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Special lecture, Part 1: Nature-guided nanotechnology for chemical tectonics of inorganic materials - Thermoelectric oxide materials for electric power generation

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Thermoelectric Oxide Materials For Electric Power Generation

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CREST, Japan Science and Technology Agency

1. Thermoelectric Energy Conversion
2. Oxide Superlattices
3. Thin Film TE Devices
Seebeck Effect

Power generation by a TE module

Voltage meter

n-Si

- +

- +

p n p n p n p n —— p n p n
“Even at the current efficiencies of thermoelectric devices, 7 to 8 percent, more than 1.5 billion gallons of diesel could be saved each year in the U.S. if thermoelectric generators were used on the exhaust of heavy trucks. That translates into billions of dollars saved.” by Prof. T. Tritt (NanoTX’07 Conference, Oct. 2-4, 2007, Dallas).
Problems of the Conventional TE Materials

Conventional materials: $\text{Bi}_2\text{Te}_3$, $\text{Sb}_2\text{Te}_3$, $\text{PbTe-Ag}_2\text{Te}$, $(\text{Bi,Sb})_2\text{Te}_3$, $\text{CoSb}_3$, etc.

1. **Low Heat Resistance & Oxidation Resistance**
   - Melting point of $\text{Bi}_2\text{Te}_3$: 580 °C
   - Comparison: Automobile exhaust gas: 800 ~ 1000 °C

2. **Limitation of resources**
   - Very small Clarke Numbers
   - $\text{Bi}: 2 \times 10^{-5} \%$, $\text{Sb}: 5 \times 10^{-5} \%$, $\text{Pb}: 1.5 \times 10^{-3} \%$, $\text{Te}: 2 \times 10^{-7} \%$
   - Ref. Pt: $5 \times 10^{-7} \%$

3. **High toxicity**

   **Oxide TE Materials are highly wanted for power generation in air atmosphere!**
SrTiO₃: Good Candidate

SrTiO₃ Single X’tal

$E_g = 3.0\sim 3.2\ \text{eV}$

$m^*_{\text{STO}} = \sim 3-10m_0$

(Frederikse et al. PR, 1964; Tokura et al. PRB, 2001)

(L. F. Mattheiss, et al. PRB., 1972)
Cubic perovskite-type SrTiO$_3$

- Excellent controllability of electrical conductivity by doping
  - High electrical conductivity, $\sigma$
- Large carrier effective mass ($m^* = 6-11\ m_0$)
  - Large Seebeck coefficient, $|S|$
- The largest $ZT$ among n-type TE oxides
  - $ZT = 0.37$ @ 1000K (SrTi$_{0.8}$Nb$_{0.2}$O$_3$)
    

Improvement in $ZT$ by reduction of thermal conductivity ($\kappa$)
and/or further enhancement of power factor ($\mu S^2$)

$$ZT = \mu S^2 T / \kappa$$
Artificial Superlattice

“If electrons were confined in a very narrow space, you would get enhanced thermopower!”


Thin layer with confined electrons

STO/STO:Nb SL

STO

STO:Nb

STO

Theory

bulk PbTe

Well thickness (nm)

$S_n \times 10^3 \mu V K^{-2} cm^{-2}$
Fabrication of SrTiO$_3$/ Nb:SrTiO$_3$ superlattice

**Growth condition**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>(100)-LaAlO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth temp.</td>
<td>900$^\circ$C</td>
</tr>
<tr>
<td>Oxygen pressure</td>
<td>$3 \times 10^{-3}$ Pa</td>
</tr>
<tr>
<td>Laser energy density</td>
<td>$\sim 1 \text{ J cm}^{-2}\text{pulse}^{-1}$</td>
</tr>
<tr>
<td>Repetition rate</td>
<td>10 Hz</td>
</tr>
<tr>
<td>Growth rate</td>
<td>$\sim 50 \text{ pm s}^{-1}$</td>
</tr>
</tbody>
</table>
RHEED intensity oscillation
Out-of-plane XRD pattern

Satellite peaks due to superlattice are clearly seen.

Topographic AFM image

Frank Van der Merwe (2D) growth

-0.39 nm (1 unit cell)

Height, Z (nm)

Intensity (a.u.)

Scattering vector, $q_z$ (nm$^{-1}$)
Diffusion of dopant Nb did not take place!
Seebeck coefficient vs. well thickness

Hall mobility
\[ \mu_{\text{Hall}} \sim 6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \text{ at } 300\text{K} \]

Electrical conductivity
\[ \sigma = 2.3 \times 10^3 \text{ Scm}^{-1} \text{ at } 300\text{K} \]

Carrier concentration
\[ n_e = 2.4 \times 10^{21} \text{ cm}^{-3} \text{ at } 300\text{K} \]

H. Ohta et al.,
The optimized ZT value in the 2DEG system reaches $ZT_{300K}(2\text{DEG}) = 2.4$, which is 24 times larger than that of the corresponding 3D-bulk SrTiO$_3$.

Cf: Bi$_2$Te$_3$/Sb$_2$Te$_3$ SL $ZT_{300K} = 2.4$
(Venkatasubramanian et al., *Nature*, 2001)

Direct Heating Test: STO/STO:Nb Superlattice

100 periods ($t = 630$ nm)

SrTiO$_3$:Nb

$i$-SrTiO$_3$

0.5-mm$^t$-LaAlO$_3$

1 unit cell SrTiO$_3$:Nb

Carrier electron concentration, $n_e = 4 \times 10^{21}$ cm$^{-3}$

Hall mobility, $\mu_{\text{Hall}300K} = 5$ cm$^2$.V$^{-1}$.s$^{-1}$

Electrical conductivity, $\sigma_{300K} = 3,200$ S.cm$^{-1}$

Seebeck coefficient, $|S|_{300K} = 350$ $\mu$V.K$^{-1}$

50 mV @ $T=140$ K

Cf: Bi$_2$Te$_3$

$\sigma_{300K} = 1,200$ Scm$^{-1}$

$S_{300K} = 200$ $\mu$V K$^{-1}$

28 mV @ $T=140$ K
High-Temp. Characteristics of STO/STO:Nb SL

**TE Conversion Efficiency of Superlattice**

- $T_c = 300 \text{ K}, \ T_h = 900 \text{ K}$
- $ZT = 2.4 @ 300 \text{ K}, \ ZT = 1.4 @ 900 \text{ K}$
- $ZT(\text{average}) \sim 1.9$ is assumed.

\[
\square = \frac{W_{out}}{Q_{in}} = \frac{T_h - T_c}{T_h} \frac{(1 + ZT_m)^{1/2} - 1}{(1 + ZT_m)^{1/2} + \frac{T_c}{T_h}}
\]

**Cf:** $\text{Bi}_2\text{Te}_3 \quad T_c = 300 \text{ K}, \ T_h = 500 \text{ K}$

$ZT(\text{average}) \sim 1.0 \sim \Box \sim 22\%$
Design Concept for TE Thin Film Module

N-type TE element: STO/STO:Nb Superlattices
P-type TE element: $\text{Ca}_3\text{Co}_4\text{O}_9$ Thin Films
P-type Layered Cobalt Oxide for TE Thin Film Module

High TE Performance of $\text{Ca}_3\text{Co}_4\text{O}_9$ Thin Film


<table>
<thead>
<tr>
<th>CCO/film</th>
<th>$\text{Bi}_2\text{Te}_3$/bulk</th>
<th>STO/SL</th>
</tr>
</thead>
<tbody>
<tr>
<td>$PF(\Delta S^2)@300K(x10^{-3})$</td>
<td>0.5</td>
<td>4.8</td>
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