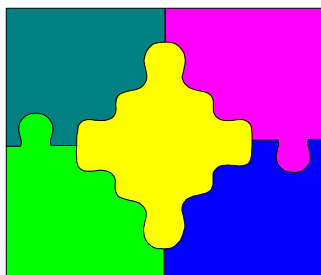


Combinatorial Methods at NIST



An overview of combinatorial
chemistry and materials science
in the Measurements and Standards
Laboratories at the National Institute of
Standards and Technology



NIST
National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

Growing impact

- Combinatorial methods have revolutionized the process of pharmaceutical discovery.
- Now, materials scientists are applying the same approach to accelerate discovery and application of new materials.
- *Chemical and Engineering News* asks: Are combinatorial methods “Redefining the Scientific Method for Discovery”?



New, more complex materials are increasingly in demand for applications in biotechnology, microelectronics and nanotechnology. The use of combinatorial methods -- which comprise a special set of tools and techniques -- enables scientists to conduct many experiments on many materials at the same time. The National Institute of Standards and Technology is using this methodology to learn more about materials and their structure, properties and processing, data which can help manufacturers accelerate the development of new materials.

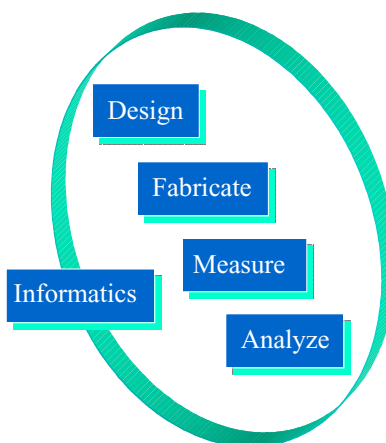
Breaking away from the traditional one-at-a-time testing of materials, combinatorial methods allow researchers to rapidly explore a wide range of characteristics of materials -- in parallel and on a miniaturized scale -- such as the effects of temperature, thickness and composition. Researchers can easily compare these characteristics, screening for what works and what doesn't, and generating data to help construct predictive models.

Two fundamental approaches can characterize NIST's involvement in combinatorial methods. "Combi for NIST" suggests the use of these methods to enhance and accelerate NIST research in areas ranging from polymers and biomaterials to electronic and optical inorganic materials. On the other side, "NIST for Combi" represents a growing effort to use the expertise gained at NIST to develop and validate research tools, establish standards and demonstrate applications of combinatorial methods for industry and academia.

A role for NIST

Why NIST?

- Drivers for industry
 - Speed, responsiveness, innovation
 - Reduction in time, material, and waste
 - Optimization for new materials needs
- Drivers for NIST
 - Rapid development of materials data
 - Validation of combinatorial measurements
 - Connections to fundamental science

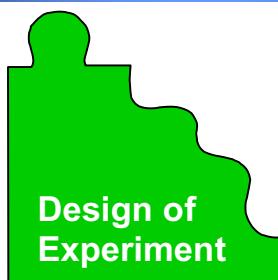


NIST Leadership

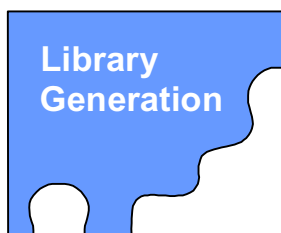
- National Meetings – National Dialogue, Vision 2020
- Tutorial Workshops – NIST, Academic, Industry
 - Library fabrication
 - High-throughput screening
 - IT infrastructure and data mining
- Demonstration Laboratory – Hands-On, Non-Proprietary
 - Industrial and academic visitors
 - Combinatorial postdoctoral training
 - Showcase for related NIST technology
 - Lowering the barrier to entry
- Internationally – Honest Broker, Method Development, Validation, Standards, Data
 - National and international meetings
 - Professional and trade organizations
 - Technical publications



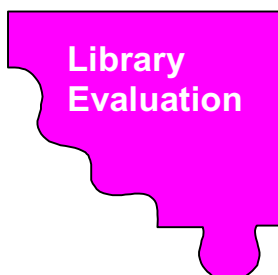
Combinatorial methodology



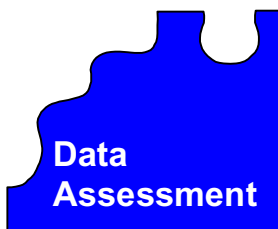
- Define sampling of parameter space
 - Molecular structure
 - Composition
 - Morphology
 - Processing



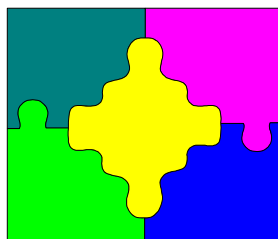
- Synthesis and creation of samples
 - Continuous gradients
 - Split and pool
 - Small/Discrete samples
 - Patterning



- Characterize materials, discriminate performance
 - Screening hits
 - Comparative performance
 - Quantitative data



- Analysis from massive data sets to information and to knowledge
 - Data management
 - Visualization
 - Data mining
 - Development of predictive models

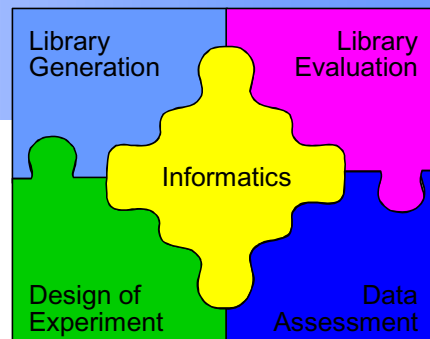


Integration of the pieces is critical to success with the combinatorial methodology

Research areas

Topics described in this brochure:

- Polymer coatings and films
- Polymer blend phase behavior
- Biocompatibility assay
- Adhesives
- Surface chemistry and modification
- Semi-crystalline polymers
- Block-copolymer ordering behavior
- Fire retardants
- High-throughput measurements
- Library production support
- Laser scanning microscopy
- Chemical microscopy by SIMS
- Data mining: Searching for patterns
- Quantitative spectral imaging
- Dielectric oxide thin films
- Metallization of GaN semiconductors
- TEM studies of combinatorial libraries
- Polarized light scattering
- Thermal properties screening
- Fluid properties microanalysis
- Service life prediction
- Microhotplate array platforms
- Modeling and characterization
- Infrared chemical imaging



Apply methods in service to NIST programs, e.g. polymer, metal, and ceramic films and coatings, biomaterials, flame retardants, electronic and optical materials.

“Combi for NIST”

“NIST for Combi”

Use NIST measurement and standards expertise to provide tools, validate methodology, assess uncertainties, provide standard reference materials and produce data libraries.

- Data base generation
 - Data bases from combinatorial libraries
 - Validation of ‘Virtual’ data base concepts
- Infrastructure
 - Robust, interoperable methods for data manipulation, storage, and mining.
 - Statistical issues unique to combinatorial approaches
- Knowledge Discovery
 - Test models and theories of complex systems
- NIST Combinatorial Methods Center - NCMC
 - Multidisciplinary effort to establish entire infrastructure focused on selected issues

Library Design and High-throughput Characterization of Formulations

- Critical Issues

- Critical challenges in formulations include developing methodologies to systematically investigate stabilization, compatibilization, reactivity and optimization of formulation properties for myriad of applications.

- Research Strategy

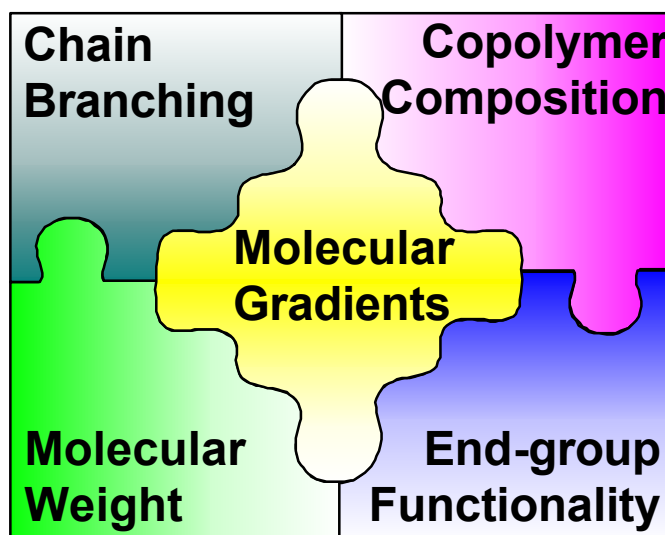
- Design and test macro and microfluidic methods for high throughput library preparation of formulations (viscous dispersions). Integrate with high-throughput spectral analysis techniques to characterize stability to flocculation and composition of dispersed phases, and develop high-throughput methods to measure rheological properties.



For more information ...

Polymer Synthesis & Characterization with Gradient Molecular Properties

- Critical Issues
 - Critical need exists to develop a simple combinatorial synthetic methods to generate libraries of ranges of polymer molecular mass, varying yet controlled architecture, co-polymers with diversity in composition as input materials for generating combinatorial maps of structure-property relationship.
- Research Strategy
 - Develop inert atmospheric ATRP based synthetic method for preparing polymer libraries with simultaneous gradients in molecular mass, co-monomer fraction, and varying molecular architecture. Evaluate composition, structure and efficiency of reaction methods using high-throughput light scattering, IR absorption, UV degradation reactions and MALDI mass spectroscopy. Utilize functionalized polymers gradients as resins for controlled testing of formulations.



For more information ...

Polymer coatings and films

- Critical Issues

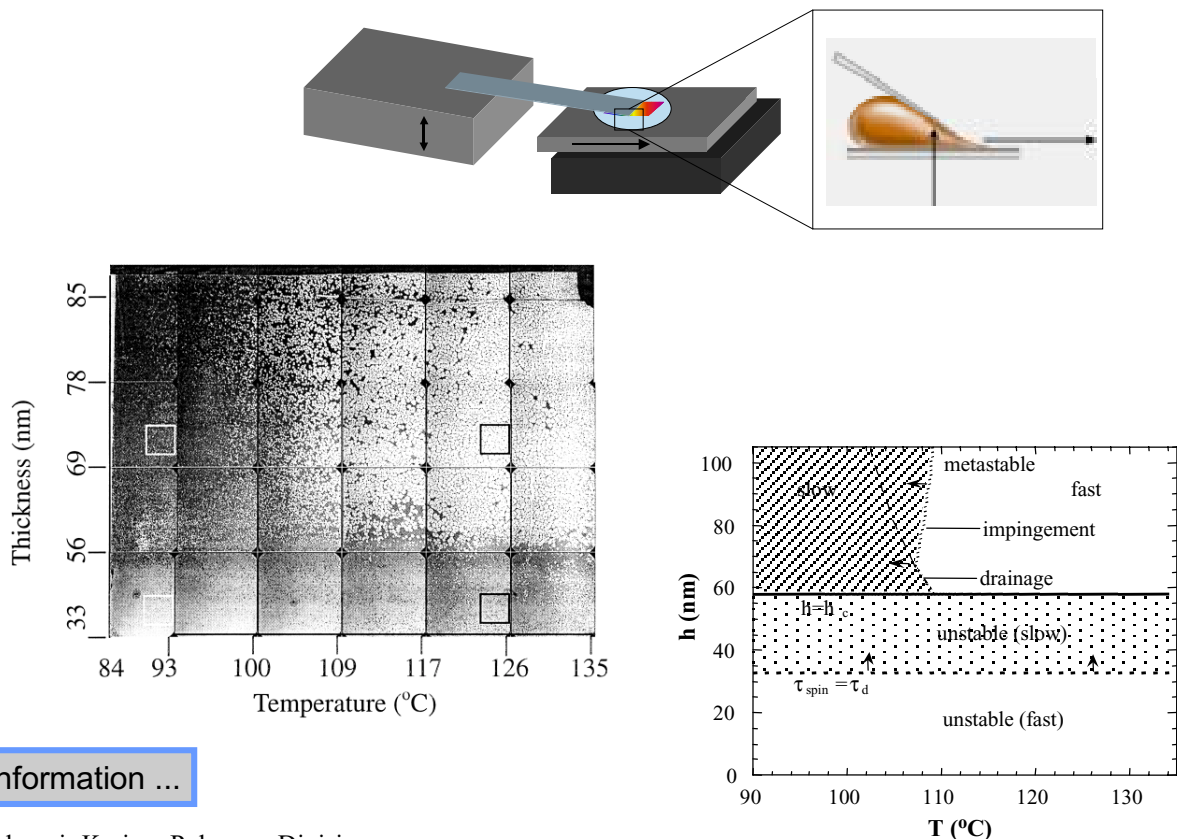
- The challenge is to achieve desired mechanical, optical or thermal properties in thin film coatings by manipulation of interfacial structure, microstructure and processing conditions.

- Research Strategy

- The goal is to develop combinatorial methods for investigating polymer coatings, for example, by creating a gradient in cross-link density in polymers. High speed automated scanning techniques such as optical and microscopy techniques can be used for evaluation of optical and other properties under orthogonally varying process variables such as temperature or stress gradients.

- Research Highlights

- Current research efforts have focused on factors affecting stability of thin film coatings. Specifically, the effect of temperature and film thickness on film wettability. Utilizing flow coating film preparation, spot ellipsometry for thickness characterization and automated optical microscopy for imaging on a temperature gradient stage, complete libraries of dewetting of low molecular mass polystyrene on Si from nucleated to thermally induced capillary wave “spinodal” dewetting have been mapped in the course of a few hours.



For more information ...

Alamgir Karim, Polymers Division

Polymer blend phase behavior

- Critical Issues

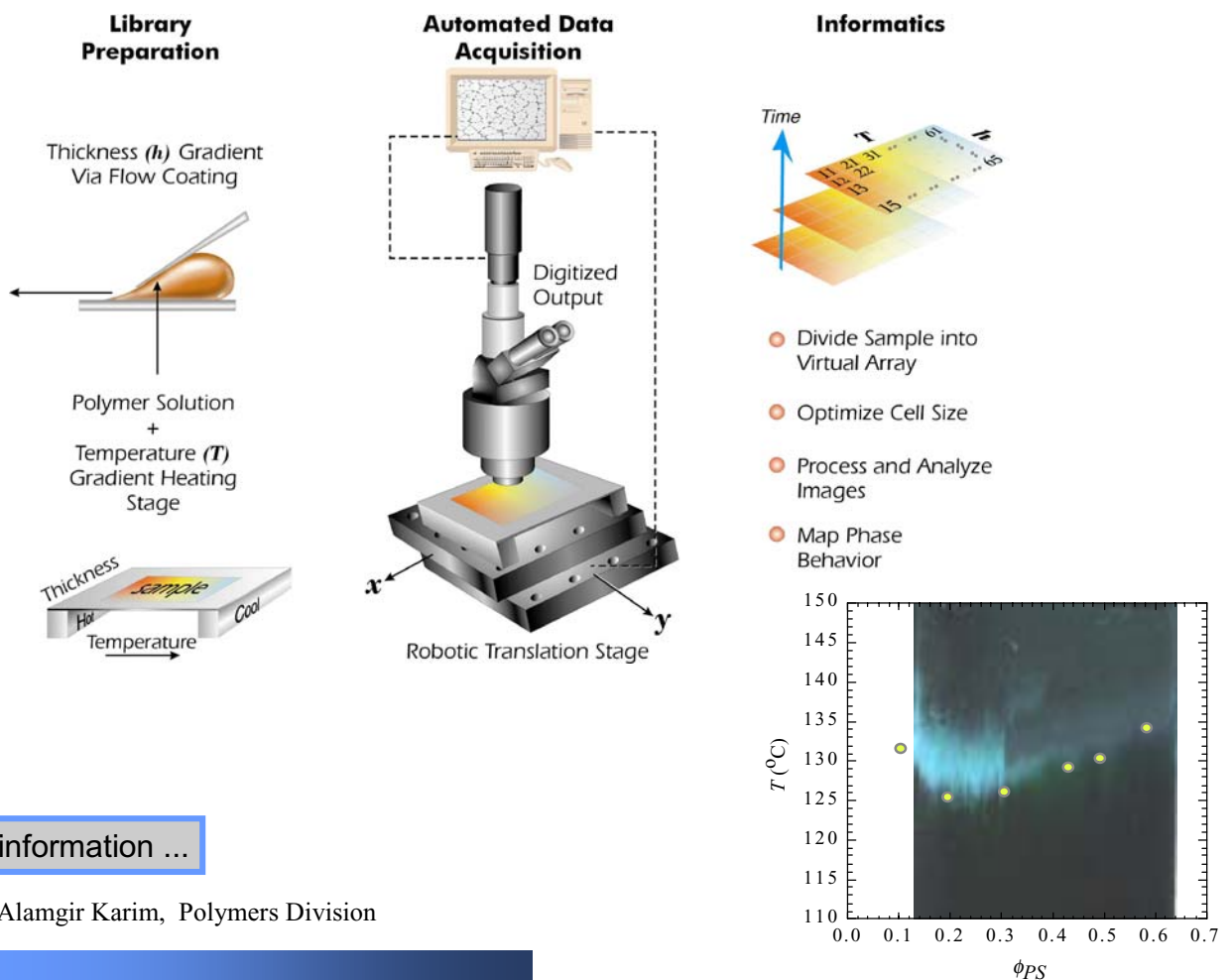
- Important factors influencing polymer blends phase behavior include effects of added compatibilizer, organic molecules, and inorganic fillers. Process variables such as temperature, supercritical fluids, in-situ reaction, polymerization, and cross-linking affect the thermodynamic and kinetic miscibility of polymer mixtures.

- Research Strategy

- The approach is to develop combinatorial methodology for applying continuously varying composition gradients of miscible and immiscible polymer blends including additives, and utilize spectroscopic characterization techniques for quantitative determination of local composition, while measuring phase boundary by automated microscopy under typical applied processing conditions.

- Research Highlights

- The composition-temperature phase boundary was evaluated and validated for model PS/PVME blend system. A prototype composition mixing apparatus has been developed for the purpose, that also allows for the introduction of suspended nanoparticles and additives to study their effects on phase miscibility.



For more information ...

Alamgir Karim, Polymers Division

Biocompatibility assay

- Critical Issues

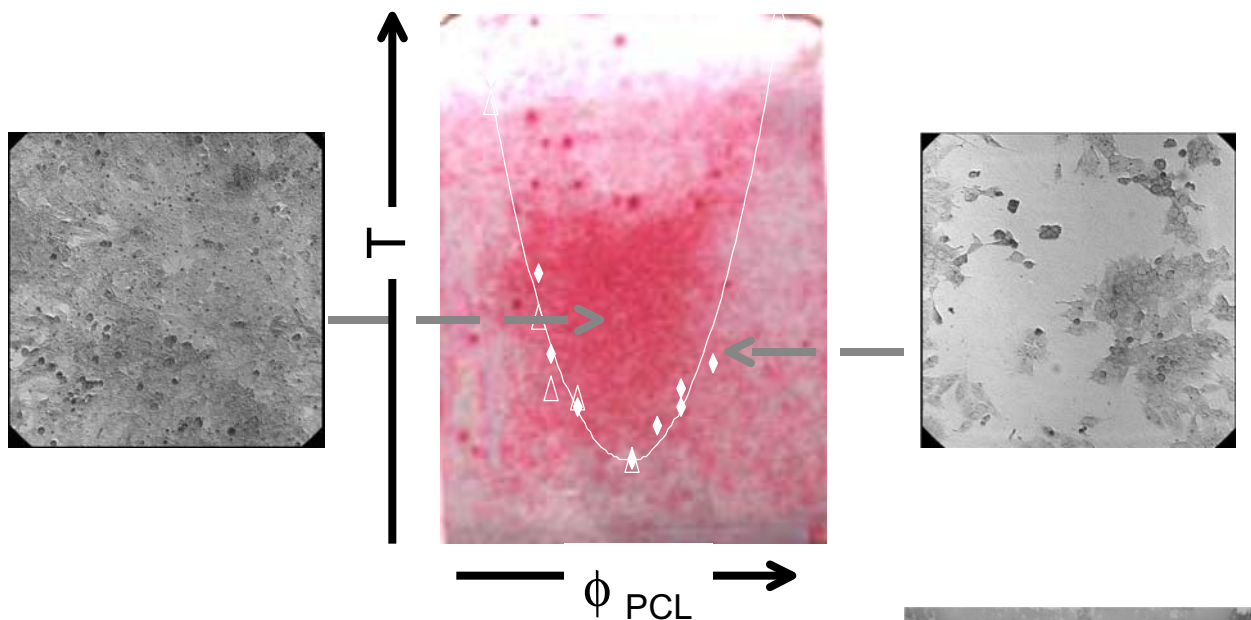
- It is widely perceived that biomaterials will become the dominant focus of materials research in the near future. Critical research areas are expected to be regenerative bioactive materials, self repair of biomaterials and implants adaptive to physiological conditions, determining in vivo performance and limitations of biomaterials, and development of novel bioactive fixation techniques.

- Research Strategy

- The combinatorial method will be advantageously used to assay biocompatibility of polymer surfaces prepared using surface assembly techniques with systematic variations of topography, chemical and geometrical patterning, hydrophobicity, charge and bioselectivity. Microscopy based high throughput screening tools will identify comparative biocompatibility as measured by protein adsorption and cell growth, adhesion and differentiation. A cell culturing laboratory has been constructed in the Polymers Division.

- Research Highlights

- Osteoblast cells were cultured onto morphologically and compositionally phase separated polymer blend surfaces of PCL/PLA, covering the full range of composition from pure PCL to pure PLA. Using staining techniques, the biocompatible region was isolated on the combinatorially prepared and assayed surface. Similar attempts are underway to investigate the effect of surface patterning of biocompatible polymers for unique biocompatibility effects.



For more information ...

Alamgir Karim, Polymers Division

Control shows uniform coverage on tissue culture polystyrene

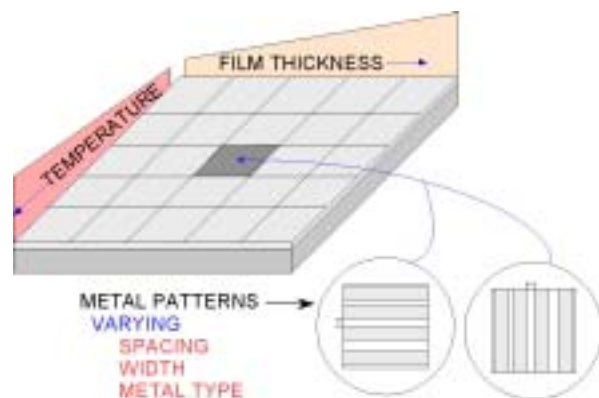
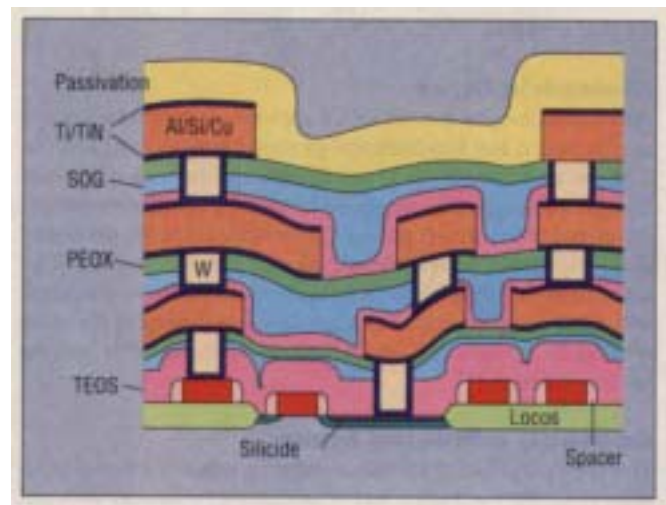
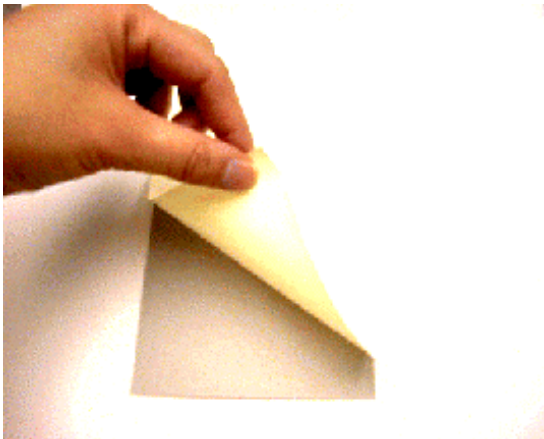
Adhesives

- Critical Issues

- Polymer adhesion is largely dependent upon the coupling of surface and bulk properties, maximizable over a given temperature range relative to the polymer's glass transition temperature. The large variety of end-use applications requires a better understanding of polymer/substrate adhesion and an efficient method of determining optimal polymer/substrate combinations.

- Research Strategy

- We are developing combinatorial methods for measuring interfacial debonding and adhesion of polymer coatings at a variety of interfaces including polymer-metal, polymer-ceramic, polymer-polymer and the polymer-biomaterials interface. The approach will be to design custom debonding and micro- libraries to measure effects of polymer coating thickness and temperature on debonding and adhesion using optical and nanomechanical test methodologies.



For more information ...

Alamgir Karim, Polymers Division

Surface chemistry and modification

- Critical Issues

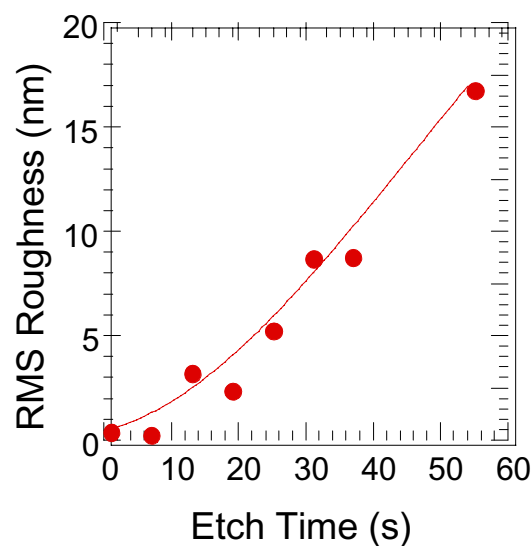
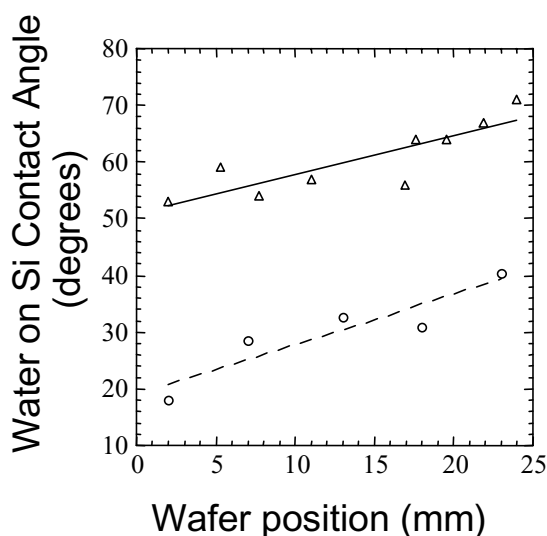
- Methods for effective surface treatments of metals and inorganic surfaces by controlled physical treatment and surface chemistry such as micro to nanoscale roughening, plasma treatment, and surface oxidation are critical to the interfacial properties of polymer coatings.

- Research Strategy

- The objective is to develop a combinatorial methodology for establishing continuous libraries of varying surface properties and quantifying them using optical and contact angle techniques for determining surface chemistry and structure. The next step is to evaluate the effect of surface modification on interfacial binding and structure of polymer layers. Microscopic techniques will include spectrometric infra-red (IR) and scanning probe microscopy (SPM) in its different modes of operation as a powerful secondary screening tool.

- Research Highlights

- The surface hydrophobicity and roughness of inorganic Si wafers was controlled by acid etch using an automated computer controlled apparatus with temperature control. The contact angle and roughness variations across differently prepared wafers was verified using an automated contact angle goniometer and atomic force microscope. Polymer films stability on the modified substrates was subsequently measured and showed a gradient of dewetted structures that correlated well with the chemical variations across the surface.



For more information ...

Semi-crystalline polymers

- Critical issues

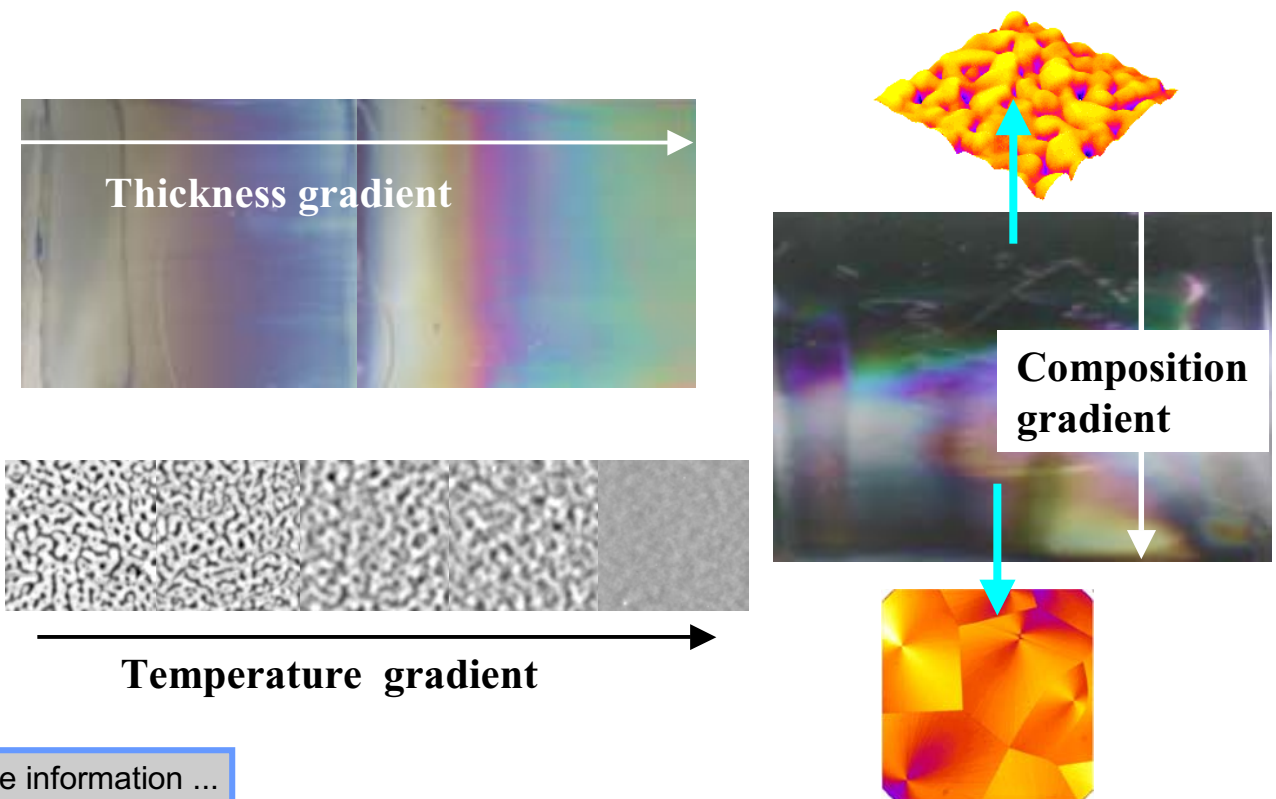
- Controlling the crystallinity and morphology of polymers and polymer blends are important in designing polymeric materials with tailored properties. Mechanisms for controlling crystallinity through nucleating agents and process variables such as degree and rate of undercooling are critical issues.

- Research Strategy

- The combinatorial preparation of crystalline polymer films involving heated solvent flow coating methodology will be developed and modified for including nucleating agents in controlled amounts. Polarized optical microscopy in conjunction with laser light scattering are expected to be primary analytical tools for the high throughput studies using temperature gradient under-cooling stage in reflection and transmission geometry.

- Research Highlights

- Model blend system of a crystalline / amorphous PEO / PMMA was combinatorially investigated as a function of undercooling rate, film thickness and composition in films containing gradients in these parameters. These material and process variables were found to strongly influence the crystalline morphology and optical properties across the film.



For more information ...

Block-copolymer ordering behavior

- Critical issues

- Controlling the morphology of block-copolymers is important in designing polymeric materials with tailored properties since they can be used to produce nanoscale morphologies. For instance, their unique properties in melts, blends and solutions leads to their use in adhesives, emulsifying agents, thermoplastic elastomers, compatibilizers etc. Mechanisms for controlling block-copolymer morphology through surface induced orientation and preferential interactions are important issues.

- Research Strategy

- The reproduction of known symmetric diblock morphological behavior with gradient libraries provides a powerful demonstration of the utility and efficacy of combinatorial methodologies for polymer physical properties characterization. Optical microscopy in conjunction with laser light scattering (under development) using temperature gradient stage in reflection and transmission geometry are expected to be the primary analytical tools for these high throughput studies.

- Research Highlights

- Gradient libraries have been employed to revisit the well-studied phenomenon of lamella formation in symmetric diblock copolymers by analyzing the effect of film thickness on the morphology of PS-b-PMMA thin films on Si substrates. The morphological evolution of the surface lamella with increasing film thickness has been observed within a single library allowing a significant reduction in experimental time. Our combinatorial approach is found to be useful in discovering and characterizing new features of pattern formation in block copolymer films. Specifically, we observe a range of film thickness where the surface remains smooth up to a constant fraction of chain length independent of molecular mass that can be attributed to an increase in the surface chain density in the outer copolymer layer with increasing film thickness. Novel bicontinuous patterns are also observed whose average size scales as an inverse power of chain length.



For more information ...

Alamgir Karim, Polymers Division

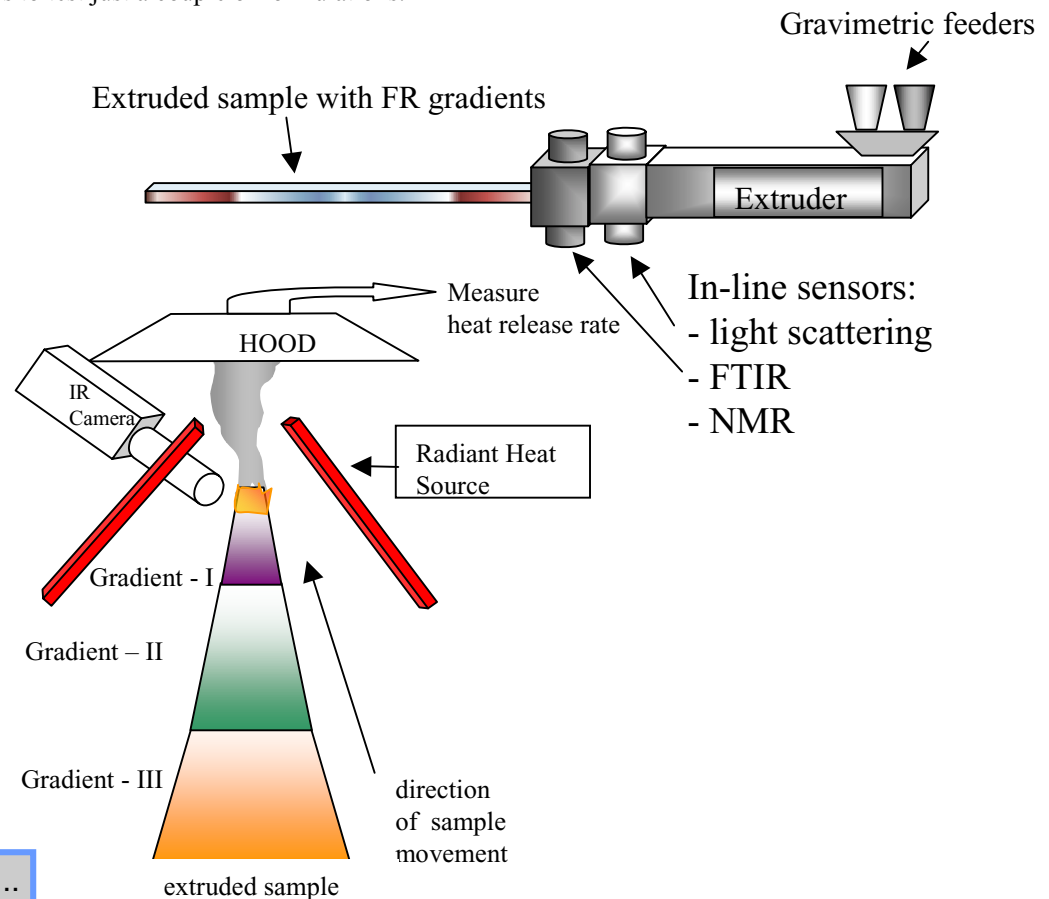
Fire retardants

- Critical Issues

- The U.S. produces about one-third of a trillion dollars in polymer products annually. Most commodity and engineering polymer resins are flammable, and fire code acceptance requirements are most often met using additives. The addition of plasticizers, curing agents, stabilizers, and pigments, which are needed in almost all commercial applications, causes a further deterioration in fire performance. Traditional trial-and-error approaches for reducing polymer flammability are expensive and time-consuming. On the other hand, combinatorial methods provide the opportunity to explore the complex interactions that govern the ultimate performance of multicomponent materials and, at the same time, offer the possibility to effect a significant reduction in the time required to bring new polymer-based products from the laboratory to the marketplace.

- Research Strategy

- High-throughput methods, based on compositional spread and non-contact thermometry, will be developed for the formulation and screening of fire resistant polymer blends and nanocomposites. Shown below is a conceptualization of a continuous flow flame test extruder that will enable researchers to screen hundreds of possibilities, as determined by variations in the relative amounts of critical additives, in the same time it now takes to test just a couple of formulations.



For more information ...

Marc Nyden, Jeffrey Gilman, Fire Science Division

Low Flammability Polymer Blends

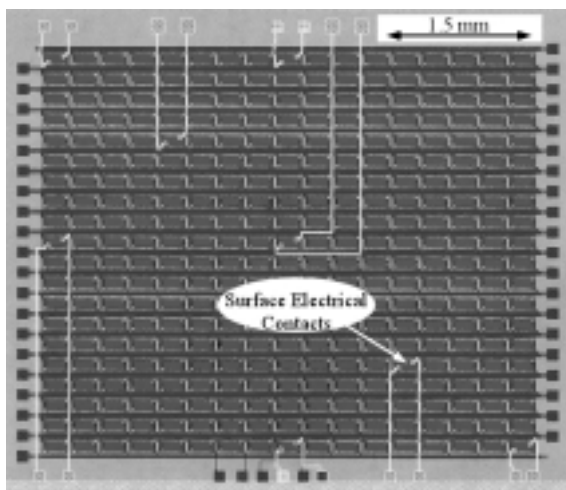
- Critical Issues

- In response to the needs of industry for more efficient research and development tools, we have initiated a research program directed at the development of high-throughput methods for the formulation and flammability screening of multi-component polymer blends and polymer/clay nanocomposites.

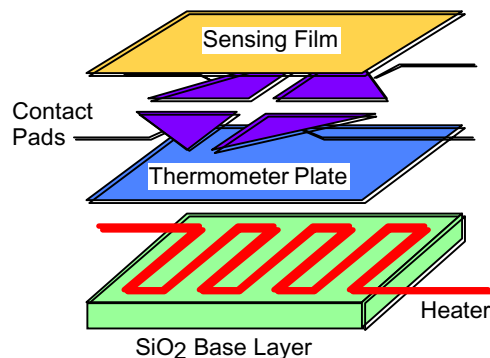
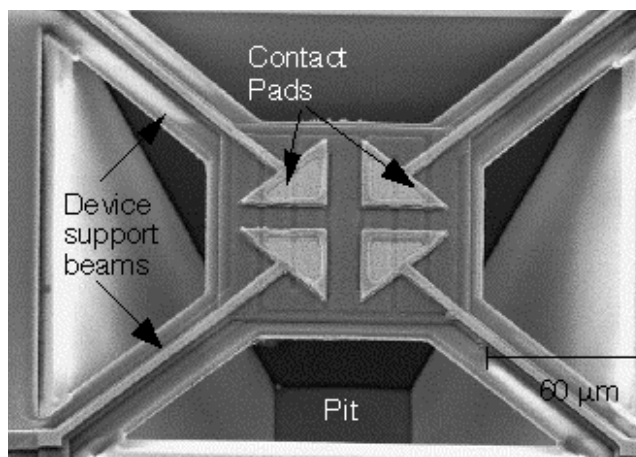
- Research Strategy

- Our first challenge is to adapt the existing technology for parallel synthesis, originally designed for discovery applications in the pharmaceutical industry, to provide the capability to create sample libraries consisting of varying amounts of polymer, clay, solvents, compatibilizers, and other additives. Commercial reactors, equipped with mixers, heaters and filtration capabilities that allow for independent control of the reaction conditions in each vessel, will be exploited in the process of removing solvents and enhancing the mixing between components. Samples of these solvent blended nanocomposites will be extracted and deposited on microhotplate arrays using piezoelectric micro-inkjet technology, electrospray deposition, or flow coating techniques, depending on their size and rheological properties. The material on each element will be heated at a specified rate representative of fire conditions. Flammability performance will be assessed on the basis of correlations between the thermal mass of the sample, as indicated by the power required to maintain the specified heating rate, and the rate of mass loss from representative materials measured by conventional flammability test methods.

340 Element Microhotplate Array



Exploded View of a Microhotplate Element



For more information ...

Marc Nyden and Jeffrey Gilman, Fire Research Division

High-throughput measurements

- Critical Issues

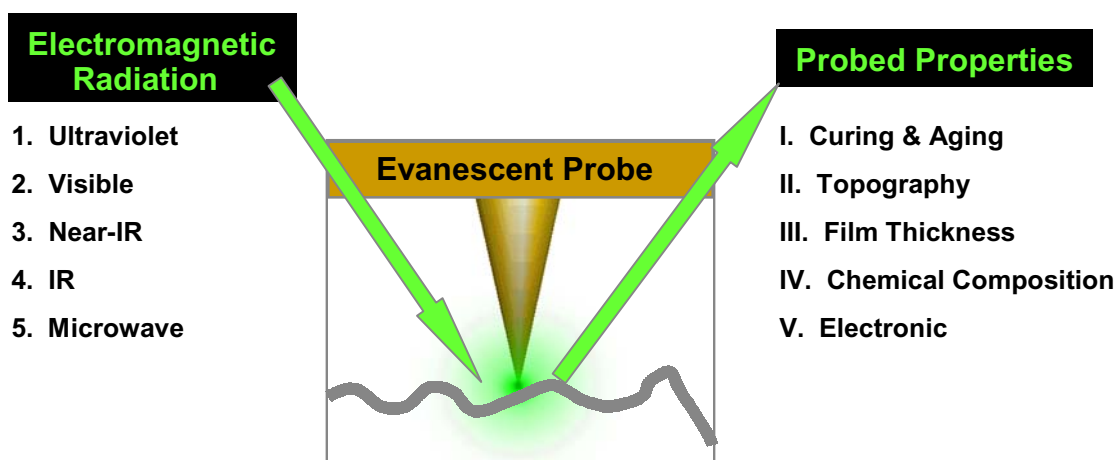
- The challenge is to determine (screen) compositional, structural, and performance characteristics of diverse samples in a time efficient fashion: need to measure in a day what you can make in a day

- Research Strategy

- The objective of our research is to develop microscopy methods for the simultaneous chemical, electrical, optical, and physical analysis of chemically textured libraries. Our approach will be to develop ultra-broadband scanning evanescent probe microscopy and spectroscopy, with the ability to simultaneously measure the topographic structure, dielectric/electrical properties, chemical composition, tribology, optical properties as well as other compositional and performance properties. This multitasking capability will provide a means of overcoming screening bottlenecks while still providing the essential information that is needed to take full advantage of high-throughput experimentation and discovery.

- Research Highlights

- Current research efforts have focused on demonstration of various contrast mechanisms that provide the needed composition and performance measurements. We are moving many chemical and spectroscopic diagnostics to smaller length scales ($< 100\text{nm}$), higher sensitivity and shorter acquisition times. With one probe structure, a sharpened metal tip, measurements will be made throughout the electromagnetic spectrum (from radio frequencies to ultraviolet) as well as on surface tip interactions (friction and shearing forces).



For more information ...

Stephan Stranick, Richard Cavanagh, Surface and Microanalysis Science Division

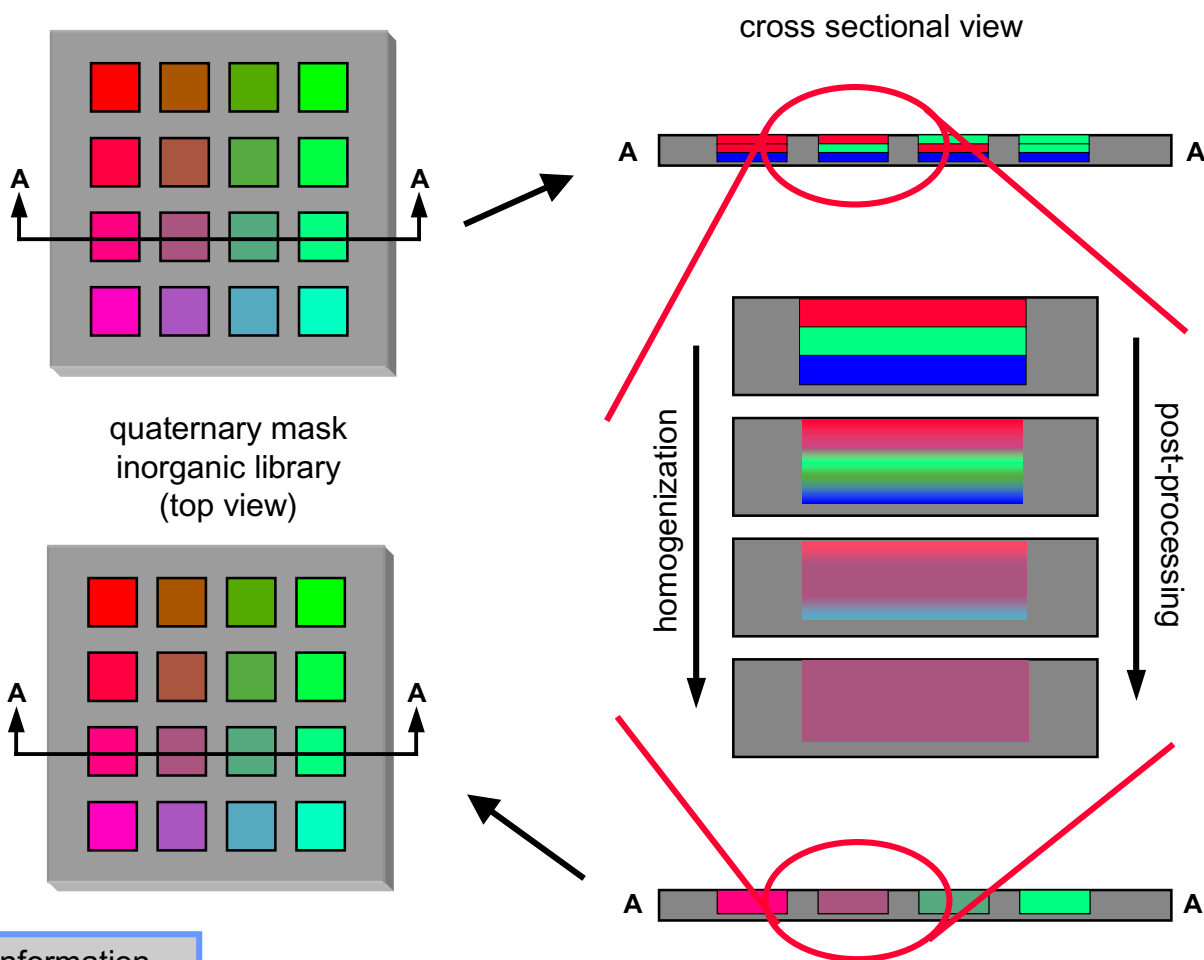
Library production support

- Critical Issues

- The production of inorganic combinatorial libraries using repeated mask-based deposition of thin films assumes subsequent processing will homogenize the components. In many specific systems the efficacy of this homogenization has not been studied carefully.

- Research Strategy

- The objective of this research is to determine the chemical and structural inhomogeneities of processed libraries synthesized by repeated deposition of thin films of inorganic components. The library cells are cross sectioned and analyzed in an analytical electron microscope using energy-dispersive x-ray spectrometry, elemental mapping, and electron microdiffraction. Information about the phase purity, degree of interdiffusion, and residual chemical gradients in the sample allow informed development of library production and processing.



For more information ...

Laser scanning microscopy

- Critical Issues

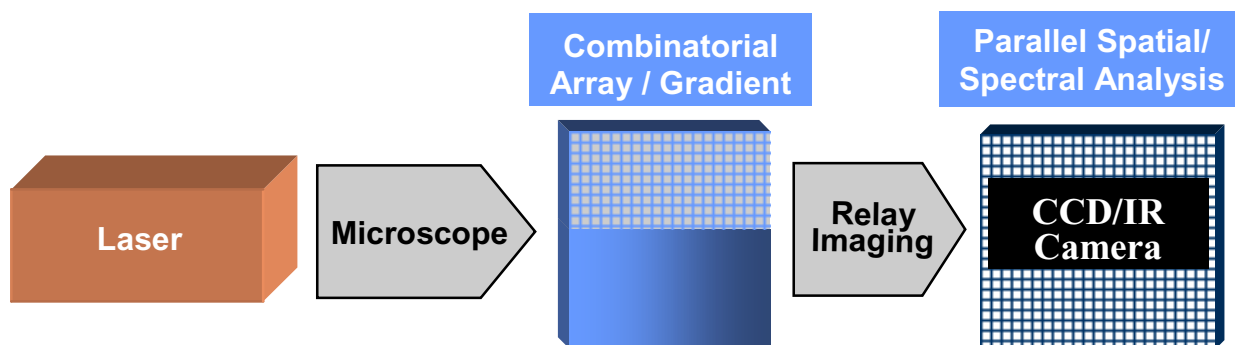
- The application of combinatorial methods to the advanced materials, catalysts, polymers, and specialty chemical industries requires the development of selective methods for identification and analysis of material composition and properties amid complex physiochemical environments. Additionally, full realization of the benefits of combinatorial synthesis demands that these diagnostic methods be highly parallel in nature.

- Research Strategy

- Our objective is to i) develop robust optical probes of chemical composition based on the parallel acquisition of spatially resolved vibrational spectra (Raman and/or IR absorption) and ii) image a series of prototype arrays/libraries of chemically nanostructured components amenable to combinatorial synthetic strategies and optical screening.

- Research Highlights

- Initial efforts have focused on the design and construction of a scanning Raman microprobe system that will be extended to allow collection of spectrally resolved, confocal Raman images. The versatile optical design will also allow for facile coupling to a state-of-the-art infrared laser source and parallel detector for confocal infrared microscopy. By taking advantage of the high degree of depth (Z) resolution available in confocal microscopy, we will develop methodologies for the non-destructive, chemical sectioning, or depth profiling, of 3D chemically inhomogeneous samples.



For more information ...

Chemical microscopy by SIMS

- Critical Issues

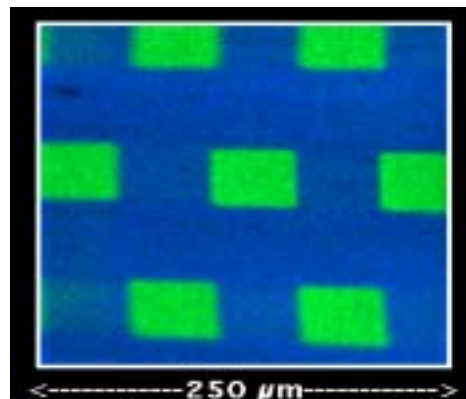
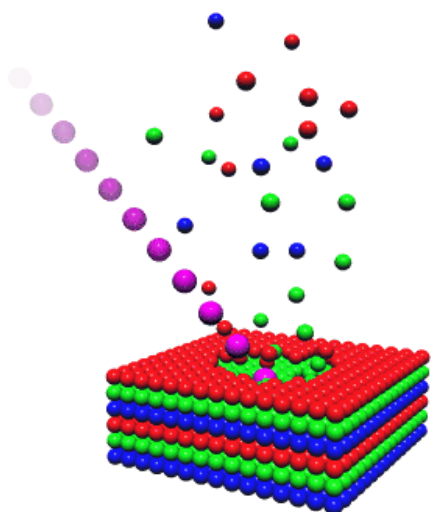
- The use of high-throughput combinatorial synthesis is of growing interest to the chemical and advanced materials industries for development of new polymer, optical, catalytic, electronic and magnetic materials. Of critical importance is the development of metrology tools for the rapid characterization of the elemental and molecular composition of both bulk and thin-film combinatorial array structures.

- Research Strategy

- The objective of our research is to apply secondary ion mass spectrometry (SIMS) imaging for high-speed elemental and molecular analysis of combinatorial arrays at micrometer spatial resolution. A unique feature of the NIST SIMS instrumentation is the ability to generate chemical maps in parallel providing very rapid screening of arrays. SIMS is ideally suited for the compositional characterization of the chemically complex materials produced using combinatorial methodologies because of its ability to detect both elemental and molecular species with a spatial resolution better than 1 μm and an in-depth resolution approaching 1 nm.

- Research Highlights

- The Analytical Microscopy Group has extensive experience in applying state-of-the-art SIMS tools for the quantitative chemical microscopy of elemental species on the micrometer spatial scale. In addition to elemental analysis, we have also developed a capability for “molecular imaging” where the spatial distribution of a compound of interest on a sample surface can be determined by ion-induced desorption of characteristic molecular ions. This is demonstrated in the figure below which shows a SIMS image of a patterned micro-array of DNA probes on a gold surface. The green and blue areas show the detected locations of the thymine- and cytosine-containing probes, respectively. Another unique feature of SIMS is a capability for probing the composition of an array element as a function of depth. This may be relevant for the characterization of combinatorial multilayer and superlattice structures.



For more information ...

David Simons, Surface and Microanalysis Science Division

Data mining: Searching for patterns

- Critical Issues

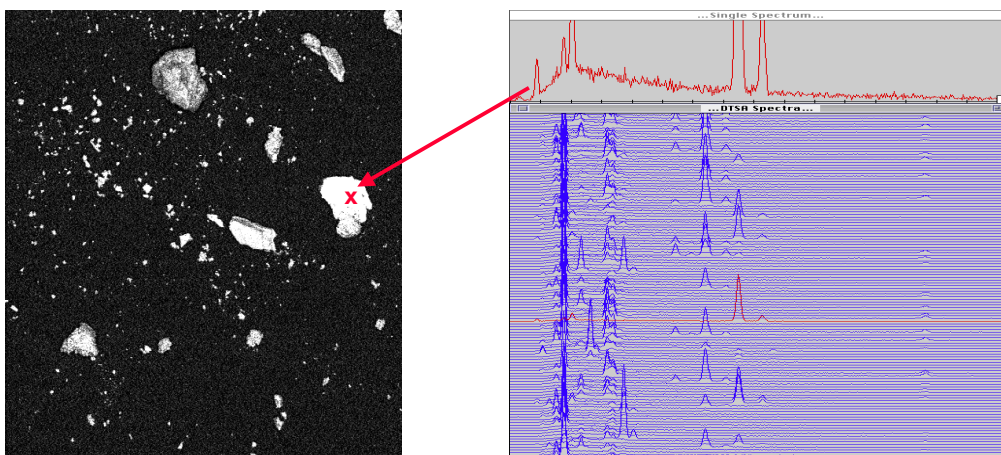
- The searching of data resulting from high-throughput experimentation often involves examination of large data sets with hundreds to thousands of features. Each feature may have one or more morphological and/or spectral images in addition to other elemental/chemical data such as x-ray spectra. We wish to classify these features using these data, where their spectra, morphology or chemical signature may not be known ahead of time.

- Research Strategy

- Our research involves development of software to automate the collection and integration of such data sets, and the development of data analysis tools for rapid visual surveying and searching. These tools are developed for Macintosh and PC platforms.

- Research Highlights

- One of the tools we are developing is the Poly Plot Package (PPP), which displays hundreds of x-ray spectra in a cascade plot, for ease of comparison. Analogous to a postage stamp display for images, the spectra can be 'clicked' to select, mark and display spectra. An individual wavelength can be clicked, and the spectra sorted by amplitude at that one wavelength. Adjacent spectra in a sorted plot can be selected and placed in a group -- these spectra will be similar if selected properly. Two or three dimensional scatter plots of amplitudes of spectra at given wavelengths (representing chemical elements) and chemical and morphological parameters also serve for comparison and selection of groups of features. All plots and images are linked so that groups of features selected in one display mode are also labeled in all other images and data sets. Together the cascaded and scatter plots, the images of the selected groups of features, and the summary statistics of each group, aid the researcher in classifying patterns in the features and finding the features of interest.



For more information ...

David Bright, Surface and Microanalysis Division

Quantitative spectral imaging

- Critical Issues

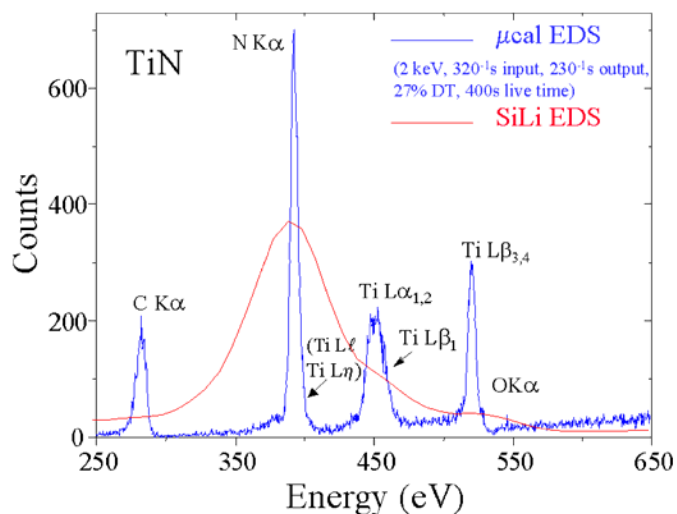
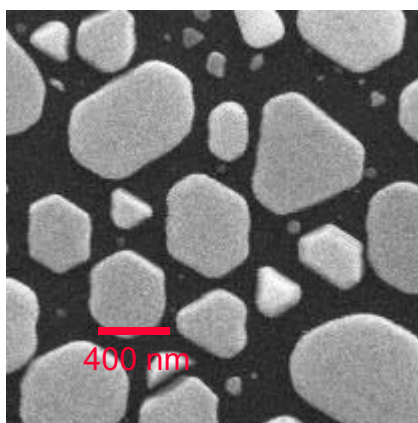
- For many of the non pharmaceutical industries that have or are currently developing combinatorial programs one of the critical issues is the rapid characterization, at high spatial resolution, of both bulk and thin-film array structures for quantitative elemental composition, and chemical information.

- Research Strategy

- The objective of our research is to develop electron microscopy methods for the simultaneous high-speed chemical and elemental spectral imaging using x-ray and Auger electron signals at submicrometer spatial resolution as well as to develop methods to rapidly process these images to obtain quantitative compositional information. As part of this effort we plan to utilize emerging x-ray detector technologies such Si-drift and microcalorimeter detectors

- Research Highlights

- The microanalysis research group has recently installed a unique state-of-the-art scanning Auger microprobe with a UHV field emission source that makes it possible to analyze ultra-fine features (< 50nm) without producing surface contamination. In addition the instrument is equipped with x-ray photoelectron spectroscopy and ion-gun sputtering capabilities. Full x-ray analytical capabilities including wavelength and energy dispersive detectors are unique to this instrument. The suite of analytical techniques combined in this instrument make it particularly well suited to provide the elemental and chemical information critical to the emerging analytical needs of industries doing high throughput experimentation.



For more information ...

John Armstrong, John Small, Surface and Microanalysis Division

Dielectric oxide thin films

- Critical Issues

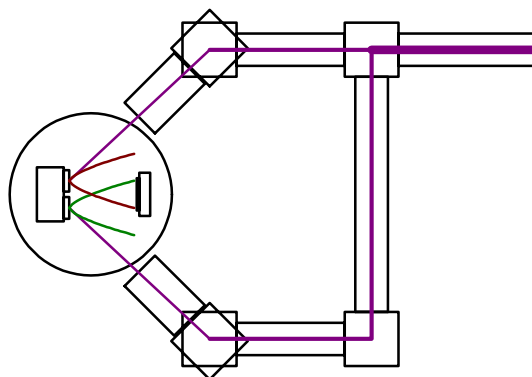
- The explosive growth of the wireless communications industry has spurred a demand for improved thin film materials with higher dielectric constant and lower loss. Detailed information on the effect of processing and composition on the dielectric properties of candidate materials is needed to identify promising materials for the next generation of wireless devices.

- Research Strategy

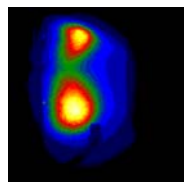
- The approach is to: 1) develop rapid prototyping tools for the fabrication and characterization of dielectric oxide thin film libraries; and 2) utilize these tools to generate processing/composition/dielectric property maps for materials systems of interest for wireless communications. The initial dielectric material selected for these studies is BaTiO_3 - SrTiO_3 , a leading candidate for voltage tunable devices.

- Research Highlights

- Thin film BaTiO_3 - SrTiO_3 (BT-ST) libraries of varying composition have been fabricated by a novel dual-beam, dual-target pulsed laser deposition process. Interaction of the two laser plumes results in a film of continuously variable composition, as confirmed by electron microprobe analysis measurements in CSTL (*NIST Chemical Science and Technology Laboratory*). Film thicknesses have been mapped by a semi-automated reflectance mode spectrophotometry technique. The dielectric properties of the libraries will be measured by a high-throughput scanning evanescent microwave microscope recently developed in CSTL. The film deposition process is broadly applicable to other ceramic materials as well as metal and metal/ceramic composites.



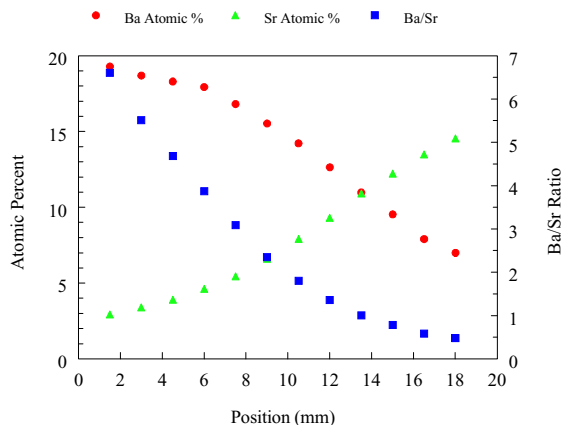
Dual-beam, dual-target system.



False color image of dual-beam deposition process



BT-ST library film on a 2" Si wafer



Composition profile of a BT-ST library film

For more information ...

Peter Schenck, Debra Kaiser, Ceramics Division

Metallization of GaN semiconductors

- Critical Issues

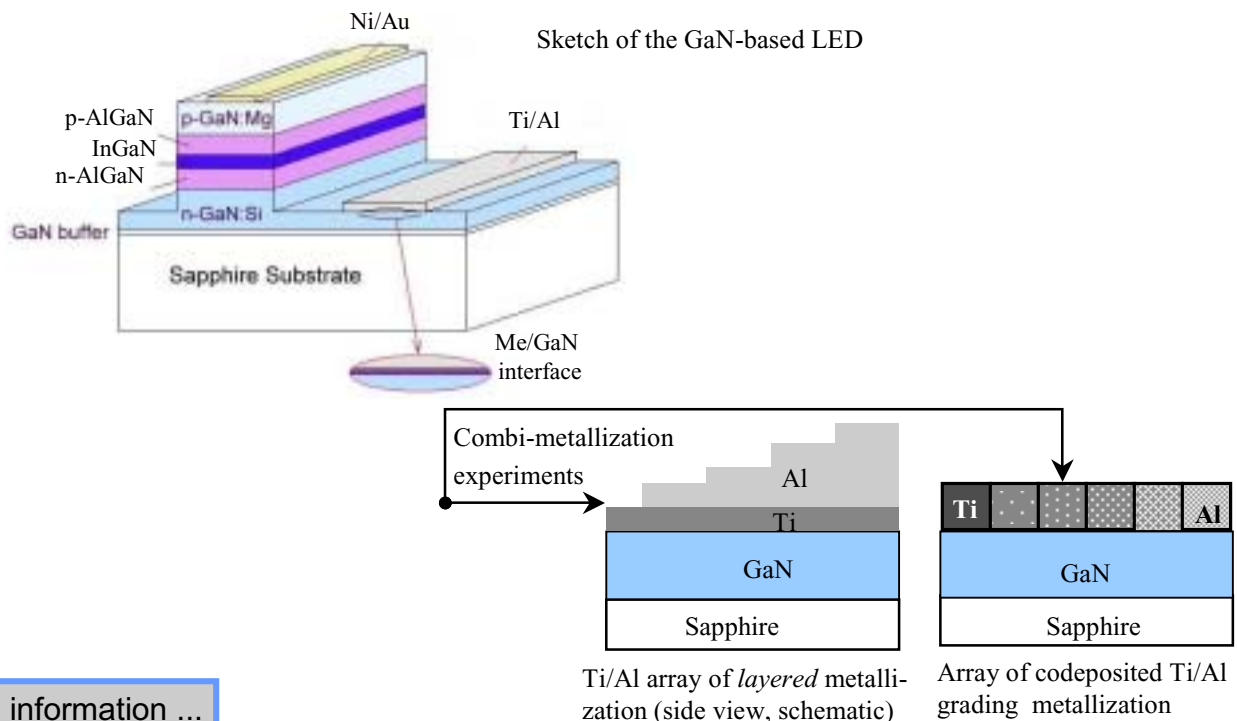
- Gallium nitride based wide band-gap semiconductors find increasing applications in optical (blue LED's, lasers, detectors) and microelectronic (high-temperature, high-power, and high-frequency transistors) devices. However, the performance of GaN-based devices is limited by several materials and engineering problems, including the difficulty in making low-resistance, thermally stable metal contacts, especially to p-type GaN and AlGaIn alloys.

- Research Strategy:

- The approach is to: 1) better understand and quantify the relationship between the resistance of metal contacts to GaN and the fundamental compositional, microstructural and electronic properties of the metal/semiconductor interface and the near/interface GaN layer. The choice of layer composition sequence in the arrays will be guided by thermodynamic and kinetic modeling of selected metal/GaN systems.

- Research highlights:

- Current research focuses on library design for contacts to n-GaN, including the optimization of contact resistivity as a function of metallization with variations of: i) semiconductor properties (doping levels, surface preparation); ii) metallization scheme (Ti/Al layer sequence, metal layer thickness and alloy composition); iii) processing schedule (annealing temperature, time, and ambient gas) .Working with the NIST Chemical Sciences and Technology Laboratory, we will develop methods to identify library elements with promising properties.



For more information ...

Albert Davydov, William Boettinger, Metallurgy Division

TEM studies of combinatorial libraries

- Critical Issues

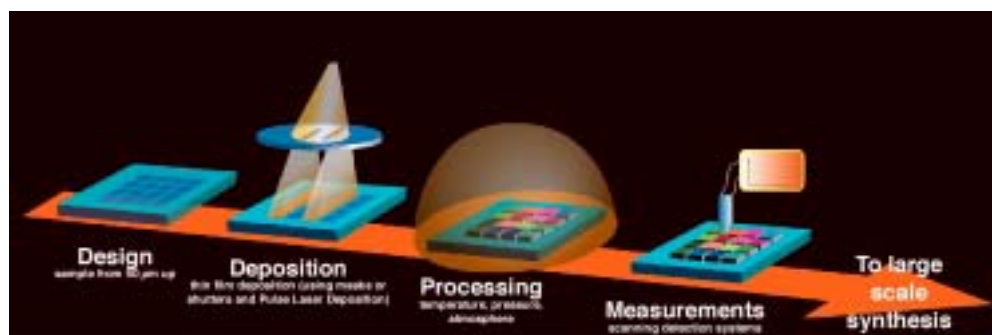
- In the search for dielectric materials for use in modern microwave communication technology, a variety of complex oxides with different chemistry and structural states are under consideration. With the ability to measure locally the relevant dielectric properties, combinatorial “libraries” are desired which are designed to either search for an optimal set of dielectric properties or study fundamentals of the relationships between crystallo-chemistry and polarization in complex oxides.

- Research Strategy

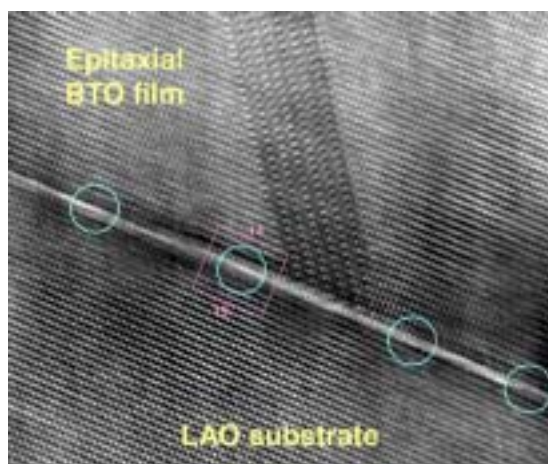
- In a collaborative effort between NIST and the University of Maryland (Prof. I. Takeuchi), we are using transmission electron microscopy (TEM) to investigate microstructural evolution in (Ba,Sr)TiO₃ thin films fabricated from amorphous precursor multilayers consisting of TiO₂, BaF₂/BaCO₃, and SrF₂/SrCO₃. The films are deposited by pulsed laser deposition (PLD) technique on a single crystal substrate using precursor materials as a target.

- Research Highlights

- Our preliminary results of high resolution TEM have demonstrated that rather high quality epitaxial perovskite film could be formed by the technique of amorphous precursor multilayer mixing, even with fairly low temperature anneals. The lower figure shows an example of high-resolution imaging obtained for such a BST film



BaTiO₃ formed via mixing of
BaF₂, TiO₂ multilayers



For more information ...

Leonid Bendersky, Metallurgy Division

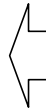
Polarized light scattering

- Critical Issues

- Light scattering is the basis for a variety of high throughput screening techniques used by industry to characterize materials. Scattering is sensitive to interfacial roughness, particulate contaminants, subsurface defects, and material inhomogeneity. However, measurements of scattering intensity suffer from lack of specificity, and the inverse scattering problem is difficult, if not impossible, to solve. However, recent work has shown that information contained in the polarization properties of the scattered light allow many of these scattering mechanisms to be distinguished. These findings suggest that new high throughput screening methods based upon polarized light scattering could be developed.

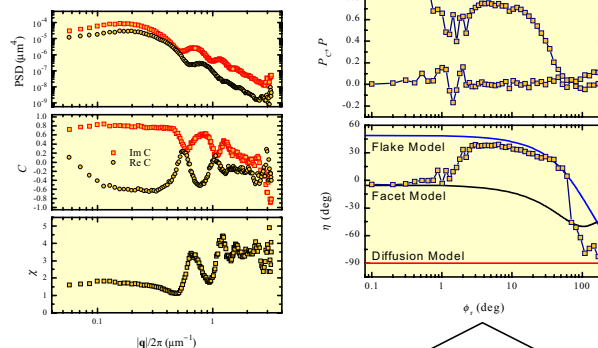
- Research Strategy

- The success of light scattering methods depends upon the availability of accurate theories for scattering. These models are developed with an aim of learning which model parameters affect which scattering parameters. Model systems are developed in the laboratory and used to test the validity of the theories. Instrumentation is also developed to demonstrate the application of polarized light scattering techniques for specific applications.

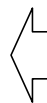


The Goniometric Optical Scatter Instrument is a high angular-resolution tool for characterizing light scattering by materials.

The roughness of both interfaces of a diblock-copolymer layer on a rough silicon layer, measured with light scattering ellipsometry.



Polarization of light scattered by a pearlescent paint showing angles at which different scattering mechanisms dominate.



The Multidetector Hemispherical Polarized Optical Scatter Instrument is a prototype for a high-throughput tool for inspecting materials.

For more information ...

Thomas Germer, Optical Technology Division

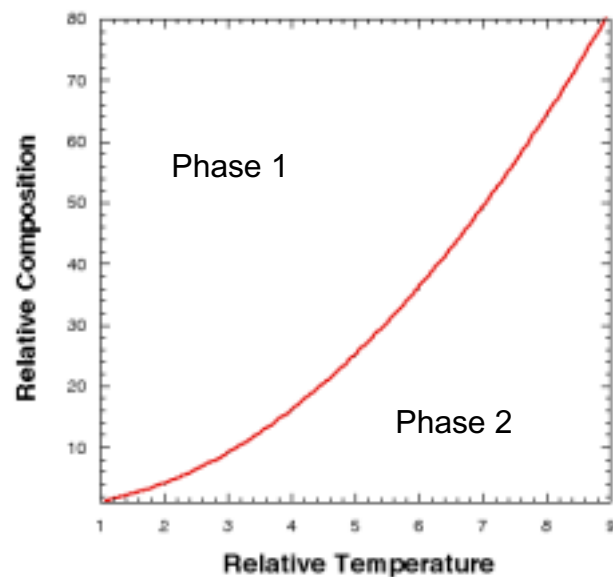
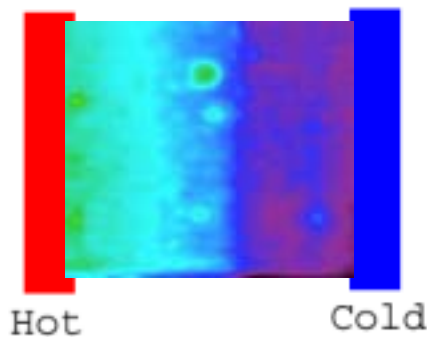
Thermal properties screening

- Critical Issues

- The challenge is to achieve desired function and properties such as mechanical, optical or thermal behavior in polymeric structures by manipulation of fillers, polymer blends, microstructure and processing conditions in manufacturing.

- Research Strategy

- The goal is to develop combinatorial methods for investigating filled and/or blended polymeric systems where a blend composition or the amount of filler must be processed within a thermal boundary in order to produce a phase with desirable properties. The phase envelope which yields these properties can be screened by viewing changes in thermal properties. An automated system is under development that uses a number of different heating methods and couples this with infrared microscopy which enables the viewing of heat flow, and therefore thermal properties, tailored to the application.



For more information ...

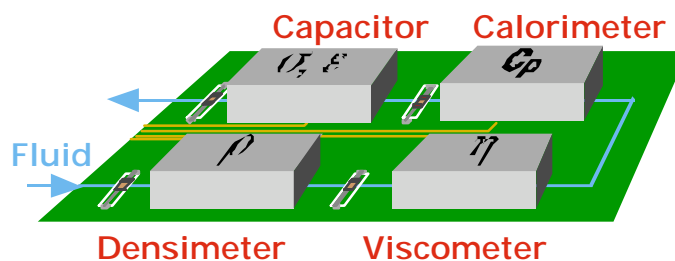
Fluid properties microanalysis

- Critical Issues

- High throughput screening and combi-chemistry generate a myriad of new compounds whose thermophysical properties (density, heat capacity, viscosity, dielectric constant etc.) cannot be measured at the production rate with conventional techniques. Massive reduction of measurement time is required.
- Besides measuring all properties of a few fluids over wide ranges of pressure and temperature, measure selected key properties of many fluids and mixtures at ambient pressure and temperature → combinatorial approach.

- Research Strategy

- Reduce sample size to speed up measurements. Initial target volume is 50 μL . Reduction by factor of 60 from smallest samples presently required.
- Develop continuous-flow microsensors for properties measurements on small sample volumes. Most conventional methods use static sample batches.
- Focus on a profile of key properties: density, vapor pressure/heat of vaporization, specific heat capacity, viscosity, electrical conductivity and permittivity. For mixtures, include heat of mixing and volume of mixing measurements.
- Microsensors for thermophysical properties of fluids have enormous market potential, e. g. *in vivo* viscosity measurements of blood.
- Combine microsensors into high-throughput continuous-flow thermophysical properties analyzer for serial measurements of the key properties on the same sample. Analyzer will have the size of a digital voltmeter combined with a laptop computer.
- Connect analyzer in series with high-throughput reaction screening and mixture preparation units.
- Harvest thermophysical properties data from combinatorially synthesized compounds to create properties libraries for the development of quantitative structure-properties relationships (QSPR).



Conceptualization of a continuous flow arrangement of thermophysical properties microsensors.

For more information ...

Service life prediction

- Critical Issues

- Current methods rely on outdoor exposure to determine service life. In the modern multi-component formulations, such as automotive coatings, the complex interactions are not explored until costly failures have occurred. This leads to long product development times and large liability exposures for new or modified formulations.

- Research Strategy

- Develop rapid high throughput screening tools using a reliability-based cumulative damage model to assess how the complex interactions between components will affect in-service performance of new materials. This involves generating high flux controlled temperature, humidity, UV wavelength and dose exposures for coating samples as well as monitored outdoor exposures.

- Research Highlights

- Current research efforts have focused on industrial based formulations such as automotive or aircraft coatings, composites and sealant. We have developed a very high flux integrating sphere that can deliver 1-65 “suns” of uniform UV radiation simultaneously to 32 individually controlled temperature, humidity, and UV exposure chambers. Each of these chambers have been designed to accommodate a wide variety of samples requirements ranging from simulated deep space to cyclic mechanical stressing. To analyze the vast richness of data generated by the exposure device several fully automated spectrometers have been interfaced to an advanced sample positioning table. These unique capabilities allow us to spectroscopically map over 30 samples/day. Each sample will contain a entire library of information about the interaction of two process or composition variables exposed to a specific environmental condition. This system will allow for rapid service life prediction and the compression of product development time.



For more information ...

Chris White, Building Materials Division

Microhotplate array platforms

- Critical Issues

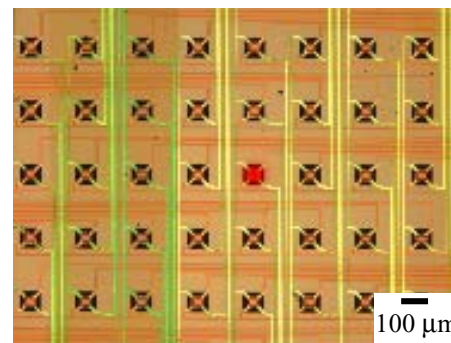
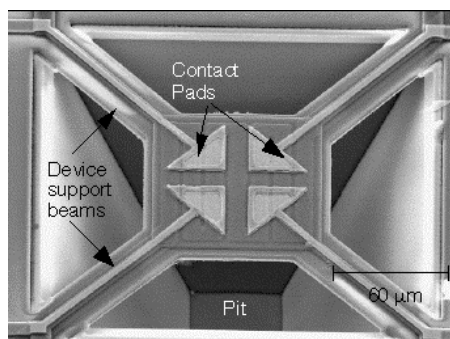
- Temperature is one of the most important parameters to control in fabricating and performance-testing materials. Parallel studies of multiple microsamples, each with its own temperature controllable substrate, can offer an efficient method for developing processing-performance correlations that permit materials optimization for a wide range of technologies, including catalysis, electronic materials, sensing, polymers, and many others.

- Research Strategy

- Microdevices called “microhotplates” have been designed and constructed using surface-micromachining of silicon. These small ($\approx 100\ \mu\text{m}$) devices can be rapidly heated ($\approx \text{ms}$) using built-in resistive heaters, and circuitry can also be included on each microhotplate to measure temperature and electrical characteristics of samples deposited over top-surface microelectrodes. The microhotplates can be easily replicated into microarrays with 10's or 100's of thermally isolated and individually addressable elements. The nominal temperature range is from $20\ ^\circ\text{C}$ to $500\ ^\circ\text{C}$, or higher. Samples can be processed onto the microsubstrate elements under a matrix of fixed or time dependent temperature programming, and the same methods can be used in evaluating the temperature dependent performance of the microsamples. The approach is particularly valuable for investigations that benefit from studies on discrete samples, such as one would encounter in developing improved or new catalysts. In addition to utilizing the individual control of temperature in processing and testing, one can also electronically address the microelements for localized electrochemical deposition and interrogation of on-chip sample electrical characteristics. Efforts are underway to expand both on-chip and external probing techniques to meet diagnostic needs in combinatorial studies.

- Research Highlights

- Microarrays of 16, 48 and 340 elements have been constructed and used, thus far, in materials studies that relate primarily to the development of new films for solid state gas microsenors. A variety of techniques for localized deposition of microsamples have been demonstrated on microhotplate arrays, including self-lithographic CVD, addressable electrochemical deposition, drying of sol-gels and suspensions, thermal lithography, masking, and micro-pipetting. Conductive films have been electrically monitored as they grow, and this approach has been utilized for automating sample fabrication. 48-element array studies of oxide-based sensing materials have been completed which demonstrate the use of on-board control and interrogation capabilities to relate film microstructures to sensing performance.

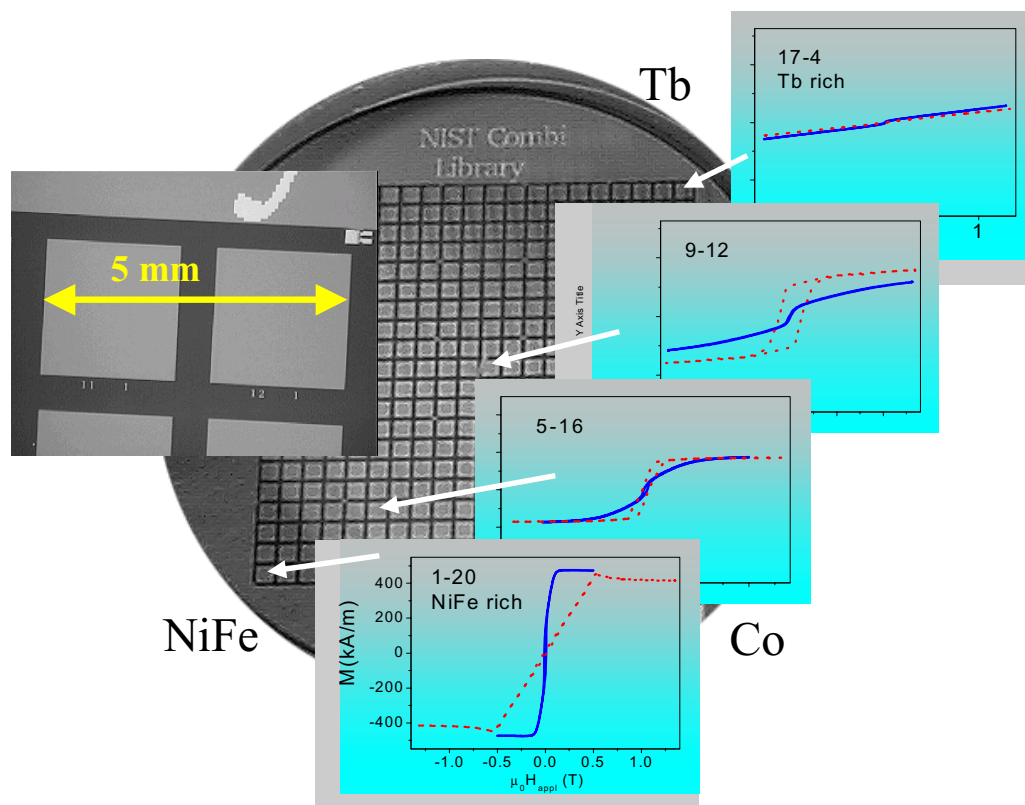


For more information ...

Steve Semancik, Chemical Science and Technology Laboratory

Modeling and characterization

- **Critical Issues:** The technical challenge lies in developing quantitative measurement techniques with micrometer spatial resolution, capable of rapidly scanning areas of a few square centimeters. New theories are required for modeling the elastic response of the library and to develop techniques for inversion of the measured values to determine the parameters characterizing the library.
- **Research Strategy:** The goal is to develop a mathematical model and measurement techniques for evaluating the structural, mechanical, and magnetic properties of libraries of new electronic, magnetic, and polymeric materials.
- **Research Highlights:** A variety of measurement techniques are being developed and adapted for library screening and characterization. Methods include x-ray diffraction, scanning acoustic microscopy, dynamic atomic force microscopy, point-probe ultrasonics, thermal screening, and magneto-acoustic techniques. A theoretical model based upon the elastodynamic Green's functions is being developed that would give the local acoustic response of the library. Libraries of giant magnetostrictive alloys have been fabricated and are one of the combinatorial systems currently under investigation.



For more information ...

Vinod Tewary, Materials Reliability Division

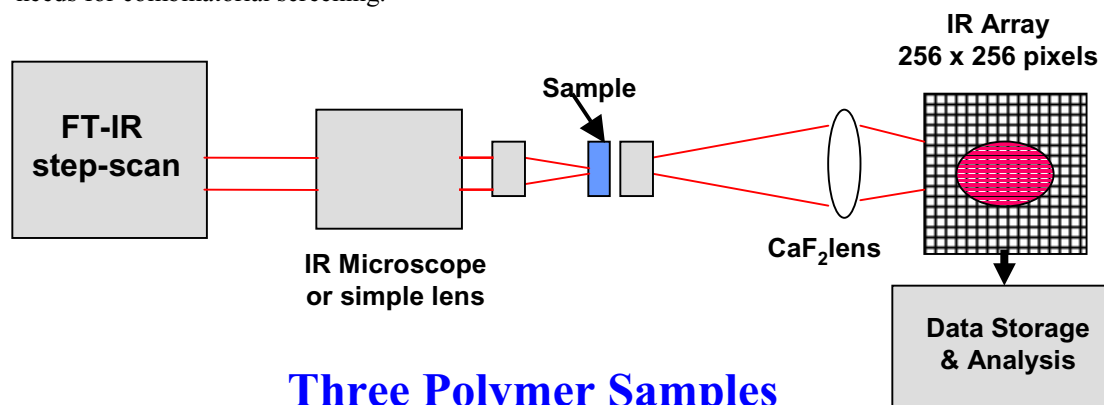
Infrared chemical imaging

- **Critical Issues**

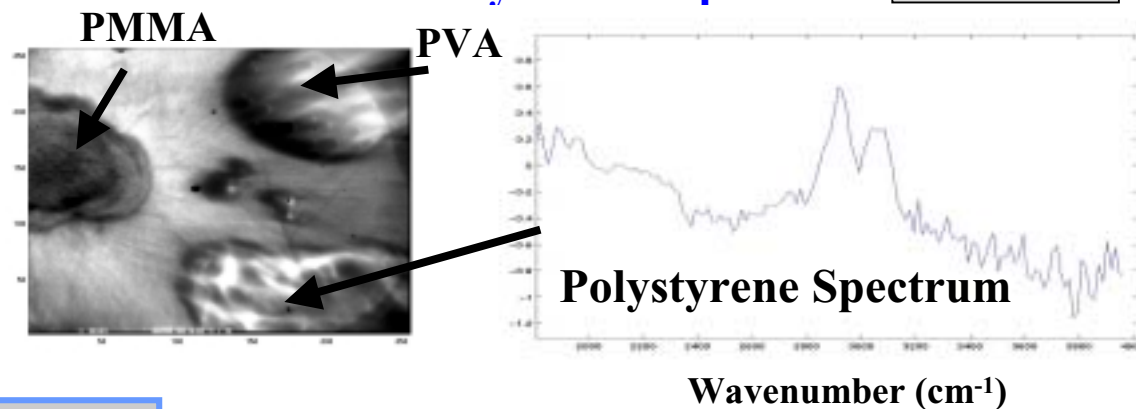
- Development of high-throughput screening methods sensitive to chemical composition and spatial dimensions will become important as varying types of combinatorial systems and libraries are generated. Rapid analysis of novel materials, catalysts, polymers, biosystems and related materials amenable to standard FTIR spectroscopic analysis will require infrared imaging methodologies and computer-aided spectral analysis. These areas demand new information, database and data analysis architectures as well as inter-laboratory standards for comparisons and improved confidence of results.

- **Research Strategy**

- Chemical imaging uses modified step-scan or rapid-scan FTIR benches combined with large-format, two-dimensional infrared focal plane array cameras. We are developing a 256x256 pixel imaging system capable of rapid data acquisition for combinatorial screening. Improvements in data quality and spectral analysis requirements will be explored to quickly assess combinatorial library elements for composition and structural information.
- Tests on gradient polymer composite films, optical density and spectral standards, and related systems will be conducted to characterize and optimize data acquisition and analysis methods pertinent to anticipated needs for combinatorial screening.

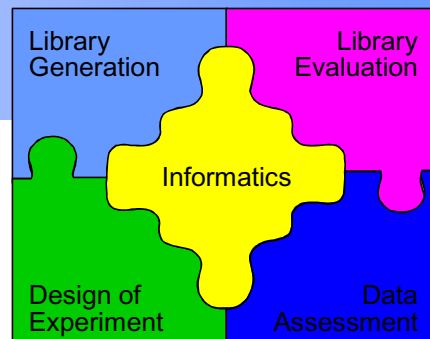


Three Polymer Samples



For more information ...

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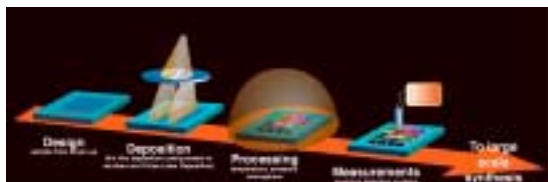
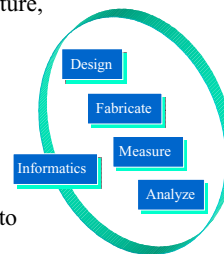
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Growing Impact

- Combinatorial methods have revolutionized the process of pharmaceutical discovery.
- Now, materials scientists are applying the same approach to accelerate discovery and application of new materials.
- Chemical and Engineering News* asks: Are combinatorial methods “Redefining the Scientific Method for Discovery”?

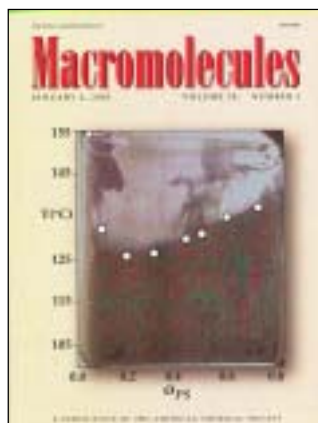
The Combinatorial Cycle

- Design- Define sampling of parameter space (Molecular structure, Composition, Morphology, Processing)
- Fabricate- Synthesis and creation of samples (Continuous gradients, Split and pool, Small/Discrete samples, Patterning)
- Measure- Characterize materials, discriminate performance (Screening hits, Comparative performance, Quantitative data)
- Analyze- Analysis from massive data sets to information and to knowledge (Data management, Visualization, Data mining, Development of predictive models)



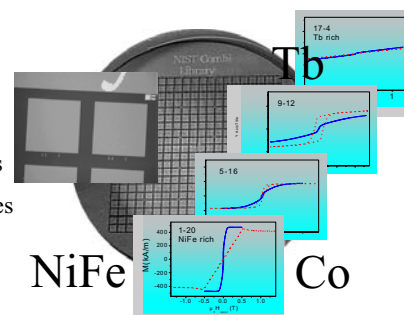
Polymers

- Polymer blend phase behavior
- Biocompatibility assay
- Adhesives
- Surface chemistry and modification
- Semi-crystalline polymers
- Block-copolymer ordering behavior
- Fire retardants
- High-throughput measurements
- Library production support
- Laser scanning microscopy



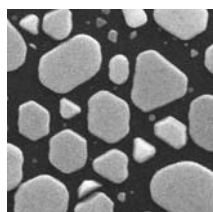
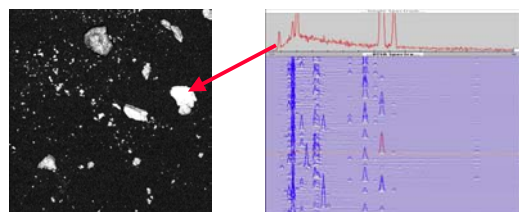
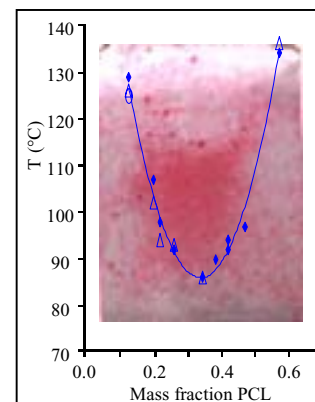
Metals and alloys

- Dielectric oxide thin films
- Metallization of GaN semiconductors
- TEM studies of combinatorial libraries
- Polarized light scattering



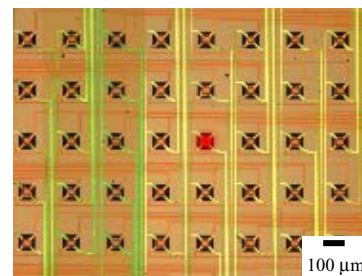
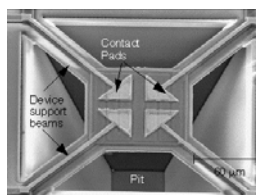
Biomaterials

- Biocompatibility assay
- Surface Hydrophobicity
- Bio-adhesion
- Cell growth and differentiation
- Patterned cellular activity



Chemical Analysis

- Chemical microscopy by SIMS
- Data mining: Searching for patterns
- Quantitative spectral imaging
- Infrared chemical imaging



Thermal Properties

- Service life prediction
- Microhotplate array platforms
- Modeling and characterization