

## Scanning Probe Diamondoid Mechanosynthesis

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One proposed pathway to atomically precise manufacturing is scanning probe diamondoid mechanosynthesis (DMS): employing scanning probe technology for positional control in combination with novel reactive tips to fabricate atomically-precise diamondoid components under positional control. This pathway has its roots in the 1986 book *Engines of Creation*, in which the manufacture of diamondoid parts was proposed as a long-term objective by Drexler [1], and in the 1989 demonstration by Donald Eigler at IBM that individual atoms could be manipulated by a scanning tunnelling microscope [2]. The proposed DMS-based pathway would skip the intermediate enabling technologies proposed by Drexler [1a, 1b, 1c] (these begin with polymeric structures and solution-phase synthesis) and would instead move toward advanced DMS in a more direct way.

Although DMS has not yet been realized experimentally, there is a strong base of experimental results and theory that indicate it can be achieved in the near term.

- Scanning probe positional assembly with single atoms has been successfully demonstrated in by different research groups for Fe and CO on Ag, Si on Si, and H on Si and CNHCH<sub>3</sub>.
- Theoretical treatments of tip reactions show that carbon dimers<sup>1</sup> can be transferred to diamond surfaces with high fidelity.
- A study on tip design showed that many variations on a design turn out to be suitable for accurate carbon dimer placement. Therefore, efforts can be focused on the variations of tooltips of many kinds that are easier to synthesize.

A patent on this approach has been filed by Zyvex [3], and continued advances along these lines are being pursued by Robert Freitas and Ralph Merkle in collaboration with various research groups [4]. This fabrication approach could meet the challenges defined by DARPA in its recently issued Broad Agency Announcement (BAA) soliciting proposals on Tip-Based Nanofabrication to make nanowires, nanotubes, or quantum dots using functionalized scanning probe tips [5].

### Motivation

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<sup>1</sup> Two carbon atoms covalently bound to each other.

The reason the DMS approach is such an attractive pathway to atomically precise manufacturing is that it directly achieves APM with existing positioning technology. The best scanning probe microscopes have the resolution (about 0.5 Å) but not the repeatability (0.5 Å repeatability needed, 10 Å achieved) required for the task, so the challenge is to push the frontier of existing nanomanipulator technology and combine it with advances in tip functionalization to pick and place atoms.

### Experimental Advances

The concept of mechanosynthesis, in general, finds a ready existence proof in the operation of the ribosome in biological systems. The ribosome mechanically forces the transfer of peptides from tRNA onto a growing polypeptide chain under positional control. As Kay, *et al.* point out [6], the first demonstration of artificial mechanosynthesis between molecular units was achieved by Itoh, *et al.* in 2004 when they mechanically drove an F<sub>1</sub>-ATPase motor backwards to synthesize ATP, reversing the hydrolysis reaction [7].

Published research provides solid evidence that scanning probe microscopes can be used to add and remove individual atoms from a crystal lattice, and to chemically bind a single atom to a single molecule. The first experimental demonstration that individual atoms can be manipulated was performed by IBM scientists in 1989 when they used a scanning tunneling microscope to precisely position 35 xenon atoms on a nickel surface to spell out the corporate logo “IBM” [2]. However, this feat did not involve the formation of covalent chemical bonds. In 1999 Ho and Lee showed that a scanning tunneling microscope could pick up a single molecule (carbon monoxide) and chemically bind it to a single atom (iron) sitting on a silver crystal surface [8]. An applied voltage facilitated the chemical reaction.

In 1998 Lyding's group showed that hydrogen could be removed from single atomic sites on a silicon surface using a scanning tunneling microscope [9]. This technique was then adapted to selectively add organic molecules to the vacant sites in a process called Feedback Controlled Lithography [10-12]. Additional examples of hydrogen abstraction are provided in [13].

The first experimental demonstration of pure mechanosynthesis, establishing covalent bonds using only mechanical forces, was reported by Oyabu and colleagues [14] in the Custance group, in 2003. In this landmark experiment, the researchers vertically manipulated single silicon atoms from the Si(111)-(7×7) surface, using a low-temperature near-contact atomic force microscope to (1) remove a selected silicon atom from its equilibrium position without perturbing the (7×7) unit cell and (2) deposit a single Si atom on a created vacancy—both via purely mechanical processes.

### Theoretical Advances

Diamondoid mechanosynthesis has undergone increasingly sophisticated theoretical analysis since its first treatment in 1992 [15]. In all cases, the conclusion is that

positionally controlled DMS can be achieved in a vacuum or machine-phase environment where undesirable species are not available to cause unwanted side reactions. The most recent computational modeling results of the transfer of carbon to and from various tip designs show that:

- The barrier to dimer transfer to bare diamond, at least for some tooltip/surface combinations, is predicted to be zero [16].
- The maximum temperature at which a tip can reliably position a carbon dimer depends on the tip design, and ranges from 80K to 300K [17, 18].
- A study on variations in tip design showed that 24 out of 53 candidate designs turned out to be suitable for accurate carbon dimer placement [19]. Therefore, initial experimental efforts can be focused on the variations that are easier to chemically synthesize.
- The positional accuracy needed for DMS is about 0.05 nm, similar to the resolution limit in one or more degrees of freedom of several scanning probe microscopes and nanomanipulators [20].
- For a germanium-based tool, if a second C<sub>2</sub> dimer is placed next to an isolated dimer that was previously placed on a flat diamond surface, there is a significant chance of defect formation (the atoms will move out of position). However, placing the dimers in alternating rows and then filling in the gaps in subsequent operations allows the atoms to retain their positions with high fidelity, even at room temperature [18].

A recent three-year study concluded that DMS can be used to build single crystal diamond, carbon nanotubes, and at least nine different DMS tool tips [21]. The theoretical analysis was rather involved, as it had to define 65 DMS reaction sequences incorporating 328 reaction steps, and account for 354 pathological side reactions to be avoided. These mechanosynthetic reaction sequences range in length from 1-13 reaction steps (typically 4) with 0-10 possible pathological side reactions or rearrangements (typically 3) reported per reaction. A Density Functional Theory (DFT)-based package (Gaussian 98) was used to perform the analysis, resulting in 1,321 unique quantum chemistry reaction energies reported.

There has also been significant theoretical work on hydrogen abstraction [22] and hydrogen donation [23], which has since been validated by experimental successes such as those reported above and in these references.

### Pathway Challenges and Milestones

Critical advances are required to verify the simulation results which show that DMS can be accomplished by positional control of a scanning probe tip. We have identified the following key near-term experimental objectives that appear worthy of immediate pursuit:

1. Design and fabrication of a scanning probe tip that can be functionalized to hold a hydrocarbon molecule and retain the carbon atoms in that molecule while the hydrogen atoms are stripped or abstracted.
2. A demonstration that carbon atoms can be added to (and abstracted from) a diamond surface via positional control of a scanning probe tip. This would be a proof-of-concept demonstration: the transfer operation would not necessarily have high reliability, and the control would not necessarily be advanced enough to pinpoint a specific atomic site.
3. Development of a low-noise SPM positioning system with highly repeatable sub-Angstrom (0.2-0.5 Å) positioning accuracy over 1-micron round-trip paths, coupled with a sub-nanometer precision coordinate system spanning at least tens of microns.
4. Development of a manipulator with rotational degrees of freedom for single molecule positioning (e.g., having workpiece rotation and tilt available during manipulation events) in early systems, and possibly to include, in later systems, the closed-loop control of a dual tip AFM system with at least 5 degrees of freedom per tooltip (6 DOF per tip would be better to ensure that we can accurately align the tooltips).
5. Methods to characterize/validate tooltips and product structures once they have been fabricated, without destroying or inactivating them—especially important in the early stages of DMS experimentation when our experience with (and understanding of) these systems is at its lowest ebb.

*Milestones.* In addition to the critical advances above, the following milestones would each be a significant advance in atomically precise manufacturing technology based on scanning probe DMS:

1. Extension of the above capabilities to multiple-tip nanopositioning systems.
2. Developing computer control of tip trajectories, rotations, and positioning, with the ultimate objective of fully automating the DMS process so that nanostructures may be fabricated according to a particular blueprint without direct intervention of a human operator for each reaction.
3. Experimental demonstration of purely mechanosynthetic (i.e., mechanical forces only, no electric fields involved) H abstraction, preferably on a diamond surface.
4. Experimental demonstration of purely mechanosynthetic H donation, preferably on a diamond surface.
5. Experimental demonstration of a purely mechanosynthetic sequence of two or more DMS reactions on or near the same reactive site on the same workpiece - for example, two adjacent H abstractions on a diamond surface, or a C<sub>2</sub> dimer placement on C(110) followed by H donation onto the previously-placed C<sub>2</sub> dimer
6. Experimental demonstration of the ability to perform a repeatable sequence of DMS operations on a diamond surface, resulting in the verifiable fabrication of a new diamondoid structure on that surface

7. Experimental demonstration of a purely mechanosynthetic fabrication of a significant 3D diamondoid nanostructure.

### Conclusions

The general concept of mechanosynthesis is not only feasible, but well-proven and ubiquitous in biological systems. Scanning probe positionally-controlled chemical reactions between single atoms and molecules has been clearly demonstrated in careful experiments under high vacuum and low temperature conditions. Theoretical analyses and simulations with high quality DFT-based models of the scanning probe *diamondoid* mechanosynthesis operation shows that diamondoid structures can be fabricated with this technology. To date, there has been no experimental verification of this conclusion (with no failed attempts reported, either). Improvements in both tip technology and positional control technology will likely advance this pathway, spurred in part by the recent DARPA BAA soliciting proposals on Tip-Based Nanofabrication to make nanowires, nanotubes, or quantum dots.

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