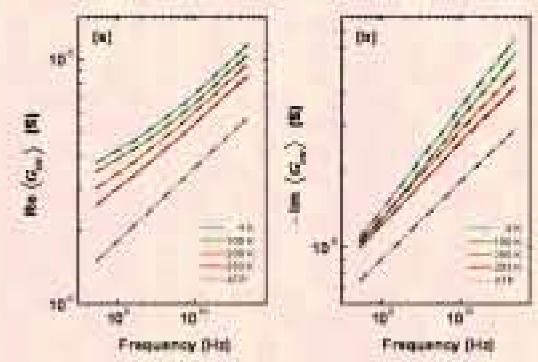
$$\frac{\operatorname{Im} G}{\operatorname{Re} G} = -\tan\left(\frac{s\pi}{2}\right)$$

→ Data fit with capacitive coupling and power-law frequency dependent $G(f)$:

$$G_{array}(f) = n_{NW}\langle G_{NW}(f)\rangle$$

$$\langle G_{NW}(f)\rangle = G_0 + A\left[\csc\left(\frac{s\pi}{2}\right) - i\sec\left(\frac{s\pi}{2}\right)\right]f^s$$

Typical SiNW Conductance Spectra



Real (a) and imaginary (b) parts of the average nanowire conductance for an array of ~10^4 n-type SiNWs in vacuum at 4 K, 100 K, 200 K, and 293 K and in atmosphere at 293 K. The dashed black lines are results of fitting the data with the sublinear conductance model. Similar results were obtained for p-type SiNWs and for undoped SiNWs in atmosphere.

- Temperature dependence consistent with bulk silicon
- Sublinear frequency dependence not consistent with bulk
  - → typical of disordered conductors ("universal" behavior)
  - → specific to nanowire morphology
- For 11 to > 50,000 SiNWs, $0.25 < s < 0.45$ → microscopic disorder
- Exponent nearly temperature independent → Not thermally activated
  - → Possibly topological disorder
- Large surface effect (ATP) suggests disorder source: SiOx charges

Surface Charge Modeling

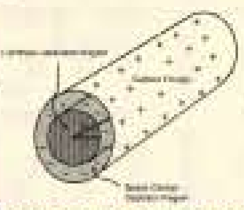
Depletion $\frac{\Delta N}{N_B} = \frac{2\pi r_0 N_S}{\pi r_0^2 N_B} = \frac{2N_S}{r_0 N_B} \equiv \gamma$

- S = surface
- B = bulk

$N = (1-\gamma)N_B$

Resistivity $\frac{\rho}{\rho_B} = \frac{\pi r^2}{\pi r_0^2} = \frac{1}{1-\gamma}$

Space Charge $n_{space} = n_s = 2\pi r_0 N_S$



Homogeneous Distribution

K. I. Seo et al., Electrochem. and Sol. St. Lett. 9 (2006)

(existing model)

- Space charge potential screened by symmetry
- Insufficient to account for resistivity
- Frequency independent

Disordered Distribution

- Disordered coulomb (space charge) potential scattering
  - → accounts for anomalously high DC resistivity
  - → carriers confined to distribution of local paths → $G(f)$

(our model)

Local Conductivity (Confined)

$$\sigma_i(\omega) = \frac{ne^2\tau_0}{m^*}\frac{1}{1 + \frac{i}{\omega\tau_i}} = -i\frac{ne^2\tau_0}{m^*}\frac{\omega\tau_i}{1 - i\omega\tau_i}$$

Ansatz Distribution

$$\eta(\tau_i) = \left[C\delta(\infty) + \frac{B}{\pi}\frac{1}{\tau_i^{1+s}}\right]$$

Nanowire Conductivity

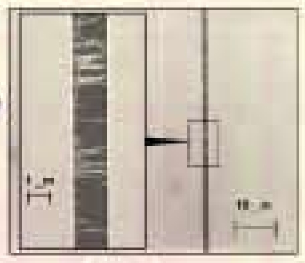
$$\sigma_{NW}(\omega) = -i\frac{ne^2\tau_0}{m^*}\int_0^\infty \eta(\tau)\frac{\omega\tau}{1 - i\omega\tau}d\tau$$

$$\sigma_{NW}(\omega) = \frac{ne^2\tau_0}{m^*}\left[C + \frac{B}{2}\left[\csc\left(\frac{\pi s}{2}\right) - i\sec\left(\frac{\pi s}{2}\right)\right]\omega^s\right]$$

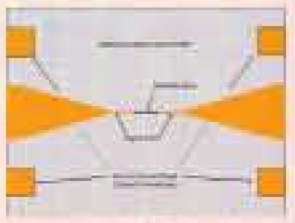
Disordered surface charge explains high DC resistivity *and* frequency response

Current Work

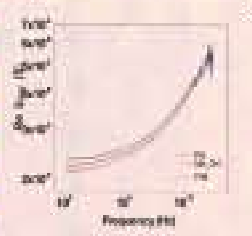
- Single wall carbon nanotube arrays measured
  - Sublinear conductance with $s \sim 0.8$
  - Exponent also temperature independent
  - DC conductivity chemically sensitive (NH_3)
  - AC conductivity not chemically sensitive
- Other nanowire efforts ongoing
  - ZnO (with J. Hsu and D. Scrymgeour)
  - InP and InAs (with J. Cederberg)
- Contact and surface effect investigations
- Individual and gated nanostructures



SWNT Array



Next generation CPW-to-microstrip test structure developed



Admittance of SWNT array exposed to NH_3 vapor

Significance

- Novel nanostructure microwave conductance spectroscopy method
  - ACDEP technique adapted to form ~ parallel nanostructure arrays
  - Highly accurate all temperature calibration scheme developed
  - Scattering data interpreted in terms of nanostructure properties
  - First direct microwave measurements of SWNTs or nanowires
  - First cryogenic microwave measurements of any nanowire or nanotube
- SiNWs and CNTs exhibit sublinear power-law frequency-dep. conductance typical of systems with disordered distribution of local conductivities
  - extension of macroscopic universality property to the nanoscale
  - may provide insight into the origins of the macroscopic phenomena
- The microwave transport is determined by the nanoscale morphology
  - Topological disorder dominates the transport due to the extremely small transverse dimensions of the nanostructures
- Significant to nanophysics and high-speed / high-frequency applications
  - Inherent mesoscopic effect
  - Indicates degree and form of some morphological effects that must be considered when designing nanostructure devices
  - Identifies directions for applications research (e.g. surface passivation)

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