

1 Introduction

This thesis is concerned with the particle-based fabrication of materials. It describes how particles can be arranged and stacked on surfaces to create materials with complex geometries and chemical compositions. This introductory chapter discusses why we want to fabricate such materials, why particles are interesting building blocks to create materials, and how this approach is conceptually different from other routes. It introduces some prior examples of particle-based materials and devices that use particles as functional components. The last section of the chapter describes the structure of the thesis.

1.1 Control of structure in materials fabrication

A paradigm shift is currently taking place in materials science and technology. So far, materials were created by varying well-known materials syntheses (and treatments) with limited control over their microscopic structure. Now, there is widespread optimism about and intense research into the creation of materials with predefined structures that have improved properties.

This shift was initiated by the advent and subsequent spread of two new fields: semiconductor microtechnology and nanoscale metrology. The advances in metrology (which included the invention of scanning probe microscopy and electron microscopy as well as the spatial reconstruction of x-ray diffraction measurements) have made it possible to correlate nanoscale structures of materials with their properties. Semiconductor technology has demonstrated that materials can be patterned with ever-increasing resolution, even at high throughput. The expectation arose that a “nanotechnology” could be developed that can create general materials with well-defined nanostructures, and thus, well-defined properties that might be tailored to solve a given problem.

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Such deterministic materials fabrication requires the solution of one central problem: the flow of information from the design to the final material. In semiconductor technology, for example, designs are first created with high-level description languages that define functionality on an abstract level. From these descriptions, an explicit design for the physical structure of the semiconductor is created (automatically or semi-automatically), which can then be translated into a set of masks for photolithography and a sequence of processing steps.

Likewise, to translate a desired materials property into the topographical and chemical structure of a material, high-level information has to somehow be translated into a physical structure. One could imagine, for example, that some future semiconductor technology will define the position and type of each atom in a device according to a design. This is not as outlandish as it might seem: at feature sizes below 10 nm that have been demonstrated in the research laboratories of semiconductor manufacturers [48], fewer than 30 atoms span the gate width. The gate dielectrics in the latest CMOS transistors are only some atomic layers thick.

For materials fabrication, however, such an “explicit” nanotechnology is inefficient in multiple aspects. The generality of the method comes at an extremely high price. After more than 30 years of continuous size reduction in the semiconductor industry, there exists a relatively robust rule for the cost of size reduction: the linewidth can be expected to drop one order of magnitude every 15 years. This decrease of the characteristic dimensions is accompanied by an increase in investments to build the necessary factory by somewhat more than one order of magnitude [37]. A lower bound for the investment required to build one production site capable of achieving atomic resolution would therefore be two trillion US-dollars. This assumes that there are no qualitatively new challenges

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involved that further increase the price, but such challenges are very likely to occur. If there are applications for which such investments would be viable, they must be using small amounts of extremely complex materials with very high added value. It is not clear whether even computer CPUs will qualify for this in the future.

Another route proposed for translating the structural information into a physical representation is the “Molecular Assembler” devised by Eric DREXLER [49]. He suggested programming a “finger” (say, the tip of a scanning probe microscope) such that it assembles reactive molecules into a material sequentially, by mechanically removing a carrier part and leaving a single atom at a time. In reply to this proposal (and some of the ideas promised to become feasible with such a fabrication method), Richard SMALLEY published an article in *Scientific American* [161], in which he famously pointed out two problems that such a molecular assembler might have, namely, its *fat fingers* and its *sticky fingers*. He argued that any computer-controlled “finger” would be too large and too imprecise to control motion at an atomic scale, and that it would stick to the molecules involved. He also argued that there was no chemical system that could replace these fingers to place atoms with the required accuracy one by one.

These limitations are still the topic of discussion, but a general problem of an additive, sequential fabrication on a molecular (or other very small) scale is the timescales involved. Even when moving at the speed of light, the finger of an assembler would need at least ten years to assemble 1 mm^3 of silicon from a heap of single silicon atoms that lie at a distance of 1 mm. Even if there were a constant supply of atoms flowing to the tip, the tip would have to travel millions of kilometers.

Several alternative routes have been proposed to avoid such problems. Many of them are based on the idea that during fabrication, the

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material itself would act as a machine that arranges its parts so that a defined structure is created. If that machine is sufficiently general, it could produce any structure required. Such concepts are often called “self-assembly”, “self-organization” or “emergence”. Their archetypes in nature are cells and viruses in which functional parts (or even entire viruses) self-assemble from its parts.

Such materials syntheses could be very efficient. The flow of information, however, is vastly more complex than in semiconductor technology or sequential assemblers. Instead of separating the assembly problem from the material’s functionality, both are now one. It is not sufficient to predict the structure required for obtaining certain materials properties, one also has predict the behavior of the disordered system and then choose a system that will arrange into the desired structure. This inverse problem in general is hard, and there is not much hope that we will soon be able to design general systems so that a given structure emerges. Thus, from an engineering standpoint, self-assembly is not yet a general method for materials fabrication.

There might be a compromise, however. Similar to what is done in classical materials fabrication (say, metallurgy or polymer formulation), we can choose systems that produce materials with interesting properties, analyze their nanostructure and bias it by changing the components or changing external parameters. We thus part with the notion of a general materials fabrication in favor of problem-oriented approaches, as they have been traditionally used with great success.

One way to bias materials fabrication in a deterministic manner is to use templates that direct the final structure in a predictable way. Such templates might be created with slower, more direct methods of nanofabrication, for example on a surface. Their order will be replicated by the self-assembling components.

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In this thesis, building blocks are arranged at predefined positions of a template. The hope is thus to combine the traditional, engineering-oriented manufacturing technique with the novel, efficient, but complex self-assembly concept. In literature, this often is dubbed the combination of “top-down” with “bottom-up”-fabrication [180].

1.2 Top-down and bottom-up, subtractive and additive fabrication

The main differences between traditional technology and self-assembly are the flow of information (summarized in the “top-down” versus “bottom-up” dichotomy) and the flow of materials. In traditional semiconductor technology and the micro- and nanofabrication technologies that have been derived from it, fabrication is mainly done by subtraction. A wafer of bulk material is etched, thin films are being applied on its entire area only to then be polished, etched or stripped away on most parts, polymer layers are exposed and developed to remove the exposed parts.

Such a subtractive strategy is in marked contrast to macroscopic manufacturing. Machines are generally built from pieces that are fabricated separately. A subtractive route, however, provides cleaner interfaces and bulk materials parts with constant properties (and even continuous crystal structure). These are critical prerequisites for semiconductor integrated devices, which subtractive technology can produce at remarkable yields.

Subtractive methods are inherently costly, however. Each step only patterns one metal or semiconductor layer, and each step involves a pattern transfer — in general, a photolithography step with a top-down flow of information — and an actual material transfer. This becomes

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problematic when making large amounts of structured materials, be it in complex thick layers, bulk pieces or large areas. Even when the desired structures are simple, repetitive or sparsely dispersed over the material, many costly fabrication steps are necessary, and many of them cannot be performed in a continuous fashion.

In bottom-up processes, where the process information is stored in the building blocks that will form the material, fabrication usually is additive. These blocks will react, agglomerate or deposit according to the information stored and self-assemble into the desired structures. Some structures are easily fabricated in this way, e.g., dense and ordered molecular "self-assembled monolayers" [175], hexagonal particle crystals (in two or three dimensions) [117], spaced particles on surfaces without particular order [63], or regular dewetting structures of diblock copolymers [72], and some of them are useful in one or the other application. However, numerous other useful structures could so far not be created bottom-up, and there is no general bottom-up process that would easily produce many different structures.

If a self-assembly process is known to create a desired structure, the actual fabrication can be remarkably simple. In contrast to thin-film technology, which commonly requires vacuum equipment, high temperatures and energetic plasmas, many of the known self-assembling systems are closer to dip-coating or spraying. The challenge lies not so much in providing extreme conditions in a relatively simple material system but rather in providing exactly the right, moderate conditions in a complex material system.

It should be possible to find bottom-up processes for many different structures. According to Brownian Dynamics simulations, complex arrangements can emerge from moderately complex building blocks (such as particles with patches on their surfaces) [194]. Such structures of-

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ten lack long-range order, as their order will decay at a length that is comparable to particle-particle interaction lengths, unless critical phenomena or kinetic mechanisms provide additional, long-range interactions. Traditional semiconductor devices have very strong long-range correlations, which is a prerequisite required to enable the typical, step-wise fabrication of standard technology. It is possible to introduce long-range order, however, using a template that confines the self-assembling structures, as has been demonstrated for the microphase separation of diblock copolymers [32].

1.3 Particles as building blocks

Instead of using molecules or atoms directly and build materials from scratch, it is easier to move to the mesoscopic level and arrange nanoparticles (or even larger particles) to create structured materials. Such particles are readily synthesized using bottom-up processes. It is a well-known strategy to introduce surface-active molecules into crystallization and polymerization processes to favor certain geometries during the growth or to seed such processes to create monodispersed crystals, polymer beads, or glassy spheres, and there are recipes available for preparing a large variety of particles from metals, semiconductors, oxides and many other materials. Detailed information on the particle syntheses used to create the particles mentioned in this work will be given in the experimental chapters later on. The reader is also referred to the large number of reviews on the subject of particle synthesis [86,123,135].

Particles can serve two different purposes: they can provide some functionality at a single-particle level, or they can interact to provide some interesting property. The vast literature on particles (in particular, on nanoparticles) contains many examples of functional particles.