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

Nano-Bio Quantum Technology for Device Specific Materials

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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

TETE MODULE

Initial Concept

Material Prepared

Si$_{1-y}$Ge$_y$ Lattice-matched condition

Produced @ NASA LaRC

Ba$_2$Te$_3$ Nanocrystals
40 – 60 nm

Metallic Nanoshell:
2 – 20 nm
Electrical conductor
Phonon scatterer

Hot Press / Low Pressure Material Process

SiGe

BiTe

High Performance Semiconductor

Home-grown Voigen

STEM Image of Au Voigen

20 nm
TE Performance Summary: Results & Projections

![Graph showing TE performance summary with various materials and temperatures.](image-url)

*Fig. 4.0

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**Tested**

- Bi$_2$Te$_3$
- PbTe

**Estimated**

- BiTe
- PbTe
- SiGe

*Need Thermal Conductivity Measurement / Validation*

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Temperature, °C

0 200 400 600 800 1000

Figure of Merit, ZT

0.0 1.0 2.0 3.0 4.0

300K 1000K

Bi$_2$Te$_3$  PbTe  SiGe

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NASA
### ATE Device for Solar Energy Conversion

#### Energy Conversion Process

<table>
<thead>
<tr>
<th>Layer</th>
<th>Input Energy</th>
<th>1st Layer</th>
<th>2nd Layer</th>
<th>3rd Layer</th>
<th>Total Harvested Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiGe System</td>
<td>1Q</td>
<td>0.3Q</td>
<td>0.21Q</td>
<td>0.147Q</td>
<td></td>
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<tr>
<td>PbTe Layer</td>
<td>0.7Q</td>
<td>0.49Q</td>
<td>0.343Q</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Be₂Te₃ Layer</td>
<td>0.49Q</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Conversion Efficiency

<table>
<thead>
<tr>
<th>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>TE Tandem System</td>
<td>Loaded</td>
<td>Loaded</td>
<td>Loaded</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Energy, Q</td>
<td>Energy, Q</td>
<td>Energy, Q</td>
<td></td>
</tr>
<tr>
<td>1st Layer (Hi T)</td>
<td>1Q in</td>
<td>1Q in</td>
<td>1Q in</td>
<td>30 %</td>
</tr>
<tr>
<td></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>0.8 in</td>
<td>0.7 in</td>
<td>30 %</td>
</tr>
<tr>
<td></td>
<td>0.81Q out</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>0.64Q in</td>
<td>0.49Q in</td>
<td>30 %</td>
</tr>
<tr>
<td></td>
<td>0.729Q out</td>
<td>0.512Q out</td>
<td>0.343Q out</td>
<td>30 %</td>
</tr>
<tr>
<td>Cascade Efficiency</td>
<td>0.271Q</td>
<td>0.488Q</td>
<td>0.657Q</td>
<td>65 %</td>
</tr>
</tbody>
</table>

#### Conversion Efficiency Diagram

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

TH > TM > TL
Si-Ge: Twin-Lattice Structure
Symmetry Breaking to 60:40

Original Crystal ~60%

Twin Crystal ~40%

\( \Psi: 32° \sim 40° \)
\( \pi: 0° \sim 360° \)
Rhombohedral Hybrid Band-Gap Engineering

Two Single Crystalline Alignments

Sapphire \{10-14\}

SiGe \{220\}, Low Temperature

60 degree difference

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

Asymmetric angles for XY mapping with Point X-ray source

Point X-ray source for mapping

2Theta-Omega Normal Scan

SiGe(111), 1.7 Mega cps, 99.9999%

Sapphire (0 0 0 6) 51 cps <0.0001%

Sapphire (0 0 0 12)

(i) Majority single crystal map

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

Sample cage created + shaped thermal shadow
Power Sources for Spacecrafts

- Fly-wheel Power Storage
- Fuel Cells
- Canister-based Battery
- 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

Artist's concepts of Mars space power station installed with WPT-ATEG system: space system (left) and ground system (right).
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 $|\mathbf{E}| = 0$,

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

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

- 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 Al₂O₃**

<table>
<thead>
<tr>
<th>RESULTS</th>
<th>B =</th>
<th>0.51 [T]</th>
<th>D =</th>
<th>0.28 [um]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier Density: x10⁴</td>
<td>Nb</td>
<td>-5.7963E+20 [cm⁻³]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>µ</td>
<td>11.50208 [cm²/V·s]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>ρ</td>
<td>9.3631E-04 [Ω·cm]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>δ</td>
<td>1.9616E-02 [Ω]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conductivity: x10⁵</td>
<td>Ns</td>
<td>-1.6280E+16 [cm⁻³]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Rh</td>
<td>-1.0769E-02 [m²/C]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>1.0630E+03 [1/Ω·cm]</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>alpha</td>
<td>0.12167</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Nb: Bulk concentration  
µ: Mobility  
ρ: Bulk resistivity  
δ: Magnetoresistance

Ns: Sheet concentration  
Rh: Hall coefficient  
σ: Conductivity  
α: W/H Ratio of Resistance

---

**Intrinsic GaN on Al₂O₃**

<table>
<thead>
<tr>
<th>RESULTS</th>
<th>B =</th>
<th>0.51 [T]</th>
<th>D =</th>
<th>0.367 [um]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>-6.6335E+16 [cm⁻³]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>µ</td>
<td>2.22096 [cm²/V·s]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ρ</td>
<td>52.87483 [Ω·cm]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δ</td>
<td>1.5200E-04 [Ω]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ns | -2.6534E+12 [cm⁻³] |
Rh | -91.39552 [m²/C] |
σ | 1.8913E-02 [1/Ω·cm] |
alpha | 0.16324 |

Nb: Bulk concentration  
µ: Mobility  
ρ: Bulk resistivity  
δ: Magnetoresistance

Ns: Sheet concentration  
Rh: Hall coefficient  
σ: Conductivity  
α: W/H Ratio of Resistance

---

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.
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.

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

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.
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

Laser (630nm) backside illumination only

Double Depth (0.8\( \mu \)m)

\( \phi \sim 150\)nm

\( \phi = 100\)nm

No Passing 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

Quartz Substrate

Metallic Film with Quantum Aperture Array

Light Injection
(Laser or White Light)

NOTE:
- Surface Plasmon Polariton (SPP)
- Electron
- Light Transmission by undisturbed SPP
- Light Transmission by disturbed SPP
Micro Spectrometer ($\mu$-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:
    - $\mu$-SM imbedded rover tires
    - $\mu$-SM imbedded Astronaut’s shoes
    - $\mu$-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**

(2µm before destructive interference height)

Photon Collection Time = 6ms

- FWHM = 465nm

- Min. ~ Min. = 1.25µm

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
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

POWER for OA

2D Measurement

3D Measurement

Interference Fringe
Two Photon Excitation
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 Fe³⁺ 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 (Fe²⁺)/ 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

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

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

Red Blood Cell

Bio-nanobattery patch installed in autonomous bio-nanorobot

Flexible Nanobattery Film

Wearable Electronics (Philips)
Bionanobattery Concept

Fe^{2+} - ferritin

Fe^{3+} - ferritin

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

Fe(OH)\(_3\)/Fe(OH)\(_2\)  \( \parallel \)  CoOOH/Co(OH)\(_2\)  \( E_{cell} = 0.66 \) V

Fe(OH)\(_3\)/Fe(OH)\(_2\)  \( \parallel \)  \( \gamma \)-MnOOH/Mn(OH)\(_2\)  \( E_{cell} = 0.20 \) V

Fe(OH)\(_3\)/Fe(OH)\(_2\)  \( \parallel \)  NiOOH/Ni(OH)\(_2\)  \( E_{cell} = 0.97 \) V
### Theoretical Values of Bionanobattery

<table>
<thead>
<tr>
<th>Anode</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>
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<tbody>
<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>
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</tr>
<tr>
<td>Hg</td>
<td>1.344</td>
<td>0.922</td>
<td>0.588</td>
<td>0.584</td>
<td>0.388</td>
<td></td>
<td></td>
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</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>(0.190)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn (1.606)*</td>
<td>(1.184)</td>
<td></td>
<td>(0.850)</td>
<td>(0.846)</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Co</td>
<td>1.416V</td>
<td>0.994</td>
<td>0.660</td>
<td>0.656</td>
<td>0.072</td>
<td>0.120</td>
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<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>

| Cathode | 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⁻ → 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>
</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

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

Thiolated Fe²⁺ → thiolated Co³⁺

0.25 V / Unit Cell
Estimation of Electrical Output

- Electrode: 1” x 1” 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 Fe²⁺-Co³⁺ 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