MissOuri Nanotechnology Alliance Spring 2004 Meeting
Friday May 14 *(Clayton-Sheraton)* & Saturday May 15 *(UM-StL)*

Notes on Friday evening
by Bernard Feldman (UM-StL Physics & Astronomy)

The meeting opened with a few comments by the Chancellor of the University of Missouri-St. Louis, Dr. Thomas George. He observed that nanotechnology is at present a very hot and fundable area of research. He mentioned his new financial commitment to furthering nanotechnology on his campus. And he expressed his hope that this meeting will lead to further cooperation among the attendees to write proposals and to cooperate with each other and with industries in Missouri.

The keynote speaker was Dr. Jingyue Liu from Monsanto. He spoke about nanoscience and nanotechnology. He defined nanoscale as sizes from molecules to proteins. He spoke about his own area of interest, catalysis, which involves surface, shape, size and interface effects. He mentioned other nanotechnologies: carbon nanotube transistors, molecular electronics, quantum dots, and magnetic particles. He defined nanotechnology as the control and manipulation of the nanoscale, and that the only successful commercial nanotechnology so far is nanolithography.

He spoke about the importance of biological applications, such as nanosensors. He gave examples as nanogold sensors to detect DNA strands, in vitro monitors, biomarkers, and biocompatible surfaces.

He ended with some advice. Nanoscience and nanotechnology are beneficial to both universities and industry. University scientists have to find fundamental problems that have practical applications. And universities need good liaison people who are knowledgeable of both science and industry to foster cooperation between universities and industry.

Notes on Saturday morning
by Keith Stine (UM-StL Chemistry & Biochemistry)

The meeting was convened at 8:30 AM by Professor Phil Fraundorf of the University of Missouri – St. Louis Department of Physics and Astronomy and the Center for Molecular Electronics. Professor Fraundorf introduced Nasser Arshadi, UM-St. Louis Vice Chancellor for Research who spoke first. Dr. Arshadi thanked the Research Alliance of Missouri for sponsoring the meeting jointly with UM-St. Louis. The Research Alliance of Missouri was formed in January of 2003 and its members are chief research officers from research active campuses in the state. The group has met with Governor Holden to discuss ways to establish an infrastructure to encourage collaborative projects involving academic and industrial scientists. The Research Alliance aims to facilitate arrangements involving state government, academic researchers, and industrial scientists so that grant support for major projects can be sought more effectively and solutions to existing industrial problems can be found. Academic scientists can learn a lot while trying to help solve industrial problems. Universities are now focusing more strongly on technology transfer and commercialization of inventions. The Center for Emerging Technologies, housing 15 start-up companies, is the UM-St. Louis incubator for many of these activities. The Information Technology incubator on campus houses 12 companies. Dr. Arshadi pointed out that his office is available to help researchers develop a business plan and seek venture capital. In the new model of university research, the distinctions between industrial and academic scientists have become smaller. Dr. Arshadi believes that there is a need for open markets to provide incentives for entrepreneurs to develop newer and better technology-based products. Dr. Arshadi thanked Phil Fraundorf for organizing the meeting and again welcomed the attendees.

Professor Paulette Spencer, University of Missouri – Kansas City School of Dentistry and Director of the Center for Research on Interfacial Structure and Properties, described research on dental materials. The Center focuses on research related to the biology of mineralized tissue, biomaterials and the engineering of mineralized tissues, and clinical research. The interfaces found in these tissues and between these tissues and engineered biomaterials are studied using micro-Raman spectroscopy, FTIR imaging, and scanning acoustic microscopy is used to characterize micromechanical properties at the interface. Dental amalgams, which contain mercury, have been used for many years in filling cavities. However, given the current awareness of the toxicity caused by the mercury that can be slowly released from them, these amalgams must now be replaced with new composite materials. The new composite materials are aesthetically attractive, but breakdown of their seal to the tooth is a serious problem. The dentin of the tooth is a tubular structure through which water and nutrients pulse and thus adhesives for use between the dentin and the composite material must be water-compatible. Using the Raman and infrared spectroscopic imaging methods, microstructural features can be identified at the interface. The scanning acoustic microscope provides information on the spatial variations of the density and elastic constants that can be used in a computational model of how well the bond between the composite and the dentin should behave under stress. Another area being studied using acoustic microscopy are the complications associated with the effects of radiation treatment for oral cancers, after which patients have problems with the enamel shearing away from the dentin on their teeth. The condition of TMJ joint disease, which affects up to 30% of the population, is also being studied. Dr. Larry Katz described the new state-of-the-art acoustic microscope at the Center and how it can be used to analyze cross-sections of bone. The microscope has a resolution of 500 nm. Changes in bone structure due to osteoporosis were clearly visible in micrographs that were shown. Atomic force microscopy (AFM) was used to study the difference between young and mature bone and differences in the structure of the collagen fibrils and embedded crystallites could clearly be seen. Dr. Katz emphasized the importance of understanding the naturally occurring nanostructures such as those found in bones and teeth.

Professor Shubhra Gangopadhyay, who holds the LaPierre Chair in the University of Missouri – Columbia Department of Electrical Engineering, Physics, and Bioengineering, spoke on her research in fabrication of a variety of nanostructures and devices. Professor Gangopadhyay joined UM-Columbia in 2003 and moved there from Texas Tech University, where she was involved in creating a nanotechnology center where research on MEMS and biosensors was carried out. Her new laboratory at UM-Columbia, scheduled to open in July 2004, will be a 3000 square foot facility, and plans are already in place to expand this to a 6000 square foot lab fully equipped for fabrication of MEMS microfluidic devices. A proposal to provide equipment for multi-wafer processing is being considered by the state. Her laboratory is developing dielectric materials, such as hafnium oxide and zirconium oxide, with for use in nanoelectronics. Tuning of the dielectric constant can be achieved by adjusting the porosity of the material by including porogens during the processing of the material. Materials in the form of thin films with a nanostructure of ordered regular pores can be used as templates to grow nanowires and are also useful as single-electron transistors. Methods for cleaning MEMS and microelectronic devices using supercritical CO_2 are being investigated. Microfluidic devices are being fabricated using soft lithography for use as biosensors. One of the applications of the microfluidic devices is that of PCR on a chip that could be used to amplify a DNA sample for testing in a period of less than an hour. In collaboration with Professor Jerry Atwood of the UM-Columbia Department of Chemistry, hydrogen sensors on a chip are being developed using calixarenes as coatings selectively permeable only to hydrogen. The development of MEMS systems for combustion on a chip is being pursued for the purpose of testing nanoengineered energetic materials for use as explosives.

Dr. Pat Kinlen, Director of Research and Development at Crosslink Polymer Research (Fenton, MO), described the company and its R&D activities. The company is located in Fenton. MO, has 25 employees, and occupies a 22,000 square foot facility. Crosslink is focused on three main business areas – illumination systems, high performance coatings, and BioMEMS systems. The illumination systems business is focused on polymer light-emitting devices (polymer LEDs), illumination in the near-infrared, and the use of nanoparticles in display devices. The high performance coatings business is focused on anti-corrosion, anti-static, and controlled release coatings. R&D in the BioMEMS area is focused on intelligent, triggered drug delivery. In addition, flexible solar panels based on organic molecules are under development. An application for the polymer LEDs in providing lighting in flexible, portable bioshelters for battlefield use is under development with the US Army. A commercial application in the area of sporting goods is also under development. Organic LEDs use low voltages and emit light very efficiently. A system modified to emit in the near-infrared is being developed for use in security devices such as maps that can only be read under an infrared viewer. Anti-corrosion coatings that release a inhibitor when corrosion is detected are under development in collaboration with Boeing for use on aircraft. Coatings that release decontaminating agents when the surface is contacted by a toxin are being developed. Organic solar cells are targeted for remote power applications needed by the military. Light emitting core-shell nanoparticles (CdS capped with ZnS) are being developed in formulations that can be printed onto surfaces. The size and composition of the particles can be varied to tune their emission wavelength. A related goal is to produce ZnS nanoparticles doped with copper inside an ion exchange polymer matrix by introducing the ions and then reducing them using sodium sulfide.

Dr. Lucio Mule'Stagno, MEMC Electronic Materials Corporation, was not able to attend and Phil Fraundorf, who has worked extensively with the company, spoke in his place. MEMC is the world's largest public company solely devoted to the supply of wafers to semiconductor device manufacturers. MEMC has been a pioneer in the design and development of wafer technologies over the past four decades. With R&D and manufacturing facilities in the U.S., Europe and Asia, MEMC enables the next generation of high performance semiconductor devices. The company is now working on Si/Ge transition layers and on Si/strained silicon. The company's main needs are in the area of characterizing silicon wafers, produced in diameters of 8" or 12".

Dr. Bob Heimann, Vice President for Research at Elisha Technologies, a subsidiary of the Orscheln Group located in Moberly, MO described R&D activities related to the production of silicon oxide coatings on metal parts, primarily for automotive applications. The silicon dioxide films are intended to replace cadmium plated onto zinc as well as chromate coatings. This is an enormous advantage from an environmental perspective since both cadmium and hexavalent chromium are toxic. Automotive and other metal parts need to be coated to prevent corrosion and the silicon dioxide coatings actually perform better than the existing methods, being more durable, creating a more uniform coating, and having better temperature stability. The European Union recently approved a directive that no heavy metals should leach out of a vehicle that is being recycled otherwise the manufacturer will face a steep fine. The process, referred to as electrolytic mineral coating, developed by Elisha Technologies rapidly produces amorphous silicon oxide coatings to encapsulate metal parts. Applications for the US Navy as coatings on door latches and ropes are also being developed. Electron micrographs of cross-sections showing steel with a zinc layer and then a silicon dioxide layer were shown. The technology works very well and is soon to be certified for use by major auto manufacturers including General Motors and Ford. The Elisha technology mimics the way that nature forms minerals by building the silicon dioxide directly on the metal surface by having the silicates adsorb onto the surface and then be hydrolyzed in the very basic environment near the surface. The technology received the Governor's Technology Award from the state of Missouri and is protected by numerous patents.

An open discussion concerning statewide efforts in nanotechnology and engaging corporations proceeded for the next 30 minutes. Questions considered included: (a) suggested recommendations to make to the Research Alliance of Missouri (RAM), (b) how can university/college laboratories have a better impact on industrial employees in the state, and (c) what issues are associated with the turnaround time for characterizing samples provided by industry. It was suggested that a list of facilities accessible across the state, along with a user fee structure, be assembled. Companies would prefer to access state-of-the-art characterization facilities at universities rather than have to purchase, develop, or maintain these instruments themselves. Dr. Jimmy Liu of Monsanto is willing to be co-PI or provide a letter of support for proposal efforts to acquire new facilities for nanoscale characterization. Outreach to industry should be recognized as a core mission of the university. The possibility of research centers where industrial and state money is spent partly on directed research and partly on open, investigator-initiated research was mentioned. A prime barrier to collaborations between especially smaller companies and universities is the university insisting on 100% ownership of any intellectual property developed during the collaboration. Investors in a small company will not tolerate such a condition. This issue is much less of a problem for open characterization facilities, and is more of a problem for collaborations that involve synthesis of new materials or fabrication of new devices. The state needs to invest money in consortia to encourage new technology development, such as that originally proposed in the area of biomaterials using the tobacco settlement money but rescinded due to the budget deficit, since the economic returns on such investments may help Missouri move away from being a state running a persistent budget deficit.

Professor Kartik Ghosh, Southwest Missouri State University Department of Physics, Astronomy, and Materials Science, described research conducted by a group of faculty at SMSU in the area of nanoparticle coatings technology. This research, funded by the Office of Naval Research, concerns the development of thin film nanocomposites consisting of nanoparticles embedded inside polymer films such as gold nanoparticles inside polystyrene-co-acrylonitrile and iron nanoparticles inside polyether ketone. The research group is interested in thin film growth, characterization of the surface and structural properties of the thin film nanocomposites, their electrical, magnetic, and optical properties and their potential use in devices. The metal ions are implanted directly into the polymer films that are then exposed to a gas reducing them to nanoparticles. Nanoparticles made of metals including gold, silver, and platinum are under study, as are nanoparticles of magnetic elements including iron, cobalt, and nickel, magnetic alloys, and tin and niobium. The formation of the nanoparticles can be seen by atomic force microscopy. Magnetic force microscopy can confirm and characterize the formation of magnetic nanoparticles in polymer films, and can determine the type of magnetism observed. Measurements of resistance versus temperature as a function of particle size for the nanoparticles of Au indicate a clear transition from metallic to semiconducting behavior as the particle size is decreased. An application of these nanoparticle composite films is in the area of infrared sensing. Applications in as biosensors are also possible. The facilities at SMSU include thermal evaporation, RF sputtering, a pulsed laser deposition system recently obtained via a grant, molecular beam epitaxy equipment, spin coaters, a mask aligner, a scanning probe microscope equipped for magnetic and electrical force microscopy, scanning electron microscope, a micro Raman spectrometer, and photoluminescence apparatus. The research involves Professor Ghosh and five other faculty and has been supported by ONR, NSF, and the Research Corporation.

Professor Jerry Jean, Curator’s Professor and Chair of the Department of Chemistry at University of Missouri – Kansas City, described activities related to nanoscience by some of the faculty from UMKC and spoke on his own work using the technique of positron annihilation spectroscopy. This is a method unique to his lab that he developed and applied over a 30 year period. Professor Jean hopes that I-70 will become a ‘nanotechnology corridor’ in the future. The PAS technique is used to measure the size of small regions of free volume inside a material. The free volume is associated with defects inside the material and PAS can measure defect sizes in the range of 0.1 – 10 nm. It is useful for characterizing polymers, coatings, surfaces, and can also be applied to biological materials. The lifetime of the positron that is accelerated and implanted into the material depends on how quickly it encounters an electron since the positron (which is a positive electron, or anti-electron) and electron annihilate each other and release gamma rays. The lifetime is longer inside a void, and is also sensitive to the elemental composition around the void. An equation, derived by Professor Jean, can be used to analyze the PAS data. The depth into the material that the positrons are inserted is controlled by the energy of the positron beam that can be varied so that free volume as a function of depth from the surface can be measured. Professor Jean highlighted the activities of some other faculty from UMKC. Professor Peng is a synthetic chemist designing nanomaterials for a number of applications including light harvesting polymers for solar cells, molecules with non-linear optical properties, ion sensors, and regularly branched polymers known as dendrimers that he will modify with multiple peptides for use as biosensors. Professor Kathleen Kilway is a synthetic chemist working on developing precursor molecules that can be used to make and cap carbon nanotubes. Professor J. David van Horn is a bioinorganic chemist studying the role of the elements uranium, chromium, and lead in biochemical systems. Professor Tom Sandrecski, formerly of McDonnell-Douglas, works in the area of conducting polymers.

Professor Amy Shen, Washington University Department of Mechanical Engineering, described research in her lab on the rheology of complex fluids and their applications to some areas of nanotechnology. Complex fluids are mixtures with many components and typically include surfactants, polymers, small particles, and/or proteins. Products such as paints, toothpaste, emulsions, clays, sands, blood, and other biological fluids are all considered to be examples of complex fluids. The distinguishing feature of a complex fluid is that it exhibits complex flow behavior and its viscosity is not linearly related to the rate of shear as would be observed for a simple liquid such as water. Her laboratory is focused on three main areas: microfluidics, biomimetic smart materials and nanocomposites, and the production of interfacial nanoporous films by dip coating of substrates into micellar solutions. A new biological nanomaterial that she is studying is called forisome, and is found in plants. Forisomes are micron sized protein aggregates that swell up when a leaf is cut and prevent the nutrients and water from flowing out of the remainder of the leaf, thus saving it from ‘bleeding to death’. The swelling of the forisomes is sensitive to temperature, pH, and calcium ion concentration. The forisomes are able to swell and contract uniformly and reversibly. A movie was shown of a forisome observed under a microscope as it swelled and contracted reversibly in response to a modulated calcium concentration. Forisomes are interesting because they might be useful in bandages and as active elements in microfluidic systems. In a second project, Professor Shen is using soft lithography to produce microchannels on a polymer surface (polydimethylsiloxane) and studying the flow of complex fluids through the channels. A movie was shown of emulsion droplets passing through a small opening into a microfluidic channel. The third project in Professor Shen’s lab involves making inorganic coatings with regularly arranged nanopores that are generated by coating a surface with a surfactant solution that also contains the precursors to the inorganic material. The surfactants arrange themselves into regular clusters by ‘self-assembly’ and when the substrate is heated to evaporate the water and burn off the surfactant, the remaining inorganic components are left as a regular pattern of pores that is related to the pattern of the original surfactant clusters.

Notes on Saturday afternoon

by Bernard Feldman (UM-StL Physics & Astronomy)

Dr. Max Bertino from the Physics Department at the University of Missouri-Rolla spoke about metallic nanoparticles (mainly Ti alloys), polyaniline nanofibers (electrically conducting polymers), and aerogels (nanoparticle composites in a SiO_2 skeleton). All materials were grown by radiolysis. The major application is biosensor materials.

Dr. Jerzy Wrobel from the Physics Department at the University of Missouri-Kansas City described the material science work in his department. It included computer simulation of electronic structures by Dr. Ching, high pressure growth and characterization of nanomaterials by Dr. Kruger, self-assembly of nanomaterials by Dr. Leibsle, XPS and ellipsometry by Dr. Wiliczka, and etching and ablation of InP by Dr. Wrobel.

Dr. Randy Tindall of the Electron Microscopy Core Facility from the University of Missouri-Columbia described the capabilities of his facility. They include TEM, SEM, microanalysis, field emission SEM, ultramicrotomy, and immunocytochemistry.

Dr. Phil Fraundorf of the Physics Department of the University of Missouri-St. Louis described his research laboratory and his various collaborations. His major research instrument is a HRTEM. He also showed a map of the state of Missouri, with a pin stuck into the location of each of his collaborators. He encouraged others to collaborate with industry and increase the number of pins in his map.

Dr. Kattesh Katti of the Physics and Radiology Department of the University of Missouri-Columbia spoke about his work in cancer diagnostics and theraputics. His group fabricates radioactive Au nanoparticles imbedded between peptide layers. This template binds to tumors. The Au is a beta emitter.

Dr. Chad Xing of the Department of Chemical and Biological Engineering at the University of Misssouri-Rolla spoke about the use of nanomaterials in energy conversion. In particular, they were studying Pt nanoparticles on carbon black as a catalytic surface for a hydrogen fuel cell. They are also looking at carbon nanotubes as a support for the 3nm Pt nanoparticles.

Dr. Pratim Biswas in Environmental Engineering Science at Washington University described the research activities in his area—aerosal science. It included photocatalysts such as titanium dioxide, magnetic nanocomposites for Stereotaxis, health effects of nanoparticles, and gas phase synthesis of nanoparticles with very uniform size distributions. He also pointed out that the state of Missouri is in the bottom 20% of states as far as attracting federal money for nanotechnology, and there are no federal funded nanotechnology centers in the state.