16th SPIE Int'l Symposium on Smart Structures and Materials

Nano-Bio Quantum Technology for Device Specific Materials

Sang H. Choi

Advanced Materials and Processing Branch
NASA Langley Research Center

March 9-12, 2009

POC: 757-864-1408, Sang.H.Choi@NASA.GOV
Areas to be discussed

- Thermoelectric Materials

- Smart Optical Materials
  - Quantum Apertures
  - Micro Spectrometers
  - Light Control Ferroelectric Materials

- Ferritin Molecules
  - Biotemplates for Nanoparticles
  - Bionanobattery
ADVANCED THERMOELECTRIC MATERIAL DEVELOPMENT

Twin Crystal with Stacking Defect: Better Material Design than Superlattice

SiGe

STEM Image of Au Voigen

Material Prepared

BiTe

Home-grown Voigen

High Performance Semiconductor

Bi$_2$Te$_3$ Nanocrystals

Metallic Nanoshell:

Electrical conductor

Phonon scatterer

Produced @ NASA LaRC

Si$_{1-y}$Ge$_y$

Lattice-matched condition

Bi$_2$Te$_3$ Nanocrystals

40 – 60 nm

Electrical conductor

Phonon scatterer
TE Performance Summary: Results & Projections

![Graph showing comparison of materials for TE Performance Summary]

- **Bi$_2$Te$_3$** (Estimated and Tested)
- **PbTe** (Estimated and Tested)
- **SiGe** (Estimated and Tested)

* Need Thermal Conductivity Measurement / Validation
# ATE Device for Solar Energy Conversion

**SiGe Layer at TH**

**PbTe Layer at TM**

**Bi$_2$Te$_3$ Layer at TL**

### Energy Input

<table>
<thead>
<tr>
<th>Layer</th>
<th>Energy Input</th>
<th>Energy Out</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Layer (Hi T)</td>
<td>1Q</td>
<td>0.7Q</td>
<td>30%</td>
</tr>
<tr>
<td>2nd Layer (Med T)</td>
<td>0.9Q</td>
<td>0.8Q</td>
<td>30%</td>
</tr>
<tr>
<td>3rd Layer (Low T)</td>
<td>0.81Q</td>
<td>0.64Q</td>
<td>30%</td>
</tr>
</tbody>
</table>

### Harvested Energy

<table>
<thead>
<tr>
<th>Layer</th>
<th>Energy Input</th>
<th>Energy Out</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Layer (Hi T)</td>
<td>0.3Q</td>
<td>0.21Q</td>
<td>30%</td>
</tr>
<tr>
<td>2nd Layer (Med T)</td>
<td>0.3Q</td>
<td>0.147Q</td>
<td>30%</td>
</tr>
</tbody>
</table>

### Waste Energy

<table>
<thead>
<tr>
<th>Layer</th>
<th>Energy Input</th>
<th>Energy Out</th>
<th>Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Layer (Hi T)</td>
<td>0.3Q</td>
<td>0.21Q</td>
<td>30%</td>
</tr>
<tr>
<td>2nd Layer (Med T)</td>
<td>0.3Q</td>
<td>0.147Q</td>
<td>30%</td>
</tr>
</tbody>
</table>

### Power Output

<table>
<thead>
<tr>
<th>TE Tandem System</th>
<th>TE FoM ≥ 1.5</th>
<th>TE FoM ≥ 3.5</th>
<th>TE FoM ≥ 4.5</th>
<th>Solar Cells</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loaded Energy, Q</td>
<td>η</td>
<td>Loaded Energy, Q</td>
<td>η</td>
<td>Loaded Energy, Q</td>
</tr>
<tr>
<td>1st Layer (Hi T)</td>
<td>1Q in</td>
<td>10%</td>
<td>1Q in</td>
<td>20%</td>
</tr>
<tr>
<td>2nd Layer (Med T)</td>
<td>0.9Q</td>
<td>0.8Q</td>
<td>20%</td>
<td>0.7Q</td>
</tr>
<tr>
<td>3rd Layer (Low T)</td>
<td>0.81Q</td>
<td>0.64Q</td>
<td>20%</td>
<td>0.49Q</td>
</tr>
<tr>
<td>Cascade Efficiency</td>
<td>0.271Q</td>
<td>27%</td>
<td>0.488Q</td>
<td>48%</td>
</tr>
</tbody>
</table>

### Efficiency

- TH > TM > TL

**Concentrated Solar Energy**

**Output Power**

**Removed Heat**
Si-Ge: Twin-Lattice Structure
Symmetry Breaking to 60:40

A37 SiGe (220) Phi Scan

Original Crystal ~60%

Twin Crystal ~40%

Ψ: 32~40°
π: 0° 180° 360°
Two Single Crystalline Alignments

Rhombohedral Hybrid Band-Gap Engineering

SiGe \{220\}, Low Temperature

60 degree difference

SiGe \{220\}, High Temperature

Sapphire \{10-14\}
Asymmetric angles for XY mapping with Point X-ray source

2Theta-Omega Normal Scan

SiGe(111), 1.7 mega cps, 99.9999%
Sapphire (0 0 0 6)
Sapphire (0 0 0 12)
SiGe(113), (220)
51 cps
<0.0001%

(i) Majority single crystal map
(ii) Defect map: Primary twin crystal rotated by 60° on (111) plane

Sample cage created + shaped thermal shadow

8
Power Sources for Spacecrafts

Fly-wheel Power Storage

Canister-based Battery

Fuel Cells

Radioisotope Thermoelectric Generators (RTG)
Advanced Thermoelectric Power Generation and Transmission System

The proposed system encompasses three subsystems:

1. Radioisotope Power (RIP) subsystem
2. Advanced Thermoelectric Generator (ATEG) subsystem
3. Wireless Power Transmission (WPT) subsystem
Solar Thermoelectrics: HAA Model with Ellipsoidal Cross-Section
Distribution of Carriers and Ionization of Deep Levels

For wide band-gap materials:
- Transparent to visible lights
- Carriers in shallow dopant levels are mobile to conduction or valence band.
- Deep levels in crystal imperfection capture or emit mobile charges.
- Bandgap structure is ionized with the loss or capture of carriers.

For $|\mathbf{E}| = 0$,
- Mobile electrons distributed uniformly in media layer.
- Most of the deep levels are neutral in this state.

For $|\mathbf{E}| \gg 0$,
- Mobile carriers (electrons in the picture) are re-distributed
- Deep levels are ionized and form new color centers.
- Absorption coefficient and index of refraction are changed
**Hall Effect Measurement**

### As Grown ScN on Al₂O₃

<table>
<thead>
<tr>
<th>RESULTS</th>
<th>B = 0.51 [T]</th>
<th>D = 0.28 [um]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nᵥ = -5.7963E+20 [cm⁻³]</td>
<td>Nₛ = -1.6230E+16 [cm⁻²]</td>
<td></td>
</tr>
<tr>
<td>µ = 11.50203 [cm²/V·s]</td>
<td>Rh = -1.0767E-02 [m²/C]</td>
<td></td>
</tr>
<tr>
<td>ρ = 9.3631E-04 [Ω·cm]</td>
<td>α = 1.0638E+03 [1/Ω·cm]</td>
<td></td>
</tr>
<tr>
<td>delta_R = 1.9616E+02 [Ω]</td>
<td>alpha = 0.12167</td>
<td></td>
</tr>
</tbody>
</table>

- Nᵥ: Bulk concentration
- µ: Mobility
- ρ: Bulk resistivity
- delta_R: magnetoresistance

### Intrinsic GaN on Al₂O₃

<table>
<thead>
<tr>
<th>RESULTS</th>
<th>B = 0.51 [T]</th>
<th>D = 0.387 [um]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nᵥ = -6.6835E+16 [cm⁻³]</td>
<td>Nₛ = -2.6534E+12 [cm⁻²]</td>
<td></td>
</tr>
<tr>
<td>µ = 2.22096 [cm²/V·s]</td>
<td>Rh = -9.38652 [m²/C]</td>
<td></td>
</tr>
<tr>
<td>ρ = 5.287408 [Ω·cm]</td>
<td>α = 1.8913E-02 [1/Ω·cm]</td>
<td></td>
</tr>
<tr>
<td>delta_R = 1.5200E+04 [Ω]</td>
<td>alpha = 0.16324</td>
<td></td>
</tr>
</tbody>
</table>

- Nᵥ: Bulk concentration
- µ: Mobility
- ρ: Bulk resistivity
- delta_R: magnetoresistance

---

ScN grown on c-axis Sapphire (Al₂O₃) shows 10,000 times higher electron concentration than intrinsic GaN. This unintentional high-background- doping gives mobile charges in the media. With the applied electric field, the redistribution of mobile charges changes the index of refraction.
ScN film shows the change in the index of refraction with the applied electric field. The electric field was applied with a few mm gap. The required voltage can be reduced in the optimized structure.
Ga$_x$Sc$_{1-x}$N Alloy System

Bandgap Energy versus Scandium Concentration in Ga$_x$Sc$_{1-x}$N alloy system.

A thin-film of scandium-alloyed gallium nitride (Ga$_x$Sc$_{1-x}$N, x=0.47) developed on a quartz substrate shows both the spectral and refractive index shifts very clearly from 3.5 eV to higher photon energy.

Index of refraction in the region below optical absorption

Extinction coefficient data shows a similar response as refractive index in the left, very clearly from 3.5 eV to higher photon energy.
Adaptive Optical Components

- The goal of Adaptive Optical Components: Adding a programmability to the conventional optical components, including lens, grating, apertures, filters and reflectors. The same optical component can be programmed for different wavelengths and polarizations.
- It can reduce the total weight of satellites and increase the working range and sensitivity of device with versatility.
**Plasmon Enhanced Transmission**

- Metal surface has the collective movement of the electrons at the surface; it is called the surface plasmon, propagating on the surface only.

- The skin-depth of a good conductive metal is very shallow; a hundred nanometer metal film is enough to block the light penetration.

- The transmission of the photons through a hole smaller than 1/4 is controlled by the surface plasmons in the hole.

- The incident light generates the back surface plasmon. Surface plasmon propagates through the surface of the hole. On the front side, the surface plasmon radiates the light again.

- Other experiments indicate there is no enhanced transmission of a long wavelength light through tiny holes in Ge, where there is no plasmon. Only a good conductor surface has plasmon.
**Nano Apertures**

- **White Light**
- **Field Generator**
- **Pin Holes**

\[ d \leq \frac{\lambda}{4} \]
Microscopic Spectral Distribution From Individual Quantum Aperture with 200nm Diameter

Transmitted Light

Center Line A: Strong Blue

Sum of Area between B and C: Close to White Light with Blue

Boundary Line B or C: Dark Red
Selected Light Transmission

Laser (532nm) + Front side illumination

Double Depth (0.8µm)
\( \phi \sim 150\text{nm} \)

Laser fringes

\( \phi = 100\text{nm} \)

Green light passes through.

Laser (630nm) backside illumination only

No Passing Red Light

No Passing Laser fringes

Green light passes through.
Dual Sensing Capable Germ or Toxic Chemical (GTC) Sensor using Quantum Aperture Array with Surface Plasmon Polariton (SPP)

Laser-induced Fluorescence (LIF): Spectral Signature of GTC element

Germ or Toxic Chemical (GTC)
Object-dependent Transmitted Light Pattern

Light Injection (Laser or White Light)

Metallic Film with Quantum Aperture Array

NOTE:
- Surface Plasmon Polariton (SPP)
- Electron
- Light Transmission by undisturbed SPP
- Light Transmission by disturbed SPP
Micro Spectrometer (μ-SM) Applications

Medical Application for Neurosensing

- Tiny form factor < 1 mm
- Flexible pin
- Sensor fusion capable
- Power & telemetry
- Redundancy feature

For Space Exploration

Leveraging Factors

Space:
- μ-SM imbedded rover tires
- μ-SM imbedded Astronaut's shoes
- μ-SM imbedded canes or darts
- Hyperspectral imaging

Aeronautics:
- Engine combustion monitoring
- Fuel leak detection
- Hyperspectral Lidar imaging

Can be used in Tumble-weed type planetary surface explorer
Sharpness of focal point P1 and PX with a green laser ($\lambda=532\text{nm}$)

10 mW Laser in 2mm diameter (0.3 W/cm$^2$) can have a focused power density $= 10^5$ Watt/cm$^2$

FOCAL POINT P1

- Photon Collection Time = 4ms
- FWHM = 620nm
- Min. ~ Min. = 1.54μm

FOCAL POINT PX

- Photon Collection Time = 6ms
- FWHM = 465nm
- (2μm before destructive interference height)

Photonic DART Technology
(Densely Accumulated Ray-point by micro-zone-plaTe)
Circular Grating: 100 rings, 750µm diameter
Aperture: 10 µm diameter

Green Laser: 532nm

Red Laser: 633nm

Green & Red Lasers: 532nm & 633nm

The human eye sees the yellow color, but the µ-spectrometer can distinguish the two lights, green and red.
μ-Spectrometer (μ-SM) Applications
Lunar & Mars Exploration

μ-SM Probes for Future Mars Lander

μ-SM imbedded Astronaut Shoes and Rover Tires

μ-SM imbedded Tumbleweed Rover
Aero-Space Application

Typical Mechanical Vibration: 0.1Hz ~ 100kHz
Beam scanner has to be faster than a few MHz!
We need Fast Solid State Optical Components!

Laser Communication

3D Measurement

Interference Fringe
Two Photon Excitation

POWER for UAV
Lithography and Etched Patterns

E-Beam Lithography

Beam Scanner Array

Single Beam Scanner

Beam Displacer
Light Control Device

Patterns made with E-Beam Lithography

All S.S. Beam Scanner Array

All-Solid-State Beam Scanner

Solid State Beam Displacer
Ferritin Protein

- Iron storage protein in biological mechanisms in human, animal, and even bacteria
- 24 subunits
- Contains up to ~4500 Fe$^{3+}$ atoms
- Stable and robust structure to withstand biologically extremes of high temperature (up to 80 °C) and pH variations (2.0-10.0)
- 2, 3, 4-fold symmetry channels for the transport of ions and molecules.
- Hydrophilic 3 fold (Fe$^{2+}$)/ Hydrophobic 4 fold
- Electron conduction through ferritin shell is possible.
- Core materials –
  - Iron (Fe), Cobalt (Co), Manganese (Mn), Nickel (Ni), Platinum (Pt), Semiconductors (CdS, CdSe) Magnetite-maghemite
  - Trimethylamine-N-oxide, etc.
Biomineralization & Reconstitution of Ferritin Core

\[ 4 \, M^{2+}_{(aq)} + O_2 \rightarrow 4 \, M(O)OH_{(s)} + 8 \, H^+ + 2 \, H_2O \]

M : Core materials ---- Fe (natural)
Co, Mn, Ni, Pt, As, P, V (successful)
CdS, CdSe (successful)
Magnetite-maghemite (ferrimagnetic)
Trimethylamine-N-oxide (superparamagnetic)
Chemically Reconstituted Ferritins

STEM image of Fe-cored ferritins

Fe-cored ferritins  Co-cored ferritins  Mn-cored ferritins

What about

- Distributed power storage?
- Flexible thin-film battery? - Designer’s dream!!
- Easy embodiment with power harvesting devices?
- Biocompatibility with in-vivo nanodevices?
- Light weight and high energy density?
- Chip scale power source?
  - Intelligent and autonomous operation

Why Bio-Nanobattery?

- Flexible Nanobattery Film
- Wearable Electronics (Philips)
- Red Blood Cell
- Bio-nanobattery patch installed in autonomous bio-nanorobot
**Bionanobattery Concept**

\[
Fe(OH)_3 + e^- \leftrightarrow Fe(OH)_2 + OH^- \quad E^\circ = -0.49V
\]

- \(Fe(OH)_3/Fe(OH)_2 \parallel CoOOH/Co(OH)_2\) \(E_{\text{cell}} = 0.66\) V
- \(Fe(OH)_3/Fe(OH)_2 \parallel \gamma\text{-MnOOH/Mn(OH)}_2\) \(E_{\text{cell}} = 0.20\) V
- \(Fe(OH)_3/Fe(OH)_2 \parallel NiOOH/Ni(OH)_2\) \(E_{\text{cell}} = 0.97\) V

Fe\(^{2+}\)-ferritin  \hspace{1cm} Co\(^{3+}\)-ferritin
### Theoretical Values of Bionanobattery

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>Cd</th>
<th>Fe</th>
<th>V</th>
<th>Hg</th>
<th>Mn</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anode</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.422</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>0.756</td>
<td>0.334</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>0.760</td>
<td>0.338</td>
<td>0.004</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg</td>
<td>1.344</td>
<td>0.922</td>
<td>0.588</td>
<td>0.584</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>0.956</td>
<td>0.534</td>
<td>0.200</td>
<td>0.196</td>
<td>(0.262)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>1.416</td>
<td>0.994</td>
<td>0.660</td>
<td>0.656</td>
<td>0.072</td>
<td>0.120</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>1.726</td>
<td>1.304</td>
<td>0.970</td>
<td>0.966</td>
<td>0.382</td>
<td>0.770</td>
<td>0.310</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Zn</th>
<th>Cd</th>
<th>Fe</th>
<th>V</th>
<th>Hg</th>
<th>Mn</th>
<th>Co</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cathode</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Zn\(^0/Zn^{2+}\): -1.246 V  
Cd\(^0/Cd^{2+}\): -0.824 V  
Fe\(^{2+}/Fe^{3+}\): -0.49 V  
V\(^{2+}/V^{3+}\): -0.486 V  
Hg\(^0/Hg^{2+}\): 0.098 V  
Mn\(^{2+}/Mn^{3+}\): -0.29 V  
Co\(^{2+}/Co^{3+}\): 0.17 V  
Ni\(^{2+}/Ni^{3+}\): 0.48 V  

(* Mn represents as \(\gamma\)-MnO\(_2\) inside Ferritin.)
Ni-Cored Ferritin

C1: NiOOH + H⁺ + e⁻ \rightarrow Ni(OH)₂

A1: Ni(OH)₂ \rightarrow NiOOH + H⁺ + e⁻

CV of physically adsorbed Ni-cored ferritin on Au electrode in 0.05 M phosphate buffer (pH 7.5 and pH 9.0) at the scan rate of 100 mV/s.

<table>
<thead>
<tr>
<th></th>
<th>Co</th>
<th>Mn</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>500 mV</td>
<td>480 mV</td>
<td>790 mV</td>
</tr>
</tbody>
</table>
Fe-Co Bionanobattery Cell – Wet Cell

Bionanobattery Demo Cell

Membrane

Fe$^{2+}$-Ferritin

Co$^{3+}$-Ferritin

0.46 V / Unit Cell
Fe-Co Bionanobattery Cell – Solid Electrodes

Thiolated Fe\(^{2+}\) ↔ thiolated Co\(^{3+}\)

0.25 V / Unit Cell
Electrode: 1”x1” gold films coated on both sides of a quartz slide
Total number of ferritin on each layer of 1” x 1” area: 4.48 x10^{12}
Total available electrons: 2 x 10^{16} per layer = 3.2 x 10^{-3} Coulomb
Charge Density per Electrode (2 x 10^5 layers): 640 Coulomb
Cell Charge Density (array of 10 electrodes): 6400 Coulomb
Operational Run-time: 6400 seconds when Fe^{2+}-Co^{3+} electrodes discharge 1 C/sec
If we connect 10 gold electrodes together, then
- Parallel connection: 0.79 V, 1 A (2844 mWh)
- Serial connection: 7.9 V, 100 mA
Conclusion

The areas discussed are still under development.

- Nano structured materials for TE applications
  - SiGe and Be-Te
  - Nano particles and nanoshells

- Quantum technology for optical devices
  - Quantum apertures
  - Smart optical materials
  - Micro spectrometer

- Bio-template oriented materials
  - Bionanobattery
  - Biofuel cells
  - Energetic materials