Sang H. Choi

Advanced Materials and Processing Branch
NASA Langley Research Center

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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

Si_{1-y}Ge_{y} Lattice-matched condition

Produced @ NASA LaRC

Bi_{2}Te_{3} Nanocrystals
40 – 60 nm

Metallic Nanoshell:
2 – 20 nm
Electrical conductor
Phonon scatterer

Hot Press / Low Pressure Material Process

Initial Concept

Material Prepared

STEM Image of Au Voigen

Home-grown Voigen

High Performance Semiconductor

Electrical conductor

BiTe

Electrical conductor
Phonon scatterer

2 – 20 nm

STEM Image of Au Voigen

SiGe

Lattice-matched condition

Produced @ NASA LaRC
**TE Performance Summary: Results & Projections**

![Graph depicting the performance of different materials (Bi\textsubscript{2}Te\textsubscript{3}, PbTe, and SiGe) as a function of temperature.](image)

- **Bi\textsubscript{2}Te\textsubscript{3}** (Estimated and Tested)
- **PbTe** (Estimated and Tested)
- **SiGe** (Estimated)

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

#### Energy Input and Output

<table>
<thead>
<tr>
<th>Layer System</th>
<th>Energy Input</th>
<th>1Q</th>
<th>0.7Q</th>
<th>0.49Q</th>
<th>0.343Q</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Layer SiGe</td>
<td>1Q in</td>
<td>1Q</td>
<td>0.9Q out</td>
<td>0.8Q out</td>
<td>0.7Q out</td>
</tr>
<tr>
<td>2nd Layer PbTe</td>
<td>0.9 in</td>
<td>0.8 in</td>
<td>0.64Q out</td>
<td>0.49Q out</td>
<td>0.343Q out</td>
</tr>
<tr>
<td>3rd Layer Be₂Te₃</td>
<td>0.81Q in</td>
<td>0.64Q in</td>
<td>0.512Q out</td>
<td>0.343Q out</td>
<td>0.343Q out</td>
</tr>
<tr>
<td>Cascade Efficiency</td>
<td>0.271Q in</td>
<td>0.488Q in</td>
<td>0.657Q out</td>
<td>65 %</td>
<td></td>
</tr>
</tbody>
</table>

#### TE Tandem System

<table>
<thead>
<tr>
<th>TE Tandem System</th>
<th>Loaded Energy, Q</th>
<th>η</th>
<th>Loaded Energy, Q</th>
<th>η</th>
<th>Loaded Energy, Q</th>
<th>η</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st Layer (Hi T)</td>
<td>1Q in</td>
<td>10 %</td>
<td>0.9Q out</td>
<td>0.8Q out</td>
<td>0.7Q out</td>
<td>30 %</td>
</tr>
<tr>
<td>2nd Layer (Med T)</td>
<td>0.9 in</td>
<td>10 %</td>
<td>0.8 in</td>
<td>0.64Q out</td>
<td>0.49Q out</td>
<td>30 %</td>
</tr>
<tr>
<td>3rd Layer (Low T)</td>
<td>0.81Q in</td>
<td>10 %</td>
<td>0.64Q in</td>
<td>0.512Q out</td>
<td>0.343Q out</td>
<td>30 %</td>
</tr>
<tr>
<td>Cascade Efficiency</td>
<td>0.271Q in</td>
<td>27 %</td>
<td>0.488Q in</td>
<td>48 %</td>
<td>0.657Q in</td>
<td>65 %</td>
</tr>
</tbody>
</table>

#### TE FoM

- TE FoM ≥ 1.5, η = 10%
- TE FoM ≥ 3.5, η = 20%
- TE FoM ≥ 4.5, η = 30%

#### Harvested Energy

- SiGe Layer at TH
- PbTe Layer at TM
- Bi₂Te₃ Layer at TL

#### System Efficiency

- 1Q in
- 0.9Q out
- 0.729Q out

#### Membrane PV

- 30 % (?) for membrane PV
Si-Ge: Twin-Lattice Structure

Symmetry Breaking to 60:40

Original Crystal ~60%

Twin Crystal ~40%

\( (2,2,0) \)

\( (2,-2,0) \)

\( \Psi: 32\sim40^\circ \)

\( \pi: 0^\circ \) \hspace{1cm} 180^\circ \) \hspace{1cm} 360^\circ \)
Rhombohedral Hybrid Band-Gap Engineering

Two Single Crystalline Alignments

SiGe \{220\}, Low Temperature

Sapphire \{10-14\}

60 degree difference

SiGe \{220\}, High Temperature
Wafer Mapping 1. (99.9999% single crystal)

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

Point X-ray source for mapping

SiGe(440) Untilted Asymmetric Phi-Scan
Power Sources for Spacecrafts

- Fly-wheel Power Storage
- Canister-based Battery
- Fuel Cells
- Radioisotope Thermoelectric Generators (RTG)
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
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 $|\vec{E}| = 0$,

- Mobile electrons distributed uniformly in media layer.
- Most of the deep levels are neutral in this state.

For $|\vec{E}| >> 0$,

- 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 Al$_2$O$_3$

- **RESULTS**
  - **B** - 0.51 [T]
  - **D** - 0.367 [µm]

  - **Conductivity:** $x10^5$
    - **$N_b$** = -5.7963E+10 [cm$^{-3}$]
    - **$\mu$** = 1.150208 [cm$^2$/V·s]
    - **$\rho$** = 9.3631E-08 [Ω·cm]
    - **$\delta_R$** = 1.9616E-02 [Ω]

  - **$N_s$** = -1.6326E+16 [cm$^{-3}$]
  - **$R_h$** = -1.0768E-02 [m$^2$/C]
  - **$\sigma$** = 1.0680E+03 [S/cm]
  - **$\alpha$** = 0.12167

  - **Nb**: Bulk concentration
  - **$\mu$**: Mobility
  - **$\rho$**: Bulk resistivity
  - **$\delta_R$**: magnetoresistance

Intrinsic GaN on Al$_2$O$_3$

- **RESULTS**
  - **B** = 0.51 [T]
  - **D** = 0.367 [µm]

  - **Conductivity:** $x10^5$
    - **$N_b$** = -6.838E+16 [cm$^{-3}$]
    - **$\mu$** = 2.2269E-06 [cm$^2$/V·s]
    - **$\rho$** = 52.8758 [Ω·cm]
    - **$\delta_R$** = 1.5200E-04 [Ω]

  - **$N_s$** = -2.6534E+12 [cm$^{-3}$]
  - **$R_h$** = -93.3952 [m$^2$/C]
  - **$\sigma$** = 1.8913E-02 [S/cm]
  - **$\alpha$** = 0.16324

  - **Nb**: Bulk concentration
  - **$\mu$**: Mobility
  - **$\rho$**: Bulk resistivity
  - **$\delta_R$**: magnetoresistance

ScN grown on c-axis Sapphire (Al$_2$O$_3$) 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.
Bandgap Energy versus Scandum Concentration in Ga$_x$Sc$_{1-x}$N alloy system.

Index of refraction in the region below optical absorption

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.

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

Pin Holes

Field Generator

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

- Center Line A: Strong Blue
- Boundary Line B or C: Dark Red
- Sum of Area between B and C: Close to White Light with Blue

Transmitted Light
**Selected Light Transmission**

Laser (532nm) + Front side illumination

Laser (630nm) backside illumination only

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

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

Laser fringes

Green light passes through.

No Passing Red Light
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

Metallic Film with Quantum Aperture Array

Quartz Substrate

Light Injection (Laser or White Light)

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**
- Medical Sensors:
  - 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
10 mW Laser in 2mm diameter (0.3 W/cm²) can have a focused power density = $10^5$ Watt/cm²

FOCAL POINT P1

Photon Collection Time = 4ms

FWHM=620nm

Min. ~ Min. = 1.54μm

Distance (um)

FOCAL POINT PX

Photon Collection Time = 6ms

FWHM=465nm

Min. ~ Min. = 1.25μm

Distance (um)

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

Mars Science Lab
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
POWER for UAV

3D Measurement
Interference Fringe
Two Photon Excitation

2D Measurement
Lithography and Etched Patterns

E-Beam Lithography

Single Beam Scanner

Beam Scanner Array

Beam Displacer
Light Control Device

Patterns made with E-Beam Lithography

All-Solid-State Beam Scanner

All S.S. Beam Scanner Array

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.

Protein subunit
Core ~ 8 nm

~ 12 nm
Biomineralization & Reconstitution of Ferritin Core

M$^{2+}$, Oxidant

Apoferititin  \[ \rightarrow \]  Ferritin reconstituted with M$^{3+}$

\[ 4 \text{M}^{2+}_{(aq)} + \text{O}_2 \rightarrow 4 \text{M(O)OH}(s) + 8 \text{H}^+ + 2 \text{H}_2\text{O} \]

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

Why Bio-Nanobattery?

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
Bionanobattery Concept

Fe^{2+}-ferritin

Co^{3+}-ferritin

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

\begin{align*}
\text{Fe(OH)}_3/\text{Fe(OH)}_2 & \parallel \text{CoOOH}/\text{Co(OH)}_2 \quad E_{\text{cell}} = 0.66 \text{ V} \\
\text{Fe(OH)}_3/\text{Fe(OH)}_2 & \parallel \gamma-\text{MnOOH}/\text{Mn(OH)}_2 \quad E_{\text{cell}} = 0.20 \text{ V} \\
\text{Fe(OH)}_3/\text{Fe(OH)}_2 & \parallel \text{NiOOH}/\text{Ni(OH)}_2 \quad E_{\text{cell}} = 0.97 \text{ V}
\end{align*}
### 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>
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<td><strong>Anode</strong></td>
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|          |     |     |     |     |     |     |     |     |
| **Cathode**| Zn0/Zn2+: -1.246 V  |
| Cd0/Cd2+: -0.824 V  |
| Fe2+/Fe3+: -0.49 V  |
| V2+/V3+: -0.486 V  |
| Hg0/Hg2+: 0.098 V  |
| Mn2+/Mn3+: -0.29 V  |
| Co2+/Co3+: 0.17 V  |
| Ni2+/Ni3+: 0.48 V  |

(*) Mn represents as γ-MnO₂ inside Ferritin.
Ni-Cored Ferritin

C1: NiOOH + H⁺ + e⁻ → Ni(OH)₂

A1: Ni(OH)₂ → 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>
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</thead>
<tbody>
<tr>
<td>Fe</td>
<td>500 mV</td>
<td>480 mV</td>
<td>790 mV</td>
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</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$^{2+}$ $\rightarrow$ thiolated Co$^{3+}$

0.25 V / Unit Cell
Estimation of Electrical Output

- 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: $4.48 \times 10^{12}$
- Total available electrons: $2 \times 10^{16}$ per layer = $3.2 \times 10^{-3}$ 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