Center for Hierarchical Manufacturing

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The Center for Hierarchical Manufacturing (CHM) is a leading research and education center for the development of precision and cost effective process platforms and tools for the manufacturing of next generation, nanotechnology-enabled devices for electronics, energy conversion, resource conservation and human health. The Center's approach involves the integration of components and systems across multiple length scales and integrates nanofabrication processes for sub-30 nm elements based on directed self-assembly, additive-driven assembly, nanoimprint lithography, and conformal deposition at the nanoscale with Si wafer technologies or high-rate roll-to-roll based production tools. The CHM effort is made comprehensive by research on device design, modeling and prototype testing in functional architectures that take advantage of the specific hierarchical nanomanufacturing capabilities developed by the Center.

The implementation of efficient nanomanufacturing strategies that are compatible with Si wafer processing or high-volume roll-to-roll processing will enable the production of high performance computing, memory, sensing and photonic/optically active media and devices as well as nano-enabled products in energy conversion, organic electronics and displays at acceptable cost. Such advances will help to transform the nation's substantial investment in basic research into products that provide substantial societal and economic benefits.

1. Fundamental and Translational Research: The CHM research structure consists of three Technical Research Groups (TRGs), *(1) Nanoscale Materials and Processes, (2) Nanoscale Devices, Systems, and Metrology* and *(3) Sensors and Environmental Monitoring*, in which fundamental research is performed. Translational research is conducted in the system-level test bed in which the key science, engineering and process barriers to the manufacturing of device nanostructures using the CHM platform tools are identified, systematically addressed and resolved.

The CHM's fundamental science and translational test bed efforts incorporate faculty and research professionals at UMass Amherst, Binghamton University, MIT, the University of Michigan, Mount Holyoke College, NIST, the University of Puerto Rico, and Rice University and benefit from collaborations with leading groups in Europe and Asia.

2. Technical Research Groups: The three Technical Research Groups, which involve nearly three dozen investigators at UMass Amherst and our collaborating institutions, are described in more detail below:

TRG 1, *Nanoscale Materials and Processes*, addresses the materials systems and processes necessary for high reliability nanofabrication and supports fundamental research on the CHM's core technologies. Essential elements include the massively parallel generation of nanostructures, their functionalization to achieve desired physical or chemical properties, and the development of models and simulations to understand and, ultimately, predict the assembly process, system dynamics, transport and materials properties. The TRG also develops functional materials sets for applications in energy conversion and storage (batteries, photovoltaics, fuel cells), separations and computing. The approaches employed reflect the unique expertise and achievements of the CHM, including directed self-assembly, additive driven assembly of hybrid nanocomposites, self-assembly of low-cost templates from commodity components for high volume applications, 3-D replication techniques in which the hierarchical morphologies achieved in soft materials are replicated in inorganic materials without loss of fidelity, nanoimprint lithography and novel conformal and spray-on deposition techniques for nanostructured films.

TRG 2, *Nanoscale Devices, Systems, and Metrology*, supports fundamental studies in magnetics, photonics and device design to generate proof-of-concept prototypes that can be assembled using advances from TRG 1 and the CHM's process platforms. It provides a balanced complement of theoretical and experimental components to guide a system-level design-for-manufacturing approach and the development of metrology methods for property characterization and nanomanufacturing control. Specific efforts include the development of high magnetic permeability ("high-μ") effective medium materials for high frequency wireless device applications, nanoscale device fabrics for computation, and plasmonic arrays for optical sensors based on the CHM's self-assembly and additive driven assembly platforms. The TRG also develops new metrology techniques based on thermoreflectance microscopy.

The efforts in TRG 3, *Sensors and Environmental Monitoring*, recognize that engineered nanomaterials provide both opportunities and challenges in environmental and health sciences. In one effort, the TRG is creating new systems for on-chip separations, diagnostics and environmental monitoring that incorporate unique and enabling technology developed in TRG 1 and the test beds. These efforts are directed towards both complex microfluidic systems and readily manufactured low-cost systems for widespread application. A second effort includes new strategies for tracking nanomaterials in the environment and assessing their stability, toxicity and biodistribution in plant and animal species. This effort is relevant not only to the use of nanoparticles in CHM projects, but also to their use throughout the nanomanufacturing and nanoscience communities.

3. Test Beds: The test beds are the heart of process and platform development where promising concepts transition from laboratory results into reliable, rapid, high-yield and transferable methodologies for nanostructure fabrication. CHM partnerships as well as a targeted Industry Advisory Board and industry consortium for the effort provide mechanisms by which these techniques may be widely distributed for use by the broader nanomanufacturing community. The center piece of the CHM test beds are roll-to-roll process facilities for self-assembled materials and devices, including micro-gravure, slot-die and roll-to-roll nanoimprint lithographic (NIL) and hybrid coating tools for preparing 30-to-1000 nm thick, ordered polymer and

Figure 1. Hybrid nanocoating tool

hybrid films (Figure 1). These efforts include demonstration projects in polymer batteries, aligned carbon nanotube composites for separations and electronics, flexible media for data storage and flexible photovoltaics. The projects are arrayed in order of increasing complexity and drive development, illustrate capability and foster commercialization of the platform. Success will be a driver for the introduction of nanotechnology enabled devices to the market by aligning manufacturing costs with market tolerance. Test beds for cost effective nanomanufacturing of next generation devices based on other technologies, including on-chip, modular arrays of functional nanochannels for biomolecule separation and detection, will be promptly introduced as prototypes emerge from TRG research.

4. Research Highlights: Significant recent developments within the CHM include:

- CHM investigators have used additive driven self-assembly to create the active device layer for floating gate memory. This approach, which allows for very high loadings of 2 nm gold nanoparticles in a polystyrene-block-poly(vinyl pyridine) block copolymer, offers theoretical storage capacities competitive with current flash memory devices. To achieve high storage densities in devices, patterning at micron and smaller length scales is required. Device patterning via roll-to-roll (R2R) nanoimprint lithography is currently being pursued. These technologies will enable the production of memory and other devices using low cost, sustainable, nanomanufacturing.

- CHM investigators have demonstrated for the first time the fabrication of flexible, low-voltage organic thin film transistors (OTFTs) by using supercritical CO_2 deposited ZrO_2 dielectric films (Figure 2). The mobility values of these flexible OTFTs are similar to the device fabricated on Si/SiO_2 substrates. Work continues on the synthesis of high-*k* metal oxide nanoparticles using supercritical fluids such that the entire process can be performed in solution and ultimately compatible with roll-to-roll fabrication.

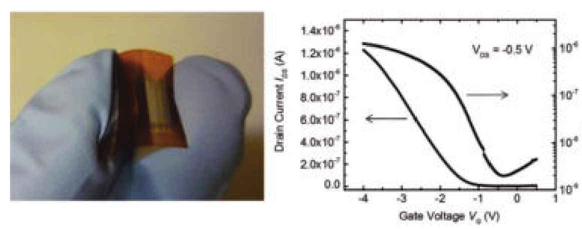

Figure 2. Flexible low-voltage OTFT

- CHM research groups have collaborated to develop new methods to overcome existing challenges in the use of nanoimprinting patterning on flexible substrates in a roll-to-roll configuration. One of the major challenges is the delamination of imprinted materials from flexible substrates such as PET films. To overcome delamination, we have recently demonstrated the use of woven substrates, rather than films, to allow mechanical interlocking to help in preventing unwanted delamination. In the process, a woven fabric is impregnated with a curable formulation which can be subsequently imprinted with a nanostructured pattern. Material and spatial limits of this approach, as well as the mechanical properties of imprinted samples, are currently being determined.

- CHM investigators prepared lines from Au NPs using advances in flow-coating methodology and measured their conductivity on inter-digitated electrodes. These line arrays exhibited an ohmic, linear current-voltage response similar to conductive material. The conductivity of the Au NP lines, measured from top contact configuration (electrode on Au NP lines) is 4 orders of magnitude higher than reported values of Langmuir monolayers of Au NPs. The performance and reproducibility of these lines were confirmed by control experiments and fabrication-characterization of numerous Au NP line arrays. These lines can also be deposited on non-uniform substrates (Au NP lines on electrode), resulting in shape-conforming conductive paths.

- CHM researchers have developed a new format of biosensor based on self-priming microfluidics that will allow for a smaller and more sensitive biosensor, as well as commercial-scale manufacturing and low materials cost. It incorporates the simplicity and reliability of a lateral flow assay with a microfluidic device thanks to the development of a single-step surface modification method which allows strong capillary flow within a sealed microchannel.

- Quantum dots (QDs) are highly fluorescent and photostable, making them excellent tools for imaging. When using these QDs in cells and animals, however, intracellular biothiols can degrade the QD monolayer compromising function. CHM scientists have developed a label-free method to quantify the intracellular stability of monolayers on QD surfaces that couples laser desorption/ionization mass spectrometry (LDI-MS) with inductively coupled plasma mass spectrometry (ICP-MS). Using this new approach it has been demonstrated that QD monolayer stability is correlated with both QD particle size and monolayer structure, with proper choice of both particle size and ligand structure required for intracellular stability.

- Development of a roll-to-roll system-level test bed program to facilitate a manufacturing platform for fabrication of low-cost, large-area nano-materials and devices using roll-to-roll processing technology. This roll-to-roll process test bed was developed to address the challenge of fabricating nanostructured thin films on a high-speed, high-reliability platform. Moving forward, this test bed will enable low-cost commercialization of nanotechnology in applications ranging water purification & filtration, batteries and thin film organic-based photovoltaics. The center accepted delivery of the first custom roll-to-roll nanoimprint lithography (R2RNIL) tool in June 2011. A similarly advanced R2R coater for nanostructured hybrid materials was delivered and commissioned in May this year. Center researchers are now routinely printing sub-100 nm features in a continuous web process (Figure 3) and currently developing new materials and processes to enable printing of features to the ten's of nanometers. Understanding flow and rheological properties is critical to the mission. Real-time inspection and metrology capabilities are also being developed for the new

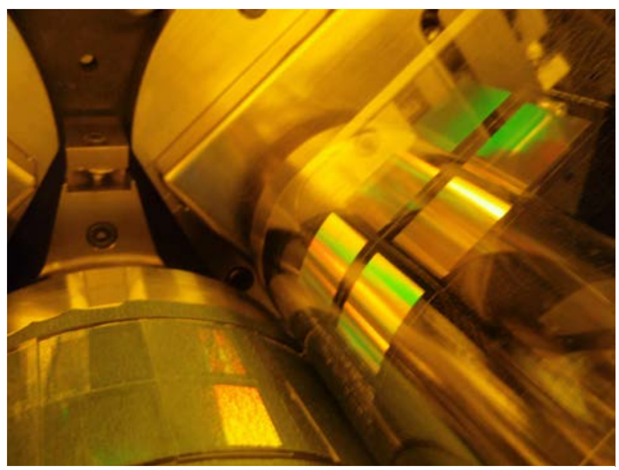

Figure 3. Nanoimprinting of 230 nm gratings on R2R NIL tool

tools.

- CHM investigators contributed new research in which nanowires are grown naturally rather than synthesized chemically. This discovery may lead to new methods for biologically-produced or biologically-inspired materials for sustainable nanomanufacturing. Pilin nanofilaments (pili), known now as “microbial nanowires”, are a class of fibrous proteins found in the sediment bacteria Geobacter. Temperature-dependent studies show the filaments possess metal-like characteristics. The conductivity can be modulated by doping, or by using an applied voltage in an electrochemical transistor configuration. Supercapacitor-level energy storage has been demonstrated with these materials.

- CHM researchers, including numerous undergraduate students, have used thermoreflectance imaging to characterize the thermal performance of operating organic light emitting diodes (OLEDs) and to inspect the temperature profile spatially. The luminance and lifetime of OLEDs decrease dramatically with increased device operating temperature due to self-heating. This problem is particularly severe in OLEDs operated at high-brightness conditions. For stand-alone OLEDs, self-heating leads to measured rises in average temperatures of up to 60°C with local hotspots of up to 200°C, reducing lifetime by 20x or more. This CHM research provides information that can increase the lifetime of high brightness OLEDs through better thermal design.

5. Educational Impact and Societal Implications: The educational activities of the CHM serve to impact a broad audience of learners including those in K-12, community college, undergraduate, graduate, professional and the public. At the K-12 level, educational lesson plans, hands-on activities and digital video tutorial modules were developed and delivered to about thirty science teachers/session for integration into their teaching curriculum during a series of six annual week-long "Nanotechnology Institute" summer workshops held at UMass Amherst to date. The learning materials integrated nanoscale science and engineering concepts into the existing science curriculum in a format compatible with state and national curriculum standards. Since each teacher contacts as many as 100 students each year, the educational impact is widespread. The curriculum materials are open access and made available to other teachers via the web. Shorter K-12 educational interactions take place in the form of one-day teacher training events, student lab tours and *Science Quest* days for more than 200 high school students at sessions held in April and October in 2012.

The CHM also has a comprehensive Nanotechnology Educational Development Group that creates digital video-based teaching modules on nanoscience and nanomanufacturing. This group includes UMass Amherst faculty, Springfield Technical Community College faculty, science teachers, and university students who design, plan, produce and test web-based modules conveying science topics through appropriate use of video, 3D animation, graphics, text and voice. Module creation and development follows an open source philosophy such that, after one module is created for a specific educational audience, it can be easily re-purposed for other audiences. Each module receives alpha and beta testing from target audiences, which provide formative evaluation for improvements. To date, these modules have had high impact since they have been customized for several educational levels (informal science, K-12, community college, university and professional) and disseminated at national events and over the web.

The CHM fostered the creation of several new university courses that include nanoscience and nanomanufacturing curriculum, including one undergraduate class, "Introduction to Nanotechnology and Nanomanufacturing", and several graduate courses have been created or modified to cover these topics. The CHM leverages methods on innovation education developed during a previous IGERT by providing graduate students training at the interface of research, business and entrepreneurship.

6. Networking, Collaboration and Information Dissemination: The CHM is the administrative hub of the National Nanomanufacturing Network (NNN) - a catalyst for U.S. nanomanufacturing-based economic development and research collaboration, a network of manufacturing facilities and expertise, a dynamic web-based information resource, and a pathway for university-industry-government partnerships. The NNN efforts include InterNano, a freely accessible digital library and information resource on nanomanufacturing. The NNN has coordinated, hosted and distributed the outcome of workshops on emerging areas in nanotechnology research, implementation and societal implications.

Providing value-added services to industry, stakeholders, and practitioners engaged in nanomanufacturing, the NNN has established a leadership role in such important activities as standards and terminology, nanoinformatics, education and workforce training, materials database federation, R&D collaborations, and archiving of nanomanufacturing relevant information. The network presently consists of centers, leaders, experts, and stakeholders from the nanomanufacturing research, development and education community representing a partnership among academia, industry and government. The core foundation of the NNN consists of the four NSF nanomanufacturing NSECs: the Center for Hierarchical Manufacturing (CHM), the Center for High-Rate Nanomanufacturing (CHN), the Center for Scalable and Integrated NanoManufacturing (SINAM), and the Center for Nanoscale Chemical-Electrical-Mechanical Manufacturing Systems (Nano-CEMMS), as well as the DOE Center for Integrated Nanotechnologies (CINT) at Sandia National Laboratories, the NIST Center for Nanoscale Science and Technology (CNST), the NanoBusiness and Commercialization Association (NanoBCA) and other affiliations.

With the goal of transitioning of the NNN into an independent network having a sustainable business plan and secure long-term support, activities have created a functioning, action-oriented network populated by leaders of U.S. R&D programs, centers and enterprises related to nanomanufacturing, including an External Advisory Board. These activities also firmly establish InterNano as the premier information site and resource of the nanomanufacturing community, and clearly demonstrate singular NNN contributions to transformational progress in U.S. nanomanufacturing. To accomplish this, the NNN has established a portfolio and database of enabling nanomanufacturing processes, capabilities, and organizations; expanded the NNN base through increased affiliations with government, industry, and academic organizations; and continued to sponsor and organize thematic workshops and conferences targeting priority challenges in nanomanufacturing. New or expanded network activities include education and training, promotion of best practices, facilitating collaborations, and promoting emerging tools supporting design for nanomanufacturing. InterNano has expanded its leadership role in nanoinformatics by organizing major workshops in 2011 and 2012, as well as database federation activities. It has also continued to increase its editorial authority through expanded nanomanufacturing content, networking and community building with expanded outreach via monthly newsletters, increased functionality on the website with new interface implementation, and new informatics tools such as middleware for automated database-centered laboratory data information management.

References

[1] For further information about the center link to: www.umass.edu/chm and www.R2Rnano.org.