The Center for Accelerated Applications at the Nanoscale (CAAN)

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ABSTRACT

The Center for Accelerated Applications at the Nanoscale (CAAN) was established in 2004 by Governor Mike Round's 2010 Initiative. It is a group of South Dakota researchers who have joined together in focused efforts to conduct applied research and development utilizing nanotechnology with the objective of pursuing various economic development activities. The Center conducts research via multi-disciplinary, multi-investigator research teams so as to form a "synergistic" multiplier to our work. The formation of such teams is the most effective mechanism to conduct applied research on focused solutions for industry. The programs initiated by the Center are chosen for their strong commercialization potential and mutual interest to potential industrial partners. In effect, following a "market pull" as opposed to a "technology push" approach. Our main technical platforms are nanoinks for printable electronics, organoclay nanocomposites, and electrical nanoprobing of integrated circuits.

Keywords: nanoinks, electronics, nanocomposites, nanoprobing, commercialization

1 TECHNICAL OVERVIEW

There are three main technological themes that form the foundation of the Center's efforts. These are:

- the development of nanoparticulate-based inks for printable electronics,
- the development of novel organo-clay based nanocomposites and processing technologies ranging from lab to pilot scale,
- performing electrical nanoprobing on sub-100 nm integrated circuits and MEMS / NMEMS.

All of the projects that fall underneath these themes either involve, or are geared towards, joint development with corporate partners.

While these are the main activities of the Center, there are a number of related and associated projects in which the Center supports and/or collaborates with nanoscience and nanoengineering faculty at the three research universities in South Dakota. These universities are the South Dakota School of Mines and Technology (SDSM&T), South Dakota State University (SDSU), and the University of South Dakota (USD). Nanotechnology research projects at these universities include :

- Nanomaterials for photovoltaics (SDSU & USD)
- Nano-sensors for toxic gas detection (SDSU)
- Electrospun carbon nano-fibers (SDSM&T)
- Nanofluids and lubricants (SDSM&T)
- Nanomaterials for the photocatalytic splitting of water and environmental remediation (USD)
- Nano-energetic materials (SDSM&T)
- Heterogeneous oxidation catalysis on MO_x / C materials (USD)
- Nanophotonics and the electronic / photonic properties of nano- and energy-materials (SDSM&T)
- Nanomaterials for industrial air filtration (SDSM&T)
- Nanomaterials for control of thermal expansion of structural composites

Our concept is one of relatively short-term research efforts with the potential for high commercial reward. A structured approach is used to establish and accelerate the realization of research, development, testing and evaluation (RDT&E) of technologies with potential commercial application. Heavy emphasis is placed on the development of prototype products and / or the establishment of technical feasibility for a product or process. Efforts are geared towards response to "market pull" as opposed to development of "technology push". Consequently, there are significant opportunities for CAAN to establish itself as an integral partner for industry working with both large and small companies to affect the ***productization*** and ***commercialization*** of nanotechnology.

2 OTHER NANOTECHNOLOGY PROGRAMS AND INITIATIVES

The 2010 Center for Nanotechnology represents just one piece of a larger and growing "portfolio" of nanotechnology programs and activities within South Dakota. Other programs include:

- A Ph.D. program in Nano-Science and –Engineering (SDSM&T – Fall 2005)
- A Ph.D. program in Materials Chemistry (USD – Fall 2007)
- A Ph.D. program in Materials Engineering and Science (SDSM&T)
- Participation in a Defense University Research Initiative on Nanotechnology (DURINT) program on nano-energetic materials (SDSM&T)
- Photoactive Nanoscale Systems (NSF EPSCoR)
- The Black Hills Nanoscale Minerals Institute (BH-NMI)
- The Northcentral States Nanoscience Consortium (NSNC)

Collectively, these programs represent approximately $18 million in investments from the State and Federal Government's in various nanotechnology efforts.

3 MAIN TECHNICAL THEMES

3.1 Nanoparticulate Inks for Printable Electronics

Direct write technologies are the most recent and novel approach to fabricate useful electronic devices. The term direct write refers to any technique or process capable of depositing different types of materials on various surfaces following a preset pattern (i.e., CAD). Another term that is prevalently used for this process is "printed electronics". It is quite common to perform the process on polymeric substrates leading to the analogous term "flexible electronics". The ability to accomplish both pattern and material deposition processes simultaneously represents a paradigm shift away from traditional lithographic approaches for device manufacturing. While direct write processing technologies are of enormous potential, there is still considerable need to develop new materials for the construction of useful devices. Materials needed to construct these devices must have a unique combination of performance properties for both electronic functionality (conductivity, dielectric and magnetic) as well as mechanical reliability (adhesion to substrates and other deposited layers, flexibility, and thermal / dimensional stability).

The deposition or prototyping technologies used for creating printable electronics emerged from a Defense Advanced Research Projects Agency (DARPA) program titled Mesoscale Integrated Conformal Electronics (MICE). The program ran from 1998 through 2003 and developed a number of advanced direct write technologies such as Maskless Mesoscale Materials Deposition (M^3D) and nScrypt. Direct write is one of the few deposition technologies that exist for the construction of crucial mid-size components such as resists, capacitors, and inductors from conductive, dielectric, and magnetic materials.

Key advantages of direct write technologies such as M^3D and nScrypt include:

- CAD driven input – no need for masks or patterns
- Reduced materials cost leading to improved cost / performance ratios
- Low-temperature processing
- Accommodates 3-dimensional, non-planar surfaces (conformal electronics)
- Facilitates conductive, insulating, and biological materials
- Significantly reduced environmental impact from reduced waste due to lithography elimination

In late fall 2004, SDSM&T established the Direct Write Laboratory which houses nearly $1.5 worth of direct write and supporting technology. Additionally, the CAAN laboratories house nearly $750,000 worth of specialized nanoprobing and materials synthesis equipment that is applicable to our endeavors. Finally, the Laboratory for Applied Electromagnetics and Communications (LAEC) houses a healthy suite of RF characterization equipment with a value well over $1 million.

While the concept of direct write and polymer based electronics is of enormous interest, it became apparent after the acquisition of the M^3D instrument at SDSM&T that highly conductive metal inks were not available on the market. Thus, we've discovered that significant opportunities exist for the development of a whole suite of deposition inks for the next generation of polymer-based electronics. As a consequence, a highly interdisciplinary group of researchers with expertise in electrical engineering, materials science, metallurgy, and chemistry formed a team to develop inks for low temperature deposition on flexible polymer substrates. Success has been achieved for producing nanoparticulate-based metal inks that work extremely well for M^3D and we are expanding our efforts to other direct write technologies such as nScrypt and industrial ink jet (Dimatix and Microfab).

A key element to these nanoparticle inks is that they require a relatively low temperature post-deposition heat treatment (< 400° C) which makes them amenable to deposition on polymer substrates such as Kapton (polyimide). Most importantly, these silver-based nano-inks result in highly conductive traces, on the order of 75 - 85% of bulk silver, which appears to be a record on low temperature substrates.

As demonstrated by the lack of "off-the-shelf" conductive inks, there is need to develop a number of new inks that can be used to make functional electronic components such as capacitors, resistors, and inductors as well as active components such as diodes, transistors, and integrated circuits. As such, these inks need to exhibit conductive, dielectric, and magnetic properties in combination with the viscosity requirements needed for deposition via direct write technologies. Yet an additional requirement that is a major driver for our work is the need for non-thermal post-deposition treatment since the use of temperature sensitive polymer substrates is of considerable interest and utility.

While we recognize the value of our efforts with conductive inks described above, we also acknowledge that a number of complimentary material "tools" are needed in order to successfully develop additional prototype, flexible, direct write electronic devices that are of interest to our program. These include:

- Gold (together with silver, good basic conductors)
- Copper (not yet been reliably written by direct write)
- Aluminum (potential for low loss and very high ε dielectrics)
- "Magnetic materials" (enabling the printing of magnetic devices for high *f* operation?)
- Transparent conductive materials (transparent electrodes and tunable electrical conductivity)
- "Alloyed" conductive inks (creation of inks for specific purposes and characteristics)
- Dielectric inks (necessary for the construction of complex, flexible, "layered" electronics)
- So-called "metamaterials" (with magnetic, microwave, and optical properties)

In terms of devices, our research team is interested in combining materials development with the prototyping capabilities of the direct write technologies to construct flexible electronic devices such as:

- Broad bandwidth antennas
- Microwave and millimeter wave circuits
- Sensors and detectors
- High impedance surfaces
- Power devices such as photovoltaic cells, fuel cells, and batteries

Finally, we have been involved in a year long project with MBA students at the University of Southern California's Marshall School of Business who have been working on a business feasibility study and development of a business plan for the creation of a small business utilizing the collective technologies that have been developed from this program.

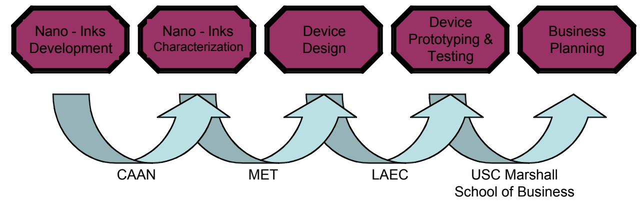

Figure 1: Interrelated Technical and Business Activities Associated with our Printable Electronics Program

3.2 Organo-Clay Based Nanocomposites and Processing Technologies

Polymer nano-composites are a new and rapidly growing class of materials that exhibit dramatically different properties compared to their macro analogs. Polymers reinforced with as little at 2 – 5 % of these particles exhibit dramatic improvements in thermo-mechanical properties, gas barrier properties, and flame retardancy. They can also outperform standard fillers and fibers in raising heat resistance, dimensional stability, and electrical conductivity. All of these benefits are available without significantly raising the density of the compound or reducing light transmission.

Most of the current R&D work in the area of nanocomposites is focused on automotive parts and packaging. The goals are physical and thermal property enhancements and reduced permeability of gases, moisture, and chemicals. Nylon based nanocomposites with montmorillonite (a.k.a., bentonite - which is prevalent in the Black Hills region of South Dakota and Wyoming) have been the first to hit the market and now there is a frenzy of activity aimed at expanding this work to other nanoscale minerals such as talc and mica as well as other commodity thermoplastics such as polypropylene and PET.

The key to achieving such useful properties and products is the proper use of surfactant technologies to promote dispersion of mineral fillers into polyolefins and increase mechanical properties, including HDT, impact, and modulus. Examples of mineral fillers amenable to this technology include calcite, talc, wollastonite, zeolite, attapulgite, and mica. Improved composite properties are achieved by unique, low-cost chemistries which enhance the physico-chemical interactions between the mineral surface and the polymer matrix.

Significant business opportunities exist with advanced organoclays and polymer-clay nanocomposites. There is an increasing demand for high performance fillers, plastics, and composites in a number of industrial and consumer

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product applications such as automotive, packaging (structural), and gas barrier (food and medical packaging).

Table 1. Projected Market Size of Polymer Clay Nanocomposites

Technology / Application	Estimated Market Size (2009)
Total polymer / clay nanocomposites	Over 1 billion pounds
Packaging	367 million pounds
Automotive	345 million pounds
Building and construction	151 million pounds
Coatings	63 million pounds
Industrial	48 million pounds
Other	67 million pounds

Source: Principia Partners - Nanocomposite Polymer Technology for the Next Century

Organoclays have been demonstrated to produce transparent nanocomposite dispersions in many thermoplastic polymers at loadings running from 2 up to 40 weight percent. The oxygen barrier properties of these nanocomposite films are more than 200,000 times better than oriented polyproplylene and over 2,000 time better than nylon-6. The technology reduces by tenfold the requirement for costly organic modifiers. These organoclay nanomaterials also improve the gas barrier properties of waxes for packaging by approximately 2,500 percent.

The data in the chart below illustrates the relative affect of a typical commercial talc and organoclay talc in polypropylene. With only 5 weight % mineral loading, the modulus is increased by 62% with the organoclay product. Note that this compares favorably with conventional talc fillers that require 20 - 30 weight % to achieve the same affect. At the highest loading levels, the organoclay product is almost twice as stiff as the conventional talc filled polypropylene.

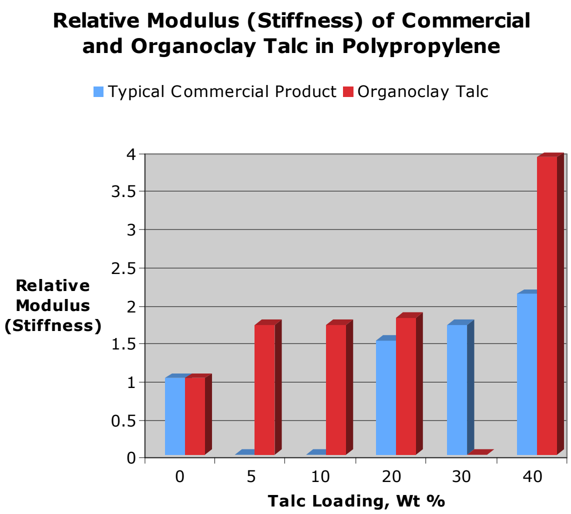

Figure 2: Comparison of Commercial and Organoclay Properties of a Structural Nanocomposite.

Some applications of these organoclay and nanocomposite materials that we are starting to work on at CAAN include:

- Barrier coatings for OLED systems
- Additives for improved gas barrier and water-resistance in polyolefins and polyolefin composites
- Nanocomposites for biomedical devices
- Cosmetic applications, e.g. greaseless hand creams, sunscreens, topical ointments and astringents
- Rheology modifiers for water- and oil-based system
- Heat transfer fluids
- Single-ion conductors for use in Li^+ batteries and proton conducting membranes
- Homeland security applications as super adsorbents - engineered clay systems contain 500 m^2/g external surface area, promising rapid mass transfer that is many times higher than conventional organoclays
- Low-cost liquid crystal systems for electronic displays (the clay platelets are highly anisotropic with aspect ratios as high as 500)
- 'Dry' lubricants especially suitable for vacuum applications
- Non-migratory surfactants to aid dispersion of polar materials into hydrophobic polymers, and are especially useful in formulating water-based, emulsion polymerization systems

3.3 Electrical Probing of Nanoscale Integrated Circuits and MEMS

The final foundational technology or activity that CAAN engages in is that of electrical characterization and nanoprobing services. We've established Nanoscale Semiconductor Testing (www.sdnanoprobe.org) to provide the service of direct contact, electrical characterization of the latest generations of integrated circuits and MEMS to the semiconductor and microelectronics industries on a fee-for-service basis. To perform these valuable services we utilize the Zyvex KZ-100 Nanoprobe System.

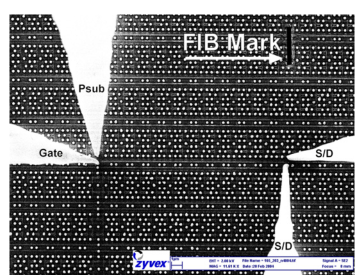

Figure 3: Four Tungsten Nanoprobes on a sub-100 Integrated Circuit (Image courtesy of Zyvex Corp.)