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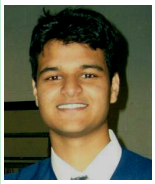
Optimization of Process Conditions for Deep Reactive Ion Etching of Silicon



By Sarvesh Varma
1st Year, Nanotechnology Engineering
University of Waterloo

As a part of my co-op term research (supervised by Dr. Todd Simpson), I was responsible to optimize processing conditions for etching Silicon using the Alcatel (Axiden) 601e deep reactive etching system in the Western Nanofabrication Lab.

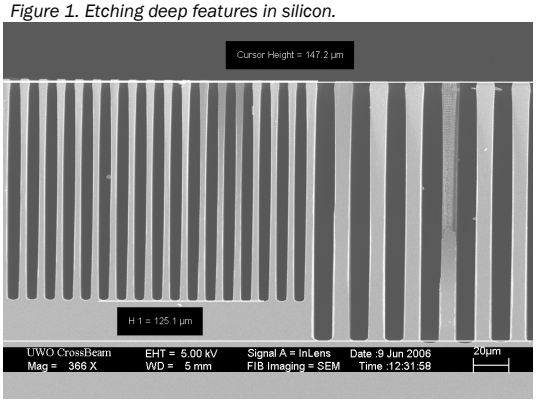
Deep Reactive Ion Etching (DRIE) is a process used to create highly anisotropic and high aspect ratio holes and trenches into a substrate. This process is highly useful in fabrication of MEMS devices, microfluidic channels and other semiconductor devices.

The 601e can operate in two modes; cryogenic and pulsed. In the cryogenic mode the substrate is cooled to -90˚C and the sidewalls are passivated by oxidation. I etched my samples with the pulsed (Bosch) process, which alternates between passivating (protecting) and selectively etching the substrate. Initially, the C_4F_8 plasma passivates (coats) the with inert polymers. Subsequently, the SF_6 plasma etches Silicon vertically (due to the substrate bias).

As a part of my optical lithography procedure, silicon wafers were primed with HMDS and then spun with a 1.4 micron layer of Shipley 1827 photoresist. The wafers were patterned by contact exposure to G-line UV. Next, they were developed and then descummed (gently cleaned) with O_2 plasma to minimize surface residue before etching. This procedure prepared the samples to be etched under different conditions and recipes.

The scope of the project was to investigate the etch sensitivity to several process parameters and to develop recipes for shallow etching (20 µm or less) and for deep etching (100 µm or more). I studied the effects of changing substrate power, gas flow and pulse interval, on the etch quality. The results were compared by analyzing the etch rate and photoresist removal rate. Furthermore, the etched feature topographies, sidewall angles and scalloping, and the surface profiles, were all studied under the SEM (Figure 1).

Figure 1. Etching deep features in silicon.



Over the course of the term, it was discovered that the process conditions for shallow etches were very different for deeper etches. Based on the results, previously used fabrication techniques/recipes were successfully optimized to achieve best quality of etches.

Future studies will concentrate on optimizing process conditions for the cryogenic etching process.

Fiducial Marks

By Dr. Todd W. Simpson
Researcher, Nanofabrication Laboratory
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An increasingly common request to the Nanofab is to produce fiducial marks at regions of interest, allowing the area to be located in other instruments for site specific analysis.

A wide variety of analytical techniques are available at Western and through the CSRF in Saskatoon for materials analysis. These include SIMS, AES, AFM, STM, nanoindentation, RBS, NRA, EDX, SEM, TEM, EXAFS and XANES. For specimens that are not uniform or bulk-like, comparing the analyses performed by different techniques require that the same region of a sample is examined with each technique. Although the individual analytical instrument may be capable of lateral resolution in the micro-scale regime, locating and measuring a particular region of interest on a macro-scale specimen is often difficult, if not impossible.

(Continued on page 4)

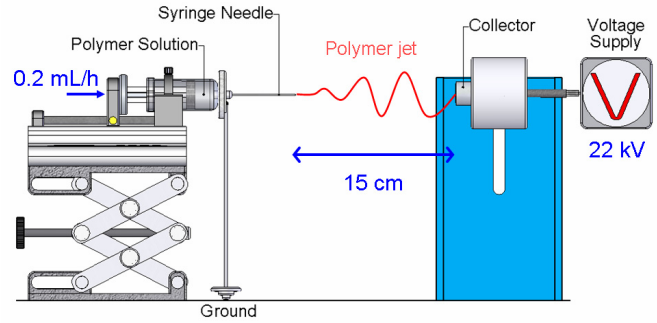
Elastic Modulus Of Individual Electrospun Poly(Vinyl Alcohol) Nanofibres

By Kenneth Kar Ho Wong, W.K. Wan, J.L. Hutter , M. Zinke-Allmang
Department of Physics & Astronomy
University of Western Ontario

Extracellular matrix and polymer scaffolds consisting of non-woven fibres are becoming the bio-medical materials of choice in many restorative and regenerative medical procedures because their basic properties, such as porosity and mechanical strength, can be tailored to suit specific applications. Definitively, the basic mechanical properties of the scaffold are governed by the composition and orientation of the polymer fibres. But the mechanical properties of each individual fibre play a dominant role on the macroscopic-scale mechanical properties of the scaffold, regardless of the orientation of the fibres of the scaffold. The elastic modulus E of each individual fibre presents some challenges to measure by conventional methods (such as uniaxial tensile testing) if the diameter reaches the nanometer regime. In this study, we propose a method to determine the elastic modulus of electro-spun fibre by using the atomic force microscope (AFM) with the assist of high resolution scanning electron microscope (SEM).

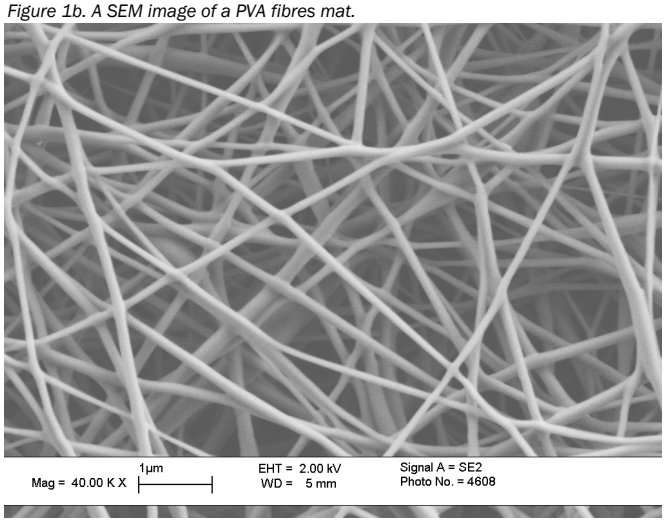
To produce non-woven polymer mats composed of fibres with diameters between 50 nm and 500nm, the electro-spinning process has been a very popular choice because of its simplicity and capability of producing fibres from a variety of materials, including proteins and polymers. Tens of kV electricity is used to create an electrically charged polymer solution jet out from a reservoir (a syringe propelled by a pump) to a collector where the jet dries and solidifies to become polymer fibre. Figure 1(a) shows the schematic diagram of an electro-spinning setup, which has an electrode connected into a collector, and the ground attached to a syringe needle, with ~1.5 kV/cm electric field in between. The value of this parameter is critical to produce uniform bead-free, non-woven poly(vinyl alcohol) (PVA) fibres mat (with the average fibre diameter of 120nm) shown as Figure 1(b) from a solution consisted of 12 wt% PVA powder (M_w = 89,000~98,000 g/mol, 99+% hydrolyzed) (Sigma-Aldrich Co.) dissolved in 80% de-ionized water and 20% ethanol.

Figure 1a. Schematic of experimental electro-spinning setup.



The atomic force microscope (AFM), with its subnanonewton sensitivity and nanometer scale lateral resolution, is well suited to the task of mechanical characterization of nanofibres. In the force-volume mode, the AFM cantilever performs 64x64 points bending test on a region with typical scan size between 4 – 5 μm, where consists a portion of a fibre suspended across a square hole of a TEM grid. A SEM image shown as Figure 2 displays the area of interest for the force-volume mode measurement. Then by selecting all the bending test data along the axis of the fibre, we can determine

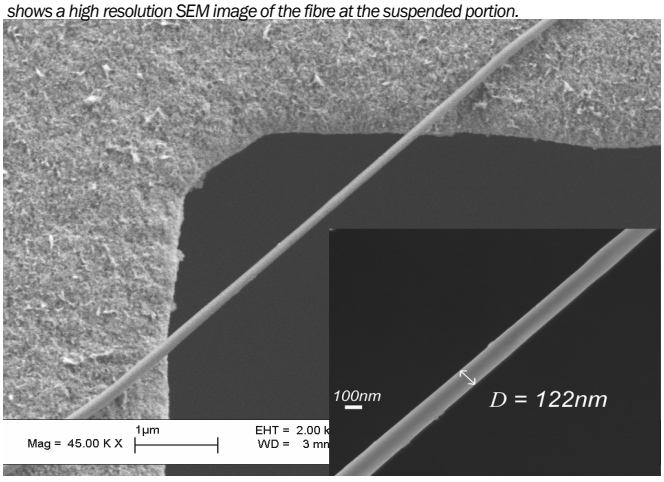
Figure 1b. A SEM image of a PVA fibres mat.



the deflection of the fibre at any point along the suspended portion.

To determine the elastic modulus, we use the clamped beam model to fit the deflection values along the suspended fibre, but some accurate measurements on the geometry and diameter of the fibre are needed. First, by comparing the AFM height and SEM diameter measurements on the portion of a fibre clamped on the grid, they show that the geometry of the electro-spun fibres is circular cylindrical. And then from a high resolution SEM image shown as the insert of Figure 2, the diameter of the suspended portion can be precisely measured, where the bending test data are obtained.

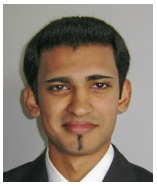
Figure 2. A SEM image of a fibre suspending across a corner of a TEM grid hole. The insert shows a high resolution SEM image of the fibre at the suspended portion.



We find that the AFM force-volume measurements with >60 deflection data points along the fibre show a very good agreement with the clamped-beam model and the elastic modulus of 30 electro-spun nanofibres has a consistant value. In the future, a better understanding of the mechanical properties of individual electro-spun fibres can help design a scaffold to mimic the natural extracellular matrix and provides a foundation to study the behaviour of live cells on nanofibres with different mechanical strength.

This work is being supported by NSERC and OPC

Biomineralization: How Does Surface Chemistry Hinder or Promote The Growth of Calcium Oxalate?



By Peter Lloyd Vincent
2nd Year Student, Department of Biology
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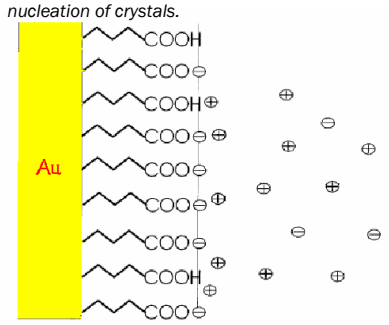
The biomineralization of calcium oxalate is of significant importance, as it is the most common constituent of renal calculi (human kidney stones). Calcium oxalate crystals usually nucleate in the tubular fluid of the renal collecting duct due to the supersaturation of calcium and oxalate ions in the fluid. After nucleation, these crystals can potentially bind to anionic molecules rooted on the apical epithelial cell surface of the renal collecting duct. Among numerous anionic molecules found on the cell surface, some like glutamate and aspartate contain anionic carboxylic functional groups that act as binding sites for calcium oxalate crystals (which subsequently aggregate and form kidney stones). My research project, in the lab of Dr. Silvia Mittler, is part of a team effort with Dr. Graeme Hunter and Dr. Bernd Grohe (CIHR Group in Skeletal Development and Remodeling, Schulich School of Medicine and Dentistry, UWO) towards examining the surface chemistry factors that affect the growth of calcium oxalate crystals on these anionic carboxylic functional groups.

In order to do so, we have taken a model system approach to elucidate some of the relationships between the surface chemistry of the renal epithelial cell surface and the growth of biominerals like calcium oxalate. In particular, we are interested in defining the role of surface charge density of these anionic carboxylic functional groups in controlling the growth of calcium oxalate. As our model system, we employed a self-assembled monolayer (SAM) containing –COOH terminal thiols on a gold layer, in order to mimic the anionic carboxylic functional groups on the renal epithelial cell surface, and to understand the events that take place during renal cell-crystal interactions (Figure 1).

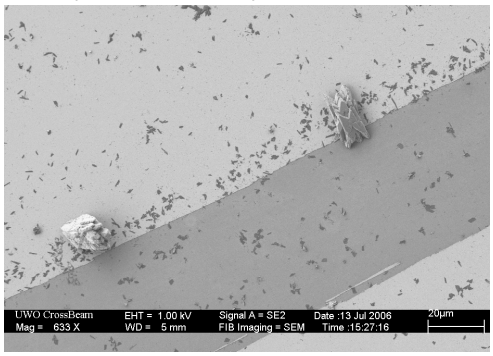
Figure 1. Model System: Calcium oxalate crystals binding to COO^- receptor sites of COOH terminated thiols on gold or COO^- "catalyzes" nucleation of crystals.



Typically, surfaces like those of the renal epithelial cell with anionic carboxylic functional groups, can undergo acid-base reactions *in vivo*, which lead to the formation of interfacial charges. These interfacial charges can be increased by raising the pH, due to the deprotonation of –COOH into H^+ and $–COO^-$. The number of $–COO^-$ sites on a surface determines the charge density of the surface. In addition, the surface charge density is shown to be dependent upon the concentration of thiol molecules, the nature of the surface, the pH and the ionic strength. Thus, we propose a novel approach of using –COOH terminated thiols to control the surface charge density on the SAM by varying parameters, such as the pH of the calcium oxalate solution, the concentration of the –COOH thiol molecules on the gold surface and the ionic strength.

While preparing our model system we had to take into consideration two main factors: the ability to mimic the renal epithelial cell surface with the deprotonated carboxylic functional groups and to simultaneously have the ability to monitor and measure the growth of calcium oxalate crystals in real time. In order to perform the latter, we used the Kretchmann configuration of Surface Plasmon Resonance Spectroscopy (SPS). Thus, for SPS measurements, the –COOH terminated thiols were self assembled on a layer of gold of suitable thickness. The shift in the Surface Plasmon Resonance (SPR) curve, before and after crystal growth, was used to determine the optical thickness of the calcium oxalate crystals embedded in solution (Figure 2). In order to prepare our samples, the gold layer below the –COOH SAM was first evaporated onto LASFN9 glass substrates using the Electron Beam Evaporator in the Nanofabrication Laboratory. The samples were then soaked in a specific carboxylic acid in order to allow the –COOH thiols to self assemble on the gold layer. After self assembly, the calcium oxalate crystals were then allowed to crystallize on the charged $–COO^-$ receptor sites. The crystal growth was analyzed using the WINSPALL® software package, which is based on the Fresnel formalism of multilayered dielectric structures. Scanning electron microscopy (SEM; LEO 1540XB, Gemini field emission column) images were taken to investigate the growth morphology and distribution of the calcium oxalate crystals.

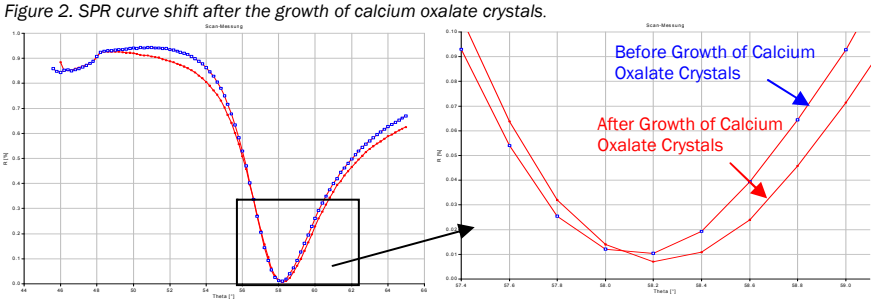
Figure 3.Two calcium oxalate crystals growing along artificially created 2-D boundary.



Various physiologically relevant concentrations of calcium oxalate solutions were tested for crystallization on –COOH terminated thiols. Ultimately, certain low concentrations of calcium oxalate were chosen, so that we could restrict and control crystal growth along the high energy 2-D boundaries of the SAM (Figure 3), that were created artificially. So far, we have also devised a method to control the pH of calcium oxalate solution at various levels within an error of +/- 0.10 units. Therefore, the next step in this project includes performing calcium oxalate crystallization experiments at various physiologically relevant pH values in the internal environment of the kidneys and varying parameters like the concentration and distribution of the –COOH thiols by employing selected laterally phase-separated SAMs.

The ultimate goal of this project is to get insights into the effects of surface chemistry and to understand the mechanisms that cause the formation of biominerals like kidney stones. It is hoped that these studies lead to the generation of therapeutic agents for the treatment of kidney stones and other forms of pathological calcification.

Figure 2. SPR curve shift after the growth of calcium oxalate crystals.



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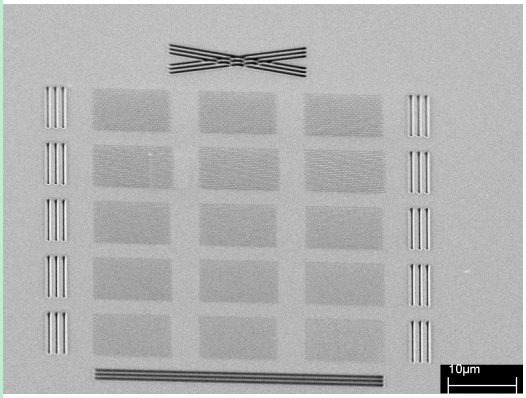
Typically, relevant features or regions can be identified in the scanning electron microscope (SEM) where there is sufficient resolution *and* contrast to identify the feature.

Figure 1. FIB milled markings surround a array of regions to be measured with Atomic Force Microscopy (AFM). S. Neretina / P. Mascher, McMaster U.



The surface can be efficiently scanned using the high precision motorized stage and composition can be determined, in situ, using energy dispersive x-ray analysis (EDX). The requirement is to produce fiducial markings in the SEM that can be located in other analytical instruments. The Nanofab CrossBeam is ideally suited to this purpose; regions are identified with the high resolution SEM and simultaneously marked by focused ion beam machining (Figures 1 and 2). Fiducial marks can also be produced by e-beam lithography and metal lift-off when the sample can be coated with pmma resist (Figure 3).

Figure 2. FIB milled markings indicate the position of a bacterial colony on filter paper to be analyzed by TOF-SIMS at the Surface Science Western Laboratory. G. Wanger / G. Southam, Western.

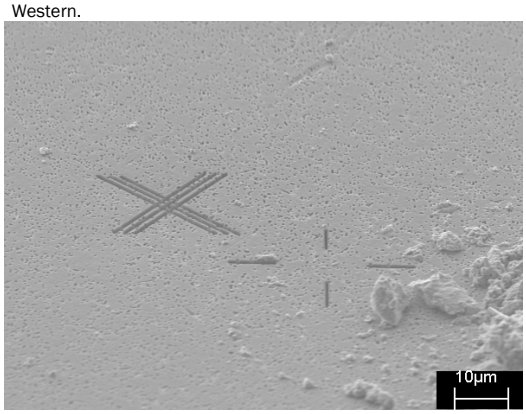
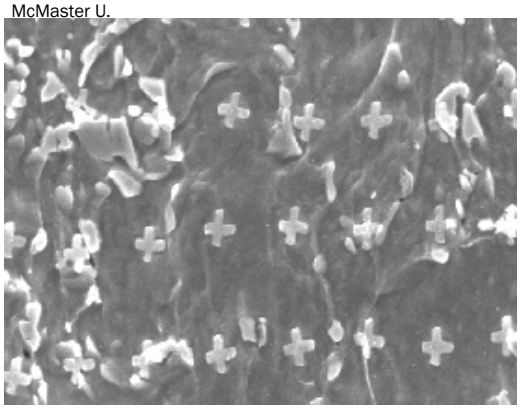


Figure 3. Grid of gold crosses (5 micron pitch) defined by e-beam lithography allows microscopic measurement of strain in dual-phase steel. Y. Ososkov, M. Jain, D.S. Wilkinson , McMaster U.



In Review: OPC 2nd Annual Showcase

The 2nd Annual Showcase of the Ontario Photonics Consortium took place on Thursday, May 25th at the University of Western Ontario in London. Following last year's successful event at McMaster University, the Showcase grew both in attendance and poster count while enhancing the interaction of researchers with their colleagues at partner institutions, and within the larger photonics community.

The morning presentations included a mix of industrial and academic presentations. In particular the two industry presentations by Trojan Technologies (water remediation) and iQ Manufacturing Solutions (photonics in metals manufacturing) provided new insight into applications of photonics in emerging fields, while generating important industry contacts for a number of the researchers.

A wide range of research topics was represented in poster presentations including optical communications, biophotonics, silicon-based photonics, nanophotonics, and materials characterization and fabrication.

A new element of this year's Showcase was the introduction of a Best Poster Award. The winning poster was: *Fabrication of Nanoparticles with Glancing Angle Deposition*, contributed by Dr. Kevin Robbie et al from Queen's University. The award was well-received, stimulating good dialogue between researchers and visitors. It is recommended that the Best Poster Award be an element of future OPC Showcases.

Registration for the event reached 130 exceeding by 30% the 100 participants reported last year. The number of posters was 59, again surpassing 2005's number of 54. Discussion with the researchers indicated that the Showcase is seen as an important opportunity for networking within the partner institutions – an important objective of the OPC. The increase in number of inter-institutional posters is an indicator of success in this regard. Fifteen people from the industrial sector participated in the event.

Very positive feedback was received from non-OPC visitors to the Showcase with two organizations offering to sponsor future events. This is a clear indication of OPC's growing relevance to the Ontario photonics community.

Ruth Rayman , OPC Business Development

Visit http://opc.mcmaster.ca for more on the OPC.