Shape Control Growth of Crystalline Lanthanum and Neodymium Hexaboride Nanostructures

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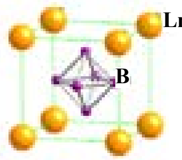
Introduction

Structures



Lanthanide hexaborides, LnB_6 crystallizes in the CsCl-type cubic lattice, space group *Pm-3m*

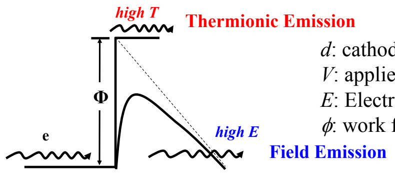
Properties

- **Low** work function (<3.1eV, compared to W ~ 4.5 eV, CNT ~ 5 eV)
- **High** thermal stability (m.p. >2000°C)
- **Low** evaporation rate at high temperature

Atomic No.	57	58	59	60	61	62	63	64	…
Ln	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	…
ϕ_{REB6}/eV	2.5	2.5	3.1	1.6	-	-	-	1.6	…

Applications

Electron source in vacuum microelectronic devices
- Electron microscopes
- Field emission displays
- High frequency detection / emission devices
- High frequency nanoklystron



d: cathode/anode separation
V: applied voltage
E: Electric field
ϕ: work function

Modified Fowler-Nordheim Equation

$$I = A\frac{1.5\times10^{-6}}{\phi}\left(\frac{V}{d}\right)^2\beta^2\exp\left(\frac{10.4}{\sqrt{\phi}}-\frac{6.44\times10^7\phi^{3/2}}{\beta V}\right)\frac{\pi kT/d}{\sin(\pi kT/d)}$$

To obtain the maximum emitting current:
1) Decrease work function ϕ
2) Increase enhancement factor β, which increases with the aspect ratio height/radius

Objectives

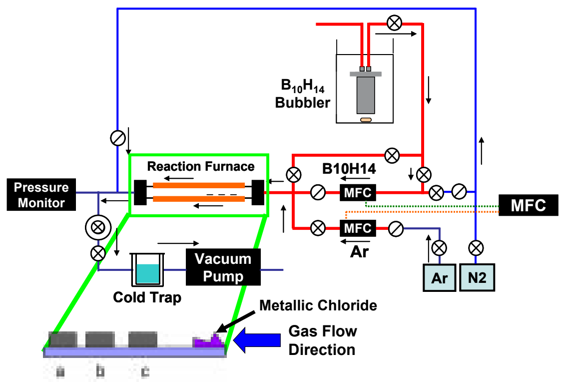
1. Synthesize high aspect-ratio crystalline lanthanum and neodymium hexaboride nanostructures with controlled shape and dimensions.
2. Verify the growth mechanism and evaluate the effect of synthesis parameters.

Reaction

$LnCl_3$(s)+ 0.6 $B_{10}H_{14}$(g) → LnB_6(s)+ 3 HCl(g)+ 2.7 H_2(g)

During the chemical vapor deposition (CVD), $LaCl_3$or $NdCl_3$ and decaborane ($B_{10}H_{14}$) serve as the La/Nd and B source. Palladium (Pd) or platinum (Pt) nanoparticles are used as catalysts.

CVD Setup and Experiments



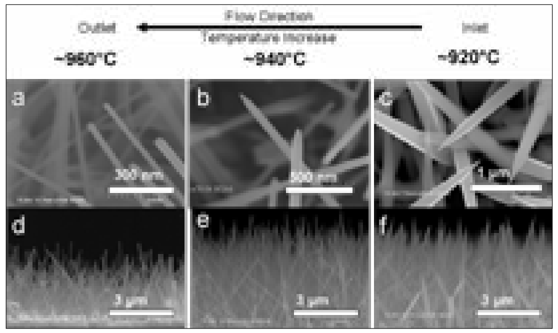
Optimize growth parameters on structural morphology

- Temperature, T_r: 900 – 1000 ºC
- Substrate Position: 10 – 16 cm from the centre of the furnace
- Gas Flow Rate: 0.25 – 0.75 sccm $B_{10}H_{14}$, 10 sccm Ar
- Catalyst Type: Pt vs. Pd
- Reaction time, t_r: 0.5 – 10 min.

Results and Discussions

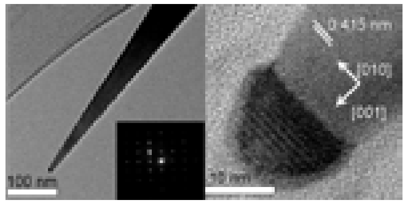
LaB_6: Pt Catalyst

Nanostructure Shape Evolution

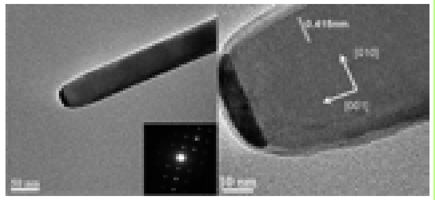


Results indicate substrate position determines shape!

TEM Characterization

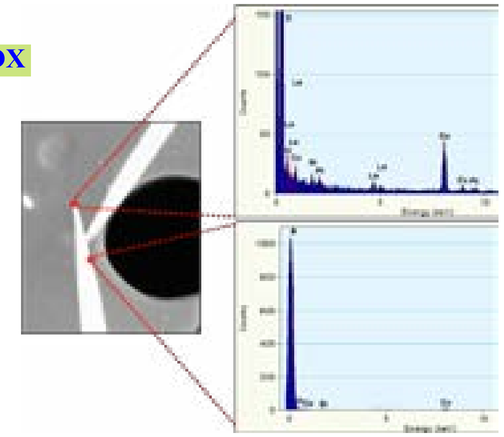


TEM of low temperature materials indicate single crystalline and a [001] growth direction!



TEM of high temperature materials indicate single-crystalline and a [001] growth direction !

EDX

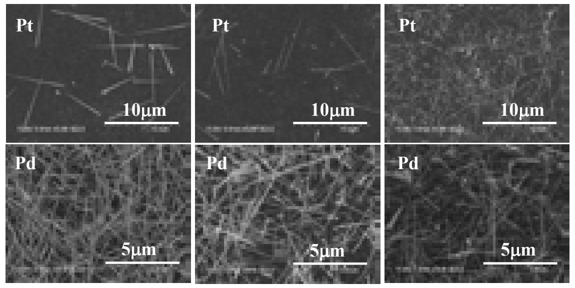


EDX indicates that the dark spot at the end of the tip is Pt and that the amorphous coating on the outside of the obelisk is B.

NdB_6: Pt vs. Pd Catalyst

Effect of Catalyst on Materials Growth: Pt vs. Pd

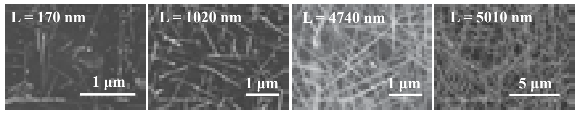
Parameters: t_r=10min, Ar 10sccm, $B_{10}H_{14}$ 0.75sccm



Compared to Pt, the Pd-catalyzed nanowire growth can be executed at lower reaction temperature (about 50°C or lower)

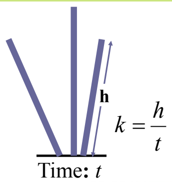
Time Evolution

Parameters: T_r=930 °C, catalyst Pd, 10 sccm Ar, 0.75 sccm $B_{10}H_{14}$, 13 cm from center of the furnace.



As reaction time increases, the length of the nanowires increases.

Estimation of Activation Energy

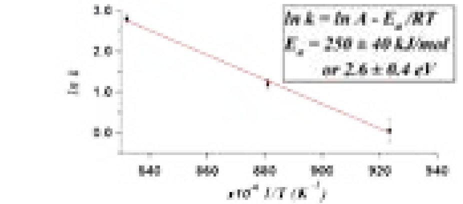


$k = \frac{h}{t}$

Assume the nanowire growth follows the Arrhenius behavior.

$$k = Ae^{-E_a/RT}$$

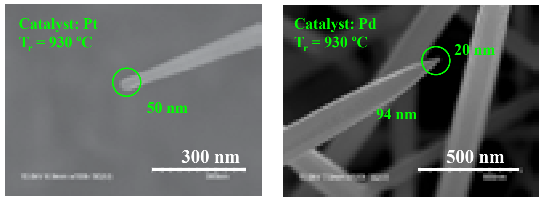
At constant flow of reactants, we may assume the reaction is pseudo first order. Thus, the growth rate constant is proportional to the growth rate.



The *ln k* vs. *1/T* plot shows that the nanowire growth agrees well with Arrhenius equation. The calculated activation energy is *c.a.* 2.6 eV.

Tip Geometry

CVD parameters: t_r=10 min, 10 sccm Ar, 0.25-0.75sccm $B_{10}H_{14}$, 12 cm from center of the furnace



Tip geometry from rod, wire to obelisk shape can be obtained by judicious selection of CVD parameters and catalyst systems.

Conclusions

1. High aspect ratio **LaB_6** and **NdB_6 nanostructures** have been grown via a metal-catalyzed CVD process.
2. Materials synthesized were single-crystalline, several microns long with tip diameters ranging from several to tens of nanometers.
3. The structural morphology of LaB_6 and NdB_6 nanostructures as **a function of temperature, reaction time and catalyst** has been investigated.
4. The **activation energy** of NdB_6 nanowires produced with Pd catalyst has been estimated using the Arrhenius model to be ~2.6 eV.

Acknowledgements

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