Layered Nanoassembly of Three-Dimensional Structures

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Abstract

NEMS (nanoelectromechanical systems) loom beyond the MEMS horizon as the new frontier in miniaturization. Nanorobots and other NEMS are expected to find revolutionary applications in science, engineering and everyday life.

Until now, nanostructures have been built primarily in two dimensions, because of the difficulties of three-dimensional (3-D) fabrication. This paper describes a promising approach to the construction of 3-D nanostructures by working in successive layers, much like the rapid prototyping techniques used in the macroscopic world. Each object nanolayer is built by nanomanipulation, or possibly by programmed self-assembly, and then surrounded by a sacrificial layer that planarizes the sample and serves as a substrate for the deposition of the next object nanolayer. Initial experimental results which show that the approach is feasible are presented.

Introduction

Rapid prototyping, also known as solid freeform fabrication and by other designations, was introduced at the macroscale more than a decade ago, and is widely used in industry. Conceptually, one slices the desired object and then builds each of its layers sequentially. The actual layer construction may use several physical processes, such as curing a polymer or sintering a powdered material—see *e.g.* [Sprow 1992] for an introduction, at the trade magazine level. Recently, the EDAM rapid prototyping process dveloped at USC was demonstrated at the microscale. At the nanoscale, however, layered fabrication has been impossible until now, and none of the macro or micro rapid prototyping techniques can be extended directly to the nanometer range. More generally, fabrication of 3-D nanostructures by any means has proven very difficult, and essentially all the nanofabrication techniques demonstrated to date have been 2-D.

In the remainder of this paper we describe a novel process for 3-D nanofabrication that is based on the robotic assembly of nanoparticles in successive layers.

Basic Process

Much like in macroscale rapid prototyping, we approximate the object by a set of layers or slices, and build these sequentially. The process is illustrated schematically in Figure 1, and has the following steps.

1. Conceptually slice the nanoscale object to be fabricated by a set of parallel planes, thus defining a sequence of layers to be produced.

2. Construct the first layer of the desired material on a substrate surface. This layer, and others to be constructed sucessively, are called here *nanoslices* and have heights on the order of a few nm.

3. Level off, or planarize the result by constructing a layer that covers the substrate but not the previous nanoslice, and whose height equals the height of the previous nanoslice. This layer is called a *sacrificial layer*. The result of this step is a new surface that will serve as a substrate for the construction of the next nanoslice.

4. Repeat Steps 2 and 3 with the successive nanoslices required to construct the entire object.

5. Remove the sacrificial layers and fuse the nanoslices to produce a solid nanoscale object.

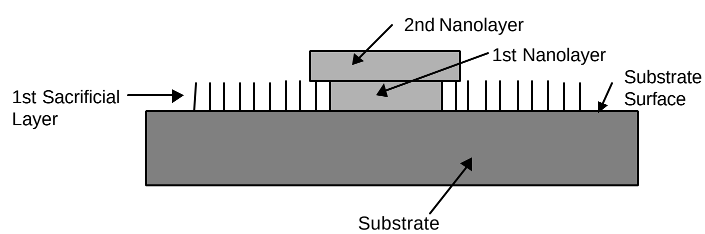

Figure 1 –Layered nanofabrication principles

In the following sections we describe in more detail Steps 2, 3, and 5.

Nanoslice Construction

We begin with a flat substrate surface, typically of (oxidized) silicon, in ambient air, at room temperature. Next we deposit (randomly) a set of nanoparticles. Typicaly these are gold nanoparticles of 5 nm diameter which are coated with hexanethiol (an organic molecule containing sulfur, which has a strong affinity for gold) and are in an organic (toluene) solution.

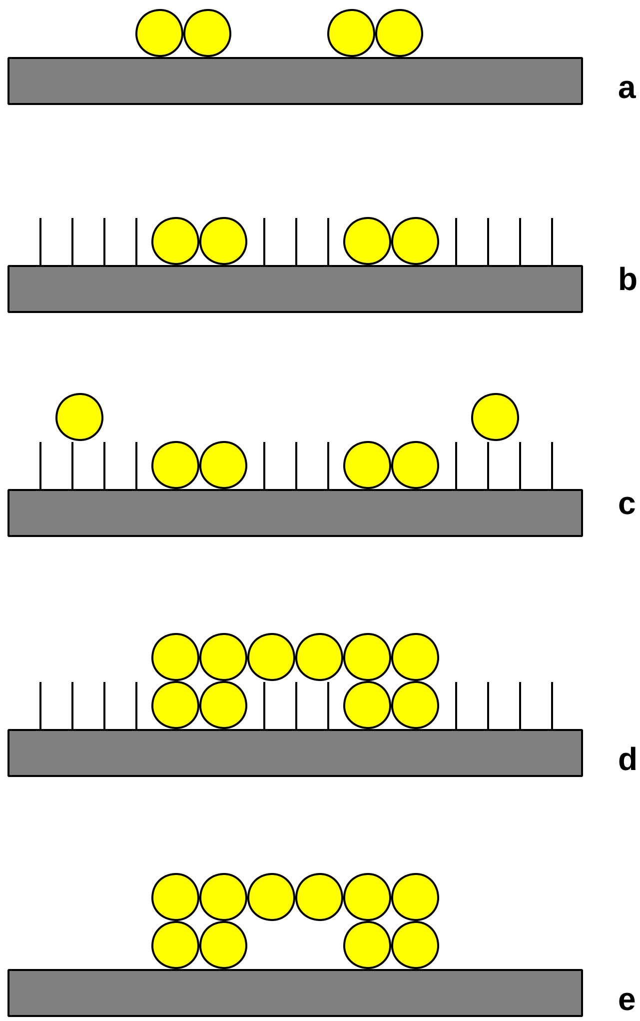

Figure 2 – Building a first nanoslice (a), depositing a sacrificial layer (b), depositing a second set of nanoparticles (c), building a second nanoslice (d), and removing the sacrificial layer (e).

The first nanoslice in built to a close approximation by assembling a group of nanoparticles, as shown schematically in Figure 2a. The assembly operations are performed with an Atomic Force Microscope (AFM) [Sarid 1994, Wiesendanger 1994], using robotic nanomanipulation techniques discussed in our earlier papers—see [Requicha *et al*. 1998, 1999] and references therein. Briefly, we proceed as follows. First we scan the sample to determine the initial, random configuration by using the AFM in dynamic, non-contact mode. Then we automatically determine the trajectories necessary to move the particles to the desired, final configuration. (This step will be reported in a paper currently in preparation.) Finally, we move each particle by disabling the AFM feedback and pushing the particle mechanically along a line that passes approximately through the particle's center.

This same procedure can be applied to successive nanoslices, as suggested in Figure 2c and 2d, provided that at each step we have a surface that can serve as a substrate for the deposition of additional particles and for their manipulation. This is the role of the sacrificial layers, discussed next.

Sacrificial Layers

Figure 2b shows schematically the result of building a sacrificial layer by (chemical) self-assembly. A sacrificial layer must satisfy the following conditions.

1. The height of the layer must equal the height of the nanoparticles, so that the combination of the nanoslice and the sacrificial layer has an approximately planar top surface.
2. The sacrificial material must adhere to the silicon substrate and to the top of the previous sacrificial layer, but not to the nanoparticles.
3. The top of the sacrificial layer must be suitable for the deposition of more nanoparticles and their manipulation with the AFM.
4. The sacrificial layers must be removable without damaging the nanoslices.

The chemists in USC's Laboratory for Molecular Robotics are currently studying various sacrificial layer materials. We are investigating three approaches.

The first is the most well developed so far. It consists of immersing the sample in a solution of OTS (octadecyltrichlorosilane) so as to deposit a layer of ODS (octadecylsilane) on the silicon substrate. (Silanes are organic molecules that contain silicon atoms.) The ODS does not deposit over the gold, and allows deposition and manipulation of newly-deposited gold nanoparticles. However, the ODS layer is not as high as the particles. Currently we are attempting to synthesize molecules similar to ODS but with longer chains. The sacrificial layer is removed by oxidation, treating the sample with ultraviolet radiation in an ozone chamber. However, it does not disappear completely. It leaves as a residue a thin layer of silicon oxide, with an height of approximately 0.27 nm. After some 20 layers this would cause the first nanoslice to be completely embedded in the silicon oxide. This is not ideal, but can be compensated for by building one or more extra nanoslices at the bottom of the object.

The second approach involves the deposition of alternating monolayers of charged polymers. The first layer is charged positively, say, the second charged negatively, and so on. Removal is achieved by oxidation. This technique has been demonstrated in the fabrication of organic light-emitting diodes and can produce layers of high quality on many substrates.

The third approach is currently being investigated by us, and involves zinc phosphonate films, which can be built to various heights. One of the most attractive characteristics of these films is that they can be dissolved in water, greatly facilitating the complete removal of the sacrificial layers.

Sacrificial Layer Removal and Nanoslice Fusion

Sacrificial layer removal is illustrated in Figure 2e. Processes for this removal operation were discussed above. They are relatively simple, and range from oxidation to washing with water. However, we do not yet know what happens to the nanoslices when the sacrificial layers are removed. It is likely that the gold will fuse automatically. If this does not happen, we can link the nanoparticles in each layer by using di-thiols, which serve as a chemical glue. We have demonstrated that this is possible, and that a robotically-assembled collection of gold nanoparticles linked with thiols is stable, and in fact can be manipulated as a whole [Requicha *et al.* 1999]. Yet another possible fusion method is sintering by using, for example, microwave radiation. In summary, nanoslice fusion has not yet been adequately studied, but does not appear to cause unsurmountable problems.

Experimental Results

Here we present initial results obtained with ODS sacrificial layers. First we deposited a set of gold nanoparticles with diameters on the order of 5 nm on oxidized silicon, as explained earlier. Then we added a layer of ODS, and a second set of 5 nm nanoparticles. In Figure 3 particle 2 was deposited in the first operation, and particles 1 and 3 in the second. The single-line scan over particle 2 shows that it has a height of 4.7 nm (Figure 5). Figure 4 depicts the result of pushing particle 1 on top of 2. The height of the resulting column is 9.9 nm (Figure 6). Although the ODS layer is much lower than desirable, these results show clearly that we can deposit successive layers of particles and we can manipulate nanoparticles that lie on top of the sacrificial layers.

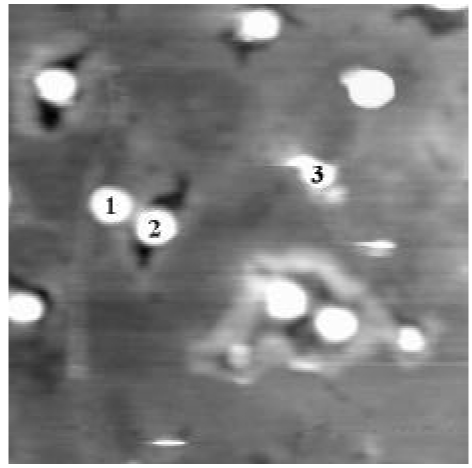

Figure 3 – Deposition of two layers of particles

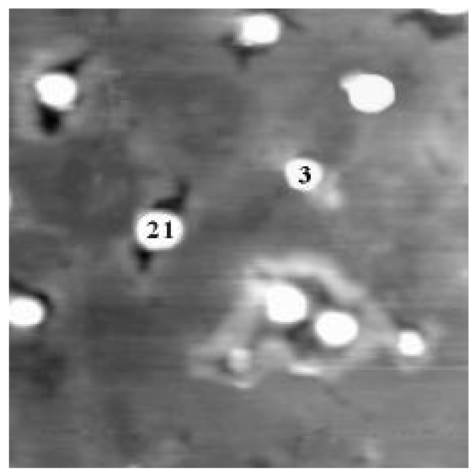

Figure 4 – Pushing particle 1 on top of 2

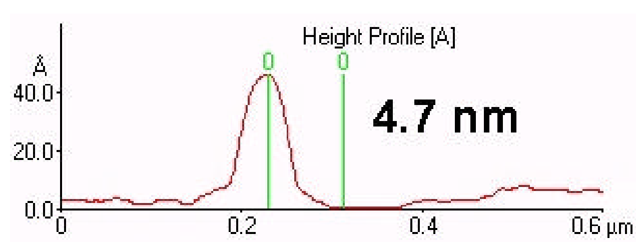

Figure 5 – Single-line scan over particle 2

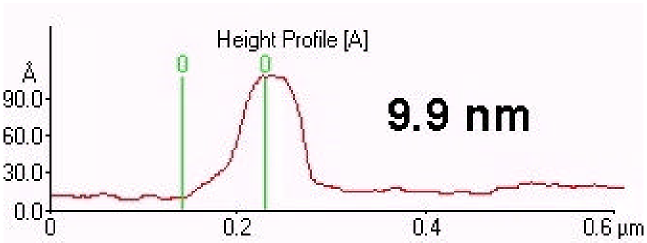

Figure 6 – Single-line scan over the column formed by particles 1 and 2

Conclusions

This paper describes a novel application of robotic nanomanipulation to the construction of arbitrarily-shaped, 3-D, nanometer-scale objects, which until now has been virtually impossible to achieve. The process is analogous to the rapid prototyping techniques used in the macroscopic world. Nanomanipulation is used to assemble nanoparticles that constitute the 2-D slices of the desired object. Assembly on successive slices is made possible by a planarization step that involves chemical self-assembly of a sacrificial layer.

Experimental results show that the process is very promising. However, much work is likely to be needed before this layered nanoassembly technique can be used routinely. Optimized materials and deposition techniques must be developed, nanomanipulation on these new materials must be studied, and so on. The limitations of the technique are not well understood and must also be investigated. In addition, lowering the overall fabrication time will require faster nanomanipulation by using AFMs equipped with the tip arrays that are currently being developed at several laboratories [Miller *et al*. 1997, Minne *et al*. 1996], and driven by the massively parallel algorithms currently being investigated in our own laboratory [Requicha 1999].

This research provides an excellent illustration of the interplay between robotic assembly and self-assembly, and of the extremely interdisciplinary nature of the work on robotics at the nanometer scale.

Acknowledgements

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