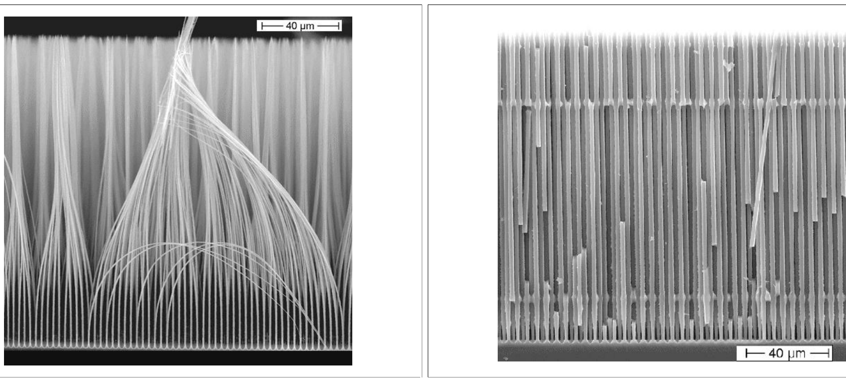
2.5 Exotic Semiconductors, Processes and Products

2.5.1 Porous Semiconductors and Product Ideas

Microporous Silicon

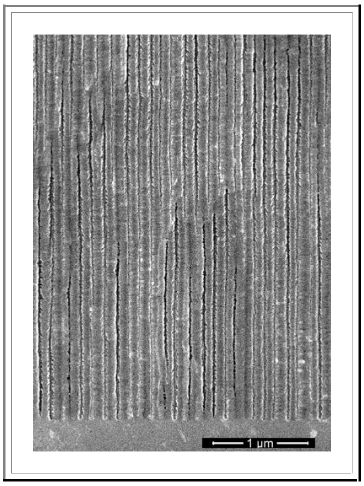
- Imagine a piece of perfect single crystalline **Si** that you have turned into a sponge by drilling holes into it that meander around like, well, just like in a sponge.
  - Now imagine that the diameter of your holes is only a few **nm**, and that the average distance between the holes is also just a few **nm**. Now ask yourself: Where is my periodic potential that I need in order to evolve a band structure? How many atoms do I need to be lined up in some periodic arrangement before I can talk about a periodic potential? Two are probably not enough, but **200** might do.
  - Tricky question. Let's simplify this a bit by considering a **quantum wire** - a **Si** crystal arbitrarily long but with a very small diameter. As long as the diameter is a few **10 nm**, nothing happens. You have a nice semiconductor, just a bit on the small side. Now decrease - in your mind - the diameter to just a few **nm**. You will now encounter "**quantum wire**" effects. With decreasing diameter the bandgap (perpendicular to the wire length) seems to increase and finally you just get a bunch of discrete energy levels - because you are loosing your periodic potential.
  - Now look back at your sponge. Between the pore, you have some quantum wire like pieces of **Si**. You must expect that the **Si** sponge behaves different from solid **Si**.
- As it turned out in **1991**, a Si sponge on a **nm** scale is extremely easy to make - all you need is a simple electrochemical cell with **Si** as the anode through which you run some current at the right conditions.
  - Your **Si** sponge actually falls into a new class of materials called "**metamaterials**"; man-made things with properties not encountered in the constituents. For reasons deeply routed in ancient chemistry, all materials with pores in the size range below **10 nm** must be called *micro*porous and not *nano*porous (s would be proper).by sone codifies convention. I know it makes not sense, but it comes from chemistry, for God's sake..
  - The properties of microporous **Si** are just amazing. To give just two:

    1. It behaves like a direct semiconductor with a band gap of **1.5 eV** or so (depends on porosity), showing strong luminescence.
    2. If you put oxygen-rich stuff in the pores (e.g. **$KClO_4$**) you have produced a high explosive with three times the bang (as measured in **kJ/kg**) than **TNT**
- Beside microporous **Si**, we have also mesoporous (**10 nm - 50 nm**) and macroporous (**> 50 nm**) **Si**; many other semiconductors can also be turned porous.
  - Porous semiconductors are objects of active research. Many possible uses have been proposed, none is on the market right now.
  - The picture below shows **Si nanowires** (actually microrwires but nowadays we call all that "nano" because it's more sexy); they were made via pore etching. The structure has been optimized for an extremely hot new application: Anodes in **Li ion batteries** with an 11-fold capacity increase relative to the state-of-the-art. If you want to know more, use the link.



Si "nanowires" made via electrochemical pore etching.

- Here is another possibly "hot" application:
  - Porous Si with a pore geometry as shown on the right has a very small **thermal conductivity**. The reason is quite simply that the wavelength of the phonons transporting the thermal energy does not fit anymore in the small space between the pores.
  - Electrons can still squeeze through, however. What that means is that the ratio of electrical conductivity to thermal conductivity increases by orders of magnitude if the pore geometry is just right.
  - This is exactly what one needs (besides some other stuff) for making efficient thermoelectric generators.



- Efficient (and cheap) thermoelectric generators are a "hot" topic right now (2010) because if we (=Materials Scientists and Engineers) can make them, "**energy harvesting**" from all kinds of hot surfaces - car exhausts for example - will be big business.