NANOMANUFACTURING PROCESSES USING MECHANOSYNTHESIS APPLICATIONS

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ABSTRACT

Quality, production capacity and production cost have been identified as the current barriers to the implementation of carbon nanotubes and nanofibers within the industrial markets and military applications where such materials offer superior performance benefits in a wide range of industries and military applications. Significant use of nanotubes and nanofibers will require substantial increases in production volume coupled with decreases in production cost of < $ 30/Kg. Based on low cost, high-volume, high yield, and ability to highly control diameter, length and chirality, a Mechanosynthesis process was selected as the most viable approach for a scaleable, top down mass manufacturing process of nanoscale structures such as nanoparticles, nanotubes and nanofibers that are continuous.

Index Terms-Mechanosynthesis, nanomanufacturing, nanoimprinting, nanofibers, material science.

I.INTRODUCTION

The challenge from an industrial manufacturing perspective is to translate scientific innovations into productive and cost-effective technology for various applications. Towards this goal, we are working on developing nanomanufacturing methods to manufacture nanomaterials, but unlike fundamental research in this area, a key metric we use to judge nanomanufacturing processes is scalability. Scalability is an important industrial manufacturing consideration wherein design for scalability reduces manufacturing cost and effort.

New techniques for patterning and engineering materials at the nanometer scale using Mechanosynthesis processes that are similar to current nanoimprinting processes will make possible the goal of nanometer scale mechanical and electronic devices at cost effective levels of manufacture.

Formidable challenges currently exist in the development and implementation of large scale nanomanufacturing of single-walled carbon nanotubes and continuous nanofiber structures. Among these are the inherently slow through-put rate of current manufacturing systems and the lack of routine reproducible production of high-quality

(zero defects) single-walled carbon nanotubes and nanofiber structures, and the lack of commercial scalability. The presence of sub-nanometer-scale lattice imperfections has been demonstrated in different nanostructures.(1,2) The properties of carbon nanotubes (CNTs), which are considered excellent candidates for the construction of electronic nanodevices, (3) can be affected dramatically by the presence of pentagon-heptagon (5-7) pair defects.(4,5,6,7) Through our efforts we seek to overcome the limitations of current nanomanufacturing processes and produce nanotubes that are defect free thus providing for an increase in quality that is several orders of magnitude better than with current manufacturing processes. The ability to manufacture defect free nanomaterials will provide for a step change in available nanomaterial quality which will greatly impact the various application needs for such nanomaterials.

NanoSource, Inc. and the MEMS and Nanotechnology Exchange with their network of 54 different MEMS and Nanotechnology foundries has analyzed the various elements of the new nanomanufacturing system and has determined the best approaches in implementation of our proposed manufacturing method, system structure and processes, conducting a technical evaluation and feasibility study of NanoSource's patent pending (Pub. No: US 20050238565 A1) "Systems and methods of manufacturing nanotube structures".

With feasibility established as to the ability to fabricate the needed structures at the nanoscale the project focus has shifted to the development of a proof of principle project that will support future efforts to produce a cost-effective, scaleable technology to manufacture and process graphene sheet material into single-walled carbon nanotubes and continuous nanofibers on a tonnage scale basis.

II.INNOVATIVE CLAIMS

We postulate a ''zipper-like'' bond rearrangement or transformation of graphene into nanotube structures that is very efficient due to the unusually low activation barrier associated with our Mechanosynthesis process. Mechanosynthesis is the chemical synthesis of a selected material controlled by mechanical systems operating with atomic scale precision wherein the material and the mechanical system are brought together in planned sequences, positions, and orientations thus allowing for direct positional selection of reaction sites of the selected material and the application of energy resulting in the desired reactions such as breaking and making bonding structures of the material wherein the innovative process incorporates the use of macroscopic diamond nanoimprinting rollers with atomically precise nanoscale features on the surface thus bridging the implementation gap between the nanoscale and macroscale wherein the Mechanosynthesis process uses mechanical energy and electric fields not high temperature growth processes thus consuming much less in energy cost for the production process and produces a highly defined structure such as chirality, diameter and length that is defect free with the future capability of introducing donor atoms for functionalizing the nanostructures formed thus allowing for fabrication of nanostructures

and materials under conditions that do not disrupt the functionality of the feed stock materials used within the manufacturing process.

To develop an understanding of the Mechanosynthesis-induced structural changes, we considered the dynamics of the atoms moving on a time dependent potential energy surface obtained as the free energy of the electrons wherein the electronic energy is obtained from the diagonalization of a tight-binding (TB) Hamiltonian with distance-dependent hopping matrix elements and core-core repulsive terms. A time-dependent electric field of loading point shape and frequency excites the system, consequently changing the electronic occupations. The application of pressure combined with the electric field pulses changes the initial ground-state electronic distribution into a time-dependent non-equilibrium distribution which then converges, because of electron-electron collisions, to a Fermi-like function which is the chemical potential which can be precisely controlled. The prior art supporting the effort feasibility within this area of voltage induced disruption and cutting of the carbon-carbon bond structure is described within reference (8) which demonstrates the capability to cut carbon nanotubes with an STM tip using a pulsed voltage of about 6.5 volts @ about 150 Hz. The optimal voltage that will be required for our project will be determined by experiment wherein the graphene sheet material may require some what different optimal voltage and frequency for graphene material within our project but the basic scientific principles used are the same.

The loading points of the nanoimprinting rollers are to be constructed of single atoms thickness of platinum nanowires or other suitable conduction atoms as described within reference (9) wherein the nanowires will provide for the conduction path for the pulsed voltages which will be used to disrupt the carbon-carbon bonding within the graphene lattice structure at the loading points.

Our objective within the proposed proof of principle project is to convert graphene sheet material into carbon nanofibers. The process will incorporate the use of electric fields (7.5 volts @ 150Hz) applied at the loading points of the nanoimprinting rollers combined with mechanical roller pressure to cause the shearing of the graphene sheets into well defined graphene upper and lower strips which lack lattice defects and are further deformed and physically placed in close proximity and joined due to the newly crated highly reactive edge bonds seeking to complete themselves thus creating a carbon nanotube or nanofiber structure in a “zipper-like” process. The zipper-like process takes place within the contact patch zone between the two nanoimprinting rollers within a few femto-seconds thus eliminating the possibility of the newly created highly reactive edge bonds from up taking unwanted atoms such as gases which would create defects within the nanotube structure. Thus the nanoimprinting rollers prevent the introduction of defects into the lattice structure of the graphene sheet material used within the process.

In the future we will examine the introduction of donor atoms and defects within the lattice structure and surfaces for the purpose of controlling the final nanotube structures formed for the purpose of functionalizing the nanomaterials formed.

III. MATERIAL CONSIDERATIONS

Current studies of direct writing of nanometer scale metallic lines by field-evaporation from a SPM tip, lithographic processes that take advantage of the nanometer-scale resolution of electrons emitted from SPM tips, nanoimprinting and nanomachining of surfaces via mechanical forces have established the ability to construct the elements required within the proposed Nanomanufacturing Mechanosynthesis processes with the ability to manufacture single walled carbon nanotubes with a diameter of 15 nanometers or less. This is based on the current capability in nanoimprinting surface features made possible using available dual beam lithographic system currently manufactured with the near future capability of 3 to 5 nanometers.

New techniques for patterning and engineering materials at the nanometer scale using Mechanosynthesis processes will make possible the goal of nanometer scale mechanical and electronic devices at cost effective levels of manufacture.

There are no technical barriers in implementing the proposed system and method of manufacturing nanotube and nanofiber structures. However, there is a need for basic scientific research along with some experimental etching and implementation aspects of integration and material handling systems that will require further investigation and refinement which is part of the scientific investigation for the proof of principle stage of the project.

IV. PROPOSAL

In studying the suitability of using nanoimprinting rollers for the manufacture of single walled carbon nanotubes or nanofibers from graphene sheet material we have devised a system and method for the mass production of macroscopic rope bundled structures of single-walled carbon nanotubes (SWNT's) and single-walled carbon nanofibers (SCNF).

A laboratory scale process is proposed for synthesizing carbon nanotubes wherein graphene sheet material is sheared in a highly controlled manner producing graphene strips, which are further, deformed and joined using Mechanosynthesis processes to form nanofibers. The customized tooling and testing performed during the proof of principle stage will focus our efforts in developing an industrial-scale demonstration pilot plant in the future and further full scale integrated commercial mass manufacturing system on a tonnage scale basis.

The goal in this research effort is to provide a proof of principle that one can in fact convert graphene sheets into carbon nanofibers using mechanosynthesis processes

wherein such basic science conducted will support further development of a hierarchical, geometrical model of the Mechanosynthesis structure, in which C atoms form hexagonal graphene sheet material that are assembled into axially aligned nanofiber structures, then finally into close-fitting bundles of carbon nanofiber material. Initial results will enable prediction of apparent fiber density, concentrations of geometrically different types of bundle structures and atoms on the external and/or internal fiber surface and/or atomic lattice structures, and further future research into the theoretical stoichiometry of atoms such as oxygen (e.g. as carboxylic acid) attached to various carbon sites on the surface which will also enable the theoretical calculation of further reaction stoichiometry of initially functionalized nanofibers with reactive monomers, polymers and oligomers.

Directions for further future refinement of the manufacturing process will also be explored, based on SEM, TEM and detailed crystallographic analysis (OD, ID, and graphene plane angle), tensile strength analysis of the final Nanofiber bundles formed.

V. KEY MILESTONES

The key milestones for our proof of principle are the customized manufacture of the component parts of the nanomanufacturing system that include but not limited to the following.

The manufacture of the diamond rollers and the etching of the surfaces which are atomically precise as to the geometry described within the patent pending and install the rollers within a thermally stable vibration free housing.

The manufacture of the true sp3 diamond rollers with platinum atoms or other appropriate conducting atoms deposited at the loading points for the purpose of conducting an electric field such that the carbon-carbon bond is disrupted (7.5 volts @ 150 HZ). We will be testing the ability of mechanical shear and voltage assisted shear to fully develop understanding of the mechanisms involved and finely tune the optimal operational aspects such as voltage, frequency and pressure between the rollers.

In addition we will examine the tool before and after the experimental runs to investigate the results of use on the rollers surface geometries and determine the impact on surface materials due to friction heat and voltages applied. With this knowledge we will proceed to experiment with the rollers in converting graphene sheet material into single walled carbon nanotubes (SWNT's) or nanofibers which would be the ultimate goal of the proof of principle wherein we would use two sheets of graphene that are sheared into strips that are joined wherein the highly reactive edge bonds created during the shearing process would complete themselves due to the physical manipulations wherein the strips are brought within physical proximity of each other within the contact patch zone between the rollers such that they join together in a "zipper-like" fashion thus forming a completed nanotube or nanofiber structure that does not introduce any defects.

Verification that we have accomplished the goal of converting graphene sheets into graphene strips and then into carbon nanotubes or nanofibers will be conducted by

examining the structures formed at the MEMS and Nanotechnology Exchange as well as third party independent verification.

VI. TECHNICAL APPROACH

The mechanosynthesis process works by breaking the bonds that exists between adjacent atoms of carbon in a graphene sheet material along the direction orthogonal to the direction of the sheet movement (see Figure 1). The spacing between the adjacent carbon atoms in the graphene sheet is approximately 1.4 angstroms, indeed an extremely small dimension. However, it is important to note that in our proposed work we shall not attempt to make the smallest single-walled nanotube possible, but instead focus on only demonstrating that the process works.

Consequently, we plan to have the diameter of the nanotubes to be on the order of 10's of nanometers, which means that the length spacing of the carbon bond shearing points is of the same magnitude. This will make alignment much easier to achieve. Also, we suspect that the graphene sheet will self align to the shearing tool due to the fact that this is the lowest energy configuration. A misaligned sheet will require the breaking of more bonds and therefore is a higher energy state than a properly aligned sheet. Lastly, even if the sheet is misaligned, we believe that it will still demonstrate the feasibility of the process since we will have demonstrated the shearing of bonds in the graphene sheet and the rejoining of the sheared bonds to form a tubular structure. If the sheet is misaligned, the effect will be a distorted nanotube structure, but would be a carbon nanotube nonetheless

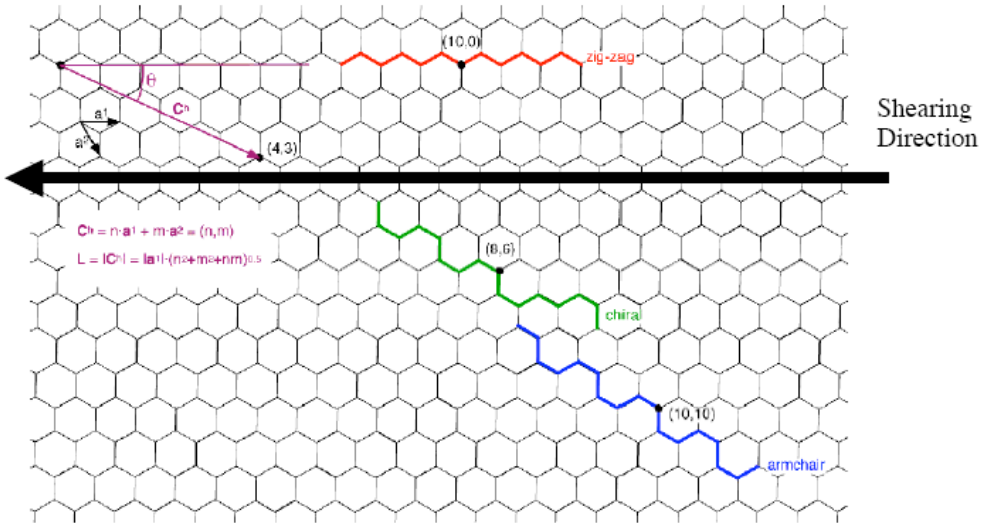


Figure 1: Plan view of graphene sheet material illustrating the direction of the shearing process (x direction) to break carbon to carbon bonds in the material.

For future work and depending on the results of the proposed work herein, if precise alignment is necessary we will utilize the capability for picometer positioning accuracy developed by NanoWave or similar company. Mechanical manipulation tools are

commercially available that use piezoelectric actuation and are capable of positional accuracy of less than a single Angstrom. This technology is now well developed and is routinely used in Atomic Force Microscopes (AFMs) and Scanning Tunneling Microscopes (STMs) to position the ultra sharp probe tip to less than a single Angstrom of the surface to be scanned.

The fabrication of the tooling for the mechanosynthesis manufacturing process is very challenging due to the extremely small feature sizes and tolerances required for the active surfaces on the rollers that are used shear the graphene sheet material. Furthermore, the process also requires that the active surfaces of the rollers to be fabricated from materials that can withstand considerable stress loading and frictional induced heating without significant degradation.

Depending on the diameter of the single walled nanotubes to be fabricated with the proposed process, the spacing of the active surfaces can vary from a few nanometers to tens or even hundred of nanometers. Consequently we believe that there is wide latitude of dimensions that can be used for this spacing distance. We envision two methods for fabricating the mechanosynthesis tools. The first involves using a Focused Ion Beam (FIB) to cut grooves of the approximate depth and width into the outer sidewalls of a cylinder of working material. FIB systems have been produced and commercially available for over a decade and are primarily used by the large semiconductor manufacturers. FIB systems operate in a similar fashion to a scanning electron microscope (SEM) except, rather than a beam of electrons, FIB systems use a finely focused beam of gallium ions that can be operated at low beam currents for imaging or high beam currents for site specific sputtering or milling as desired. As the diagram illustrates (Figure1), the gallium (Ga +) primary ion beam hits the sample surface and sputters a small amount of substrate material, which leaves the surface as either secondary ions or neutral atoms. The primary beam also produces secondary electrons. As the primary beam raster over the sample surface, the sputtered ions or secondary electrons are collected to form an image.

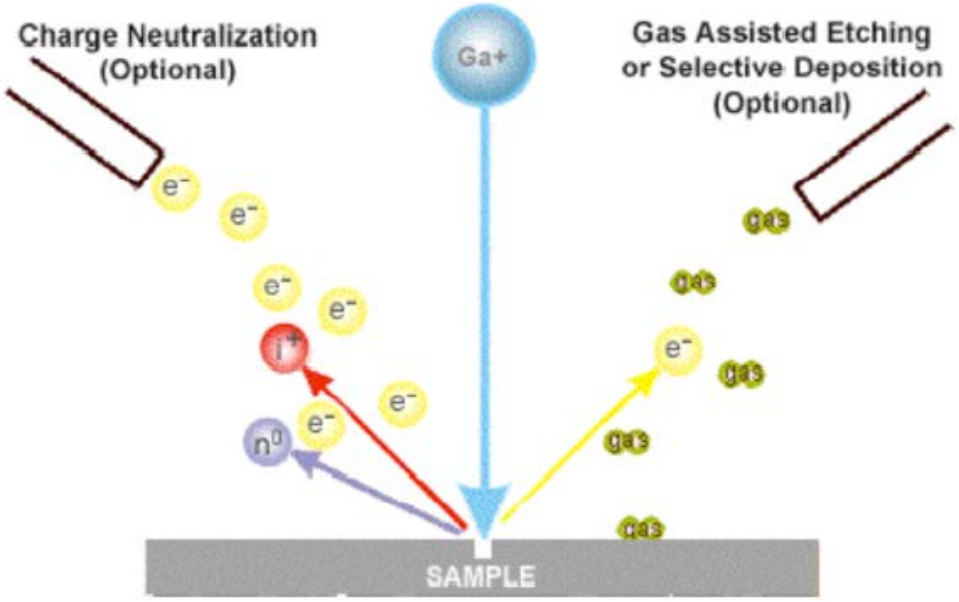


Figure 1: Diagram of the FIB process.

At low primary beam currents, a small amount of substrate material is sputtered. At higher primary currents, a great deal of material can be removed by sputtering, allowing precision milling of the specimen down to a sub micron scale (Figure 2).

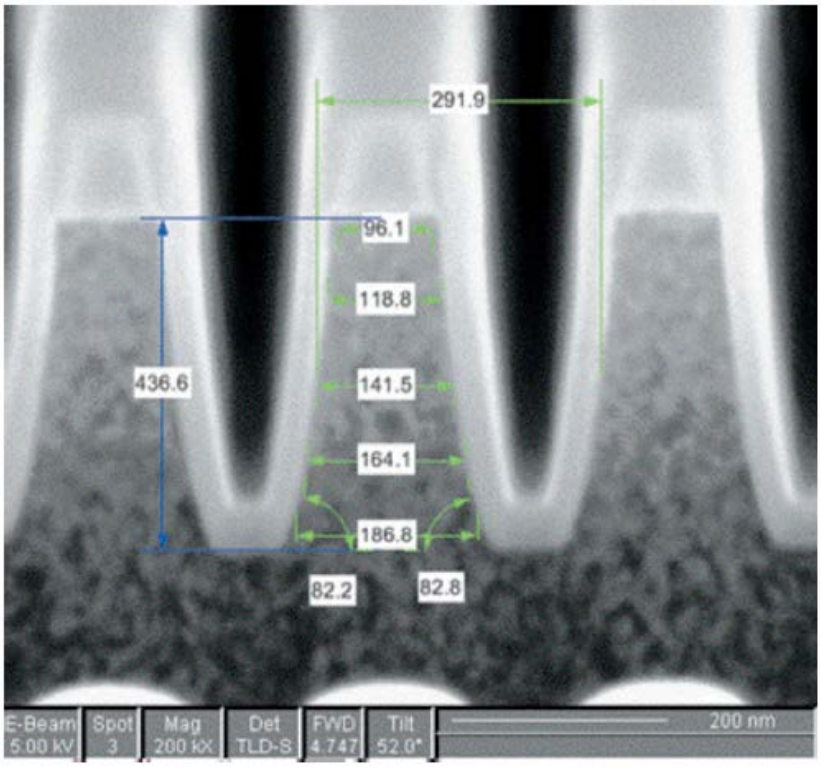


Figure 2: SEM image taken in FIB tool after cross-sectioning (cutting) process. The image scale is 200 nm and the smallest features are 82 nm. The image is displaying the trench isolation of a nanoelectronic device.

Currently available FIB tool technology is capable of making cuts into substrate surface of approximately 7 nm in beam width with extremely high levels of accuracy. The depth of the cut is controlled in the FIB tool by the dwell time and beam current as well as the sputtering rate of the material being removed. Currently available dual column FIB technology combines the exceptionally precision cutting capability of the focused ion beam with the high resolution imaging capability of the scanning electron microscope (SEM) thereby simultaneously enabling imaging during the cutting process. Another feature of the current FIB technology that is beneficial to the work proposed herein is that the cutting process is under computer control with substrate positional accuracy of a few nanometers. In addition to primary ion beam sputtering, the FIB system also permits local flooding of the specimen with a variety of gases. These gases can either interact with the primary gallium beam to provide selective gas assisted chemical etching or selective deposition of either conductive or insulating material by decomposition of the deposition gas by the primary ion beam.

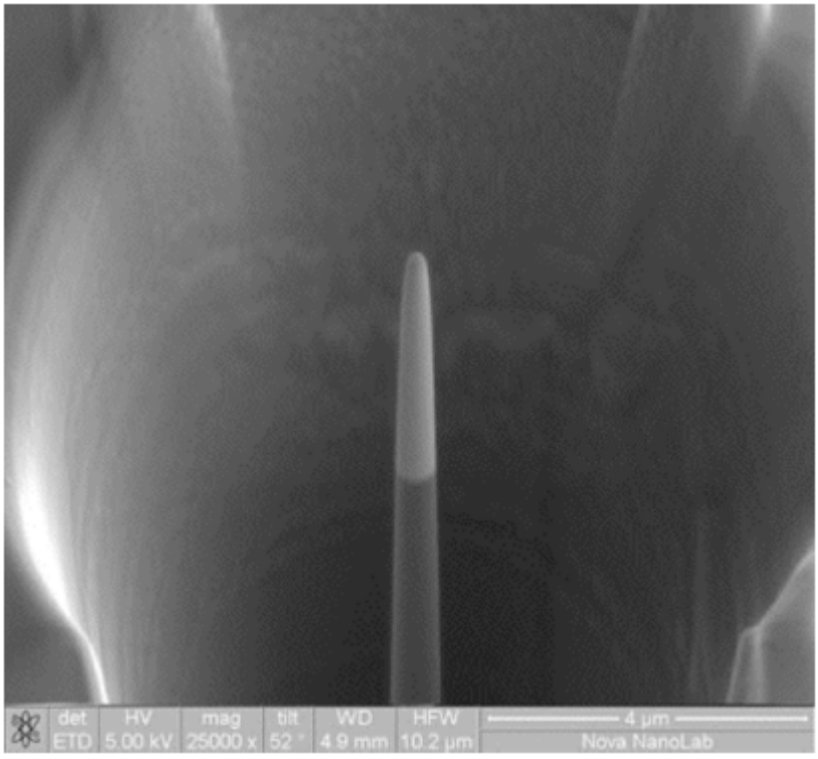


Figure 3: SEM of a needle-like structure measuring about 100 nm at the tip fabricated using FIB tool technology.

Figure 4 is an illustration of the process we envision for making the active portion of the mechanosynthesis tool. As shown, the FIB beam is positioned at an angle of approximately 45 degrees to the cylinder of substrate and the cylinder held to the FIB tool stage is rotated under computer control. Once a full revolution is made wherein a groove is made completely around the substrate, the beam is moved downward by the distance between the grooves and the cutting process is initiating again with the cylinder being rotated. The width of the groove made into the substrate material with the FIB tool is a tradeoff with the cutting time. That is, with a higher beam current, the minimum width of the groove is larger and vice versa. In our experiments we shall not attempt to push the limit of the finest feature possible with the FIB tool, but instead make grooves that are on the order of tens of nanometers and this should be sufficient to demonstrate the feasibility of the process.

In addition to the FIB tool cutting capability, we shall also rely on a technique routinely practiced in the fabrication of the extremely small diameter tips used in Atomic Force Microscopes (AFMs) and Scanning Tunneling Microscopes (STMs). These tips can now be routinely fabricated having a tip diameter that is very close to the diameter of a single silicon atom. These tips are made using a combination of bulk silicon micromachining by basically anisotopic wet etching of <100> orientation silicon terminating on the exposed <111> planes to form a pyramid structure (See Figure 5).

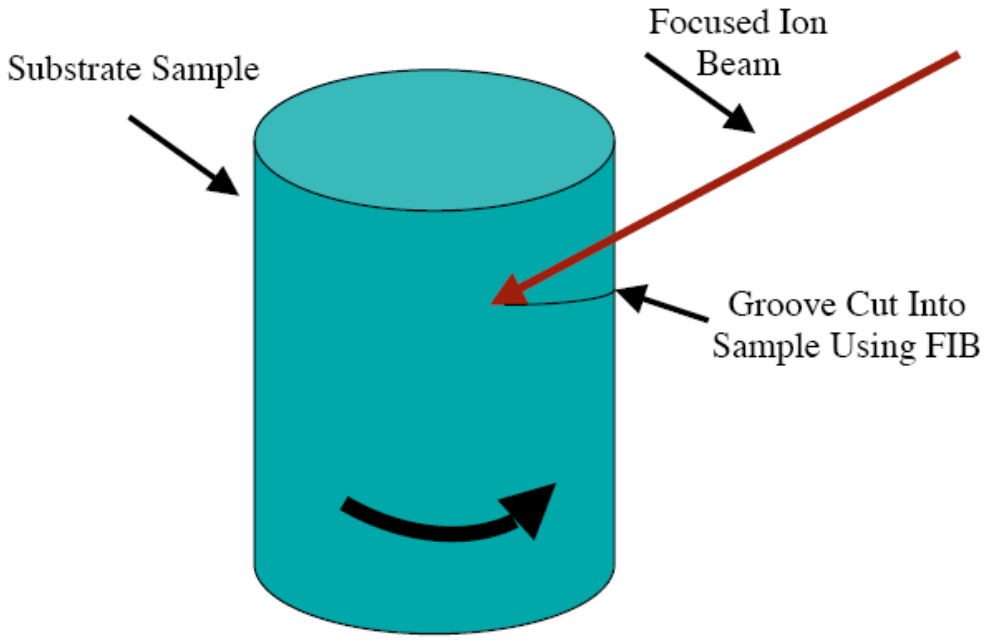


Figure 4: Illustration of the fabrication of the shearing tool to be used to demonstrate the mechanosynthesis process. However, the tip diameter after the etch may not be sufficiently small and typically an oxidation is performed of the silicon material to sharpen this tip to an extremely fine diameter. The oxidation of the silicon is performed at about 1000 C which is a temperature high enough to result in plastic deformation of the underlying silicon material. Oxidation on the pyramidal structure results in stresses to be formed between the oxide and the underlying silicon that causes the silicon to plastically deform into a considerably sharper tip. Subsequently, the oxide is removed to allow electrons to flow from the tip surface to the substrate to be imaged with the tip. We will perform oxidations on the FIB cut samples to sharpen the shearing surface of the mechanosynthesis tool to an extremely fine point. Figure 6 is a SEM photo of an AFM tip sharpens to a 40 nm point.

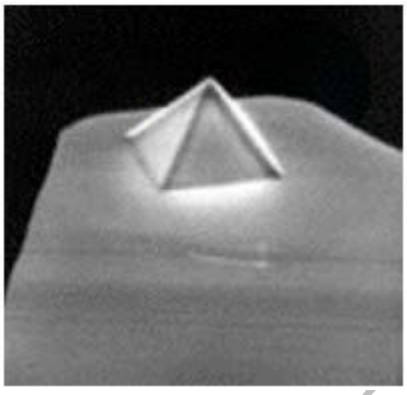


Figure 5: The pyramid structure of an AFM tip made using anisotropic wet etching of single crystal silicon. The tip of the pyramid at this point in the fabrication is approximately a few hundred nanometers in diameter, but is sharpened using either an oxidation process as described in the text or a FIB tool to trim down to a very fine point.

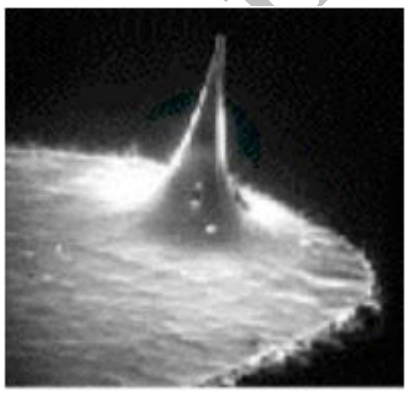


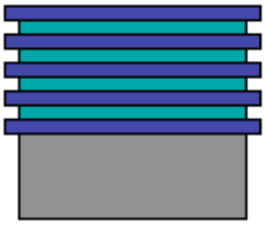
Figure 6: SEM photo of an AFM tip with an extremely sharp tip of less than 40 nm. Another method of making the shearing tools for the mechanosynthesis process is as follows. Starting with a suitable substrate, i.e., silicon, we successively deposit

alternating layers of thin films of the thickness of 3 to 4 nanometers for one material type and 5 to 10 or more nanometers of another material type (See Figure 7). We can stack as many layers using this process as desired. Subsequently, we core out a section of the substrate and then bevel the edges using a high speed wafer beveling tool. This will provide us with an extremely well-formed edge profile and a well-centered shearing disk. The underlying substrate is then etched to create an overhang of the thin films. Lastly, we perform a selective isotropic etch of the thicker thin film layer to create groove into the edges. The tool can then be mounted onto a rotational element as shown in Figure 7. In our proposed effort, we shall attempt both fabrication approaches to making the shearing tools.

Starting substrate.

Substrate A\after multiple thin film depositions.

Cored out section of substrate having diameter of 2 to 5 cm. After beveling edges to make smooth.



Cored out section of substrate after isotropically etching substrate and one of the thin film materials to create an overhang.

Figure 7: Illustration of the process to make mechanosynthesis tool using readily available fabrication processes. This approach involves deposition of alternating layers of thin films having thickness of 3 to 10 nanometers and then coring out a section of the substrate, followed by high-speed beveling to smoothen the edges. Subsequently, the substrate and one of the thin films is isotropically etched to create an overhand that can be precisely controlled. The tool would then be mounted onto a spindle and rotated such that the thin films layers that protrude shear the graphene sheet material.

In one configuration, after the initial shearing or breaking of the carbon-carbon bond of the upper sheet creating upper strips the newly created highly reactive edge bonds of the upper strips are prevented from rejoining the original bonding site by physical moving the two newly formed edges away from each other by means of staggered teeth of the rollers and nanotube formers that introduce the highly reactive edge bonds of the lower strips formed at a much closer distance thus allowing the two highly reactive edge bonds of the upper and lower strips to join in a zipper-like fashion which completes the tube structure formation process.

The throughput rate of the mechanosynthesis process is speculative at this point, but we can make some reasonable estimates of what it might be based on the physical phenomena of the process and the expected tooling capabilities. We can identify four rates of the process that are important, as follows:

1). The rotational rate of the shearing tool,
2). The rate at which the graphene sheet material can be sheared,
3). The rate at which the graphene sheet material can be fed into the system and taken up out of the system, and,
4). The rate of rejoining the sheet material at the cut Carbon bonds into tubular structures.

The upper bound on the rate is undoubtedly set by the rates at which the material can be sheared and rejoined which is on the order of a few femtoseconds that equates to 556 meters per second as the maximum manufacturing throughput rate allowed. Therefore, we can reasonably conclude that 2). and 4). will not be rate limiting steps. Considering the rotational rate of the shearing tool, we can estimate that the maximum rate at which the shearing tool can be rotated is set by the maximum rotational rate of currently available systems and this upper bound is on the order of 10,000 rpm or more. If we assume a 5 centimeters diameter shearing tool, the rate would be about 160,000 centimeters per minute or 27 meters per second. If we now consider the rate at which material can be fed into the system and taken out of the tool without problems, we can estimate that this is also about the same value as the rotational rate of the shearing tool since there are realizable manufacturing systems that operate with fed and take-out at these rates and again this is estimated to be about 27 meters per second. Therefore, we reasonably estimate the lower bound is about 27 meters per second and the upper bound to be 556 meters per second.

VII. CONCLUSIONS

The need for defect free nanomaterials at cost effective levels is of great importance in being able to deploy new nanomaterials developments in the battlefield and other commercial applications. NanoSource's top down approach to the manufacture of

nanoscale materials will be able to drive down the cost structure to levels that will make nanomaterials viable in applications that would otherwise be cost prohibitive. The scalability of the Mechanosynthesis processes will allow for mass manufacture of nanoscale materials on a tonnage scale basis providing the raw nanomaterials needed to develop technology to solve the nation's needs in the military, environment and industrial sector markets.

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