C. Research

C. 1. Statement of Research Philosophy

Materials science and engineering research is fascinating and exhilarating. I consider myself terribly blessed to make a living doing something I enjoy so immensely. I have an innate and almost insatiable desire to know “why?” and “how?” and to me there is nothing more fundamental than materials. The link between the atomic and even sub-atomic particles and their macroscopic properties whether they be mechanical, electrical, magnetic, thermal, or optical is critical to advancements in all engineering disciplines. One aspect of my job is to train my graduate students and guide them through a significant research problem to its completion. While some programs have specific goals, I like to encourage “out of the box” thinking and try to cultivate the students’ natural curiosity. When my students are curious or speculate about a particular outcome, I encourage them to think about critical experiments that would confirm or discount their hypothesis. Even when I can anticipate the answer, letting the student go through the discovery process is an important part of the educational process. Early in my graduate education, I did an internship for a small research and development company. One of the engineers I worked for encouraged me to take one afternoon a week and “play” or do an experiment just for curiosity’s sake. While I don’t quite get that luxury every week now, I try to do that vicariously through my students as I encourage them to “play” a little. Whether it be directly related to their research or just something they have an interest in, I encourage them to try new things.

Materials science and engineering is an interesting confluence of many disciplines. On one end of the spectrum, materials science is as fundamental as chemistry and physics. On the other end, materials engineering is integral to the advancement of all of the other engineering disciplines. Whether it be advanced photonic or electronic materials, advanced structural materials, or materials with better biocompatibility, it is a materials world. As such, there is a tremendous opportunity for my students and me to work on interdisciplinary teams to accomplish a goal that could not be achieved otherwise. As both a scientist and engineer, my research interests are very diverse. Some programs are very fundamental in nature where we are for instance trying to elucidate fundamental electron-solid interactions. On the other hand, some programs are more engineering oriented in which my groups main role is materials integration issues for advanced device applications. While my main expertise is in experimental materials science, I am not a pure empiricist. I enjoy correlating experimental observations to theoretical models. Making these correlations to me is the essence of materials science and once these relationships are discovered, new materials can be designed and theoretical understanding can be refined.

My specific research interests are in thin film materials and nanoscale processing for advanced materials and devices. While my research program has and continues to evolve, my research program can be divided into three focus areas, namely; 1) combinatorial thin film synthesis for rapid materials discovery, 2) materials integration and nanofabrication for advanced device applications, and 3) nanoscale focused electron beam stimulated processing. Below is a summary of these three research focus areas.
Combinatorial Thin Film Synthesis for Rapid Materials Discovery

One of the cornerstone pieces of equipment in my laboratory is a multisource rf magnetron sputtering system capable of depositing thin film metals, semiconductors, and insulating materials. The system consists of a 20” diameter stainless steel chamber pumped with a 550lps turbomolecular pump. The system is equipped with a load-lock chamber that can currently accommodate up to 6” substrates and has a routine base pressure ~ 1x10^-8 Torr. The sputtering system has 3-2” sources (scalable to 5) with in-situ source tilting capabilities which allows thin film materials (metals, semiconductors, and insulators) to be deposited in a combinatorial or layered fashion. The sources have a variable magnetron assembly for balanced, unbalanced and magnetic materials modes and are powered by 500 Watt rf power supplies and matching networks. Each source has a localized gas delivery for optimized deliver of the inert sputter gas. In addition, the substrate holder assembly has a localized gas injection for preferential delivery of reactive gases to the substrate for reactive sputtering. The compositions as a function of position can be uniform by rotating the substrate, or a deliberate composition gradient can be introduced by depositing onto a stationary substrate. By varying the individual source powers and tilt angles, large composition gradients can be realized across a single wafer leading to rapid materials discovery. To enhance/modify the thin film quality the substrate is equipped with a heater (up to 800°C) and bias sputtering capabilities. Figure 1 shows a schematic of the multi-source sputtering system and a digital photograph of the system while depositing a combinatorial ternary Fe-Cr-Ni thin film sample.

![Schematic of the multi-source rf-magnetron sputtering system and digital photograph of the system while depositing a combinatorial ternary phase diagram of Fe-Ni-Cr.](image)

This method has been used to explore Y_2O_3:Gd and Y_3Al_5O_12:Gd ultraviolet emitting materials, Y_3Al_5O_12:Cr temperature sensor materials, Mo-W high temperature electrodes, Zr-Cu-Al bulk metallic glass alloys, Ni-Cu for carbon nanofiber catalysts, and Fe-Ni-Cr phase diagram determination. To illustrate the utility of this technique, below is a brief description of the Ni-Cu and Fe-Ni-Cr combinatorial thin film studies.
Vertically Aligned Carbon Nanofiber Catalyst Development

Spatially controlled carbon nanofiber arrays are grown by plasma-enhanced chemical vapor deposition (PECVD) at pre-defined binary alloy catalyst sites. The nanofiber tip radius and fiber shape must be precisely controlled for stable electron field emission applications and intracellular probe arrays. A combinatorial Cu-Ni thin film was used as a catalyst/substrate for PECVD carbon nanofiber growth and yielded a rich variety of carbon nanofiber tip architectures strongly dependent on thin film composition. To investigate the effect that the Cu-Ni composition has on the carbon nanofiber morphology, copper and nickel were co-sputtered to form an alloy Cu\textsubscript{x}Ni\textsubscript{1-x} ranging from 0.2<x<0.8 along a 10cm long silicon substrate. Figure 2 shows a series of scanning electron micrographs of the carbon nanofiber morphology as a function of composition which reveals at ~70% copper, a high radius of curvature (~20nm) nanofiber results. These fibers are currently being explored as possible intracellular probing devices and will be investigated for their field emission properties. This combinatorial approach was successful in rapidly determining a new alloy catalyst composition, whereas a standard serial approach would have required many catalyst and nanofiber growth runs.

![Figure 2](image)

Figure 2. Scanning electron micrographs along of carbon nanofibers with varying copper concentration in the catalyst alloy prepared via the combinatorial thin film sputtering technique.

Experimental Phase Diagram Determination

Equilibrium and non-equilibrium phase diagram determination is typically a very labor intensive process requiring the preparation and characterization of numerous alloy samples. To rapidly identify the equilibrium and non-equilibrium phase diagram of Cr-Ni-Fe, ternary libraries were prepared by co-sputtering Cr, Fe, and Ni on a single-crystal sapphire substrates. Subsequent to the depositing five samples, four of the samples were annealed at 200, 400, 600, and 800C. Structural and compositional maps of the alloys were produced using synchrotron radiation and simultaneous detection of 2D diffraction patterns and x-ray fluorescence spectra. Figure 3 shows the phase diagram evolution for this ternary alloy as a function of annealing temperature. Good agreement between the measured and calculated phase diagram is demonstrated which illustrates the utility of this approach for materials development. As-deposited a very non-equilibrium structure exists with a metastable \(\alpha\)-manganese simple cubic structure (shaded area). When the
alloy is annealed the grain size increases (as determined with the Scherrer formula) and the phases evolve into the thermodynamically stable phase.

Figure 3. Phase diagram evolution for Fe-Ni-Cr ternary alloy.

Materials Integration and Nanofabrication for Advanced Device Applications
My experience at Advanced Vision Technologies and the Rochester Institute of Technology taught me a significant amount about micro- and nanofabrication. Since that time, I have leveraged my materials science background with the micro- and nanofabrication experience and have contributed to several advanced device applications. I have worked on vacuum microelectronic and optoelectronic materials and devices, electrostatic micro-electro-mechanical (MEMs) devices, and more recently bio-electronic devices. Below is a brief description of a
current device application that I am working on which describes the integration of an active matrix transistor array with a nanoscale intracellular probe device.

**Active Matrix Thin Film Transistor Intracellular Probe Array**

An enormous body of knowledge has been accumulated about intracellular processes using the classical techniques of biochemistry, in which processes and structures are analyzed in subcellular fractions, which are produced after disrupting cells. The next biological frontier is in understanding how all these processes take place within the highly organized and ordered environment of the living cell. While advances in molecular biology and imaging technology are providing enormous insight into the genetic code and cellular structure, our ability to monitor detailed, ongoing processes inside the intact cell remains extremely limited. This limitation is largely technological – our current instruments are simply not on the same scale as the cell and its components. Recent critical developments at Oak Ridge National Laboratory (ORNL) in the fabrication of vertically aligned carbon nanofiber arrays now offer the opportunity to design nanoscale molecular probing devices that function at the scale necessary to map cellular processes at resolutions well below the diffractive limit of optical microscopy, and to interface these probes between single, living cells and the macroscopic world. Initial work at ORNL utilized single probe arrays (i.e. a single nanofiber per lead). Figure 4 illustrates a VACNF single probe device. Recently I have collaborated with the group at ORNL to integrate the VACNF intracellular probes with an active matrix thin film transistor array to increase the device density.

![Exposed carbon tip, 20 nm tip radius of curvature, 400 nm](image)

**Figure 4.** An individually addressable carbon nanofiber intracellular probe on an electrical interconnect.

Figure 5 illustrates an active matrix addressed thin film transistor device coupled to a vertically aligned carbon nanofiber (VACNF) electrochemical probe and its equivalent circuit diagram.
This device is an inverted MOS device. To process the TFT, a MoW gate film is first deposited by RF sputtering on an oxidized silicon wafer. The main reason that MoW is used as a gate electrode in this work is the growth of the carbon nanofiber which is used as a vertical electrode to impale and probe cells. The VACNF is processed at ~700 °C which is not compatible with standard metallizations. Additionally, the TFT structure in this work has multiple layers that require at least 5 mask steps, therefore, the gate-etching profile should have a low taper angle as it is the bottom layer in the inverted device structure. The taper angle can be controlled with a careful reactive ion etch (RIE) process with SF₆/O₂. The taper angle is achieved by controlling the etching rate of photoresist relative to the MoW. The subsequent deposition and patterning of the insulator (SiOₓ, Si₃N₄, or SiON), active layer (poly or amorphous Silicon), and the source drain n⁺ silicon layers will be studied in detail. Each material will be investigated and various processes such as plasma enhanced CVD, low pressure CVD, and rf magnetron sputtering will be compared. A mask set has been designed with an initial 20x20 array (400 probes) with single transistor devices and test structures integrated on the die. Initially the thin film transistor characteristics will be determined with an optimum material set and subsequent VACNF integration will proceed.

Figure 5. Schematic diagram and equivalent circuit diagram of active-addressed matrix intracellular probing device proposed in this study
Nanoscale Focused Electron Beam Stimulated Processing

The ability to manipulate materials at the nanoscale is critical for the nanotechnology revolution that is occurring. While standard and emerging lithographic techniques will continue to play a critical role in nanomanufacturing, future nanoscale processing will also likely require site-selective directed assembly techniques for critical level processing. Furthermore, as geometries shrink and wafer cost-of-ownership increases, nanoscale re-manufacturing or repair techniques will be increasingly more important. Other immediate applications for nanoscale directed assembly or direct write techniques include: nanoscale device prototyping, nanoscale lithographic mask and chip repair, and site-selective metrology sample preparation for failure analysis of nanoscale devices.

To this end, we are investigating focused electron beam stimulated processing. Having successfully developed a first generation gas delivery system and explored the efficacy of nanoscale electron beam stimulated directed assembly and etching we are currently exploring three aspects of this process, namely:

1. Fundamental studies of the electron-gas, electron-solid, and gas-solid interactions
2. Engineering optimization of the precursor gas delivery and the electron beam scanning parameters
3. Development of in-situ process-monitoring schemes and demonstrate nanoscale device prototyping and repair applications.

The following summarizes some of my groups previous accomplishments for the electron stimulated processing program.

To perform the electron beam processing, a gas delivery system was designed and attached to a Hitachi S-3500N and S-4300 Variable Pressure Scanning Electron Microscope (VPSEM). The VPSEM has a tungsten hairpin source and is equipped with a backscatter detector, an energy dispersive x-ray spectrometer (EDS), and has a pump system designed to operate in high vacuum (<0.1Pa) or variable pressure mode (0.1 – 300 Pa). The gas delivery system is designed to deliver up to four gases through a hypodermic needle for localized gas injection. The injection system is mounted on a wobble stick for 3-dimensional positioning capability. Figure 6 shows a) the gas injection flange, b) the gas delivery needle, and c) an SEM micrograph of the delivery needle in close proximity (~1mm) to the substrate for localized gas delivery.

Subsequent to designing and installing the gas injection system, initial studies demonstrated the efficacy of selective electron beam etching of technologically important materials including Si, SiO₂, Si₃N₄, Ta, TaN, W, Al, Cr, C, Cu, low dielectric materials, and photoresist. Detailed studies of the etch rate of silicon in XeF₂ as a function of beam energy were performed and the etch rate was found to be inversely proportional to the beam energy (for a fixed beam current and gas delivery) [42]. Selective electron beam deposition of tungsten (from W(CO)₆ and WF₆) and carbon (from hydrocarbons) was also demonstrated and deposition rates have been evaluated as a function of beam energy and current density. Figure 3 (a) illustrates a series of tungsten nanofibers grown under various beam conditions (beam energy and current density) which shows the deposition rate and fiber geometry are a function of the beam conditions. To compliment the experimental studies, extensive Monte Carlo models of the electron-solid and electron-gas interactions were developed and the role of primary, secondary and backscattered have been investigated. Based on our experience with the electron beam stimulated process, we have made
significant progress in minimizing the effective beam width. As illustrated in Figure 7, in one year’s time we have achieved an effective beam width for focused electron beam etching of 45nm (b) and 35nm for deposition (c), which is superior to the technologically mature focused ion beam processing (~120nm). *With a more thorough understanding of the process and an optimized system, sub-10nm electron beam stimulated direct assembly and etching is believed to be possible.*

Figure 6. Photographs of a) the gas injection flange, b) the gas delivery needle, and c) an SEM micrograph of the delivery needle in close proximity to the substrate.

Figure 7. Scanning electron micrographs of a) an array of tungsten nanofibers and the smallest features obtained via electron stimulated processing: a) a 45nm selective tungsten etch, and b) a 35nm wide deposited tungsten nanopillar.