Self Catalyzed Growth of Semiconducting Sm_2S_3 Nanowires

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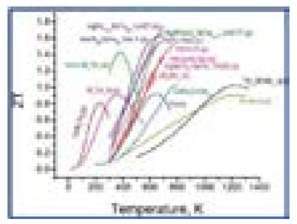
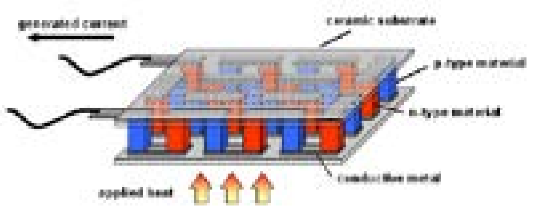
Thermoelectric Effect

- When two metals or semiconductors (n type and p type) are placed in contact with one another, a voltage develops in response to a temperature difference.
- Currently, efficiency is too low for useful power generation and use is largely limited to heating and cooling.
- **Recently, it has been demonstrated that nanostructured materials show a drastic improvement in thermoelectric efficiency[2].**
- The ideal is a dimensionless figure of merit (ZT) of 3.0 which would provide a 20% efficiency with a 500 K temperature difference.

State of the art of bulk thermoelectric materials[2]



Thermoelectric module[1]

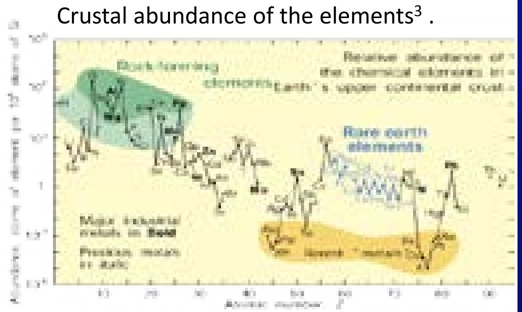


[1] http://www.sigmaaldrich.com/
[2] Kanatzidis, M.G., *Nanostructured Thermoelectrics: The New Paradigm?* Chemistry of Materials, 2010. **22**: p. 648-659.

Objective

- To create an efficient high temperature thermoelectric material.
- The Samarium sulfides were once explored as promising high temperature thermoelectric materials due to:
  a) High melting points of 1750 °C for Sm_2S_3 and 1074 °C for SmS.
  b) Naturally semiconducting.
  c) A ZT of 0.9 at 1000K for SmS[4].
  d) Relative abundance compared to bismuth, selenium, and tellurium.
  e) Good electrical conductivities.
- The thermoelectric properties of the samarium sulfides were explored before the nanostructuring impact on efficiency was demonstrated.
- **Here we present the first nanostructured samarium sulfides.**

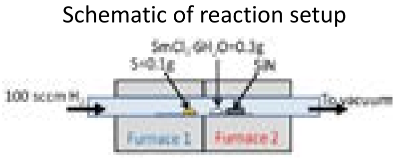
Crustal abundance of the elements[3].



[3] *U.S. Geological Survey: Mineral commodity summaries*, U.S.G. Survey, Editor. 2007: Washington, D.C.
[4] Gulubkov, A.V, *Thermoelectric Properties of SmSx (x=.8-1.5).* Inorganic Materials, 2003. **39**: p. 1251-1256.

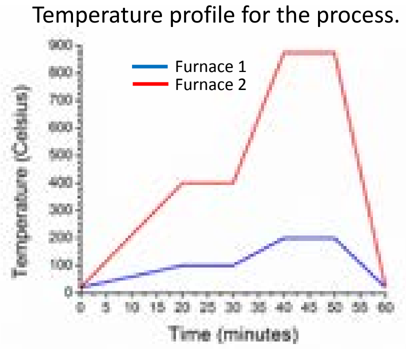
Methods

Schematic of reaction setup



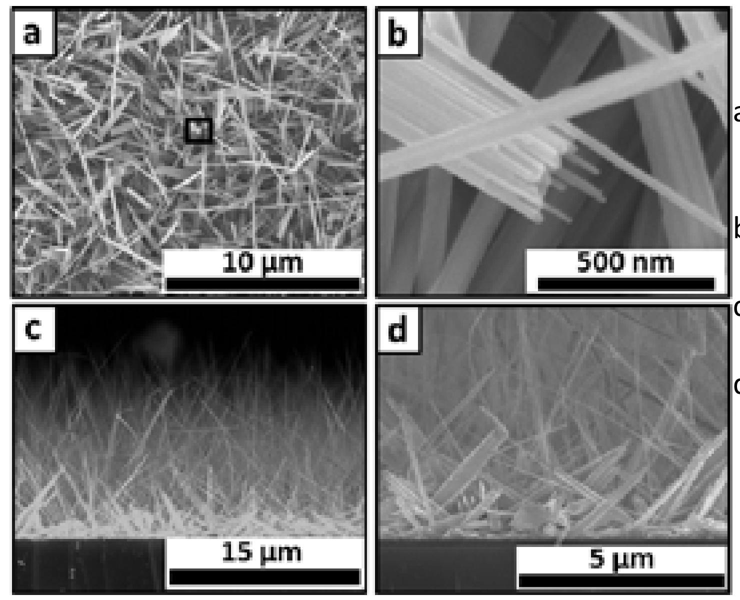
- A 1 meter long 1" diameter quartz tube was loaded with the sulfur 14 cm to the right of the center of furnace 1.
- The $SmCl_3 \cdot 6H_2O$ and the SiN coated silicon substrate were loaded 13.5 and 12 cm to the left of the center of furnace 2 respectively.
- Tube was then pumped down to a base pressure <8 mtorr followed by a 100 SCCM H_2 purge.
- The furnaces were programmed according to the temperature profile shown.
- The H_2 gas was disabled when furnace 2 reached 100 °C, and was not re-enabled until 875 °C was reached.

Temperature profile for the process.

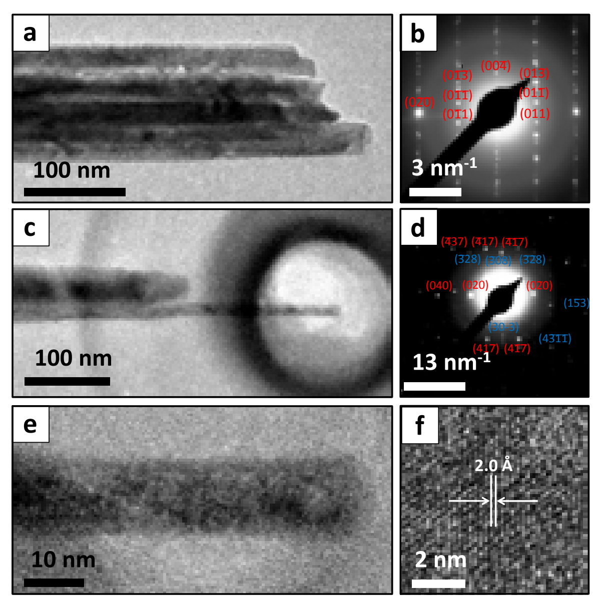


Electron Microscopy Characterization

- **Under these conditions, Sm_2S_3 wires consistently grow as highly anisotropic (up to 1000x aspect ratio) wires.**
- Individual wires have diameters of c.a. 20 nm and seem largely consistent.
- Wires are never found individually, but instead stick together into wire bundles.
- Cross sectional SEM images reveal very thick but short bundles near the substrate base while the longer bundles all remain relatively thin.



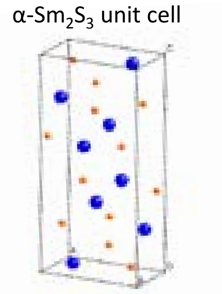
a) Typical top view of the substrate with the as synthesized wire bundles.
b) Zoom-in of the highlighted section of a.
c) Representative cross sectional view.
d) Higher magnification image from the same sample highlighting the thick bundles near the substrate.



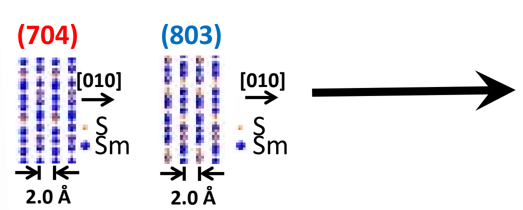
a) TEM images show wires with nearly flat terminating faces and very little tapering.
b) SAED pattern indicates a great deal of crystallinity, but many peaks. One major pattern present verifies a (100) surface.
c) Wire's proclivity to bundle makes finding individual wires difficult. Occasional long wires stand out from bundles though.
d) SAED pattern of a single wire is much cleaner than that of the bundle, but both [704] and [803] patterns present.
e) Zoom in of the single wire shows some curvature present at the tip.
f) HRTEM images show 2.0 Å lattice fringe spacing.

- **The SAED patterns all indicate a [010] growth direction.**
- Likewise, the characteristic 2.0 Å spacing is only present when viewing perpendicular to the y-axis of alpha phase Sm_2S_3
- Multi-facets strongly suggest a screw dislocation is present as shown below.
- Uncertain if the screw dislocation required for growth or anomalous to the extra long single wire.

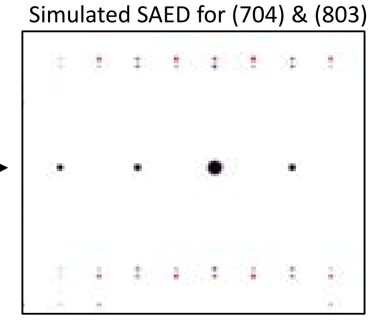
α-Sm_2S_3 unit cell



True to the HRTEM image, the indexed (704) and (803) planes show 2.0 Å fringes.



Simulated SAED for (704) & (803)



Proposed Mechanism

- Maximum wire growth occurs when the sulfur is continuously heated.
- Sulfur readily sublimes around 67 °C under these pressures.
- The samarium only later (600+ °C) sublimes into the sulfur rich system.

S+Sm binary phase diagram.

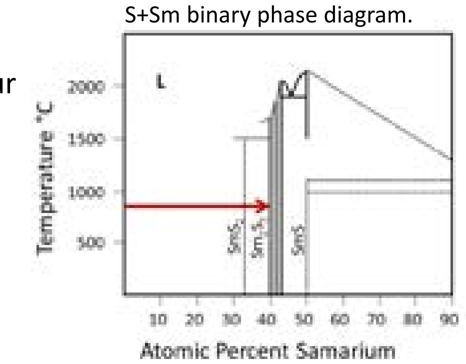
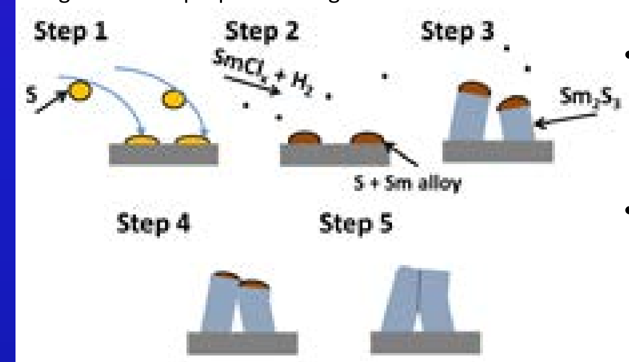


Diagram of the proposed VLS growth mechanism.

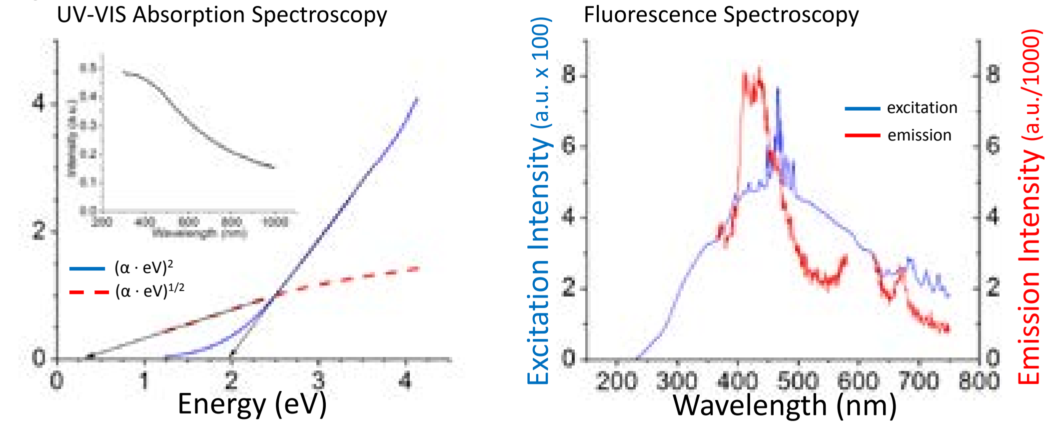


- On a surface, sulfur clusters may serve the liquid droplet collecting role for vapor liquid solid type wire growth.
- **As Sm content increases, the first stable solid phase that drops out of "alloy" is Sm_2S_3 (arrow).**

Optical Characterization

UV-VIS Absorption Spectroscopy

Fluorescence Spectroscopy



- Tauc plots and absorption (inset) of Sm_2S_3 wires in water suspension. **Tauc plot indicates a likely direct bandgap of 1.93 eV.**
- Note that alpha is absorptivity.

- Fluorescence spectra by excitation and emission. The emission spectrum's intense peak at double the excitation wavelength (300 nm) has been removed for clarity.

Conclusion

- A VLS based mechanism and the optimal conditions for wire growth has been proposed for the growth of crystalline Sm_2S_3 nanowires.
- SAED patterns indicate a [010] growth direction and the presence of screw dislocations in the wires analyzed.
- UV-VIS absorption studies show that Sm_2S_3 wires are optically semiconducting materials with a most likely direct band gap.

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