

Applications for Positionally-Controlled Atomically Precise Manufacturing Capability

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This section outlines potential near-term target applications for systems with limited capabilities to fabricate atomically precise objects via positional control. Positional control may be achieved in several different ways, thus, this analysis makes no assumptions about how the positional control is accomplished, except where noted. By “limited capabilities,” we mean:

- Little or no parallelization, limiting the number of objects that can be fabricated per unit time. This also puts realistic limits on the size of the objects—perhaps a few hundred to a few thousand atoms as a practical upper limit, depending on the degree of automation available.
- Only a few types of atoms (<5) can be used as building blocks. This implies that the tool tip set is limited as well, and can position and react only a few types of molecules.

Nanostructures fabricated via positional control would have qualitatively different characteristics from nanostructures fabricated by self-assembly, so this section focuses only on applications that take advantage of positionally controlled processes. Greater design complexity is possible at the atomic level with positional control, but the tradeoff is that the scaleup to larger systems is more difficult. In fabrication by self-assembly, scaleup is readily accomplished because the individual building block units naturally link to each other. In a positionally controlled system, scaleup of product size would be dependent on parallelization of the fabrication devices or increasing their speed of operation.

A hybrid approach might involve designing the positionally controlled structures as self-assembling subunits that can spontaneously interlock, but are mechanically guided or designed to form structures of significantly greater complexity than if the subunits simply condensed out of solution. The difference would be analogous to Lego® blocks being randomly assembled vs. crafted into clever designs [1].

Atomic Precision Matters

DARPA has recently issued a Broad Agency Announcement (BAA) soliciting proposals on Tip-Based Nanofabrication to make nanowires, nanotubes, or quantum dots using functionalized scanning probe tips [2]. Clearly, these applications are of particular

importance and worthy of mention in this section of the Roadmap. We note, however, that the BAA does not specify sufficient positional resolution to accomplish atomically precise manufacturing (Table 1). This difference in precision is important.

Table 1. Metrics in DARPA BAA for Tip-Based Nanomanufacturing [2].

<i>Metric</i>	<i>Unit</i>	<i>Phase I</i>	<i>Phase II</i>	<i>Phase III</i>
Feature Position Control	nm	50	25	5
Feature Size Control	% of dimension	10%	3%	1%
Heterogeneity		2 values of one parameter	5 values of 2 parameters	Continuous control over 2 parameters
Feature Rate		1/min Single tip	5/min/tip 5-tip array	60/min/tip 30-tip array
Tip Shape Variation	% of dimension	Height<10% Radius<20% 100 operations	Height<10% Radius<20% 10 ³ operations	Height<10% Radius<20% 10 ⁶ operations
Tip Height Sensing	nm	20 nm	10 nm	2 nm

The ability to fabricate nanodevices to atomic precision promises order-of-magnitude improvements in the performance of materials and devices—even compared with devices fabricated to nanometer precision. For example:

- Fluids pass through an array of multi-wall carbon nanotubes at velocities 1000 to 100,000 times greater than would be expected from continuum mechanics [3]. This is because nanotube walls are essentially atomically perfect, and that fundamentally changes the nature of the interaction between the fluid molecules and tube walls compared with normal microscopically-rough tubes.
- A small change in precision can have significant consequences: the affinity of the molecule *histamine-SGA* for a receptor site was changed by a factor of 14,500 by making a sub-nanometer change in geometry to the receptor site surface (replacing a CH₃ group with H) [4].
- In a theoretical analysis of diamondoid sleeve bearings, changing the circumference of the inner sleeve by a single carbon atom (only a few Angstroms) increased the energy barrier to rotation¹ ten million times [5].

Because this difference is critical, we focus on specific advantages of atomic precision for each application. For positional assembly, the pathway to achieving this is in the reverse order of that shown in Table 1, which progresses toward increasingly greater precision. By contrast, the evolution of positionally controlled APM starts from our current capability to

¹ A metric analogous to “friction.”

position a single atom on a surface, and progresses to larger and larger atomically precise structures as the technology matures.

Applications

High quality contacts for molecular electronic devices. An important problem in the development of molecular electronic devices is establishing a consistent electrical connection between molecular wires and molecular switches [6, 7]. Ideally, this requires an atomically precise interface between the two components for an optimal conductive path, but current technological capabilities limit our ability to provide this consistently. In the near term, if we could use a limited APM system to construct a defect-free interconnect, this would allow us to interface with an individual molecular switch in an optimal manner, and measure its performance more accurately. With parallelization or fast automation (such as proposed for NIST's Autonomous Atom Assembly system [8]), many molecular electronic devices could be integrated into an array of high reliability, which could then be interfaced with microelectronic systems.

Highly stable single electron transistor (SET) devices. Because they are one of the most sensitive devices for measuring electric charge, and because they can transfer individual electrons, SETs have been proposed as components for nanoelectronic systems. Single electron transistor device sensitivity is limited by low frequency noise [9], and these devices are also subject to drift of the correct operating gate voltage [10]. Both of these difficulties are caused by atomic defects in the metal or semiconductor that migrate over time. These defects, or vacancies, in the crystal lattice are artifacts of today's manufacturing processes which cannot reduce vacancy concentrations below a thermodynamic equilibrium level. With the ability to construct crystals with every atom in position, APM provides a method to produce metals with metastable vacancy concentrations near zero, and to maintain this condition by sealing the surfaces with ionically or covalently-bound films. Therefore, SETs could be manufactured that perform near their theoretical limits for highly reliable operation at maximum sensitivity.

Quantum computing. Quantum computers, once developed with capacities larger than a few qubits, may be able to significantly outperform classical computers for certain problems such as simulations of quantum mechanics and factoring large integers (useful for "cracking" many types of encryption systems). Research has therefore intensified to develop quantum computers and the market promises to be substantial if the technical challenges can be overcome. If quantum computers can be made to atomic precision, it may help to solve the problems of maintaining all the components in a coherent state, and isolating a qubit from everything except the components that are intended to access it. Qubit modules for quantum computers could be constructed, assuming positional synthesis that is capable of fabricating small planar diamondoid structures with an occasional precisely positioned guest atom (such as a phosphorus [11] or heavy-carbon atom [12]) embedded in the diamond matrix.

Room temperature superconductors. Room temperature superconductors, if possible, would have significant commercial applications for energy savings (particularly if they could be fabricated inexpensively). One of the barriers to studying the physics of high temperature

superconductors such as cuprate-perovskite ceramic materials is our limited ability to synthesize complex crystalline structures. A technology that could construct arbitrary permutations of chemically-possible crystal structures would greatly accelerate progress in our search for room-temperature superconducting compounds. Atomic precision is critical in this application, since atomic scale defects can disrupt superconducting behavior [13].

Molecular machine systems. Current efforts to build molecular machines are limited by our ability to position molecular components, fix them in place, and functionalize them to interact mechanically. For example, the Zettl Group's molecular motor based on multiwalled carbon nanotubes [14] could be used to drive other molecular machines, such as a positioning system with sub-Angstrom resolution and repeatability, if the drive nanotube could be connected to similar nanotubes with suitable gearing. Nanotube-based systems with simple gearing have been proposed [15-18]. There are still significant engineering challenges; we need the capability to:

- Synthesize atomically-precise support structures for these geared-nanotube systems
- Functionalize the nanotubes by adding gear teeth, perhaps a worm drive
- Position the molecular gears and bearings in three dimensional space
- Fix their positions with suitable welding operations (covalent bonding of the bearings to the support structures)

There is also an important opportunity in carbon nanotube-based computers, memories, and other electronics systems, since Diamondoid Mechano-synthesis (DMS) [5, 19] should also be able to fabricate at least small pieces of carbon nanotubes of any specified diameter or chirality, using hexagonal, pentagonal or septagonal rings. DMS should enable the fabrication of connection stubs between nanotube charge carriers and the underlying substrate in an atomically precise manner, and these connection stubs can be attached to any point along an insulating, semiconducting, or metallic nanotube structure. Short sections of diamond nanowires and small arrays of nanoscale pyramidal diamond field emitters might also be fabricated.

High precision atomic clock. NIST researchers [20] designed a MEMS based atomic clock by reducing the size and operating power of the core physics assembly of an atomic clock. The device had a volume of 9.5 mm³, a fractional frequency instability of 2.5×10^{-10} at 1 s of integration, and dissipating less than 75 mW of power. The NIST MEMS device has the potential to bring atomically precise timing to hand-held, battery-operated devices. Wafer-level assembly of the structures could enable low-cost mass-production of thousands of identical units with the same process sequence, and easy integration with other electronics. APM systems might be able to construct a much smaller, more precise core physics assembly for an atomic clock. This device could have both smaller frequency instability as well as much lower power dissipation. Mass production and integration with other electronic components would be a remaining engineering challenge.

High precision nanoresonator for mass sensing. Mass sensors have been constructed [21] based on a resonating cantilever or beam. The resonant frequency of the resonating cantilever

or beam is dependent on the mass of the device. By monitoring the resonant frequency change of the cantilever or beam, any changes in mass of the device can be detected. Resolution increases as device size decreases, and presumably, as structural accuracy increases with concomitant increases in tensile strength, bulk modulus, and shear modulus. In this domain, seemingly small differences make a big difference. It was found with current devices, that the Quality factor increases by a factor 400, from 70 to 28000, by operating the cantilever in vacuum.

Carbon nanotubes and molecular wires for molecular electronic devices. There are at least three short to intermediate term dimensions of improvement: (1) complex nanotube shapes that can only be fabricated using positional control, (2) fabrication of those complex structures at a specific location, and (3) adding positionally controlled interconnects between nanotubes on otherwise self-assembled nanotube electronic structures.

Complex nanotube shapes and structures could be produced by a DMS capability involving tooltips that can be manipulated with 0.2-0.5 Å repeatable precision between workpiece and tool rack. The tool rack could include a minimal toolset that can build diamondoid structures including at least C, H, and Ge atoms, and with buildable structures that include, for example, clean and hydrogenated molecularly-precise unstrained cubic diamond C(111)/C(110)/C(100) and hexagonal diamond surfaces of process-limited size, including some Ge-substituted variants; methylated and ethylated surface structures; handled polyynes, polyacetylene and polyethylene chains of process-limited length; and both flat graphene sheets and curved graphene nanotubes. These structures could provide a range of new application capabilities for semiconductor electronics, sensors, and devices.

Similarly, APM could construct small carbon nanotube structures. Without massive parallelization, we would be limited to building one-offs, so we would need to concentrate on the highest-value nanotube structures in the highest-value industries, such as molecular electronics. An example would be binding sites. These binding sites processes would be similar to conventional processes like molecular imprinting (which surrounds template molecules with polymers that solidify, then the template is removed, leaving behind binding sites for the template molecule) but would allow greater precision of binding pocket design, and would allow rational design of buildable binding sites from scratch without any need for a template molecule. These binding sites could potentially be used in nanosensor and enzymatic applications.

Research Topics That Would Address Key Challenges

There are four classes of research that would address key challenges in producing APM applications. They are: 1) standards and testbeds for programming and measuring the output of APM processes, 2) information theoretic descriptions of the nanoscale structures built by APMs, and methods for manipulating these structures that would program specific patterns of self assembly, 3) methods of interfacing and integrating APM devices into standard electronics packages and systems, and 4) methods of scaling up single APM devices using mass arrays or other parallelization techniques.

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