Growth and Properties of inorganic Nanowires

Since the discovery of Carbon Nanotubes, nanostructures have become an interesting field of research in solid state physics. The word „nano“ is put in front of nearly everything to make it sound technologically advanced. As the chip sizes are more and more shrinking, the physical limit of lithographic methods („ top-down“) in order to produce nanostructures is in sight. The „bottom-up“ method to produce self-assembled nanostructures might open the way to nanocomputers, as the nanowires grown by this method are showing interesting properties.

The idea is to let the smallest building blocks grow by self-assembly and then harvest them. Through hierarchical assembly the building blocks are put together in order to form a functional system. The field of application is expected to be large and reaches from computing to sensing and medical applications.

Depending on the properties wanted, different materials can be used for the growth of nanowires. A lot of research has been done on carbon nanotubes. Also metal nanowires can be produced, e.g. out of gold. Semiconductor nanowires are very interesting for future applications as the nanowire itself can be given a functionality. A lot of different semiconductors have been grown as nanowires, e.g. zincoxide, gallium arsenide, indium phosphate and silicon.

In order to grow nanowires by self-assembly, a great variety of different methods has been studied. The most prominent one probably is the Vapor–Liquid-Solid Epitaxy (VLS) where a metal catalyst droplet is used to grow the nanostructures. The VLS technique has already been discovered in 1964 by Ellis and Wagner and has been described in detail by Givargizov in 1975. Nowadays there is a renewed interest in this technique due to the need for the systematic synthesis of nanostructures. The whole principal consists of three main stages: (I) A metal alloy droplet is placed on the substrate where the nanowire is supposed to grow. Gold has turned out to be a good component to grow silicon nanowires. (II) Gas (e.g. Silane), containing the material out of which the nanowire is to be grown is given into to growth chamber. It condeses preferentially at the catalytic alloy droplet and increases in this case the concentration of Silicon. The droplet saturates more and more until it is supersaturated. (III) Nucleation lets the nanowire grow on the substrate. The alloy droplet remains on top of the nanowire.
As a major requirement, there should exist a good solvent capable of forming a liquid alloy with the target material, ideally they should be able to form eutectic compounds. For Au-Si the eutectic point lies at about 363°C, so a growth temperature at about 900°C allows growing from the liquid phase to a phase with liquid gold an solid silicon by increasing the silion percentage in the alloy droplet. It is important that the solubility of the eutectic metal is as low as possible in order to not destroying the semiconductor properties of the nanowire. In case of gold in silicon the solubility is 2 ppm. Thicker nanowires grow faster, to which is referred as the „Gibbs-Thomson-Effect“. The difference of the chemical potentials is the driving force when growing. This difference decreases compared to the bulk by a value, depending inversly on the diameter d: $\Delta\mu_{nanowire} = \Delta\mu_{bulk} - 4\frac{\Omega\alpha}{d}$ This also shows that there is a critical size d_c where nanowires stop growing under thermal equilibrium conditions.

A major challenge in the VLS-process is to control the localization and the density of the growing nanowires. A fast and cheap method is needed to precisely place the catalyst on the sample surface. Different methods have been tested so far. With e-beam lithography good results can be achieved, but the method is too slow. The whole surface has to be scanned and this takes very long. The same with using focused ion beams. With an AFM, single gold points can be placed in the exact position where it is wanted. It is a nice method for demonstration purposes but not at all suitable for mass production. A solution of gold crystals can be spread on the surface of the sample and as the solvent dries, the gold remains. A problem is that the gold crystals tend to cluster. Block Copolymers can be used to create nice spherical structures on the surface that then are used as a template to deposit

the metal. In nanosphere lithographie a monolayer of nanospheres funcitons as a template. Metal is sputtered against the template and on the sample surface you get a hexagonally distributed structure of the catalyst. In this method the density and the diameters of the droplets are linked. Another method is to oxidize Aluminum chemically and thus generate hexagonally distributed deep pores that can serve as a mask.
The crystall growth orientation is important for the nanowire properties. A different growth direction can lead to different atoms at the surface. The growth direction can be controlled by the crystall orientation of the substrate.

There are also other ways to create nanowires without using lithographie. For example, we use a template as a scaffold an receive a nanostructure that has the complementary form of the template. This method has a high through-put, but is limited to producing polycrystalline or amorphous nanostructures.

As said before, nanowires show interesting properties. It was observed that Germanium nanowires coated with a carbon sheath start to melt much earlier than the bulk Germanium. The low melting point allows zone refining, cutting and welding at moderate temperatures.
By deflecting Silica nanowires with an AFM the Young's Modulus has been measured. But no clear tendencies on the diameter dependence could be discovered. Different methods (e.g. Resonance vibration) lead to different results which shows that the phenomena are not yet fully understood.
The dimension of nanowires is in the region of the phonon mean free path, so interesting properties concerning thermal conductivity are expected. The importance of alloy scattering, interface scattering due to mismatch in acoustic impedance and scattering by defects and dislocation at interfaces of superlattice nanowires have been examined and confirmed. Boundary scattering greatly reduces the thermal conductivity compared to 2-dimensional structures.
Electron confinement leads to interesting electron transport properties. It turned out that for example Si nanowires with a diameter of 15 nm were insulators although Silicon in bulk is a semiconductor.
Furthermore there are promising results in the optical behaviour of nanowires. Photoluminescence has been discovered. Nanowires with flat ends can be used as resonance cavities for lasing. The Yang Group (Berkeley) managed to get ZnO nanorods to UV-Lasing at room temperature.

Nanowires can be processed as heterostructures. There is the possibility of coating an existing nanowire with a different material. Creating more sheaths and/or doping can create nanowire-based transistors. When having different chemical stabilities the inner core can be etched away in order to create nanotubes.
By changing the carrier gas during the VLS growth process superlattice nanowires can be created. With p-n junctions created, they can serve as building blocks in nano electronic circuits.

In order to create devices out of nanowires different methods for hierarchical assembly have been studied. One idea is fluidic assembly where nanowires are aligned along the streamlines of a small droplet in a microchannel. A different approach is the Langmuir-Blodgett technique where nanowires float on a water surface as a monolayer. As the surface is compressed the nanowires orientate in the same direction as the barrier and can be transferred to a substrate. Large areas can be created, but it is not possible to adress single nanowires with these methods.

There are many hopes related to nanowires for creating nanodevices. There is the hope to create displays with nanoresolution or logic gates based on photonics. Nanowires should be used to enable the production of nanocomputers. Sensing applications are profiting from the high surface to volume ratio and thus a high sensitivity to changes in the surface properties.
Still the industrial use of nanowires is far away and a lot of research and developement needs to be done.