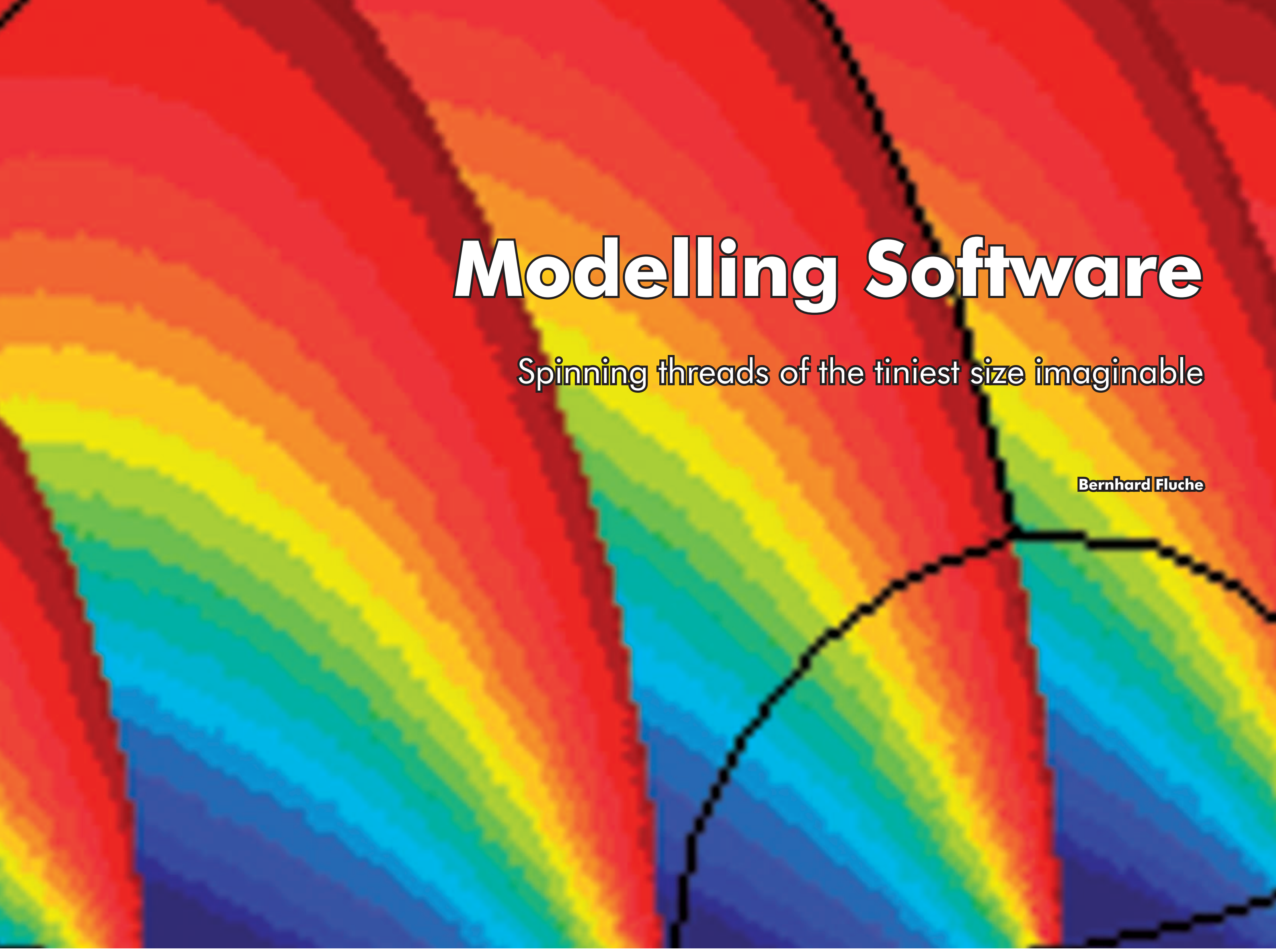
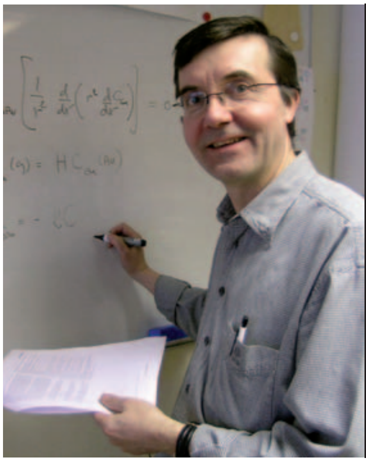
Modelling Software

Spinning threads of the tiniest size imaginable

Bernhard Fluche



The process of manufacturing nanowires – the smallest possible threads, sometimes just a few atoms wide – is not yet completely understood. Sophisticated modeling software is helping researchers rethink their previous assumptions about nanowire growth. With this newfound knowledge they can better understand and explain this revolutionary process and prepare it for commercialization.



Prof. Stig Stenström of the Chemical Engineering Dept at Lund University created a COMSOL Multiphysics model of nanowire growth to help researchers understand and better exploit the underlying phenomena.

If you've never thought of the human hair as being huge, consider that with an average diameter of 50 µm, it is roughly a thousand times wider than a nanowire. Made of materials such as silicon and other semiconductors, polymers, and carbon, these unimaginably thin threads can sometimes have diameters less than 10 nm, just tens of atoms across. Early laboratory findings indicate that these ultra-fine wires will open up a variety of remarkable applications. But until we learn how to manufacture them efficiently, these commercial uses will remain only dreams.

Researchers thought they had a good grasp on how these nanowires grow, but recent mathematical models with COMSOL Multiphysics along with laboratory calculations and observations have uncovered evidence that a completely different growth mechanism might be at work. Furthermore, the computer simulations are helping these researchers determine the process parameters that will induce the growth of hollow nanotubes rather than solid nanowires.

Exotic applications become feasible

Because of their unique and unusual properties, nanowires offer an amazing range of potential applications. They could find uses in filtration systems; serve in biomedical applications such as wound dressings and drug-delivery systems; allow the design of solar sails, light sails, and mirrors for use in outer space; develop innovative agricultural pesticides; act as structural elements in artificial organs; and help strengthen reinforced composites.

Nanowires made of glass could form the basis of optical sensors and probes that could detect biological particles; they could work as photonic devices such as liquid lenses whose focal lengths could change with an electric field; they could implement photonic switches, power splitters, filters and multiplexers, and even data-display assemblies.

A bed of nanowires can create "nanograss", which could result in products ranging from low-friction surfaces on which water or another substance glides off seemingly unimpeded; to batteries where the electrodes and electrolytes remain separated until the battery is needed, thus extending its shelf life indefinitely; and even to heat sinks. In the years to come, we can expect researchers to come up with any number of exotic devices that exploit these tiny structures.

While some of those applications might take considerable time to realize, one near-term use of nanowires is to implement the interconnects needed to wire together the next generation of integrated circuits, which are shrinking so small that conventional packaging techniques are large and cumbersome in comparison. And in some cases, crossed nanowires or those made of dissimilar semiconductor materials can themselves implement digital logic gates.

A totally new way of looking at the process

Before any of these ideas can become commercial reality, researchers must first develop a process to manufacture nanowires at a reasonable cost. In the semiconductor area, the most common method of creating one is now known as the VLS (vapor-liquid-solid) growth mechanism (Fig. 1). The process supplies the reactants in a vapor phase. They react with a liquid metallic seed particle placed on a substrate, and a nanowire grows perpendicular to the substrate. The VLS mechanism implies that the solid wire forms through precipitation on a droplet of metal that acts as the seed. The driving force for crystallization is supersaturation within the droplet, which is established by catalytic absorption of the gaseous reactants from the surroundings.

In more detail, the manufacturing process starts with a single crystalline GaAs substrate. The next step is to deposit, very precisely, size-selected gold nanoparticles on the substrate, and then the substrate with particles goes into a reaction chamber. The chamber is evacuated and heats up to 540 °C. The process then introduces reactants into the chamber as molecular beams of gallium and arsenic (a molecular beam is produced by allowing a gas at higher pressure to expand through a small orifice into a container at lower pressure; the result is a beam of particles moving at approximately equal velocities with few collisions occurring between them). Under the right conditions, GaAs forms under the gold particle but not anywhere else on the surface. The resulting nanowire can grow to be as long as 0.5 to 10 µm. The researchers at Lund University are concentrating on the para-meters that control nanowire growth so it forms different semiconductor compounds that have desirable properties. Among the factors to control are pressure in the reaction chamber, the concentrations of arsenic and gallium, and the diameter of the gold seed.

While this explanation of nanowire growth seems valid for some cases, in others, such as when growing gallium arsenide (GaAs) with gold seed particles, it leaves many unexplained phenomena and inconsistencies. Scientists clearly need a better understanding of the mechanisms governing semiconductor nanowire growth to enable the development of this promising field. One group of researchers investigating this area comes from the Nanometer Structure Consortium at the Lund Institute of Technology (Lund, Sweden). Members of the physics, mate-

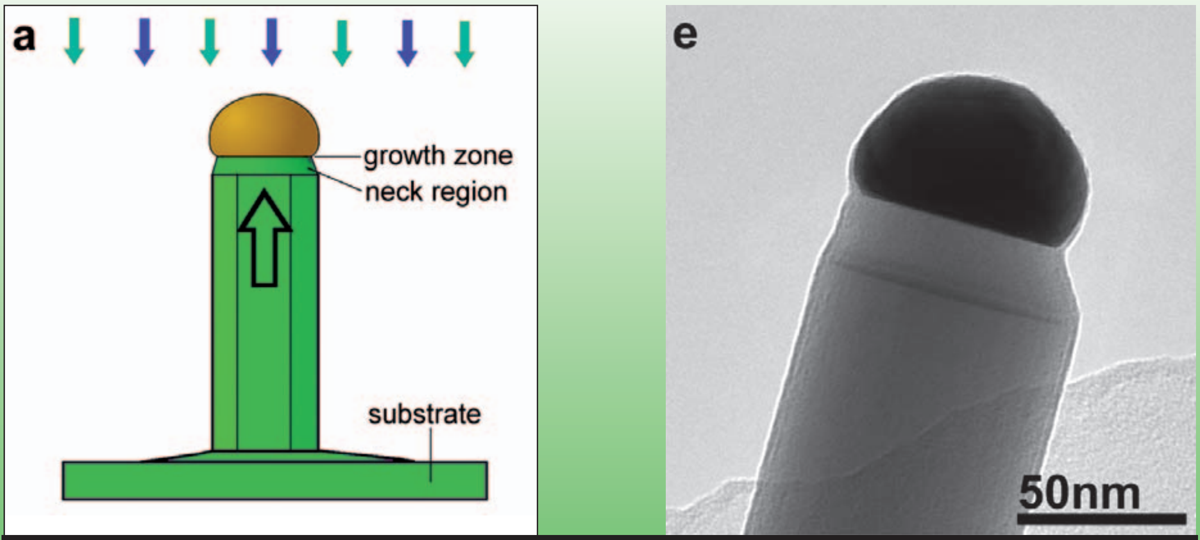
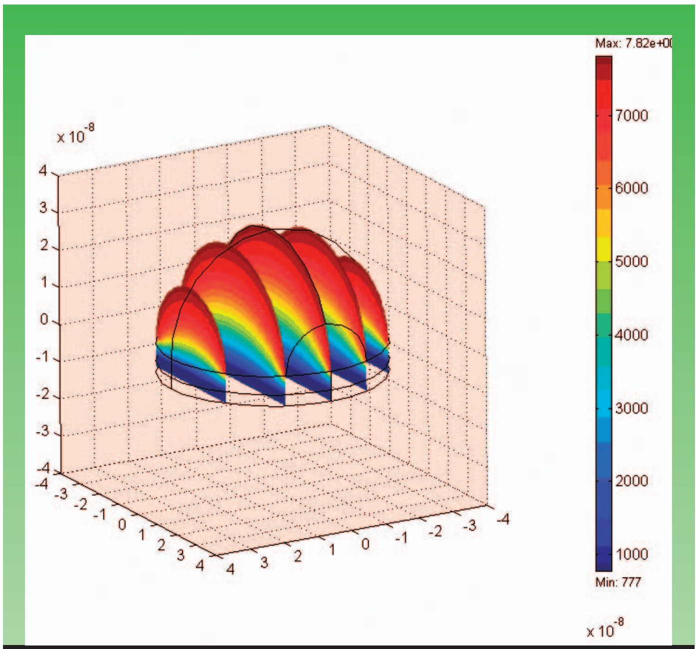


Fig. 1: To grow a nanowire, the process starts with a seed particle on a substrate (a). The nanowire's constituents, arsenic and gallium, are supplied as molecular beams, here shown coming from the top. Progressive crystal growth takes place in the zone just underneath the seed particle. The photo in (b) shows an actual nanowire with its neck clearly visible.



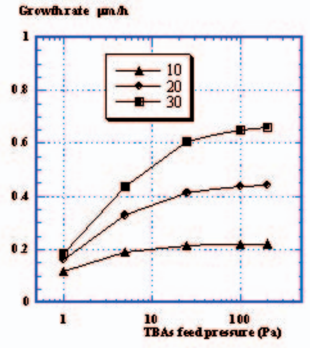


Figure 2: The COMSOL Multiphysics image above shows the gallium concentration in the nanowire for an arsenic source pressure of 200 Pa and a gallium source pressure of 27 Pa. The distance for diffusion of gallium is much shorter at the edges of the wire compared to at the centre. Thus the flux of gallium is larger at the edges, indicating the possible formation of tubular nanowires. The plot on the right shows the wire growth rate for arsenic source pressures between 1 and 200 Pa and gallium source pressures between 10 and 30 Pa. An increased gallium source pressure leads to a higher gallium concentration at the surface of the gold seed particle, resulting in a larger flux to the reaction layer and a faster growth rate.

rials chemistry, and chemical engineering departments believe that the actual growth mechanism in some cases involves solid-phase diffusion rather than the VLS mechanism. To study this concept, they perform laboratory experiments and compare the results to finite-element calculations of the mass transport and expected growth rates using COMSOL. In this way, they hope to clarify the alloying situation and the aggregation state of the seed particle, which is a key to a more complete understanding of the nanowire growth mechanism and thus the refinement of a viable manufacturing process.

A close look at the seed

To better understand the growth process and what happens in the reaction zone, the consortium enlisted the assistance of Prof. Stig Stenström from the Chemical Engineering Dept, who created a COMSOL Multiphysics model of growth including transport and the formation of the GaAs compound. This single-physics problem in 3D performs the material balance and calculates the mass-transfer rate using the Convection and Diffusion application mode. This mode's PDE templates provide the necessary description of the mass-transport equation, but Prof. Stenström had to add a custom equation that accounts for the reaction rate at the substrate layer. Further, he modeled the gold droplet to consist of a short cylinder topped with a half-sphere.

He also had to apply special techniques when creating the model geometry. The gold spray results in a semispherical droplet on the substrate, and the diffusion at the outer edge is far faster than the diffusion in the middle of the droplet. The resulting model has 4600 nodes and 23,000 elements and solves in just two or three minutes.

Fig. 2 shows a typical output plot from the model showing the gallium concentration in the seed particle and the nanowire's growth rate. By integrating the flux of gallium it is possible to calculate the growth rate of GaAs for different process conditions.

One thing that this model showed the researchers was that the previous generally accepted theory of nanowire growth, the so-called vapor-liquid-solid (VLS) mechanism, should be replaced by a vapor-solid-solid (VSS) mechanism.

Commenting on these results, Prof. Stenström says, "At this time, our model deviates with experimental data by only a factor of two. When I say 'only', I admit that in many situations that amount would be unacceptable, but in this case we think it is quite good – given the limited amount of data we have for this process. Part of the reason for these deviations stems from the fact that we don't fully understand what is going on in the reaction, so we have to make a number of assumptions."

Prof. Stenström is familiar with COMSOL Multiphysics from previous work, and he was happy to use it for this application. "It's easy to create the geometry, set up the boundary conditions, and enter the physical data for the system. I was also able to enter my own expressions for the reaction rate, whereas other codes would require us to write our own equations in a much more cumbersome fashion. Further, COMSOL Multiphysics offers good plotting facilities and visualizes results very well. Overall, the package fits in well for problems in chemical engineering such as this."

Reference

- *A. I. Persson* et al., Solid-phase diffusion mechanism for GaAs nanowire growth, Nature Materials **3**, 677–681 (2004).

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Dr. Bernhard Fluche is a physicist and CEO of FEMLAB GmbH. He founded the company in 2001 as a subsidiary of COMSOL AB, that was established 1986 in Stockholm. The company creates easy-to-use modeling software tools for solving complex multiphysics problems. The customers are researchers and engineers working for leading technical and scientific enterprises, research labs, and universities. COMSOL Multiphysics helps them to design and develop high-tech products.

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