CERSP News

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The Newsletter of the NSF Science and Technology Center for Environmentally Responsible Solvents and Processes

University of North Carolina at Chapel Hill
North Carolina State University
University of Texas at Austin
North Carolina A&T State University
Georgia Institute of Technology

"Dry" microelectronics processes

CERSP News

Center for Environmentally Responsible Solvents and Processes

Joseph M. DeSimone Director
(919) 962-2166;desimone@unc.edu
Ruben Carbonell Co-Director
(919)513-0044;ruben@ncsu.edu
Everett Baucom Deputy Director
(919) 843-6994;baucom@email.unc.edu

About the CERSP

"We use CO_2 research to develop and share scientific knowledge profitably among:

- Students
- Scientists
- Industry
- and Society

for a cleaner environment."

Mission:

To identify and enable a generation of economical and energy-efficient, clean and safe processes, especially for improved products, by developing and exploiting a robust body of fundamental knowledge in CO_2-related science and technology.

Darlene K. Taylor Editor and RICHES Manager
(919) 962-6839; dkt@unc.edu

CORPORATE SPONSORS

As the major industrial outreach component of the CERSP, the Kenan Center for the Utilization of Carbon Dioxide in Manufacturing has the advantage of its industrially supported activities being highly leveraged by federal support for CERSP. This allows for a great deal of synergy between the more applied projects associated with the Kenan Center and the more fundamental and analytical research done by CERSP. The Kenan Center is comprised of chemists, chemical engineers, and materials scientists from the University of North Carolina at Chapel Hill and North Carolina State University as well as a team of corporate sponsors. Our laboratories are uniquely equipped to help industrial partners launch research programs in supercritical fluids R&D, as well as to assist in augmenting proprietary research programs within their corporate R&D laboratories.

Kenan Center for the Utilization of Carbon Dioxide in Manufacturing

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Website: www.ncsu.edu/champagne

The Renewal of our STC

CERSP has recently been favorably reviewed by the National Science Foundation and the site visit team for the $18 million renewal of our Center. We are heartened by the strong endorsement of our Center by NSF. The formal approval will not occur until October 2003, but based on the position of the site visit report and NSF Program Officers positive recommendation, we are optimistic that we will officially celebrate in October.

CERSP has established an ambitious and far reaching vision of enabling a revolution in green chemistry through cutting-edge, integrated physical science and engineering; social science; and educational programs. Realizing this vision will require a strategically focused, highly coordinated and carefully implemented multidisci-plinary program of research, education, and knowledge and technology transfer. Over the past four years, CERSP has developed the structures, policies, and procedures that are the hallmark of well managed Centers. In particular, we have assembled a diverse and highly experienced management team, developed and refined a focused yet flexible strategic plan, recruited a qualified and motivated multidisciplinary team of scientists and engineers, and assembled a world-class collection of shared laboratories and equipment. We believe these efforts have already begun to bear fruit.

A defining characteristic of our Center is commitment to learning and continuous improvement. We have solicited input and feedback formally, through questionnaires and surveys, as well as informally. We are planning a number of changes as we approach our renewal milestone. Some of the significant changes currently underway include a refocusing on research issues that can potentially revolutionize the semi-conductor industry, especially through development and acquisition of state-of-the-art major instrumentation associated with our Dry FAB of the Future Demonstration Facility. We intend to restructure our relationship with NCA&T to emphasize development and success of undergraduates (see article on page 9). We believe these changes along with the Center infrastructure that we have created over the past four years, will help us realize our vision of enabling a revolution in green chemistry.

Our research goals have started to transition into select areas of concentration focusing on three Implementation Domains: (1) Microelectronics, (2) Macromolecular Synthesis and Engineering, and (3)

continued on back cover

Membranes are his Focus

Professor William J. Koros
Roberto C. Goizueta Chair
School of Chemical & Biomolecular Engineering
Georgia Institute of Technology

Education:
B.S. 1969, University of Texas at Austin
Ph.D. 1977, University of Texas at Austin

Professor Koros leads the Separations Focus of the CERSP where he and his group work to develop a fundamental understanding and ability to separate carbon dioxide from industrial gas streams and organic molecules .

Silpha Dample, Contributing Author

Dr. William Koros, a member of the NSF-STC Technology Center, is a faculty member at The Georgia Institute of Technology. He came to Atlanta in 2001 as the Roberto C. Goizuetta Chair in Chemical Engineering, and brought with him considerable expertise from the industrial and academic communities. His roots are in Texas, where he received both his bachelor's and doctoral degrees from The University of Texas at Austin. After working at DuPont for four years, Dr. Koros joined the department of Chemical Engineering at NC State in 1977 where he began his membranes based research program. His initial endeavors focused on barrier materials for packaging applications and emphasized diffusion fundamentals. However, he also began to investigate membrane materials for gas separations….a once small aspect of his program that later grew into a major research emphasis of a University of Texas based program which he began in 1984.

Since that time, the Koros Research Group has focused on developing membrane materials for gas separations. These *molecular scale filters* achieve selective passage of one or more components in feed streams, and are economical, compact, environmentally friendly, and help conserve energy. The Koros Group focuses on several key areas for gas separations. One aspect of the work is to develop membrane materials to produce nitrogen enriched air for economical storage of foods and to blanket fuels in transport for safety. Removing contaminants from natural gas and from flue gases to improve economic gains and protect the environment is another thrust of the research that is now based at Georgia Tech. A rather new arena of research that has begun in Austin and is being continued at Tech is the development of membrane materials for separation of organic solutes from supercritical carbon dioxide. This gas separations based research is currently supported through various sources, including both Federal and industrial funds. Federal support comes from the Department of Energy, National Science Foundation, and the National Institute of Science and Technology. BP-Amoco, Chevron-Texaco, Coke, and Air Liquide are on-going industrial sponsors.

As an academician, Dr. Koros has published over 200 articles and holds six US patents in the areas of sorption and transport of components in polymers, molecular sieve carbons, and ceramics. He is also the Editor-in-Chief of the major archival resource in the membranes arena, the *Journal of Membrane Science*, and is the Secretary of the North American Membrane Society.

Dr. Koros has earned numerous honors and awards in his 26 year career. While at NC State, Dr. Koros received the Sigma Xi Award, and at The University of Texas, the National Science Foundation Presidential Young Investigator Award. His alma matter selected him as an Outstanding Young Texas Ex in 1991, while the Department of Chemical Engineering at Texas selected him as their chairman from 1993 to 1997. From the American Institute of Chemical Engineering (AIChE), Dr. Koros has received the AIChE Institute Award for Excellence in Industrial Gases Technology in 1995, and the Clarence Gerhold Award in Separations in 1999. He was also elected as a National Academy of Engineering member and as a Distinguished Alumnus of the UT College of Engineering in 2000.

see Koros page 4

Koros continued from page 3

While his efforts in the research arena have earned Dr. Koros numerous awards and have taken him to the top of his field, it is in the sometimes forgotten arena of the classroom that Dr. Koros has made his most lasting impact. His dedication to undergraduates has earned him awards of distinction at NC State, The University of Texas at Austin, and at Georgia Tech. And the teaching does not stop with the undergraduate students. Though his days are packed and often quite long, Dr. Koros is always available to speak with and mentor his 13 graduate and 2 undergraduate students.

Besides his research and teaching endeavors, Dr. Koros, his wife, Ann, their cat (Buddy) and dog (Lucy) are enjoying their new home, which is close to campus. They have transformed their backyard into a mini nature-sanctuary. This latter feat took some effort, with their dog now wearing a "Lucy-Alert" bell to keep the many chipmunks, squirrels and rabbits apprised of her whereabouts. Lucy provides a connection between Texas and Georgia, since she was added to the clan from ***Georgia Border Collie Rescue*** where she had ended up after a short career as a Texas cattle-herding dog. Lucy also enjoys agility training and walking in the neighborhood with her handsome Georgia Tech leash to advertise her new affiliation. In addition, their 14 year-old cat, Buddy, enjoys watching the wildlife from his window perch.

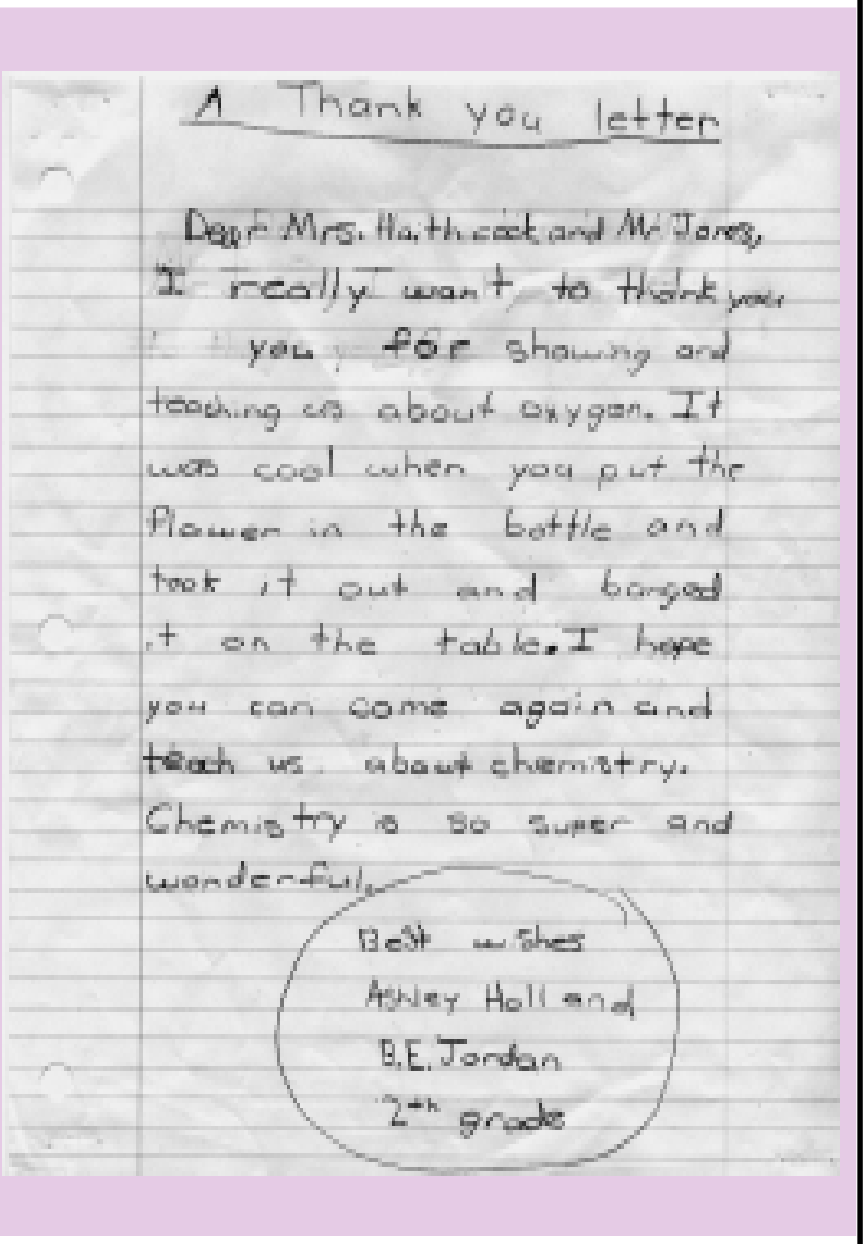
Charles Jones and Sarah Folk captured the attention of all the students during a demonstration involving carnations (top left). After the carnations were exposed to liquid nitrogen, they became brittle and were easily shattered when thrown on the floor. Students attending the demonstration mailed Thank you notes (right) along with pictures of the day's activities (bottom left).

Dancing Pasta, Frozen Carnations,

and other fun activities for elementary school students

Charles Jones, Contributing Author

Faculty and students affiliated with CERSP are given the opportunity to be active in K-12 outreach activities. Two UNC graduate students, Sara Folk (5th year) and Charles Jones (4th year) seized the opportunity on October 22, 2002 by visiting B. Everett Jordan Elementary School in Graham, NC. The school had their annual observance of Red Ribbon Week, an event geared towards helping students to become more aware about drugs and the harmful effects that drugs have on those who use them. The major event of the week, Healthy Choices Hobby Day, gave students a chance to learn about healthy alternative choices they could make for themselves and to be introduced to a variety of activities. Approximately 400 kindergarten through 5th grade students participated in the event. Many people from the community were invited to share fun activities such as soccer, gardening, and yoga, all of which can be taken up as hobbies. Students from the Center discussed how science could be fun as a hobby and even as a career. Interactive science demonstrations were presented. An experiment showing the evolution of CO_2 from baking soda and vinegar was one of the many presentations that were hits with the students. The students expressed their appreciation by writing letters and drawing colorful illustrations describing the experience. By far, the most popular experiment with the students involved freezing carnations in liquid nitrogen and then shattering the rigid and frozen flower petals as they were thrown against a wall.

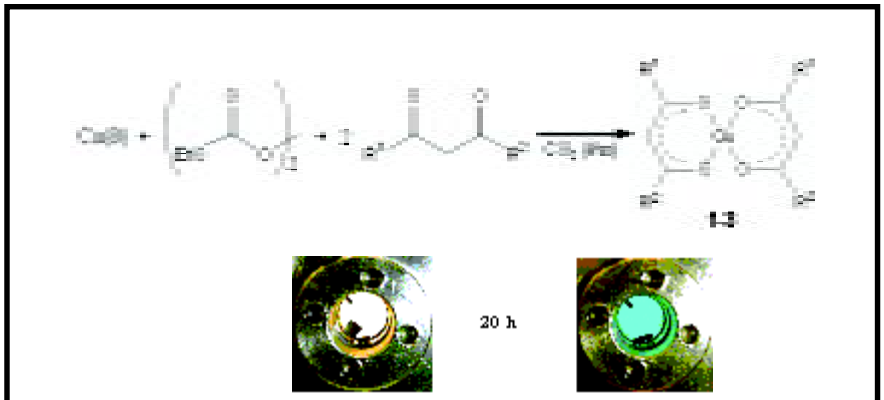


A Thank you letter

Dear Mrs. Hathcock and Mr Jones,
I really want to thank you
you for showing and
teaching us about oxygen. It
was cool when you put the
flower in the bottle and
took it out and banged
it on the table. I hope
you can come again and
teach us about chemistry.
Chemistry is so super and
wonderful.

Best wishes
Ashley Holland
B.E. Jordan
2th grade

A CO_2-Based "Dry" CMP Process is Closer to Realization



First efforts to establish a "dry" chemical mechanical planarization (CMP) process based on condensed CO_2 have been reported. The key challenge to realizing this goal is the unprecedented oxidation and removal of an elemental metal film in CO_2.

Carol A. Bessel, Ginger M. Denison and Pamela M. Visintin, Contributing Authors

The present trends in the microelectronics industry towards smaller chip dimensions (i.e., 90 nm line widths) and high aspect ratios reduce the tolerance level for defects and/or impurities.[1] Due to the superior electrical conductivity and better electromigration resistance of copper when compared to the current tungsten- or aluminum-based materials, industries have developed an interest in the use of Cu as an interconnect material.[2] In order to remove surface overburden and clean the copper surface during chip manufacture, a process called chemical mechanical planarization or polishing (CMP) is used. This process represents a combination of chemical and mechanical means: in the chemical process, the metallic copper is oxidized and chelated, while in the mechanical process, the copper surface is rubbed against a polishing pad until global planarization is achieved. A typical copper CMP slurry contains one or more of the following: chemical etchants (oxidants), chelating agents, buffers, abrasive particles, passivating agents, and co-solvent(s).[3]

We have recently reported our first efforts to establish a "dry" CMP process based on condensed CO_2.[4] The key challenge to realizing this goal was the unprecedented oxidation and removal of an elemental metal film in CO_2, a solvent that has a very low dielectric constant. The advantages to the use of CO_2-based processes are many. In particular, CO_2 processes are considered "dry" and thus, CO_2 is amenable for use in tools/chambers that can be easily evacuated and interfaced with vacuum cluster tools. These tools are standard "dry" tools used in fabs today. Unlike water, condensed CO_2 has an extremely low viscosity and a low surface tension – characteristics desired for CMP processing. Additionally, the environmental difficulties associated with the use of organic solvents (e.g., solvent toxicity and oxidation) as well as the recyclability of the organic or aqueous solvents are avoided. Finally, condensed CO_2 is easily separated from the other chemicals in the proposed CMP slurry by tuning the pressure and/or temperature.

During our experiments, copper coupons were treated with a "dry," homogenous solution in sc CO_2 containing an oxidant, ethyl peroxydicarbonate (EPDC), and a commercially available b-diketone chelating agent, often 1,1,1,6,6,6-hexafluoroacetylacetone (hfac). The reactions were performed in a 10-mL high-pressure view cell with sc CO_2 as the solvent at 40 °C and 214 bar. After 20 h, the CO_2-soluble copper product was analyzed and determined to be Cu(hfac)2.H2O. It was also estimated that ca. 2 x103 monolayers of copper were removed from the coupon. The reaction scheme represents the chemical aspects of our CMP process and also illustrates the dramatic color change observed during the oxidation and chelation process: from a clear, colorless initial solution to the

bright green of the CO_2-soluble copper complex.

We are continuing to develop many of the other processes used in semiconductor fabrication in CO_2, specifically photoresist stripping, drying, developing, spin-coating, metal deposition, and low-k interlayer dielectric material formation. We look forward to reporting on these environmental and technical advances in the near future.

References

1. (a) Steigerwald J. M.; Murarka, S. P.; Gumann, R. J. *Chemical Mechanical Planarization of Microelectronic Materials*; John Wiley & Sons: New York, 1997. (b) Singh, R. K.; Bajaj, R. *MRS Bulletin*. **2002**, *27*, 743-751. (c) Hanazono, J.; Amanokura, J.; Kamigata, Y. *MRS Bulletin*. **2002**, *27*, 772-775.

2. Stavreva, Z.; Zeidler, D.; Plotner, M.; Grasshoff, K.; Drescher, K. *Microelectron. Eng*. **1997**, *33*, 249-257.

3. Luo, Q.; Mackay, R. A.; Babu, S. V. *Chem. Mater.* **1997**, *9*, 2101-5785.

4.Bessel, C. A; Denison, G. M; DeSimone, J. M.; DeYoung J.; Gross, S.; Schauer, S. C.; Visintin, P. M. *J. Am. Chem. Soc.* **2003**, *125*, 4980-4981.

MPS Fellows Visit UNC

MPS Fellows Pat Lignon and Deborah Massengil look on as CERSP students demonstrate carbon dioxide filling a high pressure cell.

Two of the four MPS Fellows toured the CERSP facilities at UNC-Chapel Hill on July 1, 2003. As the program goes into its last phase, the Fellows are preparing to design exhibits for the discovery room at the Natural Science Museum. Additionally, Fellows will design environmental science curriculum. At the museum, interns are working with carts and the discovery room which caters mainly to 3-8 year olds. Their emphasis is on the effects of global warming on nature, carbon sequestration, and the carbon cycle. Most of the things deal directly with nature, however the interns are designing a carbon dioxide box for the discovery room. Boxes have a central theme, a book with activities, and nonperishable natural items. Items to be displayed include a tree cross section, slides of different size stomatas, clam shells, and limestone. The carbon dioxide in technology theme will be emphasized with teflon coated wires among other items displayed in the box. The box will also contain a book providing instructions on using the objects as well as exerts to integrate math, English, and social studies with stories, poems, etc. For environmental science, the objective is to help the students better understand the causes and effects of global warming and examine different solutions. The interns have designed introductory activities as well as a webquest. The webquest has the students living in an imaginary town with too much carbon dioxide and too little water. The students are to look at a lot of different websites including the Kenan Center and CERSP websites and propose a solution to the town council.

--Darlene Taylor

reaching industry

The highlights of the April 15, Kenan Center Technical Review Meeting were poster presentations by students and post-doctoral associates. A total of 38 posters were presented at the meeting.

Snapshots of the April 2003 Technical Review Meetings

Darlene Taylor,Editor
Chapel Hil, NC

Following suggestions made by our industrial partners on a previous questionnaire, the KCUCDM meeting held April 15, 2003 marked the first semi-annual meeting hosted on a Tuesday weekday format. The one-day meeting focused exclusively on research topics in microelectronics and polymer synthesis and processing featuring broad overviews by Ruben Carbonell and George Roberts respectively. The highlights of the meeting were technical presentations by students and post-doctoral associates in both poster and oral formats (38 and six respectively). CD-ROMs containing the poster presentations and a virtual tour of the CERSP laboratory facilities were distributed. A brief business meeting was conducted to discuss the future of the KCUCDM. In addition, Bob Pozner discussed patent issues with the industrial partners.

Fall 2003 Kenan Center Meeting Postponed

Due to the number of meeting hosted this year, the Fall Kenan Center Meeting, which would have been held in October 2003, has been postpone till FY2004. This will be an important meeting to attend, as we anticipate discussing major changes in the structure of the Kenan Center. The meeting will most likely fall on a week day to accommodate the requests of our industrial sponsors and is tentatively targeted for April 2004. As in the past, the entire day of activities will be held at the Friday Center in Chapel Hill, NC.

NCA&T Undergraduate Program of Excellence

A new initiative should make a significant impact in recruiting undergraduates from NC A&T to enter the graduate programs at the other CERSP campuses.

Darlene K. Taylor, Editor
Professor Leonard Uitenham, Contributing Author
Greensboro, NC

Racial and ethnic diversity have been an important goal within the CERSP during its first three years. For those years, average participation by historically underrepresented groups in our research efforts has been great: 30% of faculty, 31% of post-docs, 58% of graduate students and 71% of undergraduates have been from groups historically underrepresented in the sciences. Year-to-year differences are slight. Currently, of 127 student researchers and associates receiving CERSP support, 55% are from underrepresented groups and 76% are minority or female; 46% are women, 24% African-American, 32% of Asian extraction, and 6% Hispanic/Latino. NCA&T contributes significantly, especially among undergraduates, but we have not been very successful in recruiting undergraduates from A&T to enter the graduate programs at the other CERSP campuses. The NCA&T Undergraduate Research Program of Excellence will focus on education, including guiding/advising freshmen through seniors with a view towards increasing the number of students entering graduate school. Involvement in the program will increase as experience grows. During the freshman year, students will be exposed to the various opportunities available to scientists/engineers. The advantages of a science/engineering career path will be highlighted as opposed to more traditional professional activities such as medicine. At the end of the freshman year, it is our goal to identify at least ten "graduate school track scholars". These ten students would receive scholarships to participate in research activities and professional development seminars to help prepare them for graduate school admission. This is mostly to encourage participation in activities in which they might not otherwise participate. During the sophomore year, mentoring and tutoring services will be provided taking advance of the distributed collaboratory facilities of CERSP. At the end of the year, a new goal would be set to identify at least five students to participate in the program. During their junior year, students will host symposia at A&T and visit UNC and NCSU campuses. Support will be provided for these juniors to engage in research activities at NCSU, UNC-Chapel Hill, or industry. From the available pool of students, at least two students will be selected to continue as seniors. These students will be guided in the process of preparing for and applying to grad schools. CERSP will continue to support these students with undergrad research opportunities. In addition, a talent search will be conducted to recruit new freshseniors. Seniors will be charged with assisting in the operational details of the program for freshmen and sophomores. Summer support will be provided for NCA&T graduates who are incoming graduate students at CERSP schools. A fellowship will be provided for the top student to attend a partner university and work in the CERSP.

A post-doctoral fellow with CERSP experience will work closely with NC A&T faculty to help coordinate the NCA&T undergraduate research program. The post-doctoral fellows will commit to a multi-year program that includes research and teaching at NCA&T. Financial bonuses will be given to those faculties who best perform in recruiting, mentoring, involvement, etc. In the end, we see this new program as way of strengthen the relationship with NCA&T and providing a mechanism for a continued relationship between the CERSP affiliated universities even after funding for CERSP has officially ended.

RICHES 2003 Award

Congratulations to Ginger Denison of UNC-CH for winning the RICHES 2003 Award. The RICHES department of the CERSP annually recognizes graduate students in the CERSP who have displayed exemplary service in K-12 outreach activities as well as made significant contributions to their research projects as demonstrated by publications and oral presentations at technical meetings. A all expense paid trip to an international conference usually accompanies the award and this year Ginger attended the PASI Green Chemistry Conference in Uruguay.

Jasper Dickson of UT-Austin and Mick Hurrey of UNC-CH were also acknowledged for their outreach service and research accomplishments related to the CERSP.

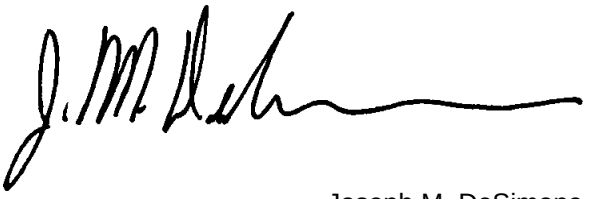
continued from page 2 Director's Letter

Nanostructures. A seed-funding program in the area of Biotechnology will be implemented to seek new leads outside current focus areas. In addition, the pervasive need for the development of separations associated with CO_2 has lead us to include a focused research program on separations. These areas of emphasis were selected for four reasons. First of all, the CO_2 platform proposed by our Center addresses the strong need of the industries targeted by CERSP to implement sustainable green manufacturing methods. Secondly, on top of the healthy environmental aspects of CO_2, its unique properties (very low surface tension and viscosity and its tunable solvent quality) make it an exceptional solvent system that addresses the technological problems faced by the microelectronics, chemical, biotechnology, and nanotechnology industries. Thirdly, these are all high value applications that can justify new technology developments. Finally, the scientific and technical challenges in these research concentration areas represent the gamut of problems likely to be encountered elsewhere; thus our experience here will be readily applicable to other industries and technologies and broaden our collective impact.

The Microelectronics Domain is a better-conceived research plan as an outgrowth of our previous domain focused on Dissolution and Deposition. The Nanostructures Domain represents a morphing of two previous domains involving small systems and interfacial studies in microemulsions. The resulting new domain will focus on what appears to be the biggest opportunity in this general area ¾ the fundamentals of nanostructures and their applications in electronic and medical fields. Significant leads have been developed in each of these areas and CO_2-based microelectronics processes are highlighted in the feature article "A CO_2-Based "Dry" CMP Process is Closer to Realization" on page 6.

The strategic plan of research in the Macromolecular Synthesis and Engineering Domain identifies important scientific and technological gaps. These research efforts have already produced valuable results and we can point to DuPont's CO_2-based production of Teflon® and CO_2-based dry cleaning franchises as examples of the development and deployment of environmentally responsible processes by our industrial partners. In addition, we have developed an educational program for K-12 students and teachers that capitalize on our findings, the environmental themes that define our Center, and the enthusiasm of our graduate students and faculty (see p. 5). This coordinated effort to impact so many students would not be possible through individual investigator grants.

In short, the concepts underpinning the organization of our Center has led CERSP on an important scientific and educational endeavor. The renewed CERSP will focus its resources and efforts to conduct world renown research, increase the diversity in the sciences and engineering, significantly contribute to educating the general public about environmentally friendly science and engineering practices, and improve science education for the Kindergartener, post doctoral fellow and everyone in between. Continued financial support from NSF and others coupled with the mindset of CERSP participants to continually improve, ensures that CERSP will be successful at leaving an unforgettable legacy that impacts science, education, and technology.



Joseph M. DeSimone
CERSP Director

On the front cover

The new ASML 550/9xx 193 DUV production stepper will be placed into the Triangle National Lithography Center (TNLC) starting October of this year. The purchase of this equipment was a joint effort between UNC-Chapel Hill and NCSU that represents an investment of over $3M. The equipment will 1) provide researchers form the Triangle and around the world a state-of-the-art multi-user facility that enable unmatched opportunities to fabricate nanoscale structures using optical lithography and 2) further the understanding of matter and processes at the nanometer length scale. The instrument should be available for use by January 2004. Professor Carl Osburn is in charge of the facilities at the TNLC. In the future, information about the facility will be posted on the new website: www.tnlc.ncsu.edu. This is an exciting opportunity for the Triangle and CERSP is proud to have played an instrumental role in making this new facility become a reality.

Triangle National Lithography Center

learn more by visiting the website www.tnlc.ncsu.edu