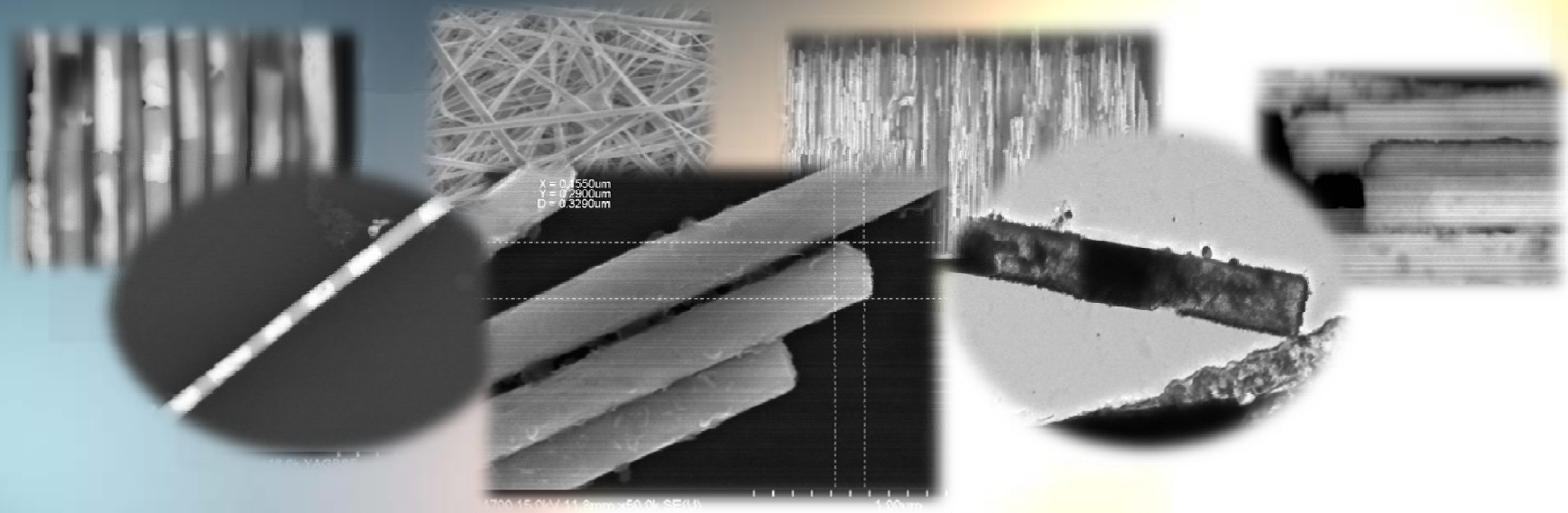
7th Korea-US Nano Forum, Seoul, Korea, April 5-6, 2010

Electrochemical synthesis of nanostructure materials for thermoelectric energy harvesting



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Introduction

Thermoelectric + Nanotechnology

- **Nanoscience and engineering for the synthesis of thermoelectric materials,**
  - **uncover the possibility of increasing of figure of merit (ZT).**
  - **allow the higher carrier mobility than alloys, and the interface carrier scattering.**
  - **provide nanoscale building blocks for fabrication of highly functional devices.**

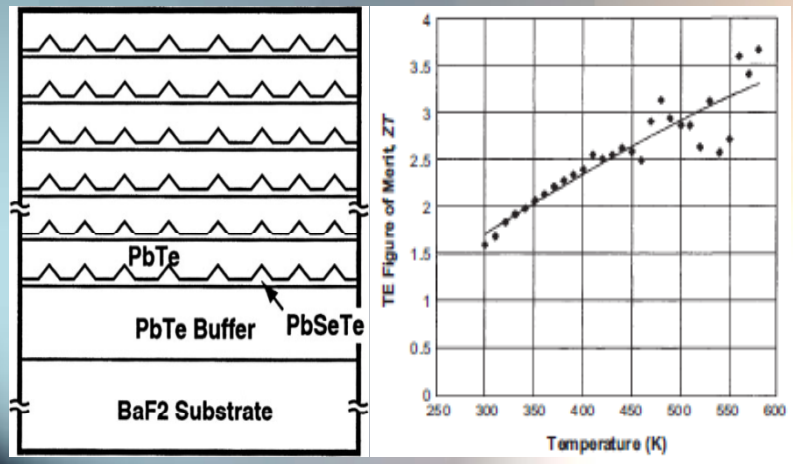


Fig. a) Schematic drawing of a QDSL and b) TE figure of merit vs. temperature for an n-type PbSe0.98Te0.02/PbTe QDSL sample

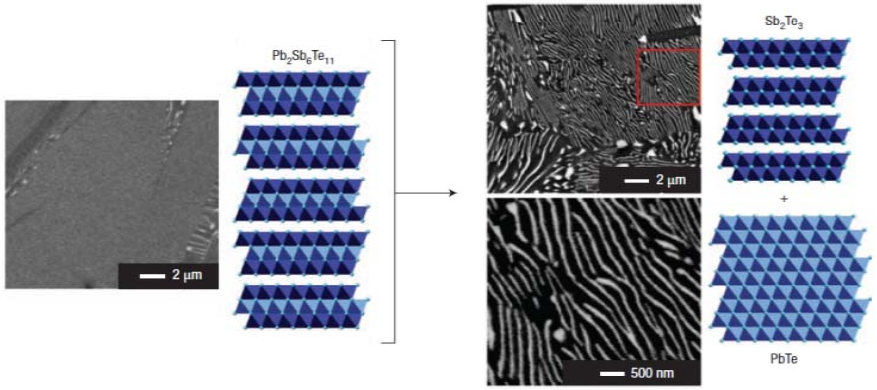


Fig. Nanostructured thermoelectrics may be formed by the solid-state partitioning of a precursor phase. The metastable Pb2Sb6Te11 phase (left) will spontaneously assemble into lamellae of Sb2Te3 and PbTe .These domains are visible with backscattering scanning electron microscopy, with the dark regions corresponding to Sb2Te3 and the light regions to PbTe. Electron backscattering diffraction reveals that the lamellae are oriented with coherent interfaces, shown schematically (right).

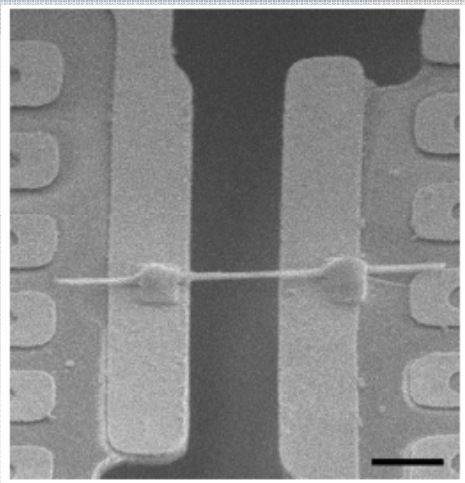
Ref. T. C. Harman, et al. Science ***2002,*** *297, 2229.*
Ref. Genqiang Zhang et al, Adv. Mater. 2008, 20, 3654–3656

Introduction

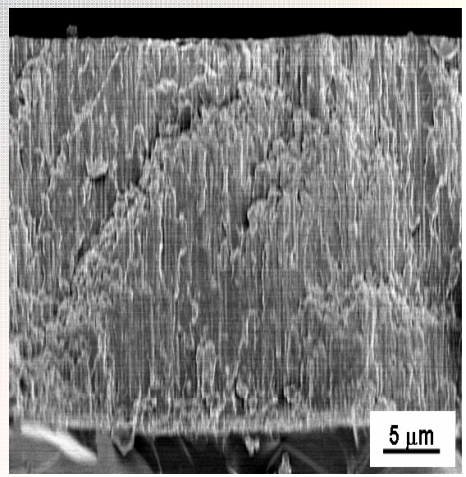
Weak aspects of nanostructure materials

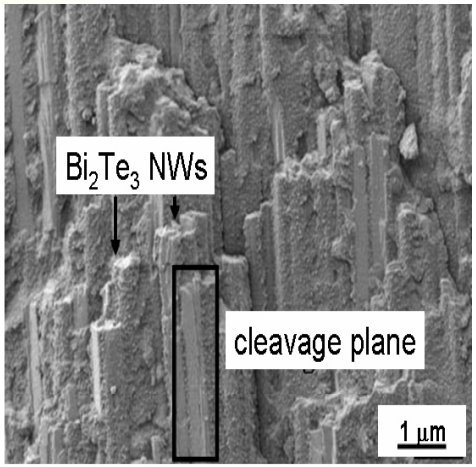
➢ **Difficult to apply on commercial devices.**

- Weak mechanical properties and difficulty on spatial controlling in the device.



Si nanowire on the TE measurments electrode needs FIB process for improving contact resistance.





Fractured nanowire array/epoxy composite showing (left) nanowires completely embedded in epoxy matrix, and (right) expanded view showing cleavage plane in nanowire.

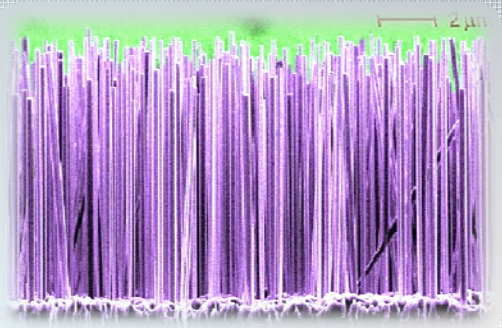
- **Vacuum based technology → Synthesis of nanostructure using cost effective electrochemical method.**
- **Mechanical stability of nanostructure must be considered to fabricate nanostructure devices.**

Ref. Allon I. Hochbaum et al, Nature 2008,451,10 .
Ref. M. H. Francombe, Structure-cell data and expansion coefficients of bismuth telluride, Br. J. Appl. Phys.,1958, Vol 9 p415-417

Outline of research

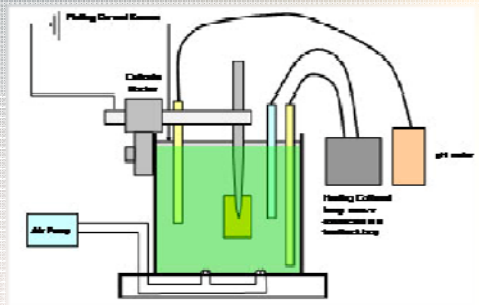
Nanostructure + Electrochemistry + Composite

1D Nano structure



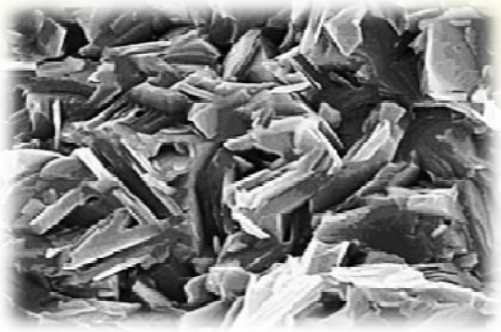
- Exist the maximum value of density of state in the fermi window system, place fermi level on nearby maximum value of density of state.
- Increase surface area as insert nano-material to phonon scattering (Interface, Boundary scattering)
- Nanowire, nanotube, nanorod, nanofiber, etc.
- Weak mechanical properties

Electrochemical method



- External electrical field or reducer give electron to anion.
- Electrodeposition, electroless deposition, galvanic displacement electrodeposition, etc.
- No vacuum, cost effective.
- Controlling the nucleation, size and thickness is utilized.

Composite/Bulk



- Figure of merit might be enhanced by adding fine, electrically conductive particles that has no reaction with the matrix.
- The addition of metal in order to explore the potential for further increasing the figure of merit of the mother alloy.
- Good mechanical properties.

Ref. Enhanced thermoelectric performance of rough silicon nanowires, Allon I. Hochbaum1, Nature, 2008
Ref. Ohnaka, H. Yasuda, I. Yamauchi, T. Ohmichi, H. Hagino, and R. Koike, in Proc 12th Inter Conf on Thermoelectrics, (Yokohama, Institute of Electrical Engineers of Japan,1993) p.121.
Ref. Yong-Ho Park et al. Mat. Res. Soc. Symp. Proc. Vol. 691

Current research

Synthesis of functional one dimensional nanostructure

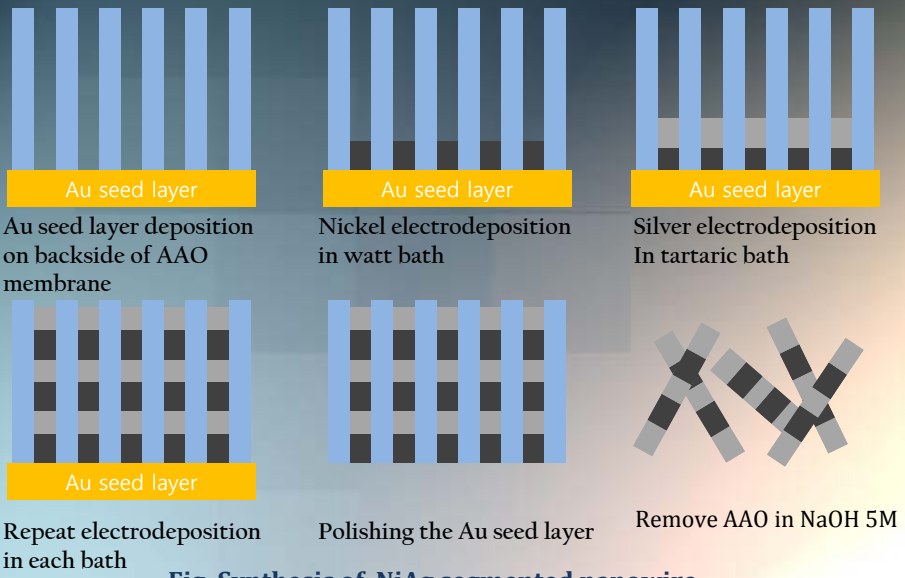


Fig. Synthesis of NiAg segmented nanowire

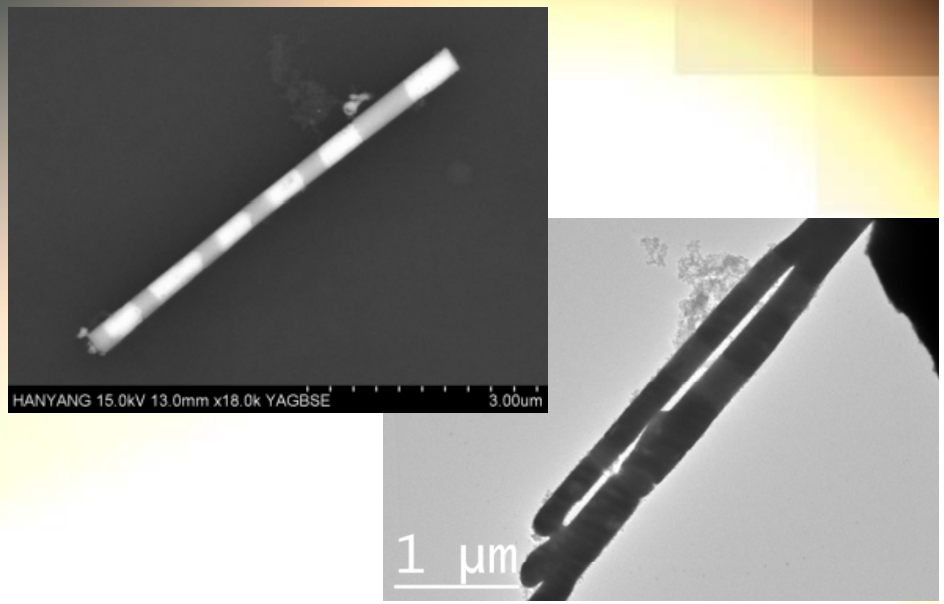


Fig. SEM image and TEM image of Ni-Ag segmented nanowire

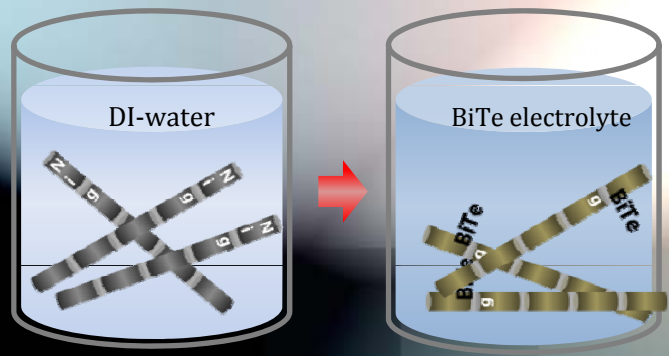


Fig. Galvanic displacement electrodepsition

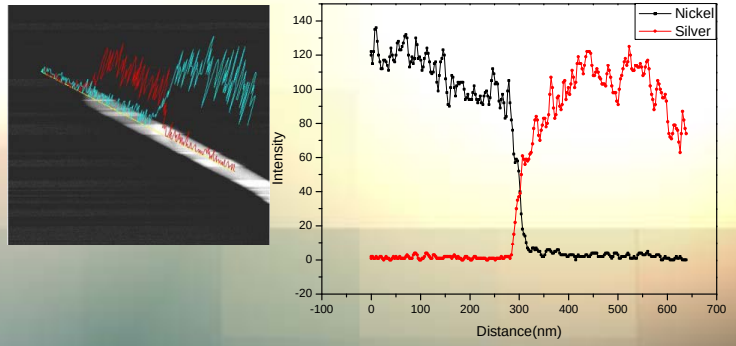


Fig. EDS line scan data of Ni-Ag segmented nanowire

Current research

Synthesis of functional nanostructure

- Pea-pod nanostructure with BiTe thermoelectric materials

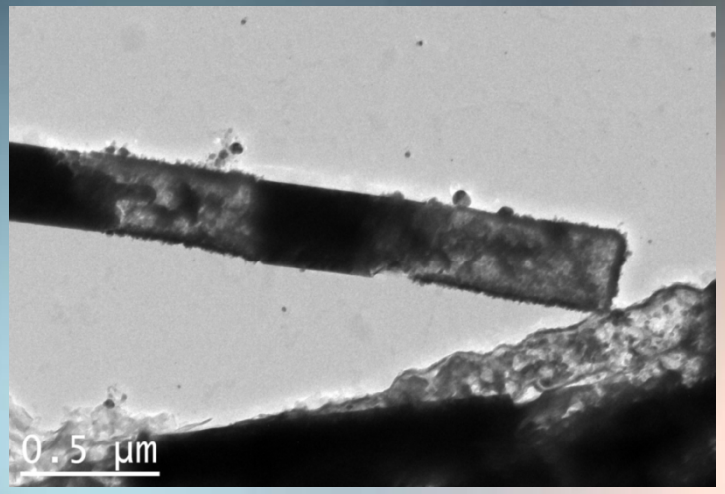


Fig. TEM image of Ni-Ag segmented nanowire
pH 0.3, in BiTe bath, 8min

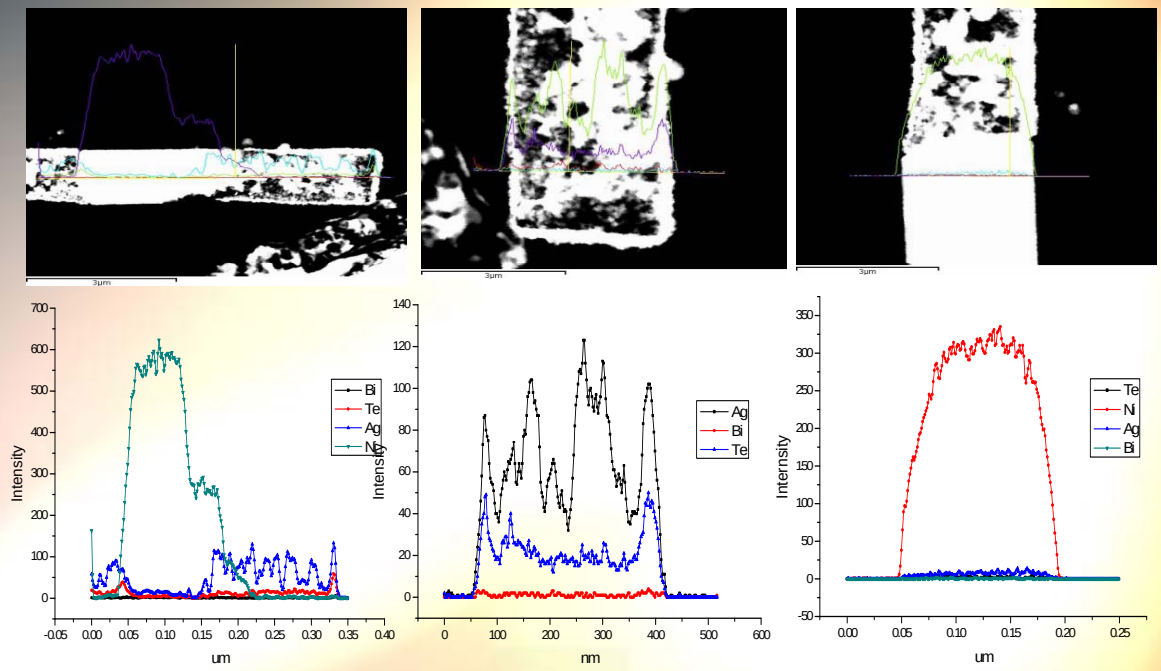


Fig. EDS line scan of Pea-pod nanostructure

Pea-pod nanostructure is successfully synthesized by displacement electrochemical reaction.

Current research

Synthesis of functional nanostructure – core/shell structures

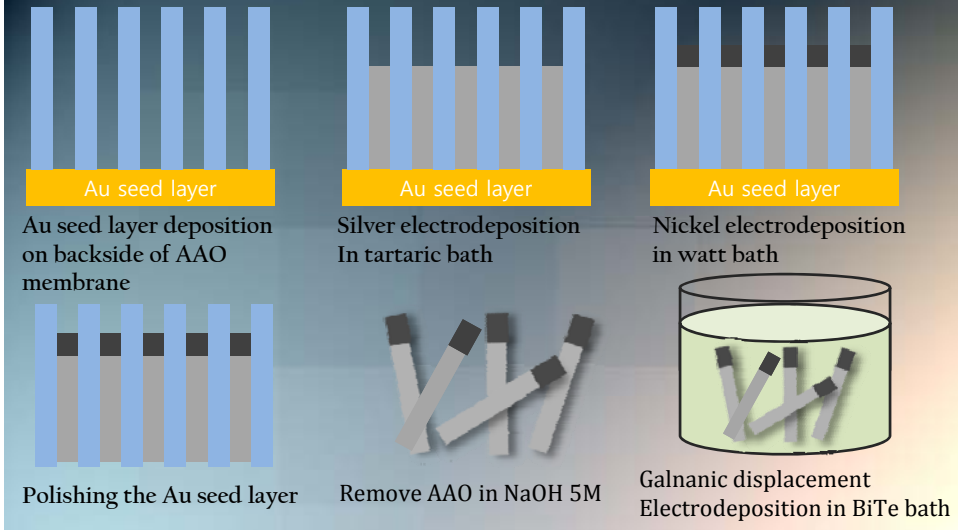
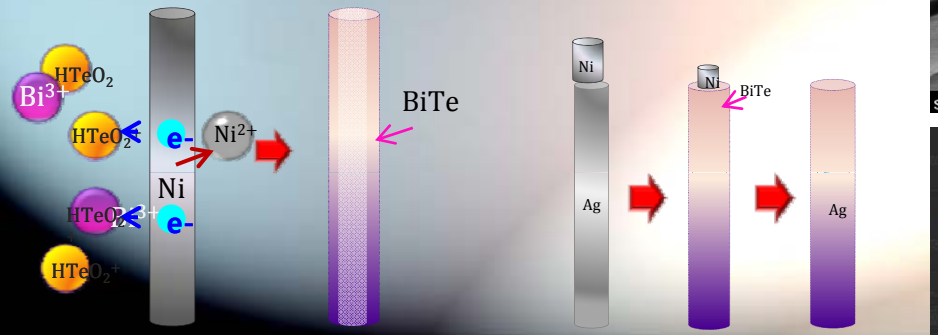


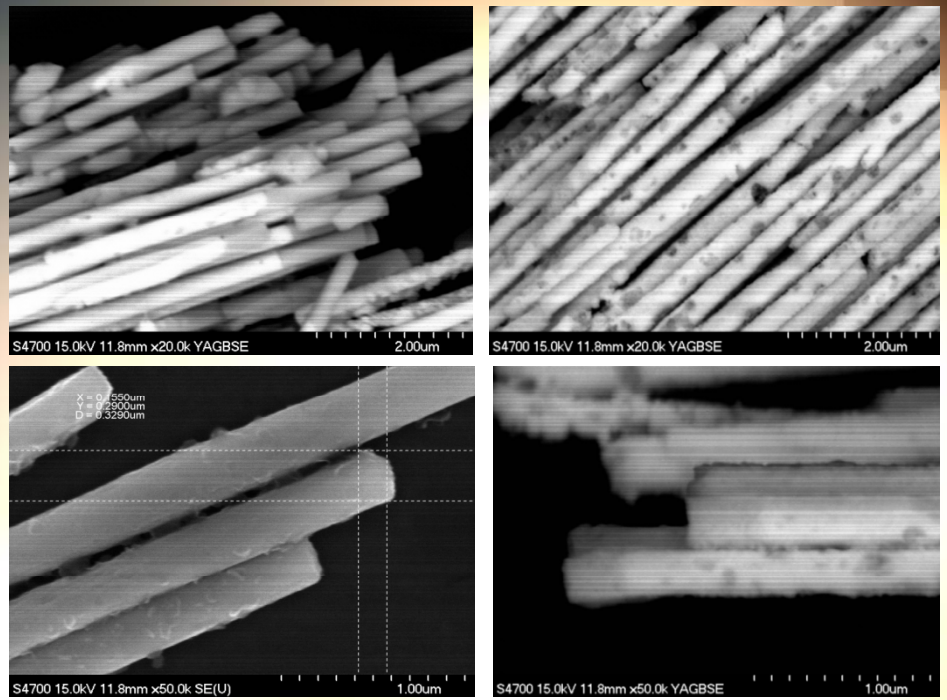
Fig. Synthesis of each 1 layer of NiAg nanowire



$$2Bi^{3+}(aq) + 3HTeO_2^+(aq) + 9Ni^0(s) + 9H^+(aq) \rightarrow Bi_2Te_3(s) + 9Ni^{2+}(aq) + 6H_2O(aq)$$

Fig. Concept of co-shell nanowire fabrication

pH 0.3, 4h



Ref. J. AM. CHEM. SOC. Bongyoung Yoo et al. 2007, 129, 10068-10069

Future study

Nano to bulk : Thermoelectric composite materials with controlled nanomaterials

Inserting nanostructure into composite

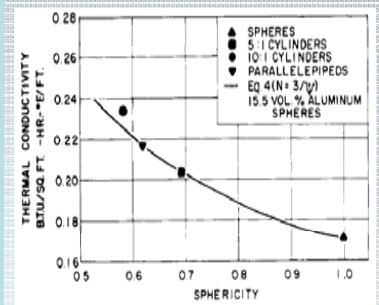
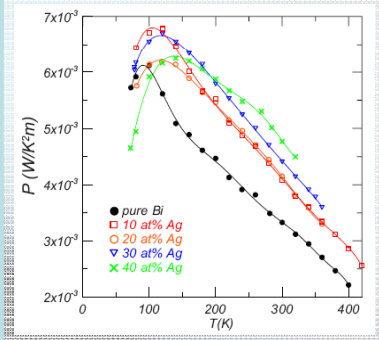


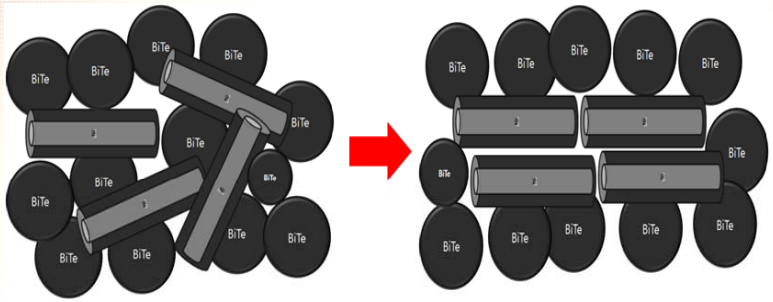
Figure 3. Comparison of Equation 4 with data as a function of particle sphericity



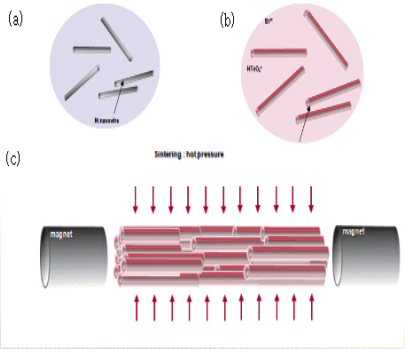
- To increase Power factor
  → 2 composite (w/high σ material)
- To increase interface scattering
  → Nano structure
- To reduce thermal conductivity
  → Particle geometry
- Ag powder in Bi polycrystalline
  → Increase the thermopower,
  But decrease the ZT.

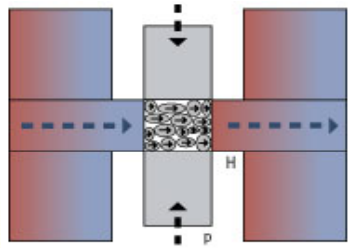
Composite thermoelectric materials

- Nanowires dispersed in bulk materials



- Arrayed by magnetic field pressing technology





Pressing of parts in transverse field (TP)

Ref. Thermal Conductivity of Heterogeneous Two-Component Systems_R. L. Hamilton_ Ind. Eng. Chem. Fundamen. 1962
Ref. Experimental study of the thermoelectric power factor enhancement in composites , J. P. Hermans, 2008


Thank you