Nano to Global: Small Structures and Their Impact on Energy Markets

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Sometimes to think big, you have to think small
Too Precious to be Expensive – The Nexus of Energy-Water-Food

• Energy
  Nothing possible without expending energy

• Water
  70% of water withdrawn from aquifers used for agriculture

• Ammonia
  The world can’t feed itself without ammonia
Ammonia Synthesis

\[ \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \]

• Why so important
Ammonia = Fixed Nitrogen

• Animals need protein (a nitrogen containing molecule)
• Most plants lousy at incorporating nitrogen (need fertilizer)
• Humans now fix more nitrogen than all natural sources combined
• >1% of world energy consumption
• Natural gas is the source of H₂
Ammonia Synthesis

\[ \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \]

- Can it really be that difficult?
- Can it really be that interesting?
Nobel Prize in Chemistry 1918

Fritz Haber
Kaiser-Wilhelm-Institut
Berlin, Germany
"for the synthesis of ammonia from its elements"

Enriching the Earth, Vaclav Smil, MIT Press (2001)
Nobel Prize in Chemistry 1931

Carl Bosch
University of Heidelberg, Germany

"in recognition of their contributions to the invention and development of chemical high pressure methods"
Nobel Prize in Chemistry 2007

Gerhard Ertl
Fritz-Haber-Institut
Berlin, Germany
"for his studies of chemical processes on solid surfaces"

Heterogeneous Catalysis
Iron nanoparticles on an oxide support

• The ammonia synthesis catalyst as revealed by high-resolution scanning electron microscopy

• 200–300 atm, 670–770 K
• 120 MMt annual production
• 1% of world’s energy consumption just to run this reaction
Modern agriculture depends on ammonia-based fertilizer.

This cannot be replaced by dung.

NH$_3$ requires fossil fuels both for H$_2$ and for the energy to run the chemical reaction.

If ammonia production were shut down, 4.4 billion people could not be supported by agriculture.
NH₃ Synthesis is, arguably, the single most important industrial chemical reaction.
Globalized trade in agriculture and fertilizer has coupled the price of food to oil

Figure 1
Food and oil prices 1990–2015. Data from Food and Agriculture Organization and EIA (111, 112).

Human Impact of Energy

- Strong correlation between HDI & energy consumption (Smil)

- To elevate Developing World to status of Poland requires equivalent of >150 Mbbl/day of oil

- Current production = 98 Mbbl/day (+17% since 2006 due to fracking)
The future is solar (and other renewable) electricity and solar fuels

Figure A-7. Cumulative additions of solar PV capacity, 2006-2014

Gigawatts (GWDC)


More energy from the Sun hits the Earth in one hour than humans use in an entire year

Nathan S Lewis, Caltech, http://nsl.caltech.edu
Solar Land Area Requirements

- U.S. Land Area: $9.1 \times 10^{12}$ m$^2$ (incl. Alaska)

- Average Insolation: 200 W/m$^2$

- 2000 U.S. Primary Power Consumption: 99 Quads = 3.3 TW
- 1999 U.S. Electricity Consumption = 0.4 TW

- Hence:
  \[ 3.3 \times 10^{12} \text{ W} / (2 \times 10^2 \text{ W/m}^2 \times 10\% \text{ Efficiency}) = 1.6 \times 10^{11} \text{ m}^2 \]
  Requires $1.6 \times 10^{11} \text{ m}^2 / 9.1 \times 10^{12} \text{ m}^2 = 1.7\%$ of Land

*More energy from the Sun hits the Earth in one hour than humans use in an entire year*

Nathan Lewis, Caltech, http://nsl.caltech.edu
Nate Lewis made this estimate using 10% efficiency. The world record for a Si solar cell is now over 22% efficient using black Si.

Pillar formation leads to low reflectivity surfaces

Pillar-covered surfaces of metals and semiconductors are black (low reflectivity) except for Cu
Laser Ablation

The vacuum chamber is mounted on translation stages along two axes. Translation at 0.01–0.1 mm s$^{-1}$ during irradiation exposes substrate to 400–8000 laser shots.

532 nm, 20 Hz
7 ns, 160 mJ pulse
1–5 mJ cm$^{-2}$
Pillars formed by Laser Ablation

Solar and wind are intermittent

Need storage and production of solar fuels

Carbon is too valuable & versatile to burn and dispose of

Make things from C & Si

Create recyclable cycles

Si outperforms graphite in theory but not in practice

- 3579 mA h g\(^{-1}\) vs 372 mA h g\(^{-1}\) specific capacity
- Poor cycling behavior because extreme volume changes in Si lead to material fatigue
- Surface electrolyte interphase (SEI) on Si surface is highly resistive

VLS Growth of Si Nanowires

A deposition process adds catalyst nanoparticles onto each graphite particle to later initiate nanowire growth from SiH$_4$ directly onto the graphite in the CVD furnace.

https://www.onedmaterial.com/
Stain etching is easy. Just mix appropriate oxidant and HF. Add silicon of any shape, size or doping level and it works.
The effects of quantum confinement are implicated both in the self-limiting nature of Si etching in fluoride solutions and in the development of visible photoluminescence when Si nanostructures drop below \(~5\) nm in critical dimension.

Stain etching of wafers can produce uniform, conformal, thick, photoluminescent porous layers when etching and drying are optimized.

- $\text{V}_2\text{O}_5$ and $\text{FeCl}_3\cdot6\text{H}_2\text{O}$: uniform, thick layers
- $\text{CeF}_4$, $\text{H}_2\text{IrCl}_6$: uniform but thin
- $\text{NO}_3^-$: nonuniform
- $\text{HIO}_3$: uncontrollable roughening
- $\text{MnO}_4^-$, $\text{HCrO}_4^-$: spotty
- Critical point or pentane drying
- Moderate etch rate
- Avoid precipitating cations

Many commercial applications (e.g. nanomedicine, consumer products and batteries) require porous Si in kg to ton quantities

Is there an economical route to porous silicon powders through metallurgical grade Si?
  – Semiconductor grade Si $10,000 \text{ kg}^{-1}$
  – Metallurgical grade Si $1 \text{ kg}^{-1}$

Previous methods of etching powder suffer from low yields, high cost, lack of control (e.g. only on small particles), incomplete etching
HOWEVER: Powders present new challenges: inhomogeneous, polycrystalline, contain 0.2 % impurities (mostly Fe and Al), high surface area, heat generation, foaming


These methods of etching powder suffer from low yields, high cost, lack of control (e.g. only on small particles), incomplete etching, fading photoluminescence.
Cross-section of a porous particle produced by stain etching

Unfortunately the porous layer is only about 200 nm thick as found in previous work. Which leaves us with a conundrum. Trade off between stoichiometry (2× more oxidant than Si), etch rate and cost.

Let’s fundamentally rethink how we perform electroless etching

In stain etching you add all the oxidant at the beginning

- High initial rate burns off porous layer
- Reaction doesn’t go to completion
- $V_2O_5$ costs $50 \text{ kg}^{-1}$
Regenerative Electroless Etching (ReEtching)

$\text{H}_2\text{O}_2 \overset{0.5 \text{ kg}^{-1}}{\rightarrow}$

$\text{H}_2\text{O}_2$ can reversibly regenerate $\text{V}^{(V)}$ from $\text{V}^{(IV)}$

$$\text{H}_2\text{O}_2 + 2\text{VO}^{2+} \rightarrow 2\text{VO}_2^{+} + 2\text{H}^+ \quad 0.785 \text{ V}$$

Use only a catalytic amount of $\text{V}_2\text{O}_5$.

Add $\text{H}_2\text{O}_2$ to establish steady state etch rate with a syringe pump. A

Amount of $\text{H}_2\text{O}_2$ added controls the extent of reaction.
Here we demonstrate complete etching of 4 µm particles. No precipitation observed with V-based etchant. Specific area up to 888 m² g⁻¹ using pentane drying. The porous region retains its crystallinity.

Ag, Au, Pd, Pt galvanic deposition of nanoparticles from HF(aq). The metals spontaneously deposit to form nanoparticles that can catalyze Si etching: MACE

Etch track pores directly primarily along <001> directions

Kolasinski, Unger, Ernst, & Aindow, Frontiers in Chemistry (almost accepted).
Metal assisted catalytic etching (MACE) leads to the formation of etch track pores. These porous layers can be exfoliated and cleaved into nanowires by sonication of porosified powder particles in ethanol.
Metal assisted catalytic etching (MACE) can be used to make porous/pillared Si powder particles.

- Deposit Ag nanoclusters from AgNO$_3$
- Etch with oxidant such as NO$_3^-$, HOOH or V$_2$O$_5$ dissolved in HF
- Can be performed on single crystal powder or polycrystalline metallurgical grade powder
Metal assisted catalytic etching (MACE) can be used to make porous/pillared Si powder particles. Electronics grade: solid core Metallurgical grade: some mesoporosity but not PL ReEtching MAC-etched powders greatly increases mesoporosity and makes both EG and MG powders photoluminescent

Mesoporosity in metallurgical grade SiNW noted by e.g. Li, Yan, Wang, Graff, Schweizer, Sprafke, Schmidt, Wehrspohn, Adv. Energy Mater. 2015, 5, 1401556; and in highly doped Si by Hochbaum, Gargas, Hwang, Peidon Yang, Nano Lett. 2009, 9, 3550–3554
H$_2$O$_2$ Injection Induces Transition from MACE to ReEtch

MACE is characterized by formation of etch track pores

ReEtching is characterized by the formation of uniform porous layer

- Weak PL
- Ag quenching
- Strong PL after ReEtching

0.025 mmol Ag

3 mmol Ag
Conclusions

- Laser ablation facilitates the formation of pillars, macropores and nanoparticles.
- Injection of $\text{H}_2\text{O}_2$ regenerates $\text{V(V)}$ which is the optimal oxidant for producing photoluminescent $\sim 4$ nm pores in porous Si (ReEtching).
- Injection of $\text{H}_2\text{O}_2$ in the presence of Ag can induce etch track pores (MACE) or weakly luminescent much smaller pores (ReEtch like process).
- Electroless etching may prove to be an economically viable route to porous silicon powders and crystalline Si nanoparticles on the kg to ton scale (ReEtch process) and Si nanowires through MACE with $\text{H}_2\text{O}_2$ injection.
- ReEtching and MACE + ReEtching facilitate the formation of hierarchical porous Si. Pores within pores, pores within pores within SiNW. Tortuous 4 nm pores inside of larger ($\sim 15$ nm) pore walls.
- ReEtched Anodic Porous Silicon (RaPSi) exhibits $> 800$ m$^2$ g$^{-1}$ unusually strong, tunable PL. ReEtched MAC-etch powder leads to luminescent SiNW.
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