Poster Session Program
NCMC-2
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   [1]Metallurgy Division / [2]Ceramic Division, NIST
   [3]Dept. of Materials and Nuclear Engineering, University of Maryland, College Park, MD

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   [1]Materials Science and Engineering Laboratory, Ceramics Division, NIST
   [2] Dept. of Chemical Engineering, North Carolina State University

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   Dept. of Materials and Nuclear Engineering, University of Maryland, College Park, MD

9. **Combinatorial Approach To Magnetic Metallic Alloys**
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   Dept. of Materials and Nuclear Engineering, University of Maryland, College Park, MD

10. **High-Throughput Characterization of Mechanical Properties in Combinatorial Polymer Libraries**
    Joe-Lahaia Sormana, J. Carson Merideth
    Dept. of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA.

11. **High Throughput Measurements of Epoxy Curing by Confocal and FTIR Microscopy**
    D. Raghavan[1], N. Eidelman[2], A. Karim[3], and E. Amis[3]
    [1]Polymer Group, Department of Chemistry, Howard University, Washington DC;
    [2]ADAHF, PRC, NIST, [3]Polymers Division, NIST.

12. **Combinatorial Mapping of Polymer Film Wettability On Gradient Energy Surfaces**
    Karen M. Ashley[1], Amit Sehgal[2], D. Raghavan[1], and Alamgir Karim[2]
    [1] Polymer Division, Department of Chemistry, Howard University, [2] Polymers Division, NIST.

13. **Rapid-Prototyping and Fabrication of Solvent Resistant Fluidic Devices**
    Joao Cabral, Chris Harrison, Kathryn L. Beers, Alamgir Karim, Eric Amis
    Polymers Division, NIST

14. **Mapping Isotactic Polystyrene Crystallization with High Throughput Methods**
    Kathryn L. Beers, Alfred J. Crosby, Jack Douglas, Alamgir Karim and Eric J. Amis
    Polymers Division, NIST

15. **Block Copolymer Thickness-Gradient Surface Patterns on Topographically Structured Substrates**
    M.J. Fasolka[1], T.A. Germer[2], A. Karim[1], E. Amis[1]
    [1]NIST Combinatorial Methods Center, NIST.
    [2]Physics Laboratory, NIST

Poster Abstracts:

4Wave Inc.

Todd Hylton, Augustus (Trey) Middleton, David Day
4Wave Inc.

4Wave, located in Sterling, VA, provides specialized process equipment, equipment prototypes, and engineering services for researchers involved in the development of novel materials. 4Wave has substantial expertise in the areas of thin films, plasma processing, vacuum systems, equipment automation and equipment design. We work researchers from leading industrial, government and university laboratories to create novel equipment and process solutions. The Combinatorial Methods Center at NIST is as an exciting opportunity for us to develop new products and relationships in this new and growing field. Please visit us to discuss your equipment and engineering needs.

The Use Of Micromachined Arrays For Efficient Materials Processing/Performance Studies.

S. Semancik, C. J. Taylor and R. E. Cavicchi,
Chemical Science and Technology Laboratory, NIST

Surface micromachining of silicon has been used to produce arrays (4, 16, 48 and 340 elements) of devices called microhotplates. The microhotplates are suspended multilayer structures which have lateral dimensions ~ 100 μm, and masses ~ 0.25 μg. They include integrated electrodes for monitoring electrical properties of deposited films, and resistive heaters and thermometry to heat (and cool) between 20 °C and 750 °C with time constants ~ 1-5 ms. We discuss the utility of microhotplate arrays in combinatorial research, focusing on the use of individually-addressable temperature control and microelectrode probing at discrete elements for efficient materials processing/performance studies. Methods used in depositing oxide, metal and polymeric films onto microhotplates (including self-lithographic CVD, and addressable potential control) are described, as are rapid survey capabilities (illustrated for gas sensing materials). Temperature-dependent processing and characterization of TiO_2 and SnO_2 films are emphasized in this presentation, although the indicated approaches can be adapted to examine many different types of materials.

Combinatorial Methods for Group III – Nitride Nano-Optoelectronics

A.V. Davydov[1], L.A. Bendersky[1], D. Josell[1], A.J. Shapiro[1], W.J. Boettinger[1], P.K. Schenck[2], J.E. Blendell[2], K.S. Chang[3] and I. Takeuchi[3]
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The performance of GaN-based optoelectronic devices is limited by several materials and engineering problems, including the difficulty in making highly transparent, low-resistance, thermally stable metal contacts, especially to p-type GaN. The optimization of the best metallization scheme and processing schedule requires extensive experimentation as well a system to organize this information for future reference. The methods of high throughput research are ideal for this problem.
This paper presents the results of on-going combinatorial study of Au/Ni bi-layered metal contacts to GaN aiming at identifying elements with optimum optical and structural properties as a function of Au/Ni thickness and annealing schedule. An array of 88 Au/Ni contact elements of various compositions

was e-beam deposited on 2" n-GaN/sapphire commercial wafer. Post-deposition annealing in a rapid-thermal-annealing (RTA) furnace for 60 s in the 400^{o}C to 900^{o}C temperature range is in progress. Spectroscopic reflectometry and transmission is used for measuring optical properties of metal contacts. XRD and electron back-scattered diffraction (EBSD) techniques is employed to assess crystalline quality of metal films. Morphology of metal layers is characterized with optical microscopy, AFM and plane-view SEM. Comprehensive characterization of combinatorial library of as-deposited and successively heated samples is used to better understand and quantify the relationship between the characteristics of metal contacts (light reflectance/transmittance, crystalline quality and thermal stability) and the fundamental microstructural properties of the metal/semiconductor interface.

Pulsed Laser Deposition as a Combinatorial Tool for Inorganic Thin Films

Peter K. Schenck and Debra L. Kaiser
Ceramics Division, NIST

A pulsed laser deposition (PLD) system has been modified for the production of compositionally graded inorganic thin films. PLD is a good tool for the production of inorganic thin films as congruent vaporization of the target preserves the stoichiometry of the target in the film. The PLD beam delivery system has been modified to include a beam divider which apportions the laser energy between two beam delivery paths with independent adjustment of beam focus and alignment. The normal PLD target has been replaced with a dual target holder which allows for the rotation and rastering of the targets relative to the laser impact points. The combination of rotation and rastering reduces the production of particulate formation due to surface modification. In-situ diagnostics including a high speed imaging system and dual deposition rate monitor are used to adjust the dual PLD plumes to obtain the desired composition gradient in the library film. Systems under study include $BaTiO_3$ – $SrTiO_3$ (dielectric, ferroelectric films for memory devices) and Au –NiO (transparent electrodes).

Spectroscopic Reflectometry as a High Throughput Tool for the Analysis of Combinatorial Thin Films

Peter K. Schenck, Debra L. Kaiser and Albert Davydov
Materials Science and Engineering Lab, NIST

A spectroscopic reflectometer based on miniature fiber optic coupled spectrometers has been assembled to characterize the thickness and optical properties of combinatorial library films. A bifurcated fiber optic probe illuminates the surface under study as well as collects the reflected light from the thin film surface. The film under study is rastered in two dimensions, under computer control, to map the reflectance spectra of the film with a resolution of 0.5 mm. The resulting reflection spectra are periodic in wavelength. The periodicity is proportional to the product of the film thickness and real part of the index of refraction. The depth of the oscillations in the spectra is related to the ratio of the complex index of refraction of the film to the index of the substrate. Analysis of the collected spectra involves fitting the thickness and an appropriate model for the complex index of refraction to the data. Systems characterized include $BaTiO_3$ – $SrTiO_3$ (dielectric, ferroelectric films for memory devices), Au –NiO (transparent electrodes) and Au – Ni on GaN (electrical contacts).

Imaging Chemical and Molecular Nano Properties : Combinatorial NEXAFS, Pictures & Movies

Daniel A. Fischer[1] and Jan Genzer[2]
[1]Materials Science and Engineering Laboratory, Ceramics Division, NIST
[2] Dept. of Chemical Engineering, North Carolina State University

NIST operates a soft-x-ray (C,N,O,F) materials characterization facility to study the structure and chemical nature of diverse materials at the National Synchrotron Light Source (Upton, NY). We utilize polarized soft x-rays as a searchlight for chemical bond identification, orientation and quantification by measuring Near Edge X-ray Absorption Fine Structure (NEXAFS). We describe a new parallel process combinatorial methodology for the production of NEXAFS chemical pictures and reaction kinetics movies of nanostructured materials. Possible applications include the surface orientation and chemistry of continuously graded polymer films and graded or patterned self-assembled monolayers that exhibit tunable surface properties of potential use in nanotechnology. A one dimensional chemical NEXAFS picture of a semifluorinated gradient monolayer is presented that illustrates our current ability to measure chemical bond concentration and orientation of molecules on surfaces.

Adapting Sequential Material Property Techniques for Higher Throughput Experimentation

Steve Robbins and Michael Rusak
Air Products and Chemicals, Inc.

APCI Physical Testing Laboratories routinely provide material property analyses for polyurethane chemicals (foams and elastomers), polymer emulsions (adhesives and water based coatings) and epoxy curatives. The need for comparative material characterization places a high dependency on performing industry standard test methods with specific data results. Our approach to meeting test requirements has been to develop rapid sequential experimentation that uses standard instrumentation and sample techniques. This poster will illustrate several of our higher throughput experimentation techniques that reflect the need for accurate macroscopic, or bulk, property determination.

Combinatorial Approach To Functional Metal-Oxide Thin Films

Kao-Shuo Chang, Maria Aronova, Olugbenga Famodu, J. Hattrick-Simpers, I. Takeuchi
Dept. of Materials and Nuclear Engineering, University of Maryland, College Park, MD

We present our general capabilities for pursuing combinatorial investigation of a variety of functional metal oxide systems. We use our combinatorial pulsed laser deposition systems to fabricate libraries and composition spreads of different designs. Our rapid characterization tools include scanning microwave microscopy. Examples of investigation of ferroelectirc materials, gas sensor materials, and optical materials will be presented.

Combinatorial Approach To Magnetic Metallic Alloys

Olugbenga Famodu, Maria Aronova, Kao-Shuo Chang, C. Ziegler, I. Takeuchi
Dept. of Materials and Nuclear Engineering, University of Maryland, College Park, MD

We use our combinatorial ultra high vacuum magnetron co-sputtering system for fabrication of composition spread samples using three 1.5” parallel guns. Wavelength dispersive spectroscopy is used to map the spreads onto ternary phase diagrams. Magnetic properties are mapped using room

temperature scanning SQUID microscopy. Structural information of the materials is obtained using our scanning x-ray microdiffractometer. Recent results from investigation of ferromagnetic shape memory alloys and other Heusler systems will be presented.

High-Throughput Characterization of Mechanical Properties in Combinatorial Polymer Libraries

Joe-Lahaia Sormana, J. Carson Merideth
Dept. of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA.

Combinatorial libraries of segmented polyurethaneurea with gradients in curing temperature and curative composition were prepared and characterized using a novel high-throughput mechanical instrument. Stress-strain profiles taken at different positions (cure temperature and curative composition) on the libraries showed an optimum curing temperature of 94 ^{o}C and curative composition of 85 mole %. A structure-property relationship between microstructure and mechanical properties was established by correlating AFM and FTIR measurements with stress-strain profiles. These results demonstrate the feasibility of rapid and accurate characterization of mechanical properties, and their correlation to structure, by using gradient combinatorial polymer libraries.

High Throughput Measurements of Epoxy Curing by Confocal and FTIR Microscopy

D. Raghavan[1], N. Eidelman[2], A. Karim[3], and E. Amis[3]
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High throughput measurements techniques were used to study the chemistry and network structure of cured epoxy. A mixture of diglycidyl ether of bisphenol A epoxy (DGEBA) resin, fluorescent dye (dimethylamino-p-nitrostilbene), and 10% Arcamine curing agent was flow coated on glass substrate and cured for 1 hr on a continuous temperature gradient hot plate (45^{o}C to 90^{o}C). The changes in the chemistry with epoxy curing were studied by following the changes in the IR absorption of the epoxy groups using FTIR-Reflectance Microscopy (FTIR-RM) mapping technique. The high throughput results were validated by comparing with individual standards annealed at constant temperature. Confocal microscopy was used to map the apparent changes in the network structure of epoxy resin. A distinct break in the slope of the fluorescence intensity maximum versus temperature was detected close to a curing temperature of 60^{o}C. This observation closely mirrors the results observed by FTIR-RM technique. From the processing standpoint, these results can be potentially useful to develop protocols for calibrating, tuning, and optimizing the curing of thermoset resin systems.

Combinatorial Mapping of Polymer Film Wettability On Gradient Energy Surfaces

Karen M. Ashley[1], Amit Sehgal[2], D. Raghavan[1], and Alamgir Karim[2]
[1] Polymer Division, Department of Chemistry, Howard University, [2] Polymers Division, NIST.

The control of film stability, or conversely dewetting, is critical for the application of coatings as photoresists, paints, adhesives, lubricants, or biomaterials. We demonstrate the use of 2-D combinatorial libraries to investigate the influence of substrate interfacial energy and variables such as temperature and film thickness on the dewetting of thin films. Substrate libraries with gradients in contact angle (θ) were prepared by a 'chemical etch method' and by the ozonolysis of a self assembled monolayer by ultra violet light. The chemically etched gradients were prepared by immersing Si-H (passivated Si) in Piranha solution ($H_2SO_4/H_2O_2/H_2O$) at a controlled rate giving a systematic variation of solvent (water

and diiodo methane) contact angles across the surface. In the UV ozonolysis approach, chlorosilane SAMs on Si surfaces were exposed to a linearly varying dosage of UV radiation such that a range from hydrophobic to hydrophilic was obtained across the surface (~4cm). Libraries of thin films of PS coatings on gradient energy surfaces orthogonal to gradients in film thickness for the chemical etch method were screened for dewetting behavior using automated optical microscopy. The number density of polygons of the dewet films was found to obey a power law relationship with both film thickness and substrate surface hydrophilicity as characterized by contact angle studies. We also observed a non-linear trend in film stability with temperature. At lower equilibration temperatures, the crossover from dewetting to wetting occurs at higher surface energies with increasing temperature. This crossover surface energy however asymptotes as the temperature is raised further. We describe combinatorial gradient energy methods to rapidly investigate not only the effect of surface energy on the structural organization of thin polymer films, but also to quantify polymeric interfacial interactions with temperature in a self-reporting fashion.

Rapid-Prototyping and Fabrication of Solvent Resistant Fluidic Devices

Joao Cabral, Chris Harrison, Kathryn L. Beers, Alamgir Karim, Eric Amis
Polymers Division, NIST

We describe a rapid prototyping technique for the fabrication of fluidic channels in a solvent-resistant polymeric matrix. Using conventional contact lithography and a commercially available thioelene-based adhesive, we demonstrate the fabrication of 600 micron deep fluid channels with width of one millimeter, dimensions that challenge conventional photolithography techniques. These channels are impervious to a wide range of aggressive solvents, including toluene. Additionally, we demonstrate that siloxane-based elastomer molds of these channels can be readily made for aqueous applications.

Mapping Isotactic Polystyrene Crystallization with High Throughput Methods

Kathryn L. Beers, Alfred J. Crosby, Jack Douglas, Alamgir Karim and Eric J. Amis
Polymers Division, NIST.

Combinatorial methods are utilized to study the influence of film thickness and crystallization temperature on the crystallization and mechanical properties of isotactic polystyrene. Films with continuous gradients in film thickness were prepared by flow coating and crystallized on an orthogonal gradient temperature stage under an optical microscope. Growth rates were measured as a function of film thickness and temperature, as determined from an optical micrograph library of numerous subregions within the gradient films. We observed that the growth rate had a maximum near 180 °C and varied inversely to film thickness. A transition from hexagonal plate to circular growth was observed with increasing under-cooling in the thickness range between 23 nm and 80 nm. Both hexagonal and branched dendritic morphologies formed in ultra-thin regions where the film thickness is less than the radius of gyration. Thickness gradients were also floated onto ductile copper grids. As described previously, subsequent irreversible plastic deformation of the copper grid induced uniform, locally isolated strain on each square of the grid and prevented relaxation of the film upon release of the grid. Craze structure was probed using optical and atomic force microscopy.

Block Copolymer Thickness-Gradient Surface Patterns on Topographically Structured Substrates

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Design schemes for thin film, multilayered, opto-electronic devices depend upon control of both in- and through-plane film architecture. To this end, we examine the self-assembly of volume-symmetric (lamellar) block copolymer (PS-b-poly(octyl-methacrylate)) films supported by topographically structured substrates using a high-throughput approach. In particular, a film thickness gradient up to the first two lamellar periods was deposited onto substrates patterned with a pseudo-random array of cylindrical pits having micron sized diameters and 9nm depth. Atomic Force Microscopy and high-throughput image processing techniques were used to analyze the resulting annealed film surface morphologies (i.e. “island” and “hole” formation) along the thickness gradient. Interestingly, it was found that the substrate pits could nucleate island formation, resulting in a series of thickness-dependent film architectures that relate to the substrate structure in a variety of novel ways. Specific thicknesses, for example, exhibit film surfaces that anti-correlate with the substrate topography. The diverse set of observed film structures will be discussed, as well as how the library of these structures was used to aid in the development of an off-specular polarized light scattering formalism used for characterizing thin films.