Background and Overview:

The ability to deterministically place nanoscale features at specific points on a pre-existing surface with nanometer scale accuracy requires the development of several key technological capabilities. Rather than try to synthesize nanoscale objects in a remote location and use physical manipulation of the objects to place them at a deterministic location on a substrate, we will be pursuing a method to electrochemically synthesize the nanoscale features at the end of an AFM like tip in-situ, real time, as the tip is placed at the point of interest. This method has the advantage that the synthesis and placement of the features happen simultaneously, with a resultant improved connectivity and contact with the substrate, compared to separate synthesis and placement processes. It also allows for independent control of parameters for the nanoscale feature at the time of synthesis, allowing a large degree of customization to be achieved in the synthesis of each nanoscale feature, and therefore to the degree of deterministic heterogeneity achievable on the surface. To achieve this goal, we feel there are a number of separate areas of effort that must be approached and integrated into a whole system that is capable of rapid, high throughput synthesis of nanoscale features with deterministic placement and variable control of feature parameters. Each area of effort is outlined separately below, and the principle team members and their areas of responsibility within each area of effort are outlined. In Figure 1, we show an overview of the system, with each technical challenge area detailed out to give an overall concept image of how the integrated system will be capable of operating.

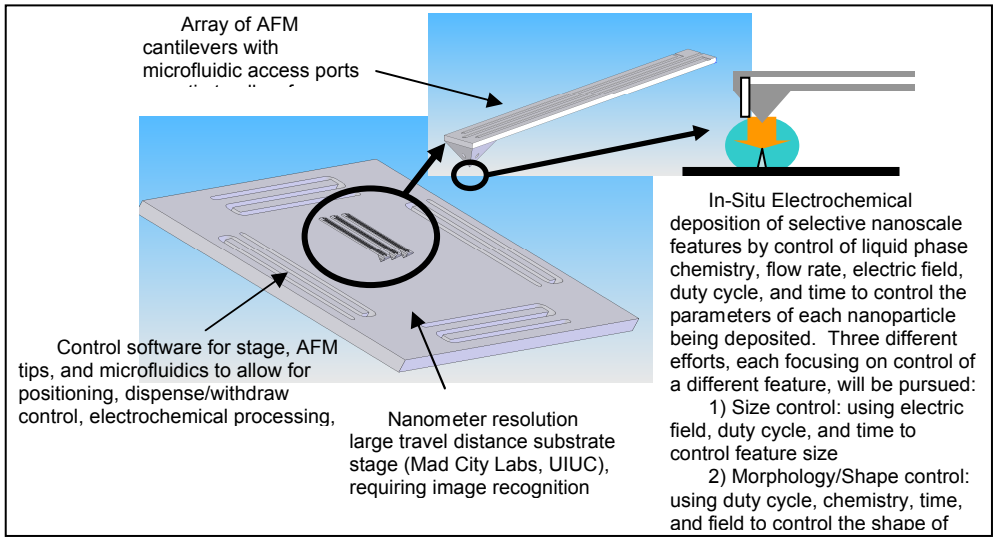

Figure 1: Program Overview, demonstrating key technical areas to achieve deterministic placement of asymmetric nanoparticles on a substrate, and the principle responsible team members for each area.

To accomplish the development of both a tool capable of fabricating a nanoscale feature at a deterministic position on a substrate, we have combined a team incorporating Sandia National Laboratories, who has expertise in AFM fabrication of nanoscale features, as well as highly accurate control of systems at the nanoscale level. For position control, the team includes Mad City Laboratories, a large commercial, US owned manufacturer of precision stages that have resolutions into the sub-nm level. To help in the understanding of the fundamental aspects of nanometer scale growth and control, Dr. Min-Feng Lu's group at the University of Illinois, who has demonstrated nanoscale deterministic deposition of nanoscale rods, springboards, and bridges. Each of the team members has specific tasks associated with the development of the fabrication platform, as well as development of the methodologies for nanofeature deposition. A

Table 1: Work Breakdown Structure of High Level Tasks for each of the Team members, by primary task

	I	II	III
Fabrication of Microfluidic AFM Tips			
Development of single tip with microfluidic channels	Sandia		
Development of locally positioned peristatic MEMS pump for fluid control	Sandia	Sandia	
Integrate First AFM microfluidic tip with early stage positioners	Sandia/MCL		
Fabrication of AFM tips with waveguides		Sandia	
Development of small scale multitip array of microfluidic tips		Sandia	
Integration of small array with improved positioning stage with thermal control	Sandia/MCL		
Demonstration of multitip manufacture of nanofeatures		Sandia	Sandia
Development of large scale multitip array			Sandia
Nanopositioning and Stage Control			
New design for long range positioners (invar)	MCL		
Piezoelectric motor development	MCL		
Development of dual interferometric position sensors	MCL		
Development of thermal control systems	MCL		
DSP development of two stage solution	MCL		
Increase translation distance		MCL	
Tip/Tilt control		MCL	
Nanoradian control of rotation		MCL	
Advanced Thermal control for multitip integration		MCL	
Novel long range positioners in composites			MCL
Thermal control for all stage and components			MCL
Integration of Multitip array with stages			MCL/Sandia
Microfluidic Dispense and Tip control			
Modelling of system for thermal and mechanical response	Sandia	Sandia	
Development of microfluidic control system for pL dispense	Sandia		
Development of closed loop temperature sense/control with 0.1 degree accuracy	Sandia		
Development of AFM tip drive software for force neutralization	Sandia	Sandia	
Integration of control loops with single tip on first gen stage		Sandia	
Development of integrated microfluidic/temperature control with heat loss		Sandia	Sandia
Development of close loop detection of tip position against stage		Sandia	Sandia
Development of sense/feedback from AFM tip for metrology			Sandia
Development of multitip alignment capability for multitip assembly of heterogeneous structures			Sandia
Development of optical control for optically initiated chemistry in-situ			Sandia
Development of integrated high accuracy X Y Z Theta control			Sandia/MCL
Overall System Integration			
Phase I system Integration	Sandia/MCL		
Phase II system integration		Sandia/MCL	
Phase III system integration			Sandia/MCL
Feature fabrication			
Development of early droplet control	Sandia		
Development of initial electrochemical deposition methods	Sandia/UIUC		
Development of metrology methods for tip	Sandia		
Demonstration of 2 size printing using single tip	Sandia/UIUC		
Transfer of deposition of nanoneedle from UIUC onto integrated platform	Sandia/UIUC	UIUC	
Development of nanoneedle process	UIUC	UIUC	
Demonstration of size and morphology variation	UIUC	UIUC	UIUC
Demonstration of 2 separate chemistry depositions on substrate		Sandia/UIUC	Sandia/UIUC
Demonstration of heterogeneous chemistry in single nanofeature			Sandia/UIUC
Demonstration of large number of heterogeneous structures			Sandia/UIUC
Demonstration of continuous control of chemical heterogeneity			Sandia/UIUC
Final Report			Sandia/UIUC/ MCL

proposed organization in the form of a high level work breakdown structure by phase, is shown

in Table I. Throughout the program, strong interactions between the three principle team members in the form of weekly conference calls, on site meetings, and written communication will keep the team focused on the delivery of prototype hardware for manufacturing the nanofeatures, and on developing chemistries compatible with the fabrication hardware.

Several challenges arise as a result of the consideration of integrating such a device with real time chemistry, and are broken down into 5 basic areas. The first is the actual manufacture of the AFM tip incorporating the microfluidic channel, and the optical waveguide to support photolytically initiated deposition. The next is the design and implantation of a nanopositioning X-Y stage controller that is capable of long travel distances at high speeds to meet the manufacturing needs. The third is the closed loop system control design for both the control of the tip itself as well as the microfluidic controllers necessary to accurately dispense pL droplets at the AFM tip. The fourth major task is the development of the chemistries that will actually produce the nanofeature on the substrate of interest, and modulate the properties of the nanofeature in size, morphology, or chemistry. The final is the overall system integration and demonstration of fabrication of arrays of nanoscale features with deterministic positioning and fine control over the size, morphology, and chemistry of individual features. Each major task group is discussed in more detail in the following sections.

Manufacturing of AFM tips with Microfluidic and Waveguide Features

Sandia National Laboratories has a nearly 20 year expertise in the fabrication of MEMS based technology, including the development of specialty sensors and actuators in the microfluidic regime, and force based sensing and actuation at the microscale. Several standard process flows exist to produce a wide variety of devices, and we intend to utilize this process experience to modify existing processes to build the special microfluidic AFM tips necessary for this application. Arrays of microfabricated devices have also been demonstrated by Sandia in the past, and the use of microlithographic capability allows us to expand on early designs for single isolated microfluidic AFM tips into conjoined arrays of tips. A sample process flow to manufacture an early stage Phase I) tip is shown in Figure 2. In this process, a standard methodology for the fabrication of AFM tips is modified to include the incorporation of a fluid channel into the cantilever, with a release of the droplet occurring at the base of the tip. Capillary forces will then carry the picoliter droplet to the end the AFM tip, allowing subsequent positioning and deposition of a nanofeature once emplaced. Despite Sandia's fabrication experience in this area, several technological hurdles exist to the fabrication of such tips. For example, large or high aspect ratio tips cannot be fabricated with this process flow because severe topography will limit our ability to planarize top surface for channel fabrication. If it is found that a high aspect ratio tip is needed either for fluidic control at the tip, wetting, or precise positioning, alternative methods to fabricate the mold layer of the silicon, such as high aspect ratio etching, will be substituted for the simple wet chemical KOH etch. Placing both a waveguide and a microfluidic channel together has not been previously demonstrated in this technology, and may require additional lithography levels, with their inherent manufacturing risk, in order to achieve this integration. Placement of the fluidic port at the base of tip is the easiest to achieve, but if the port is required to be on a facet for wetting or AFM stiffness reasons, the design could be accommodated, with an additional complexity of the silicon nitride tolerance to etching coming into the design. Use of highly selective dry etching and careful control of processing may alleviate these concerns for integration.

Of more concern is the sharpness of the tip. An as-fabricated atomically sharp tip is not typically done. Instead, a post fabrication sharpening step of oxidation and stripping is done, but

this process is complicated by the existence of the microfluidic channel. Methods of sharpening the tip first, followed by release of the microfluidic channel, may solve this integration problem. This is compounded with a need for a very long chemical release time for the fabricated channel to remove the molding silicon oxide. Engineering a "keyhole" in the channel to locally allow wet etch chemicals has been previously demonstrated, and can be employed in this case as well. Finally, the tip will be located well below the backside of the wafer during final assembly, which will complicate the assembly of the finished device to the microfluidic control and delivery system.

It is also possible that, due to the needs of the control system for microfluidic dispensing, a micromachined peristaltic pump will need to be integrated into the base of the AFM tip to allow for minimizing the distance between the control point and the dispense point. If this turns out to be the case, additional mask and fabrication complexity will be necessary before an integrated AFM tip can be fabricated. Sandia has developed several prototypes of peristaltic integrated MEMS pumping systems with pL accuracy, and these can be implemented into the fabrication of the microfluidic tip if necessary for accurate control of the fluid dispensing.

Nanometer Accurate Stage Positioning with High Accuracy, High Speed, and High Travel Distance

The difficulties in achieving the positioning requirements of the BAA are all a result of the long range of motion required. At present, it is well understood that a flexure guided motion stage using an integrated position sensor which is driven by a piezo actuator can achieve sub-nanometer precision with response times of a few milliseconds over a range of approximately 100 microns. Simply "scaling up" the range of motion for such a stage does not result in a high speed, long range of motion nanopositioner. For every incremental increase in the range of motion, the stage's response time increases, the positioning errors increase, and the problems due to thermal expansion increase. These detrimental effects result from increased strain in the hinges and the scaling of positioning errors present in the integrated sensors. The stiffness and expansion limitations in the piezo actuators themselves also make it impossible to simply "scale up" the range of motion in a modern, state of the art, nanopositioner without losing at least one desirable attribute.

Our proposed solution to this "scaling up" problem is to develop a different design concept so that the detrimental effects on both speed and precision will be minimized when long range of motion is achieved. The concept is a hybrid motion system which combines a high speed, high precision, short range of motion stage with a long range of motion stage. The displacements of the two will sum together to produce the total system displacement. The long range motion stage will be fairly high speed, with step response times in the 20 msec range, while the short range motion stage will be ultra high speed with step response times in the1-2 msec range. The ultrahigh speed stage will be used to control growth locations in a 50 μm x 50 μm area while the long range motion stage will be used to position the ultrahigh speed stage across the entire area of interest. When the device is used to scan (AFM imaging for example), the two stages will be used in tandem to achieve the highest possible speed over long range of motion. The difficulties we expect to encounter in building such a device are numerous and include: the position sensor, the guidance mechanism, the driving force, the choice of materials, the control system, and thermal stability.

Thermal expansion will be a major concern throughout the entire design process. To illustrate its importance - the linear thermal expansion of 1 cm of Si is 260 nm per degree C. Obviously temperature stability to less than 0.1 degree C will be of critical importance. Thermal stability

strongly affects the fundamental system design. Selecting position sensors with low heat output and materials with low thermal expansion will minimize temperature changes and the effect of those changes. In addition, the effects of thermal expansion can be minimized by keeping the entire system as small as possible.

The guidance mechanism and driving force of the long range motion stage are also critical. The best choice is likely to be a piezo motor actuating a long range flexure hinge. The flexure's inherent repeatability and stiffness are significant advantages when compared to mechanical bearings. The potential benefits of these design choices are a low heat output actuator combined with a stiff guidance mechanism which is potentially capable of high speed motion. Potential difficulties with this approach are the relatively low forces generated by commercially available piezo motors and the limited range of motion produced by current flexure hinge designs. New piezo motor designs will be needed to move the proposed flexure stage and new flexures will need to be developed which are capable of the required range of motion. This is complicated by the fact that low CTE materials such as invar and super invar make very weak flexures with poor speed characteristics. Composite materials, which offer anisotropic control of material properties and can have low CTE may need to be used - especially in phase III.

Position sensing and control will have to be greatly improved relative to current nanopositioning system design. Currently we can achieve 50 picometer resolution with repeatability of 0.5 nm on a stage with 100 microns of motion. Scaling this up to 1 cm of travel translates to a resolution of 5 nm and a repeatability of 50nm. Piezo sensors only measure linear motion and do not correct for orthogonality. Capacitive sensors have the same orthogonality problem but produce lower positioning resolution. We feel that an interferometer based measurement system is the proper choice. These systems are available with nanometer resolution but require a design effort to reduce the optical path length while also eliminating the effects of the laser heat output. Control will necessarily be done with a DSP since it is envisioned that additional sensors inside the shorter range motion stages will also be used for control.

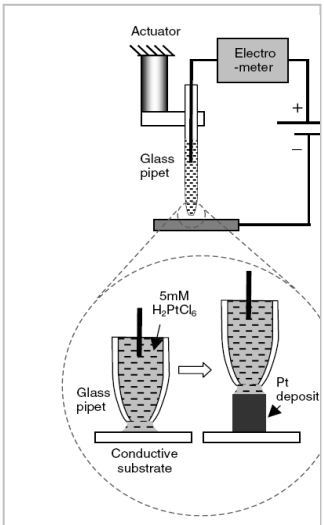

Fig. 3: Schematic showing the setup for ec-FPN deposition of Pt

Microfluidic Dispensing, Retraction, and AFM Positioning Control

System identification and control of the system will be of primary importance when the positioning system is combined together with the tip-based end effectors. Any structural resonances of the selected positioning device will have to be identified for appropriate control algorithm development. Customized tips will also need to be analyzed to identify bending modes and spring constants for appropriate feedback control.

Process control of picoliter volumes of liquid is an extremely difficult and challenging task as well. At these particular scales nonlinear effects such as viscous forces and surface tension will dominate. In order to deposit the appropriate amount of fluid it will be necessary to model the force applied relative to the amount of fluid released at the tip. In order to reduce the moving mass of the tip, a MEMS based fluidic delivery systems will be of primary importance. Problems to be addressed will include but not be limited to position and impedance control of the tip, tip contact angle, fluid spreading after contact, and a MEMS based fluid deposition.

In-Situ Fabrication of Nanofeatures with Size, Shape, and Chemistry Control

Feature control of the deposited nanofeature is the critical component, and the design element against which the physical fabrication device technology outlined above will be implemented. At the most basic level, control of the size of a nanoscale feature allows the demonstration of all of the most basic design elements of the deposition and control system. To meet the early phase goals of the BAA, we will modify the size of the deposited nanofeature between two discrete sizes. These will be controlled by the amount of delivered liquid in the precursor phase, and the control of the time of deposition in the electrolytic deposition of the nanofeature. Once this capability has been established for a single tip in Phase I, additional capabilities that stretch the capability of the platform will be implemented.

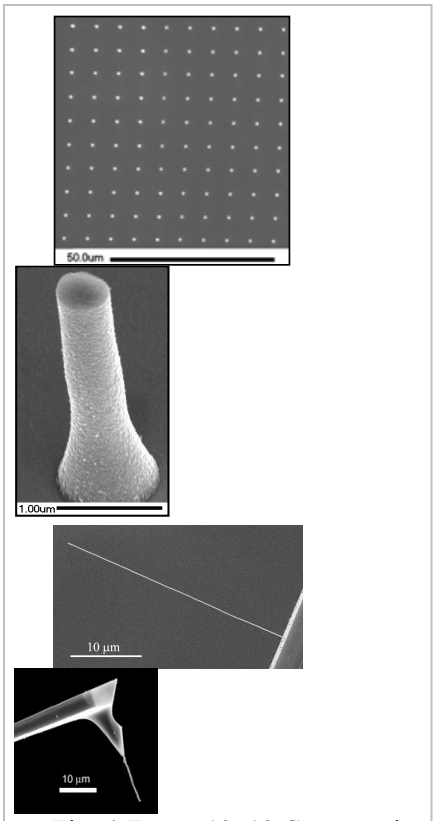

Fig. 4 Top: a 10×10 Cu nanowire array and a close-up view of a nanowire. Bottom: a freestanding Pt nanowire 150 nm in diameter and 30 µm long and a Pt nanowire deposited directly on an SPM tip.

The next level of challenge for control of the platform is to deposit features with controlled variation in the shape of the deposited feature, making them vary in aspect ratio or move to more complex geometries. The ability to control the shape of the as-deposited nanostructures greatly expands the utility of the proposed technology and allows manufacturing-scale fabrication of complex three-dimensional (3-D) structures with nanoscale dimensions.

The team member at the University of Illinois has, in prior practice, developed a unique electrochemical deposition process, electrochemical fountain pen nanofabrication (ec-FPN), that goes beyond the traditional planar electroplating and surface deposition, and realizes the fabrication of 3-D nanostructures in ambient environment, such as high aspect ratio out-of-plane nanowires, interconnect nanoscale bridges, curved and coiled nanostructures and ultimately, complex-shaped nanostructures and nanostructure arrays. The main concept involves a two-step process, as schematically shown in Figure 3: first, the use of an electrolyte-filled nanopipette with nanoscale aperture to supply electrolyte and the initiation of local electrodeposition within the nanoscale liquid meniscus formed between the nanopipette and substrate surface; and second, the controlled withdrawal of the nanopipette from the substrate surface while maintaining the meniscus formation between the nanopipette and the growth front of the deposited material to continuously grow off-surface nanowires and other types of 3-D nanostructures, with their diameters limited by the size of meniscus and their lengths limited by

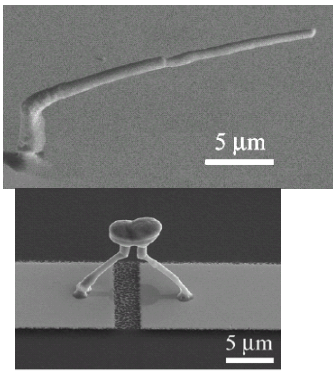

Fig. 5: Left: SEM images showing a tilted Cu nanostructure on a Cu post continuously fabricated with the same nanopipette. Right: an interconnect bridge.

the withdrawal distance of nanopipette, as shown in Figure 4. Instead of being driven straight up from the substrate, the nanopipette can also be driven sideway to fabricate tilted nanostructures, as shown in Figure 5.

This probe-based ec-FPN technique thus shows a number of advantages not existed in any other technologies. The technique is essentially a direct-write technique, which renders its flexibility and versatility; it is capable of producing structures with nanoscale features in ambient environment, which makes it compatible with existing manufacturing processes; it is inherently a 3-D fabrication technique, which opens up new venues for practical nanomanufacturing; and it is based on electrochemical deposition, which ensures low cost nanofabrication of a wide range of materials accessible to electrochemistry.

In this proposed project, we will explore the deposition with electrochemistry of other materials that are important for certain applications, for example, magnetic metal materials (Ni, Co), semiconductive materials (III-V and II-VI compounds), and conductive polymers (polypyrrole, polyaniline, and their derivatives). To successfully make nanostructures of those material types with ec-FPN can open up new opportunities for application, and most importantly, allow the direct local fabrication of nanoscale electronic and sensing devices consisting of multiple components. The appropriate electrochemical deposition routes will be identified based on existing literatures on electrochemistry, the characteristics of the related electrochemistry will be studied with cyclic voltammetry integrated with the existing ec-FPN setup, and the optimal conditions (electrolyte concentration, electrodeposition potential, withdrawal speed, humidity and temperature) for the electrodeposition and shape control of nanostructures will be explored. We will also explore the direct use of the developed microfluidically accessible AFM probe for 3-D nanostructure fabrication. New issues deemed important for the electrodeposition and shape control of nanostructures with this new probe will be studied, such as meniscus formation and stability, surface mediated liquid transport at nanoscale, ion transport at nanoscale, and potential distribution and its effect on nucleation and electrodeposition of materials at nanoscale. The studies will in turn provide practical design parameters for the optimization of the proposed microfluidic AFM probes for tip-based electrochemical nanofabrication.

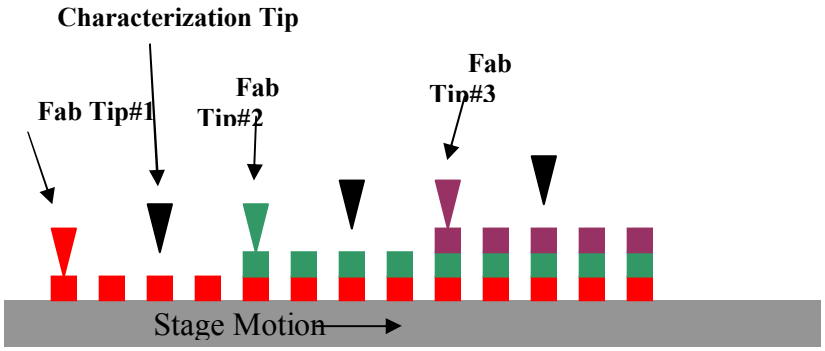

Figure 6. Fabricating a nanowire heterostructure in Z axis.

The highest level of complexity, which will be fully implemented in Phase III but have significant research in all three phases is the concept of a chemically heterogeneous nanoparticle. To make tip-based nanolithography truly useful, one must consider a system that can create heterostructures of different materials with nanometer precision. To accomplish this we propose to develop a multi-tip nano-fountain pen system where each tip has the capability to deposit single material. This will eliminate the problems with

developing a tip-based liquid dispensing system that has to deliver several different solution through microfluidics.

Figure 6 shows a schematic of the proposed assembly process. In this scheme, tip #1 delivers and assembles a nanostructure of material 1. A high precision stage will be used to shuttle the initial nanostructure to tip #2, where material 2 will be deposited either in the lateral plane or along the z axis (vertical structures). This nano-assembly line concept could be used to create a large variety of heterostructures that will have novel electronic properties. In this arrangement, the tips will be organized into unit cells where some tips will be used for fabrication and other used for high fidelity topographic characterization.

In this method, one tip will be used to deposit a pL-aL droplet on the base substrate, while the other tip will be used to perform the electrochemical growth and topographic characterization. The cantilevers supporting the tips will be designed to independently control tip-sample separation. The dispensing tip will be a microfabricated cantilever with integrated microfluidics for delivering precision droplets of fluids. The tip of this lever will be brought into physical contact will the surface for a brief amount of time. Capillary forces will pull solution from the cantilever reservoir onto the substrate. Once fluid has been deposited, the tip will be pulled back from the base substrate, preventing uncontrolled deposition of additional fluid. The motivation behind developing a delivery system that deposits well-controlled amount of fluids is to aid in the control of the feature size. By control droplet volume, we hope to gain the ability to tune the volume so that during the electrochemical growth, all of the material in the droplet will be depleted after fabricating a feature of known size, leaving behind only a droplet containing salt. This eliminates the need to handle droplet waste before the next fabrication step. If the drop is too large to deplete, they will be manipulated away from the deposited nanostructure using the tip. In addition to controlling droplet volume, the

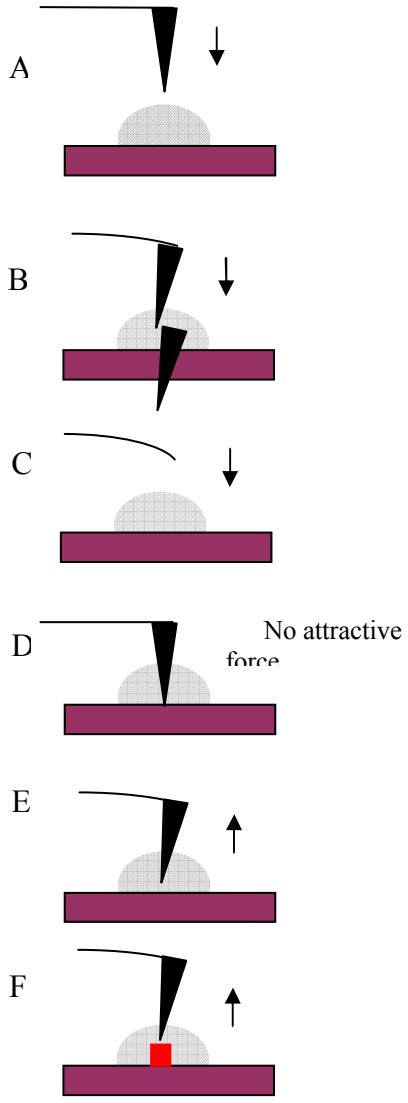

Figure 7. Fabrication sequence. A) Approaching the droplet. B) Droplet penetration. C) Contacting the surface. D) Finding the zero-load condition. E) Pulling the tip back to a known gap. F) Applying electric current to deposit nanostructure.

molarity of the plating solution will be adjusted so that it will be completely depleted after the deposition of a known feature size.

Once the droplet is deposited, the stage will be used to position the drop under the tip used for the electrochemical deposition. The tip used to perform the actual electrochemical growth will be made of a conducting material.

To initiate the electrochemical growth, the tip will initially be positioned slightly above the base substrate within the deposited liquid droplet. Since the tip used for growth needs to be positioned very close to the surface (closer equals better feature resolution and control) without physically touching the surface, care must be taken in the design of the cantilever supporting the tip. To accomplish this, the self-actuating cantilever supporting the tip will advance the tip thought the droplet and into weak physical contact with the surface. During the tip's approach to the surface, there will be a Z position where the surface forces will overwhelm the restoring force of the cantilever. At this point the tip will snap into contact with the surface, shorting the tip-substrate. Although shorting to the substrate is a problem for the deposition, this physical configuration has the advantage of allowing the control system to locate the surface just prior to deposition of the nanostructure. By continuing to load the cantilever until its deflection returns its free non-deflected value (zero load), the control system now knows where the substrate is in Z. After this position is determined, the control system will pull the tip off of the surface (snap-free) and reset its position with a well controlled tip-substrate gap, enabling a high degree of control of feature size. Since the tip is located in the droplet, the surface adhesion forces will be extremely weak due to screening of the van der Waals force, reducing any wear to the tip's apex. After electrochemically depositing the feature, the tip will be used to perform a topography analysis, similar to a contact or non-contact SPM, to determine the feature size. Figure 7 summarizes this process.

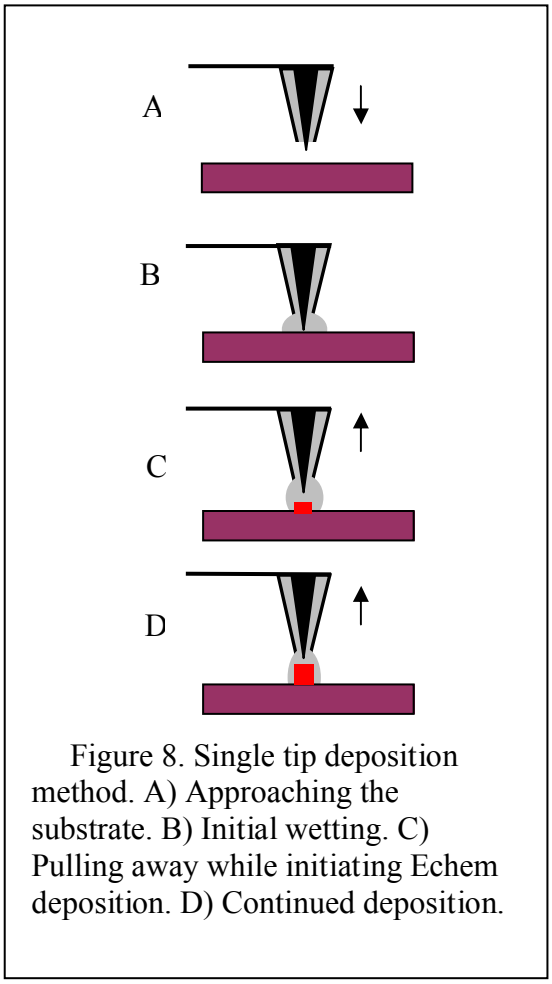

Figure 8. Single tip deposition method. A) Approaching the substrate. B) Initial wetting. C) Pulling away while initiating Echem deposition. D) Continued deposition.

In this method a single tip with built-in microfluidics will be use to electrochemically deposit a nanostructure. Initially, the tip will approach the surface. Once in contact, fluid will be pulled for the dispensing tip unto the surface. At this point the tip will pulled away for the surface while an electric current is sourced through the tip-sample gap in the meniscus. The speed of withdrawal will be selected to maintain a liquid meniscus between the tip and the growing nanostructure that is being electrochemically deposited. Figure 8 summarizes the process.

In parallel with the electrochemical method of nanofeature production, a parallel pathway of photolytically initiated nanofeature formation will be pursued. The advantage of this methodology is that the production of the features is independent of the substrate, i.e., this method does not require electrical conductivity of the substrate in order to fabricate the nanofeatures. Since this is a liquid delivery, the molarity of the dissolved reagent can be used to control the amount and number of nanoparticles. The synthesis methods would include reactive precursors and nanofeature growth using selected activation (photothermal and thermal) across the drop. A schematic of the general approach is shown below, with the target of being able to synthesize a single nanofeature per droplet of precursor.

The precursors of interest for this process would include metal alkyls or amides in organic solvents. This family of compounds is specifically selected due to their high reactivity upon exposure to atmospheric conditions (i.e., oxygenation, hydrogenation). Based upon conditions, the nanofeatures could be made into the oxides or the metal. This uniform exposure does not lend itself to morphological control. One way to induce morphological changes is to control the temperature gradient across the drop upon exposure to circumjacent reactive atmospheres. Several of these compounds are not stable at room temperature. Therefore upon reaching room temperature, the compounds will decompose and again with a gradient, directional morphological modalities may be realized. Further, mixtures of solvents within the drop can control morphological tendencies (i.e., DMF/water). The precursors could also have two types of surfactants that require different source activators. Therefore, nanofeatures of one type can be generated followed by another activator. With the proper 'lock-key' functionalization, these newly selected nanofeatures can be then be activated to link together.

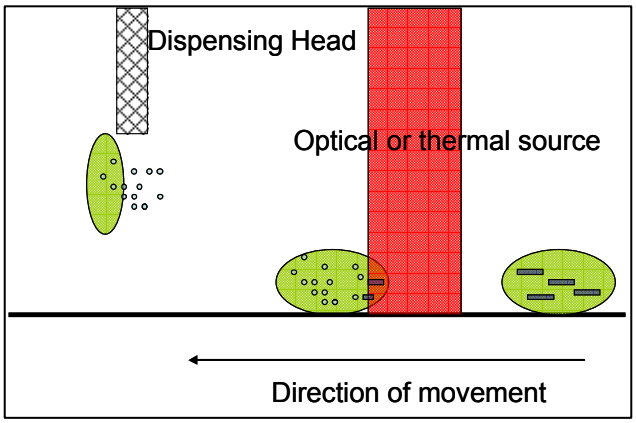

Figure 9: Schematic of Photolytically initiated nanofeature growth, showing droplet dispensing followed by optical beam initiation of feature formation.

Another method is to photoactivate (*hν)* the decomposition of the reagents, as shown schematically in Figure 9. Several metal salts (i.e., Ag, Au, Sn) can easily be activated to decompose into the parent metal. In addition, metal oxide (i.e., TiO_x, SnO_x) and semiconductors (i.e., CdE E = S, Se, Te) NPs can be generated using aqueous solutions and *hν* activation. One concept to vary the morphology in this situation would be to use a scan of the *hν* across the particle which would initiate directional growth. Selected active sites on polymers will allow for controlled pockets of nanofeatures formed upon activation. The size and shape of the pockets can be manipulated through the assembly of the polymers. The polymers could then be selectively grafted to the surface in a controlled manner. Coupling these two reactivities will allow for specific deposition of controlled morphological nanoparticles.