

The logo for 'cientifica' features the word in a white, lowercase, sans-serif font. A small, stylized graphic of a pencil or pen nib is positioned above the letter 'i'.

Bottom-up
Production Techniques

Technology White Papers
nr. 15

The background of the cover is a dark, almost black, field filled with numerous small, out-of-focus, multi-colored spots. These spots, in shades of purple, blue, green, yellow, and red, are arranged in a way that suggests a perspective of looking down at a large number of tiny objects, possibly representing a microscopic view of a material or a data visualization. A thin, horizontal band of purple and blue light is visible near the top of this section.

Paul Holister
Cristina Román Vas
Tim Harper

BOTTOM-UP PRODUCTION TECHNIQUES

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Authors

Paul Holister
Cristina Román
Tim Harper

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Origin of content

The free reports in this series are extracted from the technology reports that make up the Nanotechnology Opportunity Report collection and are designed to offer an introduction to the variety of technologies that fall under the nanotechnology umbrella. The full reports also include 'opportunities' sections, covering the various applications of the technology and their effects on markets, and a list describing the companies involved in the technology.

Bottom-up production techniques

The distinction between bottom-up and top-down production techniques is often made in writings on nanotechnology. Top-down techniques take a bulk material and form and modify it into the desired product. This often, but not always, involves removing some material in the form of wastage. An example would be the machining of a metal engine component or the nanostructuring of metals through deformation (the latter not involving wastage). Bottom-up techniques build something from more basic materials. An example would be the building of an engine out of the component parts. In general there is less likely to be wastage with bottom-up approaches, but this is not necessarily true (a component in a self-assembling system, for example, might need a co-component to assist the self-assembly process but which is not wanted in the resulting product and would need discarding).

Self-assembly

Self-assembly is a bottom-up production technique that has excited many because of the potential economies in having products that simply "make themselves". It is, of course, not that simple. Nor is self-assembly anything new. Biological systems are built predominantly using self-assembly and even age-old industrial chemical reactions could be described as self-assembly.

The aspect of self-assembly that is somewhat newer, and attracting all the interest, is our increasing ability to control it to make structures such as layers (for coating flat surfaces or nanoparticles, for example), nanocapsules, nanowires or even basic molecular electronics components. Dendrimers are a classic example of relatively complex self-assembly, although many would simply describe this as polymer chemistry.

Because of the wide variety of nanotechnologies to which self-assembly may be applicable, it is normally dealt with in the appropriate sections elsewhere in the report, the exception being self-assembled monolayers, covered below. However, self-assembly as a general approach does warrant some discussion.

In nature, self-assembly is used to make some remarkably complex systems (though nature does also have approaches other than self-assembly, such as the creation of proteins by ribosomes, which resembles a production line). At present, our mastery of self-assembly is limited to relatively simple systems. The trick to making more complex systems is hierarchical self-assembly, where the products of one self-assembly step become the basis of the next, assembling again into something more complex.

Multiple layers of self-assembled monolayers and the building of dendrimers already require some of the planning and design of hierarchical self-assembly. Ultimately, it may be possible to make complex structures such as computer processors only using self-assembly. The hurdle to overcome here is the design of such hierarchical processes, which can be expected to require many stages. The undertaking is not a trivial one, but the potential rewards are great, the promise being of the manufacture of large quantities of complex structures simply by a sequence of steps analogous to bulk manufacture of chemicals, such as in the pharmaceuticals industry.

Self-assembled monolayers

Self-assembled monolayers (SAMs) are produced when a substance spontaneously forms a layer one molecule thick on a surface. Additional layers can be added, leading to laminates where each layer is just a molecule in depth. Research in this area began in 1983 and has seen an increasing number of published papers every year. Research into SAMs coincided with the maturation of scanning tunneling microscopy following its invention in the early 80s.

SAMs are produced when a substrate, for example a metallic or porous surface, is placed in contact with a solution of organic molecules, which then spontaneously align themselves with respect to the substrate. The coated material can then in turn be the substrate for a layer of a different compound.

Whereas various approaches to creating metallic and ceramic films are well established, they cannot generally be applied to creating organic films because they usually involve extreme conditions that would destroy organic molecules. SAMs, however, can now be created under very moderate conditions and the use of organic materials is opening a new range of possibilities (they offer improved control over charge transport for electronic applications, improved adhesion control and greater biocompatibility). Notably, SAMs are generally close to perfect in structure, although they don't initially form this way but undergo a process of reorganization and become extremely well-ordered.

SAMs are one technology that can contribute to biosensors, such as DNA chips, which consist of arrays of immobilized single-stranded DNA probes. Significant work still needs to be done on creating the ideal film structure and composition for attachment of the DNA probes.

SAMs are also widely used in microcontact printing, a form of soft lithography (covered in a separate section).

Sol-gel technology

First discovered in the late 1800s, sol-gel processes started to be used extensively in the early 1930s. More recently, processes to make gels at low temperatures and convert them to glasses have been developed.

The sol-gel process is a versatile process for making ceramic and glass materials from solutions or colloids (where a particle is not dissolved in a liquid but also does not settle out, as it does in a suspension). In general, the sol-gel process involves the transition of a system from a liquid "sol" into a solid "gel" phase. Applying the sol-gel process, it is possible to fabricate ceramic or glass materials in a wide variety of forms: ultrafine or spherical powders, thin-film coatings, ceramic fibers, microporous inorganic membranes, monolithic ceramics and glasses, or extremely porous aerogel materials.

The starting materials used in the preparation of the sol are usually inorganic metal salts or metal organic compounds such as metal alkoxides. In a typical sol-gel process, the precursor is subjected to a series of hydrolysis and polymerization reactions to form a colloidal suspension, or a sol. Further processing of the sol enables one to make ceramic materials in different forms. Thin films can be produced on a substrate by spin coating or dip coating. When the sol is cast into a mold, a wet gel will form. With further drying and heat treatment, the gel is converted into dense ceramic or glass articles. If the liquid in a wet gel is removed under a supercritical condition, a highly-porous and extremely low-density material called an aerogel is obtained. As the viscosity of a sol is adjusted into a desired viscosity range, ceramic fibers can be drawn from the sol. Ultrafine and uniform ceramic powders are formed by precipitation, spray pyrolysis, or emulsion techniques.

Sol-gel processing of nanoparticles has potential for making low-cost preforms. Typically, a mix of nanosized silica and additives are cast into molds. Drying of the wet gel is then required, which takes some careful control to avoid cracking. The material can then be further processed into clear glass.

Catalytic substrates have been made using salt-based routes to nanoparticulates with ceramics (such as Al_2O_3 and Ni-YLaO_3).

Sol-gel processes can be used to accurately control the doping of titanium or germanium nanoparticles in sol-gel silicon dioxide films to control the refractive index of the material. Fibers can be spun or drawn from precursor solutions or coated with thin films.

Deposition

Classical deposition techniques are well established and wouldn't normally be classified as nanotechnology. However, they can indeed make nanoscale thin films, nanoparticles, nanotubes and other structures and, though the basic technologies are

old, they are finding new applications and being revisited as a result of nanotechnology.

Though there are a variety of deposition techniques, one, chemical vapor deposition (CVD), has recently shown particular promise in creating certain nanoscale coatings.

CVD, put simply, takes a substance in a gaseous form (usually at high temperatures and pressures) and encourages it to deposit itself on a surface. Recently, the technique has been used to create diamond films with good fine structure on the nanoscale, i.e. they are particularly smooth.

The main interest in diamond is in microelectromechanical systems (MEMS), which are normally made from silicon using traditional lithographic techniques. Diamond has a number of advantages over silicon for MEMS—it is much more physically durable than silicon, repels water, and is chemically and thermally very stable—it doesn't expand or contract much with temperature changes, effects that can lock up silicon-based MEMS. Additionally, biological systems hardly react to diamond. Diamond films have also been investigated recently for use in field emission devices for flat panel displays.

CVD approaches to the creation of nanotubes also hold great promise. This is covered under the section on nanotubes.

Manipulators

The scanning tunneling microscope and atomic force microscope can be used as manipulators but are covered under the section on microscopy.

Optical tweezers

The technique of using a single focused laser beam as an atom trap was first applied in 1984 at Bell Laboratories, though trapping techniques using pairs of laser beams predate this. Since then the use of both single and double laser beams to manipulate particles has been widespread. At the lower end of the scale it is possible to hold individual atoms and then propel them at a chosen velocity with the tweezers. At the higher end of the scale, an individual bacterium can be lifted out of a culture without damage or organelles can be moved around within a cell. The company Arryx was created to commercialize this technology.

Nanomanipulator

An application of the STM that stands out, at least for its potential to capture the imagination of journalists, is the Nanomanipulator. Developed at the University of North Carolina and commercialized by 3rd Tech, this device integrates an STM and virtual reality-style techniques to allow researchers to "feel" individual atoms and place objects on the atomic scale. NASA was the first customer.

3D printing

Also known as solid freeform fabrication, this is a prototyping technique that is becoming very popular. As yet it does not operate on the nanoscale, nowhere near, in fact—currently resolution is only sub-millimeter, but the approach is worth keeping in mind since there is no reason that it, or something similar, will not be scaled down to the nanoscale, offering the ability to create precisely-defined 3D nanoscale structures. Atom lasers, as covered in the previous section, may ultimately prove capable of performing such tasks.

The technology uses ink-jet type printing approaches to build up layers of a variety of materials, including ceramics, metals, polymers and composites, into a three-dimensional object that can have quite complex geometries. Throughput is already pretty good, allowing the creation of an object the size of a soda can in around twenty minutes. Machines are around the size of a photocopier and relatively inexpensive. A good overview can be found at the MIT 3D printing site (<http://web.mit.edu/tdp/www>).