SYMPOSIUM W
Combinatorial Chemistry and Materials Science
April 25 – 26, 2000

Chairs
Bruce van Dover
Lucent Technologies, Bell Labs
Murray Hill, NJ 07974
908-582-6540

Martin Devenney
Symyx Technologies
Santa Clara, CA 95051
408-764-2038

James R. Engstrom
School of Chemical Engr Dept
Cornell Univ
120 Olin Hall
Ithaca, NY 14853
607-255-3515

Symposium Support
DuPont
Symyx Technologies

*Invited paper
8:30 A.M. #W1.1
CONTINUOUS COMPOSITIONAL SPREAD APPROACHES TO NEW MATERIALS STUDIES. Lynn F. Schneemeyer, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

A combinatorial-type approach that we call the continuous compositional spread, CCS, approach has proven of value in the search for new high dielectric constant amorphous thin films and the identification of $n$-Zr$_2$Si$_2$O$_7$:$TiO_2$. Our CCS thin film technique employs independently applied coating systems, and is particularly suited for exploration of metastable materials and for development of materials that will ultimately be used in thin film form. Fascinating opportunities exist in the identification and optimization of materials. We will discuss our work with the lead magnesium niobate system which contains the relaxor ferroelectric PMN.

Increasing the number of materials that are studied provides increased understanding of composition/property relationships and increases the probability of breakthrough material discoveries.

9:00 A.M. #W1.2
GENERATION OF OSCILLATING PROPERTIES IN SILICON CARBIDE THIN LAYERS SYNTHESIZED VIA AUTOCATALYTIC POLYMER FRAGMENTATION. Milind Sardesai, Josh Carter, Nancy McCourt and Ann-Marie Chacko, Bishop's Univ. Department of Chemistry, Lennoxville, Quebec, CANADA.

Polymer-Assisted Vapor Deposition method (PA-VD) is currently developed in our group for the synthesis of thin ceramic and semiconductor layers on large surfaces in conditions rendering Chemical Vapor Deposition inapplicable. For example, a specific characteristic of the procedure is the fast deposition rate of silicon carbide on large, irregular or dielectric substrates. The method uses the gaseous species generated via fragmentation of various organosilicon polymers exposed to specific thermal and chemical conditions. A recent development is the induction of space-oscillations in the characteristics of thin films of Nitrogen-doped silicon carbide deposited on electronic grade silicon and aluminium single crystal wafers (see picture below), in an atmosphere containing a certain partial pressure of ammonia. This way, a 2D-array of precisely positioned areas of SiC-film with different characteristics is created on the substrate that becomes this way a library-substrate that could be used in the experimental design and optimization of semiconductor SiC devices. The mechanism of the process is under current investigation, but preliminary research points to an oscillating reaction in the gas phase involving the polyaniline-precursor formation when ammonia is carried over solid poly(dimethyl)alumine during PA-VD. We think that these oscillations appear as a result of an auto-catalytic transmutation step in the fragmentation of polysilanes under higher order analysis is required to prove this statement. Since silanes are known precursors for N-doped SiC, the transfer of these oscillations over the deposition area inside the reactor lead to the space-oscillating properties of the films. It is known that species during chemical reactions can be transferred, in general, into space-oscillations via local perturbation of the reaction medium. The appearance of oscillations in our case is induced via local perturbation of the gas flow supply of gaseous silane precursors over the substrate.

9:15 A.M. #W1.3
EXPLORING COMPLEX MATERIAL SYSTEMS USING COMBINATORIAL MATERIALS CHIPs. Xino Dong Xiong, Lawrence Berkeley National Laboratory, Berkeley, CA.

Conventional approach to mapping phase diagrams or exploring new materials is to make and characterize samples of discrete composition one at a time. Since 1995, in an effort to speed up this process, combinatorial materials chips (CMCs) in a format of discrete material chip and continuous phase diagrams (CPDs) are fabricated by thin film deposition of elemental precursors through combinatorial mask or linear shutters. Followed by proper annealing processes, thousands of distinct compounds or an entire continuous ternary phase diagram can be formed, in either polycrystalline or more often epitaxial thin film form, on a single substrate. Various physical properties, including electrical impedance, optical, magnetic and structural properties, of these compounds are then mapped using various imaging instruments. We are routinely applying this approach to explore unknown materials systems and to study well materials phase diagrams. Application areas include exploring superconductors, ferroelectrics/dielectrics, electo-optical, luminous, piezoelectric and magnetic materials. I will discuss some of recent studies on phase diagram mapping new ceramics and metal alloys.

10:15 A.M. #W1.4
APPLICATION OF COMBINATORIAL SYNTHESIS TO THE DEVELOPMENT OF NEW LASER AND SCINTILLATOR MATERIALS. Richard Schlechté, Sundor Erdei, Lasergraphics Corporation, San Jose, CA; Xin-Dong Xiong, Gang Wang, Yi Dong, Lawrence Berkeley National Laboratory, Berkeley, CA.

Combinatorial synthesis and high throughput screening are being used to develop a wider and larger range of new inorganic materials. Lasergraphics and Lawrence Berkeley National Laboratory are applying this method to the development of new laser and scintillator materials. We will describe our results in these two areas.

We fabricated a material chip (MC) set of 256 MCs of YVO$_4$ on lanthanum aluminate. The dopants were holmium, erbium, thulium and chromium from zero to 10% concentration. These fluorescent dopants are important in many laser materials not only because of the wide range of laser wavelengths possible but also because they serve as sensizers, as cascade laser sources and as up-converters.

These processes are very concentration dependent as are the level lifetimes and fluorescent efficiency. Therefore, to study a whole series of dopant concentrations using the usual crystal growth techniques would require years if not many decades of research.

Nuclear and high energy physics experiments, medical diagnostic equipment, industrial measurement, safety control and earth resource search equipment all use scintillators that must have greater time and energy resolution, higher radiation hardness and larger crystal sizes than exist today. Currently, the materials that are closest to meeting the needs of DOE and other users are scintillators doped with cerium. We are applying the techniques of combinatorial synthesis to a wide variety of scintillators to search for and develop new scintillator materials with much improved performance and greater crystal size. The studies we will report on are concentrated on the chlorines, the garnets and the sapphire.

Our objective is to develop new scintillator materials having faster response times, higher energy resolution, greater radiation hardness and greater physical size which are needed for research in nuclear and high energy physics, in medical diagnostics (e.g. XRT and PET equipment), in industrial measurement and security inspections, and in the search for natural resources such as oil, gas and uranium.

10:45 A.M. #W1.5
COMBINATORIAL APPROACHES TO DISCOVERY OF NEW AMORPHOUS SILICON BASED MATERIALS USING HOT-WIRE CHEMICAL VAPOR DEPOSITION. Qi Wang, National Renewable Energy Laboratory, Golden, CO.

Combinatorial approaches greatly increase the experimentation throughput. Applying this technique to hot-wire chemical vapor deposition (HWCD), the time of exploring new hydrogenated amorphous silicon materials has been greatly reduced. It also provides a systematic way to examine the materials that depend upon multi-composition parameters. For example, material that transition from amorphous to microcrystalline silicon, which depends on multi-composition parameters, is one of many promising materials that have a high hole mobility and show less the light-induced-defect degradation. To explore this material, a series of more than 120 samples were deposited on glass substrate at substrate temperature of about 250°C as a function of silicon flow rate, hydrogen flow rate and chamber pressure using combi-HWCD within a couple of weeks (normally take a few months). Raman spectra or UV reflectance measurement was used to determine the structure of the materials. At a given silicon flow rate, the transition material depend on both hydrogen flow rate and chamber pressure. Material, in general, becomes microcrystalline silicon with increasing hydrogen flow rate and chamber pressure.

11:00 A.M. #W1.6
COMBINATORIAL METHODS FOR FORWARDING AND OPTIMIZATION OF MATERIALS AND DEVICE PARAMETERS IN OLEDs. Christoph Schmidt, Peter Poehl, Yvonne Heinrich, Mukundan, Thiebaek and Hans-Werner Schmidt, Makiromolekulare Chemie I, Universität Bayreuth, Bayreuth, GERMANY.

Electroluminescence displays based on organic materials are presently in a stage of materials screening and optimization of device structure and performance. The concept of combinatorial methods has been successfully applied to various fields such as peptide chemistry and development of catalysts for polyelectrolytes [1,3]. Recently we applied this method to the optimization process of multi-layer OLEDs using e.g electron transport materials as additional layer in such devices [4,5].

In this contribution we present several additional examples for the applicability of this method concerning the optimization of different parameters in OLEDs such as deposition thickness, the simultaneous selection of the ratio of layer thickness and device configuration and the optimization of different layers in multi-layer devices. We also applied...
the method to the screening of new synthesized materials for the use in OLEDs. The devices were prepared by vapor deposition using a combinatorial set-up consisting of a movable mask stage and a turntable substrate holder placed in a vacuum chamber. To analyze the specific data of the libraries current-voltage-electroluminescence measurements were carried out. In this work the thickness of layers of typical devices ITO/HI/EMI/Al and ITO/HI/EMI/EThE/AI can be optimized in one single experiment. Experiments using several newly developed low molecular weight and polymeric hole transporting materials were performed. Furthermore, we tested novel phenanthrene containing europium (III) chelate complexes which were investigated as electron transport and emitter materials in an ITO/NPD/Eos-complex/Al configuration. The optimized devices show red electroluminescence with sharp emission bands originating from the europium complexes.

References:

11:30 AM *W2.1 COMBINATORIAL PLASMA PROCESSING OF AMORPHOUS MATERIALS AND DEVICES. Hisakazu Kawanuma, Kazuo Naito, Nobuyuki Masumoto, Hidetoshi Shibata, Yoshinobu Akiba, Wataru Minano, Sato Chiba, Tokyo Institute of Technology, Ceramic Materials and Structures Laboratory, Yokohama, JAPAN. Tako National Institute for Research in Inorganic Materials, Tsukuba, JAPAN. T. Chikyo National Research Institute for Metallurgy, Tsukuba, JAPAN.

Conventional combinatorial approach to solid state materials mainly uses thermodynamically equilibrated process, i.e. deposition of thin films at room temperature and subsequent sintering. For extending the method to nonequilibrium processes using photo and plasma excitations, we need to take into account additional factors that could provide significant effect on reaction process and product.

Combinatorial pulsed laser deposition was developed for parallel syntheses of solid soded oxides and superlattices by using deposition temperature and oxygen pressure as additional parameters. Here, we report our combinatorial approach to two types of plasma chemical processes; one is rf glow discharge plasma for the fabrication of amorphous silicon alloys and field effect devices and the other is atmospheric pressure cold plasma for the discovery of its new applications. Combinatorial plasma CVD was applied to the optimization of structure and fabrication process of amorphous thin film transistors and field effect solar cell. Typically, library of 7X7 single layer films or bi- or tri-layers heterojunctions was fabricated on a substrate by operating a pair of fixed and moving mask and 80 degree substrate rotation. Chemical control of defects in a-Si:H and its interfaces was also investigated in a combinatorial way using chemical species and treatment conditions as variable parameters. We developed new plasma generators that could activate chemical species into release processes below 100°C. A time resolved combinatorial method is being tested to seek for new application of this unique plasma for such purposes as surface costing and modification of polymers, CO2 fixation by plasma copolymerization, and sterilization of food packaging materials.

SESSION W2 COMBINATORIAL CHEMISTRY OF MATERIALS Chair: Martin Devenney Tuesday, Afternoon, April 25, 2000 Toc 15 (Marriott)

12:00 PM *W2.2 NEW SOLID SUPPORTS FOR COMBINATORIAL CHEMISTRY: POLYSTYRENE GRAFTED TEFLOMN MEMBRANES. Jochen Thiele, Andy E. Atseghu, M. Nuria De Francisco, Valery Y. Antonenko, Affymax Research Institute, Santa Clara, CA.

Teflon membranes have the unique combination of thermal and mechanical stability, high pore surface area, and porosity. Irradiation grafting of poly(styrene-co-vinylbenzylic chloride) creates a large number of reactive groups in the polymer, which can be utilized after the removal of the graft polymer and because of that the concentration of reactive groups was optimized by varying the irradiation dose, the polymerization temperature, the duration of the polymerization reaction and the position of the membranes. The maximum concentration of reactive groups we were able to reach was 0.33 mmol/g, which corresponds to 14.4 mmol/cm². We have demonstrated in a variety of experiments that further organic reactions could be carried out on this new solid support leading to products with high purity and yield. The porosity of the membrane allows pumping the reactants through the membrane without diffusion problems. The possibility of tailoring the size and the shape of the membrane to the needs of a specific application opens new ways in the development of new technologies in combinatorial chemistry.

3:30 PM *W2.5 COMBINATORIAL METHODS APPLIED TO PIGMENT RESEARCH. Rakesh Jain, Fritz Herren, Drinan Higdik, and Faleh Salameh, Symyx Technologies, Inc., Santa Clara, CA.

We have developed methodology for the rapid, automated synthesis of mixtures of acid- and base-soluble organic pigments with the aim of identifying new binary and ternary crystal phases. Characterization of the libraries is performed using parallel generation of paint samples followed by rapid serial measurement of reflection spectra. We have also developed techniques to measure X-ray diffraction patterns of the pigment mixtures in the powder form. This provides a convenient method to map out the entire phase space for novel crystal phases for a given number of components. For example, we have generated complete binary and selected ternary phase diagrams for about 20 pigment components.

4:00 PM W2.6 PHASE SEPARATED BLEND FILMS AS TEMPLATES FOR
COMBINATORIAL ASSAY OF PROTEIN ADSORPTION. J. Caron Meredith, Alangir Karim, Eric J. Amis, Polymers Division, NIST, Gaithersburg, MD.

Combinatorial methods were initiated to study protein adsorption and cell behavior on blend films of plasma-sprayed biodegradable polymers, poly(caprolactone) and poly[(caprolactone)]. As measured by light scattering, the poly[(lactide)/poly[(caprolactone)] blend system has a lower critical solution temperature (LCST). Coated blend films of constant composition poly[(lactide)/poly[(caprolactone)] were exposed to a one-dimensional temperature gradient (crossing the system LCST of 86°C) on a hot-stage under vacuum. This resulted in a range of crystalline and phase-separated microstructures of poly[(lactide)] and poly[(caprolactone)]. This was expected to lead to a reduction in protein for adsorption selectivity tests. The morphology of adsorbed protein A was found to be sensitive to the blend microstructure induced by LCST phase separation, demonstrating that libraries containing systems-specific properties could be used to study polymer and cell-polymer interactions. Work is underway to assay osteoblast-like cells on temperature-controlled combinatorial libraries.

4:15 PM #W2.7 COMBINATORIAL LIBRARIES OF SELF-ASSEMBLED DENDRITIC MODULES Virgil Pierce, University of Pennsylvania.

ABSTRACT NOT AVAILABLE

SESSION W3: HIGH THROUGHPUT SCREENING, CATALYSIS
Chair: Bruce van Dover
Wednesday, April 26, 2000
Salon 15 (Murrill)

8:30 AM #W3.1 MICROMACHINED ARRAYS FOR COMBINATORIAL MATERIALS PROCESSING AND MULTISAMPLE CHARACTERIZATION S. Semancik, R.E. Cavichi, M.C. Wheeler, G.E. Poirier, Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, MD. B. Pachonkowsky and D.L. DeVoe, Institute for Systems Research, University of Maryland, College Park, MD.

Surface micromachining of silicon has been used at NIST to produce miniature temperature-controlled structures called microhotplates. Microhotplates are suspended multilayer devices which have nominal lateral dimensions ~100 μm, and masses ~0.25 μg. Integrated resistive heaters and thermometers are used to heat (and cool) these structures between 20°C and 750°C with time constants ~1.5 ms. Electrodes mounted on the microhotplate surfaces can be used to monitor electrical properties of deposited films. These devices have been used singly and in arrays as platforms for the development of an application-specific solid state gas microsensor technology. In this presentation, we discuss the utility of microhotplate arrays in combinatorial research. The research we have conducted, to date, involves arrays with 4, 16, 48 and 340 discrete elements. We focus on the use of individually addressable temperature control of multiple microsubstrates for efficient material processing and materials performance studies. We also describe functionality that can be included on-chip for electrical and calorimetric characterization of each microsample deposited within an array, the use of external probing techniques with the arrays, and the potential for mixing gas microsensor arrays as diagnostic in array-based material performance studies. We illustrate the range of methods that have been used in depositing oxide, metal and metal-oxide films onto microhotplates (including self-lithographic CVD, and addressable potential control), and we also indicate results of experiments that examined the importance of cross-talk among elements when one forms or monitors microsamples which are separated by only hundreds of microns.


9:00 AM W3.2 MATHEMATICAL MODEL FOR ACOUSTIC SCREENING OF COMBINATORIAL LIBRARIES OF COMBINATORIAL MATERIALS V.K. Tewary, National Institute of Standards and Technology. Materials Reliability Div, Boulder, CO.

A mathematical model will be described that gives the elastic response of a library of combinatorial materials to an ultrasonic probe. The objective of this work is to examine the feasibility of screening and nondestructive characterization of libraries of combinatorial materials using devices such as high frequency acoustic microscopes and short-pulsed lasers. We consider a typical library containing an array of several hundred thin-film samples on a substrate of a few sq. cm area fabricated by using quantum masking techniques [H. Cho et al., Appl. Phys. Lett. Vol 72, p 3185, 1998]. An elastic wave incident on such a sample will suffer dispersion because of multiple reflections and scattering at the interfaces between materials of mismatched elastic constants. The mathematical model is based upon the elastic field representations [V.K. Tewary, Phys. Rev. Vol 86, p 15695, 1995] of the elastodynamic Green’s function and accounts for the dispersion, internal reflections, and scattering processes. Continuity of displacements and traction are used as boundary conditions at each interface. Zero traction is prescribed as the boundary condition at the free surfaces. The model is used to calculate the velocities and waveforms of bulk elastic waves as well as the Rayleigh wave on the delaminated surface. The model also gives resonant frequencies. Some resonant modes can be identified which are essentially localized at the interfaces. The complete acoustic map of the library can yield useful information about the interfaces and elastic constants of various materials in the library and would supplement results obtained by other measurements.

9:15 AM #W3.3 COMBINATORIAL X-RAY STUDIES OF MULTICOMPONENT SYSTEMS. Damian A. Hajduk, Rakesh Jain, Faleh Subramany, Synexus Technologies, Santa Clara, CA.

Advances in combinatorial materials synthesis are of little utility unless accompanied by corresponding improvements in characterization techniques. As the field has evolved, such techniques have expanded beyond the "bookcase" screens reminiscent of pharmaceutical binding assays to encompass rapid quantitative chemical and structural characterization of library elements. X-ray scattering is well suited for the latter application due to the potentially nondestructive nature of the probe, the ability to obtain data from very small specimens, the speed with which measurements can be conducted, and the high information content of the resulting data. Prior work has employed synchrotron radiation for this purpose, but advances in instrumentation permit useful measurements to be obtained with conventional X-ray generators even from systems with intrinsically low electron density contrast. I will illustrate these points with results obtained from several different classes of self-assembling organic materials, including both synthesis and formulation studies. One study required six months and over 10,000 materials to survey a "known" composition phase space that had taken ten years to map by conventional techniques. High-throughput X-ray scattering correctly identified all of the known compositions of interest while simultaneously detecting a number of new morphologies which would have been difficult to identify by other means.

10:15 AM #W3.4 POLYMER COMPOSITE SENSOR ARRAYS: COMBINATORIAL METHODS AND SMEAR DIGITIZATION. Bruce Herrman, Beth Munoz, Greg Steinthal, Steven Sunshine, Cyrrano Sciences, Inc., Parsippany, CA.

Polymer composite sensor arrays were first invented nearly eight years ago. The functionality of these systems requires the fabrication of a number of different compositions which vary in polymer or filler type. While initial sensor arrays were made using traditional combinatorial methods, it was recognized early on that combinatorial methods could be applied to these systems. Combinatorial methods offer the ability to create added sensor diversity with minimal synthetic complexity. Results of several combinatorial approaches will be outlined. In addition to using combinatorial methods in the fabrication of sensor arrays, these arrays hold promise as a simple characterization method for combinatorial discovery strategies. Polymer composite sensor arrays can provide chemical information in a small region and in a very short time frame. These analysis attributes are important for evaluating combinatorial synthesis methods that involve chemistry (e.g. catalysis). Recent results on the use of sensor arrays in combinatorial discovery will be presented.

10:45 AM W3.5 COMBINATORIAL SYNTHESIS OF METAL OXIDE CATALYSTS. Heidi M. Reichenbach, Paul J. McGin, University of Notre Dame, Department of Chemical Engineering, Notre Dame, IN.

Combinatorial synthesis has been used to produce libraries of mixed metal oxide catalysts for the CO oxidation reaction. An in-situ dispensing technique was adapted to systematically generate the compositional libraries of each system. Solutions of metal nitrate or chloride precursors were deposited into microtiter plate wells. Subsequently, aluminum catalyst supports were impregnated with the solutions. Here we report on results from an examination of the CeO2-CuO system and the perovskite-like Li9Sr2Co9O19 system. The libraries of compounds were screened for catalytic activity by infrared thermography. The effects of various process parameters will be discussed.

366
11:00 A.M. W3.6 COMBINATORIAL AUTOMATED HYDROTHERMAL SYNTHESIS OF MOLECULAR SIEVES. Nicole Hillbrandt, Thomas Bertsch, Department of Chemistry, University of Munich, Munich, GERMANY; Kangwook Choi, David Gardner, Department of Chemistry, Purdue University, West Lafayette, IN.

The development of combinatorial approaches for the hydrothermal synthesis of molecular sieves (zeolites) depends on methodologies for rapid synthesis under harsh conditions and for effective structural screening protocols. We have developed a new methodology based on automatic dispensing of reagents into autoclave blocks, followed by synthesis, isolation, and structural analysis. The autoclave blocks can be heated to at least 170°C. After synthesis, the samples can be repeatedly washed and then completely transferred onto sample holders using centrifugation. A complete experiment (from mixing of reagents to x-ray structural analysis) can be performed without manipulation of any of the individual samples. We will present several examples illustrating this methodology, including the synthesis of aluminophosphate and aluminosilicate molecular sieves. Crystalization fields of these and other phases as well as the effects of template structure, mixed organometallic-organic templates, solvents, framework precursors, and temperature on the resulting microporous phases will be discussed.

11:15 A.M. *W3.7 HIGH THROUGHPUT METHODOLOGIES FOR ADVANCED MATERIALS R&D. John D. Hewes, Advanced Technology Program, National Institute of Standards and Technology, Gaithersburg, MD.

The widespread implementation of high-throughput experimentation (combinatorial methodologies) represents a significant technical challenge for the United States, and discontinuous innovation will be necessary to drive down costs and facilitate its use throughout the technology-driven processes of the chemical and materials sectors. The NIST Advanced Technology Program cost-shares technically risky applied research with U.S. companies. The ATP encourages proposals in all areas of advanced materials R&D, for example in electronic materials, polymers, biomaterials, smart materials, catalysts, etc. The FY 1999 competition resulted in a technology cluster Combinatorial Methods for Materials R&D at the ATP with three projects in catalysis and polymers and funding requests of $2.6M over five years. An ATP technology cluster provides an atmosphere for awardees to discuss non-competitive synergies, facilitates interaction with NIST Laboratories, and catalyzes growth into other industries. This presentation will describe the ATP technology cluster in combinatorial methods for R&D and discuss the current business and technology climate surrounding combinatorial methods.