Synthesis and Characterization of Calcium Hexaboride (CaB₆) Nanowires

NSF- REU 2007 at UIC

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Overview: Project Goals

- Department of Energy (DOE)
  - Use of hydrogen as an energy carrier
    - Research and development of hydrogen production, storage, and usage

- Use of Hydrogen as an Energy Carrier:
  - alternative energy strategy
  - reduce greenhouse gas emissions and dependence on foreign energy sources
Hydrogen Storage – Complex Metal Borohydrides

Ca(BH$_4$)$_2$

- Thermodynamical stability of Metal Borohydrides
- Boron: lightweight and forms complex hydrides
  - Nanowires increase diffusion rate
  - Favorably high surface to volume ratio of nanowires
- High gravimetric densities of Hydrogen in Metal Borohydrides
  - Theoretically 9.6 weight% Hydrogen in Ca(BH$_4$)$_2$
Gas Release Upon Phase Transition

Desorption Reaction for Ca(BH$_4$)$_2$ at 350°C

$$3\text{Ca}(\text{BH}_4)_2 \rightarrow 2\text{CaH}_2 + \text{CaB}_6 + 10\text{H}_2$$

Adsorption Reaction for CaB$_6$ and CaH$_2$

$$\text{CaB}_6 + 2\text{CaH}_2 + \text{H}_2 \rightarrow \text{Ca}(\text{BH}_4)_2$$

- at 400°C and 700 bar with 80% Yield

Ronnebro et al., 2007 Hydrogen Program Review available at
Vapor Liquid Solid Mechanism

1) Solid substrate with catalyst
   - forms liquid alloy upon heating
2) Gaseous reactant dissolves onto catalyst alloy
3) Supersaturation of liquid droplet
4) Growth of nanowire at solid-liquid interface by precipitation


Synthesis of CaB$_6$ Nanowires

- **Temperature** in 900-1025°C range
- **Pressure** about 175-180 mTorr under Argon flow
- **Wafer** (SiO$_2$ substrate) with randomly layered CaO - Thermally evaporated Nickel catalyst for coating

**Gas introduction:**

1) Argon gas inflow for 55 minutes  
2) Diborane (B$_2$H$_6$) gas (1.08% in Argon) for 20 minutes  
3) Cooled under the flow of argon for 3 hours

\[
\text{CaO(s) + 3 B}_2\text{H}_6 (g) \rightarrow \text{CaB}_6 (s) + \text{byproducts}
\]
Low Pressure Chemical Vapor Deposition Apparatus

1) Diborane Gas Source
2) Flow meter Controller
3) Ceramic Heating Chamber
4) Liquid Nitrogen Trap
5) Bubbler Tube
6) Connection to Mechanical Pump
Observed Nanowire Morphologies

- SEM images of Wafer 1: Figures A and B
- SEM images of Wafer 2: Figures C and D
- Different nanowire morphologies across Wafers

**Potential Explanations:**
1. Different temperatures experienced across Wafers
2. Different amounts of gaseous introduction experienced
TEM and Electron Energy Loss Spectroscopy Data

TEM image of nanowire using 10.8 mg Ni with 20 sccm $\text{B}_2\text{H}_6$ gas flow rate at 900°C.

TEM image of nanowire with core and shell structure

Line Scan: Ratio of Ca:B on nanowire

![Graph showing atomic percent of B and Ca along a line scan on the nanowire.]
EELS Collected Data of Two Nanowires

- Synthesis performed at 925°C with 20 sccm B$_2$H$_6$, using 2.7 mg Ni
- TEM image of two distinct nanowires from sample (Right)
- EELS collected data from line scan of 2 nanowires (Left)
  - Detected relative atomic percentages of Ca, O, and B
  - Varying elemental composition of nanowires across same sample
  - Suggests reaction resulted in a mixture of different nanowires
Future Works

- Continue Synthesis and Characterization of CaB$_6$ nanowires and other metal hexaboride nanowires
- Vary reaction time along with temperature and flow rate
- Perform FTIR studies of reversible hydrogen storage materials
  - Initial steps of Calcium Borohydride dehydrogenation
  - Initial steps of Calcium Hexaboride Hydrogenation
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