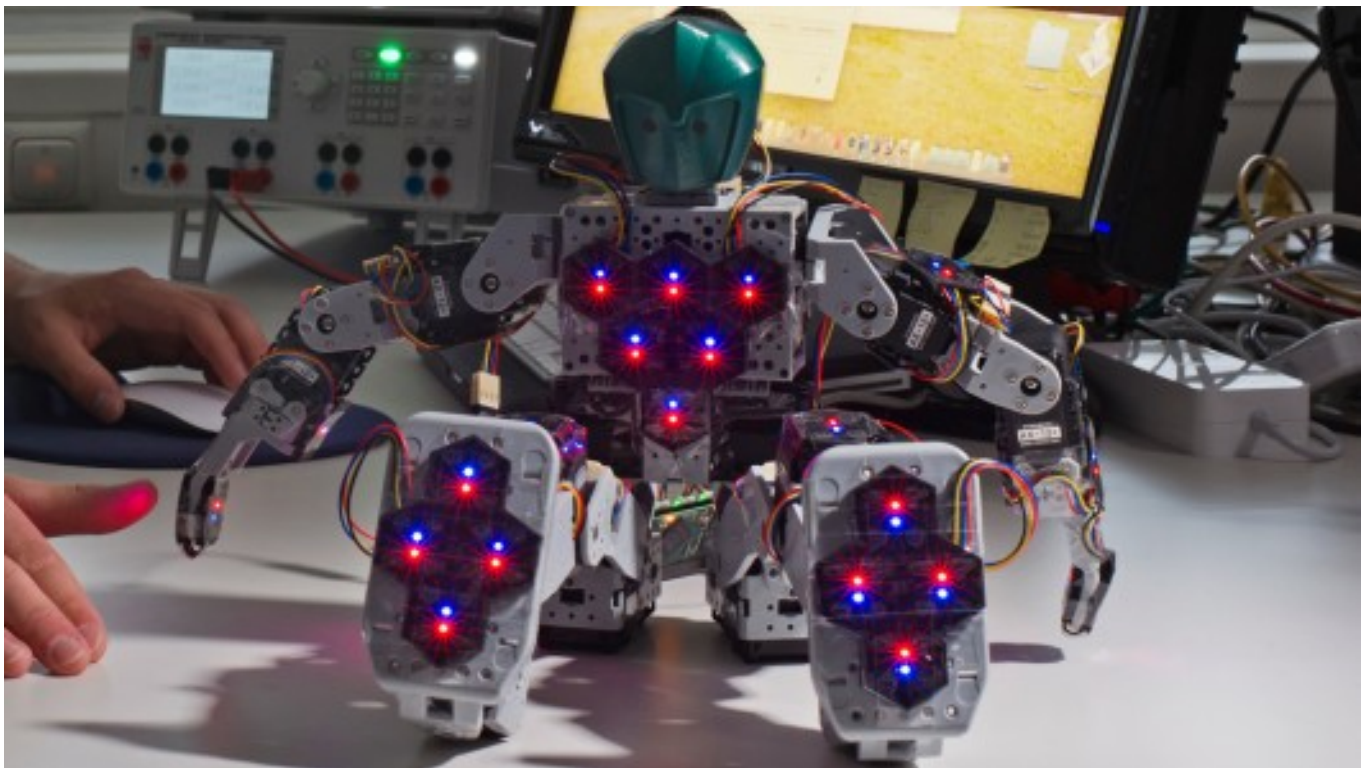


Managing Emerging Technologies

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Term Project Diamond Nanoprobe Tips demonstrate Success in Nanomanufacturing

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Current Technological Gap

Nano manufacturing changed the way things are and opened new resolutions to long lasting issues. However, in Nano world of Fabrication, there are several problems since the start of working at the Nano scale such as accuracy and reproducibility. These problems limited the expansion of MEMS/NEMS applications (1).

Therefore, most MEMS/NEMS devices currently under development are mainly based on silicon because of the available surface machining technology adapted from the silicon-based microelectronics and microcircuits batch fabrication technology. However, due to the relatively poor mechanical and tribological properties of silicon, it limited its application to only areas simple devices involving bending and flexural motion such as cantilever beams, vibration sensors, accelerometers (3).

Moreover, probes applications such as sensing, multiple probing, arraying and actuations have been also limited due to the short lifetime of probes due to the repetitive mechanical failure in operation and handling, pickup of sample material and particles from the samples, and wear (2).

Other attractive futuristic applications might be those involving more mechanical rolling or sliding operating environments and more complex shaped components such as gears, wheels, micromotors and geartrains requiring high mechanical and tribological properties, and the reliable performance in such environments. Methods of lubrications as in the macro machines and gears are not considered viable due to minute scale and difficulties of maintenance (1).

The problem being investigated is regarding the materials of the Atomic Force Microscope (AFM) probe tips having minimal durability and low wear and friction resistance subjecting them to experience wear, flattening and fouling, or picking up the substrate materials at severe environment. Nano-scale wear have been considered to be the main limiting factor for conventional atomic force microscopy (AFM) probes and other nanolithography probes that results in decreased resolution, accuracy, and reproducibility in probe-based imaging, writing, imprinting measuring, nanofabrication and nanomanufacturing applications (4)

Diamond is considered the solution to the above addressed problems for its high mechanical strength, incomparable chemical inertness, and great thermal stability. For instance, the brittle fracture strength of diamond is 23 times that of Si, and the wear resistance is 1000 times higher than that of Si (1)

Furthermore, earlier trials of using diamond were not practical since diamond grain size is large and hard to fabricate (1). Other methods of using relatively small grain size diamond such as diamond films and diamond-like coatings were considered impractical due to the low bonding energy because of the columnar inter-granular formation and high surface roughness (1). Also, the other disadvantage of this technique is the additional thickness it adds to the initial tip radius of the probes (10–20 nm) (2)

Moreover, other attempts of using boron-doped diamond layers grown by chemical vapor deposition (CVD) showed the feasibility of employing conductive diamond in probe manufacturing, but found not suitable for integration such that cantilevers had adhesion and stiction phenomena (2). On contrary, UNCD is the ideal probe material due to its unparalleled hardness and stiffness, its low friction and wear, and its chemical inertness. However, the nanomanufacturing of such probe tips dimensions, shape consistency and reproducibility has not been previously achieved (5).

Technology at hand

The newly reported technology is regarding the UNCD probe tips integrated with doped Silicon Atomic Force Microscope (AFM). It is proposed to be used in tip-based nanomanufacturing, imaging and scanning where wear resistance and anti-fouling is essential. These diamond tip Nano-probes have minute radii of 15 nm. They also have shown the ability to retain their shape when scanned for more than a meter at high temperatures and under high loading forces (4).

Performance Testing

Several mechanical destructive testing schemes such as bending, hardness and torsional were previously performed on similar specimens such that the mechanical properties are still retained at the nanoscale. (6). The technology device was also tested and it showed an extraordinary performance in nanomanufacturing in harsh environments. Mainly, the issue was to investigate the wear resistance of this new combination of the AFM probe tips. The new AFM with the UNCD tips of radii of 15 nm were tested on different substrates materials of quartz, silicon carbide, silicon and UNCD. The AFM probes were used at a speed of 25 $\mu\text{m/s}$ to scan more than one meter. The test was applied on the AFM with loads up to 200 nN at a temperature condition of from 25° to 400°C (7). The same test conditions were applied to the other AFM with the same geometry with silicon probe tip. After the tests were complete, both tools were examined. The UNCD tip showed no signs of wear, or delamination and exhibited a great fouling resistance. On contrary, the Silicon tips were found partially or totally worn out. Moreover, the UNCD tips retained their shapes under the high loading forces, demonstrating no signs of distortion (4).

Significance of the AFM Tip

It is imperative with a real application that suffers. The tip plays a critical role in the image quality, when used for scanning. Also, some probes of nanoelectronics or lithographic masks require the tip to scan long distances over hard surfaces such as silicon, silicon dioxide, quartz, and various other metals(8). Thus, having a uniform and unchanging shape is a vital characteristic of the AFM performance. When the tip wears out during the scanning operation, it gives faulty results (9). Moreover, the AFM scanning is considered a very rough task, especially with the contact mode scanning (9). The common requirement for different approaches of nanomanufacturing is using similar tips. An important factor of nanofabrications is tip stability, which is essential for repeatable and consistent fabrication. Hard and chemically reactive substrates, long scan distances, high tip loads, and high temperatures all cause tip wear, deform, and foul, such that make continuous manufacturing unachievable. Testing the UNCD tips integrated into heated silicon AFM cantilevers gives a good reliability test of the accuracy levels and performance measures (10).

UNCD Impact

Diamond is the hardest of all known single phase materials, with hardness values around 100 GPa, depending on the crystalline direction. Also, crystalline diamond films have similar characteristics such that hardnesses up to 95 GPa have been obtained. However, a wide spread of varying hardness values were achieved, but the challenge has been on having a uniformity of structures and morphology (12). Moreover, in thin film form, to obtain such properties with minute (nano) geometries reliably and economically has been a challenge (8).

The Ultra-Nano-Crystalline Diamond (UNCD) was first grown by researchers in the former USSR in the 1960s by detonation of carbon explosive materials and pure-phase UNCD films synthesized by chemical vapor deposition (CVD)(11). Since then, several UNCD diamond coatings have been synthesized on a variety of materials using different methods of chemical vapor deposition technology yet all were considered uneconomically viable and showed amorphous microstructures(11). With the Nano world boom, other methods of growing UNCD were investigated for its attractive features. UNCD films has an average grain size between 3 to 5 (nm) with not more than 8% by volume of grain sizes larger than 10 nm. UNCD is manufactured by combining methane and hydrogen to create plasma, then in a Microwave argon rich plasma technique using CVD process, where an energy is applied to a vapor of acetylene and hydrogen in an inert with the volume ratio of acetylene to hydrogen between 0.35 and 0.85 to break their bonding at a processing temperature between 600-800 °C to form a UNCD film (11)

Thin film UNCD diamond are now developed by Advanced Diamond Technology (ADT) and considered a commercially available material for different applications whose properties and performance characteristics can be characterized and reproduced. Furthermore, there are several grades of this material

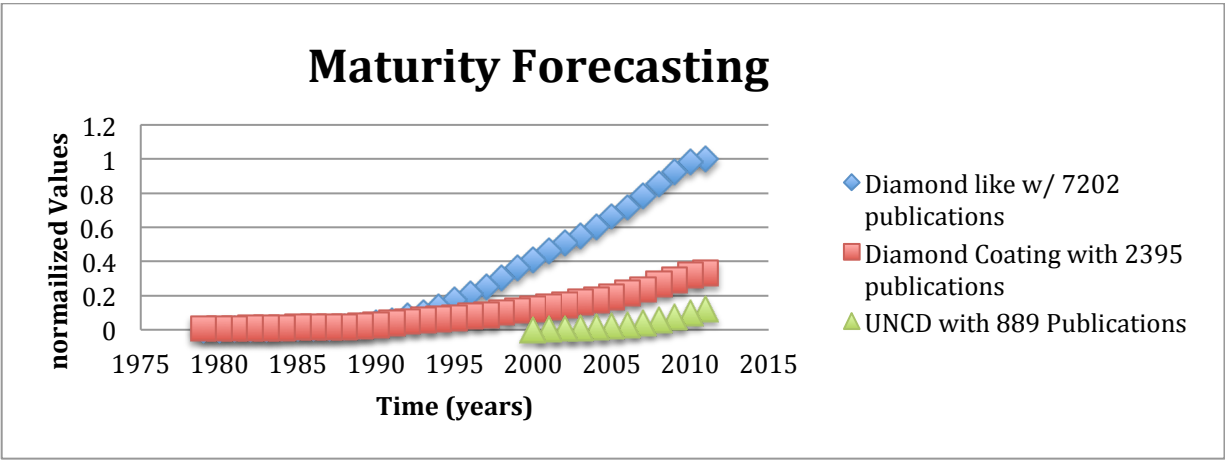
with variation of properties of these films as desired such as smoothness, thermal conductivity, electrical conductivity, and optical properties. Therefore, these thin film diamonds can be adjusted in a controllable and reproducible manner. For example, ADT is offering different grades of UNCD Aqua series with different roughness values (13).

Significance of this technology

The significance of this technology is that it can lift most of the limitations encountered earlier with, not only AFM operations, but all of the nanofabrication processes by bringing diamond to the nano world with the industry requirement of micro/nano geometries, reproducibility and affordability. Diamond features of renowned durability such as low stiction properties and strength have been desired such that the instruments can perform effectively, i.e., no fouling or delamination. Unlike other types of diamond at nano scale, UNCD proved to have smooth, dense, pure (no voids), and can be deposited effectively on a wide variety of materials and high-aspect-ratio structures (11) The UNCD also proved its reliability and economical feasibility in several applications. For microfabrication, UNCD coatings proved its conformity for coating high aspect ratio structures with different geometries. The use of diamond wafers will greatly affect the MEMS/NEMS component and put them in real applications. This new technology made it possible to economically and reliably create minuscule patterns onto a material, tip-based nanofabrication operations subject tools to harsh conditions (4). The earlier technologies of MEMS/NEMS such as microgears, microfluidics and other similar devices can have real reliable and economical applications.

The Technology Status

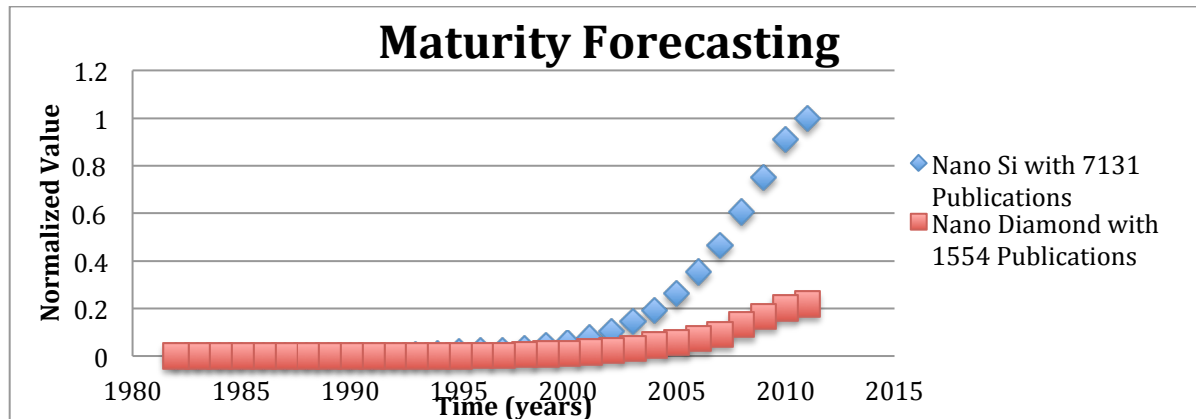
UNCD films have graduated from the laboratory to become a practical industrial material whose properties and performance characteristics can be well defined and reproduced. In general, we can consider most of its applications at the technical development stage. UNCD films were developed and patented at Argonne National Laboratory in 2003 and was funded by DARPA. Advanced Diamond Technologies (ADT), a spun-off company from ANL, has been developing UNCD for commercial products (14). In general diamond coatings are considered an emerging technology, as there are more than 35,000 patents registered for this technique of coating. On the other hand, there are 3487 patents registered for diamond at nano scale, of which only 29 for UNCD (15). However, looking at the bibliometric of the papers and research works and assuming that the diamond-like material is approaching its maturity level, we can see that UNCD is growing and just starting to climb up the curve in the start of the emerging technology region. By comparison, we notice that it roughly took Diamond like around 25 years to reach its maturity, so we can expect UNCD to be mature by year 2025.



Moreover, for this type of materials “UNCD”, its applications have been growing in different fields. At a macroscale, the materials were successfully produced for several applications such as mechanical seals and

tools. Also, broader range of grades have been achieved and applied. At a microscale, diamond in general were preferred, but has been limited due to nano/micro manufacturability difficulties. On the other hand, UNCD has been successfully produced for a number of wafers, and other microscale devices and tools (13).

The use of diamond at nanoscale has been considered. In fact, there are 3487 patents for Nano Diamond compared with 14680 patents for the nanoscale Si (15). Moreover, the bibliometric graph shows that there have been tremendous works with regards to Nano diamond applications as it is catching up with the Si nano applications, yet it appears to be in the emerging technology region .



The critical path is developing shapes and coating MEMS and NEMS components in a reliable, uniform, scalable and economically feasible trends. Also, Diamond based MEMS/NEMS applications are being considered in several areas such as AFM, Micro/Nano-fabrication and photolithography tools, resonators and switches, telecommunication devices, display panels, in-vivo biomedical implants (such as joints and spine) and biosensors as they offer great performance as well as reducing lifecycle costs (4, 13, 16)

Depending on the applications of this material, its development status differs. For example, in the thin filming application of UNCD such as on multipurpose pump seals, several researches were completed to aid John Crane on improving plasma uniformity and automating the diamond seeding process to produce UNCD layers on large area substrates with uniform thickness and microstructure (17).

The application of the Probes, Nanolithography probes or arrays for parallel imaging, writing, reading, recording and/or nanofabrication tools for drilling, cutting and milling are also being considered. Similar applications under this category are independent sensors, actuators, arraying, microfluidics and scanning probes. The status of such applications is just existing the laboratory doors, as several probes have been made successfully with the AFM, which were used for contact mode scanning, and proved to be reliable and reproducible (6). There have been also several researches and successful trials for mass production of diamond probes for SPM, nanofountain, nano pen and nano probe heaters, which are all used for nanofabrication purposes (4 & 18). For such applications, the technical developments by the major players are taking place, which might take some years to reach full production for some of them.

Other applications with regards to in-vivo implanting and complex shapes are being researched in several areas. The use of UNCD , with its overall biochemical, electrochemical inertness, and gears with the unrivalled durability to wear, and very low surface roughness, is being seriously researched. The broader impacts of this research are the advantages they offer such as the elimination of anticoagulants for patients with implanted medical devices, making different patients safely use advanced devices such as heart pumps, and the reliability of small machines that can be applied in several areas. Several companies such as the pharmaceutical, biomedical and nano machineries are also considering this technology for serious researches (13 & 19).

Technology Owner

The UNCD was funded by DARPA to the Argonne National Lab (ANL) to develop high performance integrated diamond MEMS. ANL partnered with ADT, IMT, MEMtronics Corp, Peregrine Semiconductor and academic partners such as U-Penn, UW-Madison, Northwestern University, U-Chicago, and UI-Urbana Champaign. ADT is now the licensed company of producing products with diamond films for industrial, electronic and medical applications. Also, ADT is licensing recipes of some products which enable engineers and product developers to reliably and affordably design micro devices and sensors out of diamond (14).

The Major Players

Currently, ADT is producing a variety of products for different applications, especially with the well established market of the probe tips, tools, and some other specific products. Their name has found its position into this technology, and they are distributing the products through other companies which have more experience with the end products and specifications. However, due to its promising market penetrations, other products will be developed by others who have the expertise to use the material and productize them into real applications.

First, the players of the Probe Tips might take over very soon as their main interest is manufacturing of nano/micro probe tips such as Nanoscience Instruments, SPI, Nanosensors, Accurion, LLC and others. Also, other players would be the manufacturers of the nano/micro lithography machines and wafer processing equipment such as NanoInk, Molecular Imprints, Mad City Labs, Anvik Corp., EV Group, Nanonex and others. In fact, Nanoscience Instruments already have some products in cooperation with ADT (20). Such players will need to first obtain the required core competences, develop the technical knowledge, as it is somewhat different from the existing techniques. Yet, their brand identity, well established distribution channels and customer's knowledge will require them to speed up the process of acquiring the knowledge and coming up with full scale production in at most 5 years period.

Other end users that might be interested in similar devices that use UNCD tips, chips or wafers can broadly range from switches, sensors, biomedical equipment to communication. This is an established market, and the players already have the market knowledge, distribution channels and other required skills. It would be a short period of time to change to this new type of materials, and develop the required technical knowledge and acquire the missing core competences. In general, micro/bulk manufacturing of the UNCD wafers, are done in a similar fashion to those of the Silicon wafers, but there are some technical knowledge that might be developed as well. Currently, MEMtronics Corporation is already making switches of UNCD in collaboration with ADT that showed outstanding longevity of operations (22). There will be others who would follow, but it might take time (5 to 8 years) before they reach full production as different products have different requirements and regulations/code requirements..

As for the emerging market of MEMS/NEMS, the market is growing, but with this new material, its potential of growth will be skyrocketing. The current key player in this market is IMT. They already have products out of UNCD, they are considered a MEMS foundry, who are specializing in offering complex shapes of MEMS/NEMS (21). Nonetheless, other major players in the MEMS world such as Micralyne, MEMS Industry, Tronics and others will surely pick up this technology. This however will take longer time to develop since they have to develop all the required knowledge as for MEMS it has to be developed all in the same place. This market will take longer time, and I personally expect it to be projected over the upcoming 10 to 15 years, but depending on the products, the timing will vary.

Biomedical, pharmaceutical equipment, and other medical related equipment are also being researched and some successfully tested products were obtained. JarvikHeart is already testing some products related to heart. This might take the longest period of time due to the extended regulations and clinical trials (13 &19).

Reference List

- 1- Krauss, Auciello, Gruen, Jaya, Sumant, Tucek, Mancini, and Meyer, "Ultrananocrystalline diamond thin films for MEMS and moving mechanical assembly devices", *Diamond and Related Materials*, Sept. 01
- 2- Kim, Moldovan, Horacio, Espinosa, Xiao, Carlisle and Auciello, "Novel Ultrananocrystalline Diamond Probes for High-Resolution Low-Wear Nanolithographic Techniques", *Nanolithography Probes*, Aug.05.
3. Srinivasan, Hiller and Auciello, "Piezoelectric/ultrananocrystalline diamond heterostructures for high-performance multifunctional micro/nanoelectromechanical systems" *APPLIED PHYSICS LETTERS* 90, 134101 (2007)
- 4- J. Jackson, "The World's First Diamond Nanoprobe Tips Demonstrate Success in Nanomanufacturing" *Calyx Consulting*, June 10.
- 5- Grierson, Moldovan, Notbohm, O'Connor, Sumant, Carlisle, Turner and Carpick, "Preventing nanoscale wear of atomic force microscopy tips through the use of monolithic ultrananocrystalline diamond probes" *UW-Madison Pubs.* May 10
- 6- Espinosa, Prorok, Peng, Kim, Moldovan, Auciello, Carlisle, Gruen and Mancini "Mechanical Properties of Ultrananocrystalline Diamond Thin Films Relevant to MEMS/NEMS Devices" *Experimental Mechanics*, Sept. 03.
7. QMED, "Diamond Nanoprobe Tips May Outperform Silicon in Nanomanufacturing Processes" *MPMM MedTech*. Jun. 10 [available online:] (<http://www.qmed.com/mpmn>)
8. Fletcher, Felts, Jacobs, Woo Lee, Sheehan, Carlisle, Carpick, and King, "Wear-Resistant Diamond Nanoprobe Tips with Integrated Silicon Heater for Tip-Based Nanomanufacturing", *ACS Nano*, Feb. 10
- 9- U-Texas "AFM Manual" [Available Online] (<http://uweb.txstate.edu/~ab35/manuals/AFMmanuals/AFMLabManual.pdf>)
- 10- Fletcher Felts†, Jacobs‡, Sheehan, Carlisle, Carpick and King, "Wear-Resistant Diamond Nanoprobe Tips with Integrated Silicon Heater for Tip-Based Nanomanufacturing" *ACS Nano* May 10
- 11- Olga Shenderova and Gary McGuire *Nanocrystalline Diamond* International Technology Center, Research Triangle Park, North Carolina, 2006.
- 12- Cyril, and Favaro, "Mechanical properties of ultrananocrystalline diamond (UNCD) films" *CSM Instruments SA*, 2002.
- 13- Products of ADT (online Website Address: <http://www.thindiamond.com/technology1/what-is-uncd/>)
- 14-Catherine Foster "Diamond technology to revolutionize mobile communications" *DOE/Argonne National Laboratory*, Aug. 06 [Available online] http://www.eurekalert.org/pub_releases/2006-08/dnl-dtt080806.php
- 15- US Patent and Trademark Office (website Search: <http://www.uspto.gov/>)
- 16- Hamiton, Carpick, Sawyer, and Konicek, "Low-friction and long-wearing diamond films", *Micro/Nano Lithography, SPIE*, Oct. 08 [Available online]: <http://spie.org/x27566.xml?ArticleID=x27566>
- 17- US. Dept. of Energy, Energy Efficiency and Renewable Energy, "Development of Ultrananocrystalline Diamond (UNCD®) Thin Films for Low Friction/Low Wear Applications" *INDUSTRIAL TECHNOLOGIES PROGRAM*, 2007 [Available online]: http://www1.eere.energy.gov/industry/imf/pdfs/1798_uncdcoatings.pdf
- 18- Espinosa, "The World's Smallest Fountain Pen?" *NSF Nanoscale Science and Engineering Center for, Illinois* Aug. 05

19- Carlisle, "Development and Characterization of Bio-inert UNCD films for Implantable Devices to Eliminate Blood Clotting" *National Science Foundation*, 2009

20- Nanoscience Inst. Website: <http://store.nanoscience.com/store/pc/viewCategories.asp?idCategory=155>

21- IMT website <http://www.memtronics.com/>

22- Memtronic website: <http://www.memtronics.com/>