SYMPOSIUM JJ

JJ: Combinatorial and Artificial Intelligence Methods in Materials Science II

December 1 - 4, 2003

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* Invited paper

SESSION JJ1: Combinatorial Approach to Magnetic and Electronic Materials

Chairs: Radislav Potyrailo and Ichiro Takeuchi
Monday Morning, December 1, 2003
Independence West (Sheraton)

8:30 AM *JJ1.1

Combinatorial synthesis and characterization of multifunctional thin film materials. Ichiro Takeuchi, [1]Small Smart Systems Center, Center for Superconductivity Research, University of Maryland, College Park, Maryland; [2]Dept of Materials Science and Engineering, University of Maryland, College Park, Maryland.

We have developed a methodology for rapid synthesis and characterization of a variety of functional thin film materials. Combinatorial pulsed laser deposition is used to fabricate libraries and composition spreads of oxide systems, and combinatorial UHV co-sputtering system is used for investigation of metallic alloy systems. High-throughput studies are carried out in order to explore novel compositions as well as for facilitating quick mapping of composition-structure-property relationships. Rapid characterization tools include scanning probe microscopes such as non-linear microwave microscopy and room-temperature scanning SQUID microscopy and MEMS device libraries. One of our emphases is on multiferroic materials which display co-existence of different ferroic properties. They have rich multifunctional phase diagrams and are of great interest for novel sensor and actuator applications. Different types of continuous composition spreads are fabricated for pursuing ferroelectric-ferromagnetic materials. In particular, artificial magnetoelectric materials are designed and synthesized using composition spreads where one end of the spread is a pure ferroelectric material and the other end is a pure ferromagnetic material. Structural phase transitions which often accompany ferroic properties are identified using a scanning x-ray diffractometer. Examples of multifunctional phase diagram mapping will be discussed for ternary metallic systems which contain ferromagnetic shape memory alloys. We will also discuss an example of a composition spread device, where the entire composition spread acts simultaneously as one integrated device. This work is performed in collaboration with K.-S. Chang, M. A. Aronova, O. O. Famodu, J. Hattrick-Simpers, C.-L. Lin and M. Murakami.

9:00 AM JJ1.2

Magnetic and electrical properties of transition metal impurities in TiO_2. Murugan Palanichamy, Rodion V. Belosludov, Hiroshi Mizuseki, Takeshi Nishimatsu, Masashi Kawasaki and Yoshiyuki Kawazoe; Institute for Materials Research, Tohoku University, Sendai, Japan.

As extensive and potential applications of diluted magnetic semiconductors, it has elaborately been studied in many field of research, such as opto-electronic and -magnetic studies, superconductor and intelligence systems, etc. Addition of impurities into these materials changes the electric and magnetic properties drastically. Looking at combinatorial screening approach, the sizable soluble amount of transition metals, like cobalt in TiO_2 anatase, is upto 8%. Another interesting thing is that, this anatase material, $Ti_{1-x}Co_xO_2$ (x=0.07), remains ferromagnetic, even above room temperature with saturated magnetic moment $0.32\mu_B$ per cobalt atom [1]. In this work, we have studied the magnetic properties of different double impurities of transition metals into TiO_2, instead of single impurity. Two different transition metals (double impurities in this work) has naturally existed in double perovskite structured compounds. This work is performed by using the VASP code [2] with the electron exchange-correlation energy within generalized gradient approximation (GGA), coupled with ultrasoft Vanderbilt pseudopotential and plain wave basis set. Here, we assumed that transition metal impurities are substituted in place of Ti atoms. Computational screening of different double impurities of transition metals in TiO_2 was performed. In order to find exact sites of impurities in TiO_2, the lowest distance between Fe_{Ti} and Mo_{Ti} has identified from energy minimization as the most stable configuration. After establishing the equilibrium state of stable configuration, magnetic moment and density of states (DOS) are evaluated. The oxidation state of transition metal impurities in TiO_2, rutile is obtained by plotting the DOS. By the present work, it is obtained that in case of Fe-Mo impurities in TiO_2 rutile, the antiferromagnetic superexchange interaction between the $3d^5$ (Fe^{3+}) spin and $4d^1$ (Mo^{5+}) spin produces large ferrimagnetic magnetization (total = $3.99\mu_B$). 1. Y. Matsumoto et al, Science **291**, 854 (2001) 2. G. Kresse and J. Fürthmuller, Phys. Rev. B **54**, 11169 (1996).

9:15 AM JJ1.3

Combinatorial Methods of Screening, Optimization and Snalysis of Materials and Device Characteristics of Thin Layer Opto-electronic Devices. Hans-Werner Schmidt[1], Christoph Schmitz[1], Markus Baete[1], Mukundan Thelakkat[1], Helmut Haensel[2], Heiko Zettl[2] and Georg Krausch[2]; [1]Makromolekulare Chemie I, Universitaet Bayreuth, Bayreuth, Germany; [2]Physikalische Chemie II, Universitaet 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 polyolefines. 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. In this way the correlated layer thicknesses of typical devices: ITO/HTL/EML/Al and ITO/HTL/EML/ETHBL/Al can be optimized in one single experiment. Experiments using several newly developed low molecular weight and polymeric hole transporting materials were carried out. In this contribution we present several additional examples for the applicability of this method concerning the optimization of different parameters in OLEDs and in thin layer organic solar cells such as layer-thickness, the simultaneous variation of layer thickness and device configuration and the composition 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 same method can also be used for the combinatorial preparation of solar cell libraries. The devices were prepared by vapor deposition using a combinatorial set-up consisting of a movable mask sledge and a turnable substrate holder placed in a vacuum chamber. To analyze the large amount of data of these libraries current-voltage-electroluminescence measurements were carried out in an automated set-up. By exchanging the light detection unit with an illumination light source, the analytical set up can also be used for the study of durability and degradation of solar cells. The majority of the results are published in various journals as given below. Literature: [1] C. Schmitz, M. Thelakkat, H.-W. Schmidt, Adv. Mater. 1999, 11(10), 821 [2] C. Schmitz, P. Poesch, M. Thelakkat, H.-W. Schmidt, Phys. Chem. Chem. Phys. 1999, 1, 1777. [3] H.-W. Schmidt, C. Schmitz, P. Poesch, M. Thelakkat, Proceedings of SPIE, 1999, 3797, 58 [4] C. Schmitz, P. Poesch, M. Thelakkat, H.-W. Schmidt, Macromol. Symp. 2000, 154, 209 [5] M. Thelakkat, C. Schmitz, H.-W. Schmidt, Adv. Mater. 2002, 14, 577 [6] H. Haensel, H. Zettl, G. Krausch, C. Schmitz, R. Kisselev, M. Thelakkat, H.-W. Schmidt, Appl. Phys. Lett. 2002, 81, 2106

9:30 AM *JJ1.4

High-Throughput Screening of Thermoelectric Materials; Application of Thermal Probe Method to Composition-Spread Thin Films. Atsushi Yamamoto[1], Dmitry Kukuruznyak[2], Parhat Ahmet[3], Toyohiro Chikyow[3] and Fumio S Ohuchi[2]; [1]Energy Electronics Institute, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki, Japan; [2]Department of Materials Science and Engineering, University of Washington, Seattle, Washington; [3]Nanomaterials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

Recently, various thermoelectric materials are under exploration and the target has been shifted from binary systems to ternary or quarternary systems after the stimulating findings of the high-performance filled-skutterudite family such as $Ce_yFe_{1-x}Co_xSb_3$ and the layered cobaltite family such as $NaCo_2O_4$, $Ca_2Co_2O_5$. In principle, evaluation of a thermoelectric material requires three independent parameters such as the electrical conductivity σ, Seebeck coefficient S, and the thermal conductivity κ for the identical sample to estimate the total thermoelectric performance in a form of $Z = \sigma S^2/\kappa$. An efficient material screening can be constrained by the availability and capability of thermal and electrical evaluation techniques. In this paper we describe a new attempt of high-throughput screening of thermoelectric materials using the combinatorial MBE system to fabricate composition-spread library and the scanning thermal probe method to measure the distribution of the transport properties of the library. The scanning thermal probe apparatus developed at AIST consists of a hot thermocouple probe, and a sample holder mounted on a computer-controlled X-Y stage. The system is capable to visualize the distribution of the temperature difference, and the thermoelectric voltage produced across the sample thickness simultaneously and outputs color maps of calculated Seebeck coefficient and thermal conductivity for given composition-spread library. The resolution of each pixel is 20-50 micrometer. The information of the electrical contact between the sample and the probe is also displayed as a color map, which enables us to judge the reliability of the Seebeck coefficient information. We will discuss the experimental results of triangular composition-spread library of transition metal manganese oxide and applicability of this approach to the high-throughput screening in thermoelectric materials in this paper.

10:30 AM *JJ1.5

Novel Ge-based Magnetic Semiconductors and Heterojunctions. Frank Tsui[1], Liang He[1], Lei Ma[1] and Yong Chu[2]; [1]Physics and Astronomy, University of North Carolina, Chapel Hill, North Carolina; [2]APS, Argonne National Lab, Argonne, Illinois.

There is considerable interest in high T$_{C}$, group IV element-based magnetic semiconductors, owing to their potential compatibility with current Si-based processing technology. In order to achieve this, doping levels in access of several at. % and relatively high processing temperature would be some of the basic requirements. However, they also have been the main obstacles for the synthesis, since they tend to promote phase separation of dopant rich compounds, resulting in disordered and inhomogeneous materials. We describe combinatorial MBE synthesis of stable epitaxial films of Co-Mn doped Ge, and the resulting characteristic properties of the system. In-situ RHEED experiments, and ex-situ x-ray diffraction, x-ray fluorescence spectroscopy and cross-sectional high resolution transmission electron microscopy measurements show that the presence of several dopants alters the local energetics and kinetics so that the tendency to phase separate can be controlled during non-equilibrium synthesis. The magnetic and transport properties of the system exhibit high T$_{C}$, large magnetoresistance effects, and p-type conduction with low-temperature behavior dominated by hoping, all of which can be controlled systematically by the doping concentration. Heterojunction diodes made from these materials exhibit large magnetization-dependent rectification effects.

11:00 AM JJ1.6

Composition-spread exploration of thin-film optical amplifier materials. Karen E. Downey[1], John E. Graebner[2], Lynn F. Schneemeyer[1] and R. Bruce van Dover[1]; [1]Materials Sci. & Eng, Cornell University, Ithaca, New York; [2]Triquint, Breinigsville, New Jersey.

The demand for optical communication bandwidth continues to grow exponentially, a trend that motivates the demand for photonic components with ever-increasing functionality and complexity yet at low cost. Planar waveguides have achieved high performance and represent the most promising path toward low-cost integration of optical functions. Integration of an amplifier material is needed to compensate for absorption and scattering loss in planar waveguides, as well as losses due to splitting, coupling, etc. The planar-waveguide analog of the Er-doped fiber amplifier might prove the basis for such an amplifier material, but the intra-$4f$ transition is parity forbidden and has a small cross section, therefore requiring a high Er concentration to achieve sufficient amplification in a cm-scale waveguide. For high concentrations of Er in SiO2, the Er atoms interact and create nonradiative channels for dissipation, decreasing the gain. Adding substituents such as La and Al to the amorphous Er:SiO2 has been shown to improve the performance(1). We have conducted a high-throughput search for alternative substituents, using the composition-spread approach. Films were prepared by off-axis sputtering, and evaluated using a custom-built diode-pumped fluorescence apparatus. Hits were identified using the product of fluorescence amplitude and lifetime as a figure of merit. Compositions in the Er-Bi-Al-Si-O system were found to exhibit a response threefold higher than any composition in the benchmark Er-Ln-Al-Si-O system. We will report on the systematics of the composition dependence of fluorescence in a wide range of chemical systems, and identify the most promissing materials for further study. (1) Bruce, A.J., et al., Erbium-doped planar optical device. 1996, Lucent Technologies Inc.: US Patent 5563979.

11:15 AM JJ1.7

Combinatorial Material exploration to discover a new gate insulter with higher dielectric. Toyohiro Chikyow, nanomaterial labs., NIMS, Tsukuba, ibaraki, Japan.

T.Chikyow* and P. Ahmet, COMET-NIMS, National Institute for Material Science, Nanomaterial Research Laboratories, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan K. Nakajima, N. Okazaki, K. Fujimoto, and M. Watanabe COMET-NIMS, National Institute for Material Science, 1-1 Namiki, Tsukuba Ibaraki 305-0044, Japan K. Hasegawa, T. Tamori, T. Hasegawa, T.Aoyama, and H. Koinuma* ** Materials and Structures Laboratory, Tokyo Institute of Technology 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan * CREST-JST ** COMET-NIMS, National Institute for Material Science, A ternary phase diagramming for discovering new gate insulator was demonstrated using combinatorial synthesis and characterization. HfO2-based ternary oxide was found to be a candidate as a new gate insulator which had stable amorphous structure with higher dielectric property. In the modern large scale integrated circuit (LSI), due to the scaling down of the transistors, gate oxide material becomes the most serious problem year by year and a lot of efforts have been made to find new candidates of having higher dielectric property. The requirements for the new materials are 1) higher dielectric property, 2) amorphous material 3) low interfacial states at oxide/Si interface. For this puorpose, HfO2 or ZrO2 has been proposed and the property has been investigated. The problem of these materials is that they tend to be crystalline around 300 C and have rather poor electric property. To improve the properties, binary alloying with SiO2 or Al2O3 has been attempted. However the answer was not found yet. To discover a stable amorphous oxide of higher dielectric, newly designed combinatorial growth system was applied to find the candidate in a ternary alloys. Dielectric properties are characterized by scanning microwave microscope as well as conventional C-V measurement. Structures are investigated by combinatorial x-ray measurement system and transmission electron microscopy combine with micro sampling technique. To investigate the vacancy density, a position annihilation method was applied. Throughout the experiments, a new candidate for the gate insulator was proposed. The authors wish to thank the members of the research project "High-k Network" for their fruitful comments and discussion.

11:30 AM JJ1.8

Epitaxial Combinatorial Library for Oxide Electronics. Tomoteru Fukumura[1], M Ohtani[1], Y Yamada[1], J Nishimura[1], H Sakurada[1], X Zhao[2,6], H Sugaya[2], K Nakajima[2], A Ohtomo[1], A Yamamoto[2], Y Matsumoto[3], T Chikyow[4,6], T Hasegawa[5,6], H Koinuma[2,6] and M Kawasaki[1,6]; [1]Institute for Materials Research, Tohoku University, Sendai, Japan; [2]Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan; [3]Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, Japan; [4]National Institute for Materials Science, Tsukuba, Japan; [5]Department of Chemistry, University of Tokyo, Tokyo, Japan; [6]Combinatorial Materials Exploration and Technology, Tsukuba, Japan.

Transition metal oxides exhibit various attractive functionalities so that there is much room for discovery of novel compounds and properties. We have developed various methods for fabrication and characterization of combinatorial library made of transition metal oxide epitaxial thin films, in order to make a lot of the compounds, to optimize and tailor the thin film structures, and to discover novel functionalities. Here, we talk about the recent combinatorial approach toward gigantic nonlinear optic material, room temperature ferromagnetic semiconductor, as well as the optimization techniques to fabricate various combinatorial libraries. In addition, we shall mention the characterization techniques such as composition mapping and high throughput screening of optical and magnetic properties. Also, we shall talk about recent progress in a room temperature ferromagnetic semiconductor discovered by combinatorial approach, Ti1-xCoxO2.

11:45 AM JJ1.9

Development of Magneto-Optical Imaging for High-Throughput Characterization of Combinatorial Magnetic Thin Films. Xiaoru Zhao[1], N Okazaki[1], Y Konishi[2], K Akahane[2], Z Kuang[3], T Ishibashi[3], K Sato[3], H Koinuma[1,4] and T Hasegawa[1,5]; [1]National Institute for Materials Science, Tsukuba, Japan; [2]Neoark Corporation, Tokyo, Japan; [3]Department of Applied Physics, Tokyo University of Agriculture and, Tokyo, Japan; [4]Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan; [5]Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, Japan.

A new magneto-optical (MO) imaging system for high-throughput characterization of combinatorial magnetic thin films has been developed. The instrument allows us to measure both Faraday rotation and ellipticity maps at various wavelengths (400 nm∼1000 nm), different magnetic fields (0∼2000 G), and different temperatures (12 K∼300 K) for wide variety of materials. We used the magnetic circular dichroism (MCD) modulation technique to map MO properties, relatively free from substrate effects. The superiority of this system is that magnetic hysteresis curves of numerous specimens with different compositions prepared by the combinatorial technique can be simultaneously measured at one sweep of magnetic field, providing an efficient characterization method for combinatorial magnetic materials. We also confirmed that the system possesses enough spatial resolution and sensitivity for detecting MO signals of individual pixels contained in a combinatorial library. Detailed results will be reported in the presentation, including the specifications and some experimental results.

SESSION JJ2: Combinatorial Approach to Electronic and Inorganic Materials

Chairs: Frank Tsui and Qi Wang
Monday Afternoon, December 1, 2003
Independence West (Sheraton)

1:30 PM *JJ2.1

Examples of Inorganic Materials Discovery and Optimization

using the Combinatorial Approach. Martin Devenney, Symyx Technologies, Santa Clara, California.

Examples will be shown of how the combinatorial approach has been successfully implemented and used in inorganic materials discovery programs at Symyx Technologies. High throughput syntheses and screening techniques and materials discoveries from combinatorial programs directed towards X-ray storage phosphors, phosphors for lighting applications and materials for microelectronics applications will be presented to demonstrate the utility of the approach.

2:00 PM JJ2.2

Evolution of microstructure in epitaxial Zn(1-x)MgxO composition spreads. Leonid A. Bendersky[1], I Takeuchi[2,3], W Yang[3], K.-S. Chang[2], R.D. Vispute[3] and T Venkatesan[3]; [1]MSEL, NIST, Gaithersburg, Maryland; [2]Department of Materials Science and Engineering, University of Maryland, College Park, Maryland; [3]Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, Maryland.

Wurzite ZnO is a wide gap semiconductor with a bandgap of 3.3 eV whose potential applications in optical devices include UV lasers, transparent conducting layers for solar cells and phosphors. Recently it was demonstrated that by mixing MgO (bandgap 7.8 eV for the NaCl-type structure) with ZnO, one could obtain a tunable bandgap. In order to study the effect of mixing on properties and microstructures in a wide range of compositions, Zn(1-x)MgxO continuous composition spreads were fabricated by shutter-controlled pulsed laser deposition (PLD). Structural evolution of phases across the spread has been mapped using x-ray microdiffraction, and selected compositions were investigated with cross-sectional transmission electron microscopy (TEM). Three regions of different microstructures were identified and analyzed: (1) for $0.6<x<1.0$, the microstructure has columnar grains belonging to one of two variants of the [111]-oriented cubic Mg(Zn)O phase; (2) for $0.0<x<0.4$, the microstructure is an epitaxial [0001]-oriented wurzite Zn(Mg)O with high density of planar defect. The defects appears to be the sites accommodating the excess of MgO in a form of intergrowth; (3) for $0.4<x<0.6$, the microstructure consists of two phases, wurzite Zn(Mg)O and cubic Mg(Zn)O, with Mg(Zn)O presents in both [100] and [111] orientations. The new orientation relationship between the c-oriented hexagonal Zn(Mg)O phase and the [100] oriented cubic Mg(Zn)O phase will be discussed in the paper. We will also discuss the solubility of MgO in ZnO, either by atoms' substitution or by intergrowth of MgO layers.

2:15 PM JJ2.3

Combinatorial chemical vapor deposition of hafnium, zirconium and tin silicates. Lijuan Zhong[1], Fang Chen[2], Stephen A Campbell[2] and Wayne L Gladfelter[3]; [1]Dept Chem Engn & Mats Sci, University of Minnesota, Minneapolis, Minnesota; [2]Dept Elect & Comp Engn, Univ Minnesota, Minneapolis, Minnesota; [3]Dept Chemistry, Univ Minnesota, Minneapolis, Minnesota.

Tri (tert-butoxy) silanol and the anhydrous nitrates of hafnium, zirconium and tin were used to grow continuous compositional spreads of MO_2/SiO_2 (M= Hf, Zr or Sn) on Si (100) substrates in a modified low-pressure chemical vapor deposition (LPCVD) reactor. At deposition temperatures as low as 130°C, film compositions ranged from 5% to 60% ($M/(M+Si)\times100\%$). The chemistry involved in determining the film stoichiometry will be discussed. The dielectric properties of the amorphous films were measured by creating an array of 100μm x100μm platinum electrodes. The correlation between the dielectric constants and film composition will be described.

2:30 PM JJ2.4

The Linear Combinatorial Synthesis Achieved By Multi-Layer Stacking CdO-SnO2 Structure. Xiaonan Li, Mailasu Bai and Timothy Coutts; 5200, National Renewable Energy Lab., Golden, Colorado.

The linear combinatorial synthesis completed by a low-pressure metal organic chemical vapor deposition (CVD) has been used to fabricate cadmium oxide (CdO)-tin oxide (SnO2) ternary compound thin films. The change in the thickness of each layer in a CdO/SnO2 multi-layer stacking structure was used to alter the compound film properties. The X-ray diffraction was used to assess the phase structure and the X-ray photoelectron spectroscopy was used to analyze both the composition and layer structure of the films. The crystal structure of the compound films was mixed with cubic CdO, spinel Cd2SnO4 and tetragonal SnO2 dependent with the ratio of CdO-to-SnO2. The thickness of each layer in the multi-layer stacking structure also plays an important role for the phase formation of the compound films. In this study, we will report the electrical and optical properties of the compound thin films changing with the layer thickness and thus the crystal structure of the films.

3:15 PM *JJ2.5

Combinatorial Studies on Ti/CrN, Cr/ZrN and Nb/VN Libraries. David S. Ginley[2], C W Teplin[2], M F.A.M Van Hest[2], M Dabney[2], C Perkins[2], L Gedvilas[2], B To[2], P Parilla[2], B Keyes[2], J Alleman[2], J D Perkins[2], Y Lin[3] and Y Lu[3]; [1]PV&EM, NREL, Golden, Colorado; [2]NCPV, NREL, Golden, Colorado; [3]Guardian Industries, Auburn Hills, Michigan.

The various transition metal nitrides are of increasing interest for electro-optical, corrosion resistant and tribological coatings. We have employed combinatorial techniques to explore a wide range of ternary nitrides from the binary Ti-Cr, Cr-Zr and Nb-V systems. Libraries were sputter deposited from metal targets in controlled nitrogen ambients to produce compositional gradients in the metals and nitrogen. New optical characterization techniques, including simultaneous reflection and transmission and ellipsometry, have been developed to rapidly survey the libraries key properties for electro-optical applications. Electrochemical characterization has been used for evaluating stability and XRD to identify phase formation. Improved data handling approaches have been investigated to handle the over 20,000 data files generated. A wide range of compositional phase space has been covered indicating that the properties of the nitrides can be effectively tailored to potentially address a wide range of possible applications.

3:45 PM JJ2.6

High-Throughput Investigation of Inorganic-Organic Hybrid Materials. Norbert Stock, Sebastian Bauer and Thomas Bein; Department of Chemistry, Ludwig-Maximilians University, Munich, Germany.

High-throughput methods applied to materials discovery have attracted much attention over the last few years. The incorporation of hydrothermal synthesis procedures has been particularly challenging. Based on previous work in our group [1] we have recently developed a multi-autoclave that permits the investigation of 48 different hydrothermal reactions at one time. The methodology now includes automatic dispensing of solids and liquids in mg and ml quantities, respectively, followed by homogenization, pH-measurement, synthesis, isolation, washing, as well as automated phase analysis by X-ray diffraction without the manipulation of individual samples [2]. This methodology was applied to the investigation of inorganic-organic hybrid materials based on phosphonic and phosphonocarboxylic acids. Special attention was given to the use of amino bis(methylphosphonic) acids since they have been rarely investigated in the synthesis of metal phosphonates. For example, the following systems were investigated employing discovery as well as focused libraries: (1) $Zn(NO_3)_2$ / $H_2O_3PCH_2\text{-}C_6H_4\text{-}COOH$ / NaOH, (2) M^{II} / $(H_2O_3PCH_2)_2N\text{-}(CH_2)_4\text{-}N(CH_2PO_3H_2)_2\cdot 2H_2O$ and (3) $M^{II/III}$ / $(H_2O_3PCH_2)_2N\text{-}CH_2\text{-}C_6H_4COOH$ / NaOH. In a typical example (system (2)) a discovery library was set up by keeping the water content constant, choosing four molar ratios metal : phosphonic acid of 1:1, 4:1, 1:4 and 2:3, and varying the nature of the metal ion (M = Mg, Ca, Sr, Ba, Mn, Fe, Co, Ni, Zn, Cd, Sn, Pb). In a second experiment the growth of products having larger crystallite sizes was investigated. This led to the formation of single-crystalline products $M[HO_3PCH_2)_2N(H)\text{-}(CH_2)_4\text{-}(H)N(CH_2PO_3H)_2$, which are the first metal tetraphosphonates described in the literature having a three-dimensional framework structure. Literature: [1] K. Choi, D. Gardner, N. Hilbrandt, T. Bein, Angew. Chem. Int. Ed. 1999, 38, 2891. [2] N. Stock, T. Bein, Z. Anorg. Allg. Chem. 2002, 628, 2150.

4:00 PM JJ2.7

Achievement of Combinatorial Experiment in Ni-Ti Thin Films By Laser Interference Structuring. Kaiwen Liu, Carsten Gachot, Peter Leibenguth and Frank Muecklich; Materials Science-Functional Materials, Saarland University, Saarbruecken, Germany.

It is well known that phase transformation can be induced by laser irradiation. With laser interference configuration, the laser power is distributed periodically according to the interference pattern. Therefore, phase transformation can be induced only in the local region within each interference period where the local laser energy exceeds the critical phase transformation ignition energy. By selecting different shutter window sizes and the velocities of substrate, various compositional spreads are prepared conveniently in ion-gun sputtering facility. Combinatorial experiments are achieved on the periodically structured thin films by applying laser interference technique on thin film composition spreads. In this report, the laser interference structuring technique, preliminary results on composition spread by compositional spread will be presented. The microstructural evolutions obtained by laser interference structuring are compared with the those obtained by conventional isothermal annealing. Periodically structured NiTi thin films with variable compositional spreads are prepared by laser interference irradiation using a Nd:YAG laser.

4:15 PM JJ2.8
The Combinatorial Search for Red Long Persistent Phosphors. Xiaonan Liu[1], Hanwei Gao[2], Yun Tang[3], Sunxiang Huang[2], Jun Bao[1] and Chen Gao[1,2]; [1]National Synchtron Radiation Lab., University of Science and Technology of China, Hefei, Anhui, China; [2]Department of Physics, University of Science and Technology of China, Hefei, Anhui, China; [3]Deparment of Chemical Physics, University of Science and Technology of China, Hefei, Anhui, China.

Recently, many oxide long persistent phosphors have been developed, and their life time, intensity and chemical stability surpasses the previous zinc sulfide. But most of their fluorescence are varied from violet to yellowish green, the performance of the red long persistent phosphors are not very good. Considering that the mechanism of the long persistent phosphors is not clear now, the search of new red long persistent phosphors is a big challenge for material scientists. In this report, the combinatorial method was used to search the new red long persistent phosphors. The sample library was synthesized by a home-designed multi-inkjet deliver system; the emission spectrum of the samples were detected by a fiber spectrometer; the persistence of the samples fluorescence were characterized by a scientific CCD in a parallel way, which can dramatically save the time of the sample characterization and accelerate the process of the new persistence phosphor finding. Finally, a serial of Mn^{2+} doped alkaline earth aluminosilicate were screened and some good red persistent phosphors were identified.

4:30 PM JJ2.9
Combinatorial Preparation of Hydrogen Sorbing Metal Alloys. Charles H. Olk, Materials & Processes Lab, General Motors Research Development & Planning, Warren, Michigan.

The discovery of hydrogen storage alloys that exceed the capacities, have lower thermodynamic stabilities, and faster kinetics than existing candidates is imperative to the development of clean hydrogen energy systems. We introduce the use of thin-film combinatorial methods to synthesize Mg-based hydrogen storage compounds. Using a combination of pulsed laser deposition (PLD) and magnetron sputtering, multi-compositional samples were produced for hydrogen sorption studies that consist of 16 separate Mg-Ni-Fe ternary pads and 32 Mg-Ni or Mg-Fe binary pads.

4:45 PM JJ2.10
Abstract Withdrawn

SESSION JJ3: Combinatorial Approach to Electronic, Inorganic and Magnetic Materials

Chairs: Alfred Crosby and David Ginley
Monday Evening, December 1, 2003
Independence West (Sheraton)

8:00 PM *JJ3.1
High-Throughput Investigation of Semiconducting-Insulating Thin Film Stability. J. Carson Meredith and Santanu Chattopadhyay; Chemical Engineering, Georgia Tech, Atlanta, Georgia.

I was invited by Alamgir Karim. Developing a robust ability to coat or deposit stable thin film polymeric conductors, semiconductors, and insulators is a necessity for many proposed nanoscale materials. These materials offer great promise to enhance the capabilities of sensors, microcomputers, optical devices, and biomaterials. However, our understanding of the onset and control of instability in polymer thin films, particularly those with large Hamaker constants (e.g., conductors and semiconductor polymers), is far from complete. In this talk we report a study of the van der Waals stability and dewetting that occurs for thin films of semiconducting polythiophene, as well as the more complex case of a polythiophene / polystyrene bilayer. In particular, using a combinatorial experimental strategy, we search a large number of thickness and annealing temperature combinations for these thin films, and characterize film dewetting mechanisms using image processing and informatic techniques. We are able to detect the onset transition thickness for van der Waals instability in these films, which allows a description of the conditions necessary for forming stable nanoscale films and bilayers. In addition, we illustrate how the dependence of van der Waals instability onset on film thickness is not captured by current theory in the bilayer case. Finally, we describe a very interesting dependence of the semiconducting polymer's stability on chain alignment and heterogeneity.

8:30 PM JJ3.2
Combinatorial Approach for Investigating Acid-Diffusion in Photoresists. Michael X Wang, Eric K Lin, Alamgir Karim and Michael J Fasolka; Polymers division, NIST, Gaithersburg, Maryland.

Developing and formulating materials for sub-100 nm lithography requires a detailed understanding of photoresist properties and processing conditions to achieve the necessary critical dimension and line-edge roughness control of patterned structures. High throughput combinatorial methods enable rapid and efficient evaluation of material properties and are well suited for the investigation of photoresist processing parameters. These methods can be used to extract parameters such as the acid diffusion coefficient for input into simulation tools or to map-out the processing parameter space likely to yield an optimal photoresist formulation. Using combinatorial methods*, we have studied acid diffusion and the deprotection activation energy in poly(p-tert-butoxycarboxystyrene) (PBOCST) matrix via a poly(4-hydroxystyrene) layer containing a photoacid generator (PAG) and functioning as an acid feeder. Utilizing a small sample set on designed film gradients such as temperature gradient, exposure dose gradient, or thickness gradient, we investigated the effects of PBOCST thickness, and the concentration and structure of PAG on acid diffusion. The surface roughness of the developed PBOCST layer was measured by atomic force microscopy (AFM) and correlated with varying deprotection activation energy and acid diffusion rates. * Work performed at the NIST Combinatorial Methods Center (NCMC)

8:45 PM JJ3.3
Combinatorial Fabrication and Studies of Small Molecular Organic Light-Emitting Devices. Lijuan Zou, Kwang-Ohk Cheon, Gang Li and Joseph Shinar; Ames Laboratory - USDOE * and Department of Physics and Astronomy, Iowa State University, Ames, Iowa.

Various combinatorial matrix arrays of UV-violet, white, and blue-to-red organic light-emitting devices (OLEDs), fabricated using a sliding shutter technique, are described. In the ultraviolet-violet devices, which contains a UV-violet emitting layer of 4,4'-bis(9-carba-zolyl)biphenyl (CBP), the optimal radiance R and external quantum efficiency η_{ext} were determined with respect to the thicknesses of the hole transporting layers. In the blue-to-red devices, which contained a blue-emitting layer of 4,4'-bis(2,2'-diphenyl-vinyl)-1,1'-biphenyl (DPVBi) and a red-emitting 5 wt.% dye-doped guest-host layer, the color of the devices evolved continuously from blue to red as the thickness of the doped layer increased from 0 to 35 Å. The (nominal) 2 Åthick doped layer device exhibited the highest brightness $L \sim 120$ Cd/m^2 and external quantum efficiency $\eta_{ext} \sim 4.4$ % at a current density of 1 mA/cm^2. In the white OLEDs, which were similar to the blue-to-red devices but only lightly doped, the highest brightness L_{max} was over 74,000 Cd/m^2; in all devices L_{max} exceeded 50,000 Cd/m^2. The maximum efficiencies were 11.0 Cd/A, 5.96 lm/W and 4.6% at 5.8 V, 0.6 mA/cm^2, and 68 Cd/m^2 in a 0.25 wt.%, 2 nm-thick doped layer device. *Ames Laboratory is operated by Iowa State University of the US Department of Energy under Contract W-7405-Eng-82.

9:00 PM JJ3.4
A Neutron Scattering Study of Rare-Earth Intermetallic Compound $La_3Co_{29}Si_4B_{10}$. Heng Zhang[1], M. Hofmann[2], S. J. Kennedy[3] and S. J. Campbell[1]; [1]School of Physics, University College, University of New South Wales, Australian Defense Force Academy, Canberra, Australian Capital Territory, Australia; [2]Technische Universitat Munchen, Garching, Germany; [3]Bragg Institute, Australian Nuclear Science and Technology Organization, Menai, New South Wales, Australia.

A quaternary rare-earth intermetallic compound $La_3Co_{29}Si_4B_{10}$ has been synthesized by using arc melting. The crystal structure and magnetic structure have been investigated by using in-situ neutron scattering. The Neutron scattering study and Rietveld refinement indicate that $La_3Co_{29}Si_4B_{10}$ is isostructural with $Nd_3Ni_{29}Si_4B_{10}$ tetragonal structure [1]. The magnetic scatting study indicates that the magnetic moments of the Co sublattice lie in the basal plane as a collinear configuration. Refinement of the low temperature neutron diffraction pattern indicates a mean magnetic moment for the Co sublattice of 0.47 μ_B/Co, or 13.6μ_B/F.U. Full details of the study will be addressed in the presentation. This work was support by Australian Research Council (ARC) and Australian Institute of Nuclear Science and Engineering (AINSE). Reference [1]. Heng Zhang, E. Wu, S. J. Campbell, S. J. Kennedy, H.-S. Li, A. J. Studer , S. R. Bulcock and A. D. Rae, "Structural study of the Rare-Earth Transition-Metal intermetallic compound $Nd_3Ni_{29}Si_4B_{10}$", J. Alloys and Compounds 278 (1998) 239

9:15 PM JJ3.5
Rapid growth temperature optimization of ferroelectric $Sr_xBa_{1-x}Nb_2O_6$ epitaxial thin films by a temperature gradient method. Isao Ohkubo, Hans M. Christen, Sergei V. Kalinin, Gerald Earle Jellison, Jr, Christopher M. Rouleau and Douglas H. Lowndes; Condensed Matter Sciences Division, Oak Ridge

National Laboratory, Oak Ridge, Tennessee.

Transition-metal oxides continue to attract significant attention due to their interesting electric and magnetic properties. However, obtaining single phase thin films of such complex metal oxides with excellent crystalline quality is generally time-consuming because of the numerous growth parameters to be optimized. Here we present a temperature-gradient substrate approach which allows a parallel, multiple-sample optimization of film growth conditions. The method has been applied successfully during pulsed laser deposition to optimize strontium barium niobate ($Sr_xBa_{1-x}Nb_2O_6$: SBN) film-growth conditions, thereby demonstrating the approach's capabilities. SBN is an attractive ferroelectric material because it exhibits an *exceptionally* large electro-optic (EO) coefficient, r_{33}, making it a potential material for miniaturized EO modulators, real-time holography applications, and information storage technologies. A smooth temperature gradient ranging from 200 °C to 830 °C over the film deposition surface was achieved by using a specially designed substrate holder. During film growth onto this temperature-gradient substrate holder, a position-dependent laser repetition rate was used in combination with reciprocating linear motion in order to achieve spatially uniform film-growth. For rapid evaluation of optical and ferroelectric properties, spectroscopic ellipsometry, x-ray diffraction and piezo-response atomic force microscopy were employed. Variations in optical properties and ferroelectric domains structures were clearly observed as function of growth temperature, and these physical properties can be related to their different crystalline quality. The results indicate a sharp "step" in the refractive index near 650 °C but full crystallization occurring only at slightly higher temperature. Research sponsored by the U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, and in part by the Laboratory Directed Research and Development Program.

9:30 PM JJ3.6
Optical Non-Contact Conductivity Mapping of Transparent Conducting Oxide Thin Film Libraries. John D Perkins[1], Brian M Keyes[1], Charles W Teplin[1], Lynn M Gedvilas[1], Jeff L Alleman[1], Matthew S Dabney[1], Maikel F A M van Hest[1], Matthew P Taylor[2], Xiaonan Li[1] and David S Ginley[1]; [1]National Renewable Energy Lab., Golden, Colorado; [2]Colorado School of Mines, Golden, Colorado.

For the development of transparent conducting oxides (TCOs), both the conductivity and the optical properties are critical properties which must be measured. For a combinatorial discovery and optimization approach, this must be done rapidly across an entire library. Furthermore, since, for TCOs, the infrared optical properties are largely determined by the optical response of the mobile conduction band electrons, in principle both the optical and electrical properties can be determined from the infrared optical measurements. Optical techniques are also inherently non-contact and hence amenable to automated mapping applications. We have developed, and are applying, infrared optical reflection and transmission mapping over the spectral range of 1.7 to 25 microns to characterize composition graded thin film TCO libraries. A Fourier Transform Infra-Red (FTIR) spectrometer is used in conjunction with an automated motion stage to produce sequential but spatially correlated reflection and transmission maps. A numerical Drude (free-electron) model is used to determine the local conductivity from the measured infrared optical spectra. We find that it is critical to measure both the reflection and the transmission in order to determine the electrical conductivity from the optical spectra via modeling. The development, application and limitations of this approach to non-contact conductivity mapping will be discussed using examples taken from our on-going work on the combinatorial development of thin film TCO materials. Specific material systems to be discussed include Zn-Sn-O, Cd-Sn-O, Zn-Al-O and Zn-In-O.

9:45 PM JJ3.7
SQUID magnetometry investigation of $Ca_xSr_{1-x}RuO_3$ films obtained by a compositional-spread technique. Isao Ohkubo, Hans M. Christen, Peter Khalifah, David George Mandrus and Douglas H. Lowndes; Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

The composition-spread method is an efficient way to fabricate films with continuously varying composition of a solid solution system. $Ca_xSr_{1-x}RuO_3$ (x = 0∼1) is known to have metallic conductivity and unusual magnetic properties. $SrRuO_3$ is a ferromagnet with a T_c of about 160K, whereas the susceptibility of $CaRuO_3$ shows a negative Weiss temperature suggesting a tendency toward antiferromagnetism. In order to investigate the magnetoelectric properties of the $Ca_xSr_{1-x}RuO_3$ system, we have used a pulsed laser deposition-continuous composition spread (PLD-CCS) approach [1] for fabricating epitaxial $Ca_xSr_{1-x}RuO_3$ films on various substrates. Here we report on the details of their magnetic properties over the entire composition range (x = 0∼1) as measured by SQUID magnetometry. The influence of the composition variation across each individually measured sample will be discussed in detail. Research sponsored by the U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC, and in part by the Laboratory Directed Research and Development Program. [1] H.M. Christen, C.M. Rouleau, I. Ohkubo, H.Y. Zhai, H.N. Lee, S. Sathyamurthy and D.H. Lowndes, Rev. Sci Instrum. in press.

10:00 PM JJ3.8
Combinatorial Co-Sputtering of Metal Nitrides and Transparent Conductive Oxides. Maikel F.A.M. van Hest, C. W. Teplin, M. S. Dabney, J. D. Perkins, J. L. Alleman, P. Parilla and D. S. Ginley; National Renewable Energy Laboratory, Golden, Colorado.

Combinatorial research is one of the approaches in the search for new materials, which can be used to rapidly explore material phase space by performing only a few depositions. The use of combinatorial co-sputtering from two or three different targets to produce both mixed metal nitrides and transparent conducting oxides films on 2″ x 2″ glass substrates will be reported. The sputtering targets are located in such a way that the composition of the deposited material is highly dependent on the location on the substrates. This allows for a large composition gradient across the deposited film. When using two targets material ratios can be mapped in a range from 0 to 100 % in as little as five depositions. The successful application of this combinatorial approach will be demonstrated for transparent conductive oxides, e.g. Zinc Tin Oxide, Zinc Indium Oxide, Zinc Indium Tin Oxide, and metal nitrides, e.g. Chromium Titanium Nitride, Chromium Zirconium Nitride and Vanadium Niobium Nitride. For the deposition of these mixed metal materials both metallic and oxide targets have been used. The targets have been sputtered using RF as well as DC power in an argon gas atmosphere with and without admixing oxygen or nitrogen. The importance of the combinatorial approach will be illustrated by showing correlation of optical and electrical properties with the material composition for the sputtered libraries.

SESSION JJ4: Combinatorial Approach to Polymers and Coatings
Chairs: Vladimir Mirsky and Ulrich Schubert
Tuesday Morning, December 2, 2003
Independence West (Sheraton)

8:30 AM *JJ4.1
Combinatorial Electropolymerization: Concept and First Results. Vladimir M. Mirsky, Institute of Analytical Chemistry, Chemo- and Biosensors, University of Regensburg, Regensburg, Germany.

An electropolymerization is used in different fields of science and technology as a simple method for preparation of polymer layers with a controlled thickness. It allows one to form multilayer systems and is compatible with inorganic electroplating. A concept of electrochemical synthesis and characterization of combinatorial libraries formed by different polymers and polymeric structures is presented. A control of electrical potential of single electrode groups on the array allows one to perform an addressable electrochemical polymer synthesis on defined electrodes only. Afterwards, an analysis of electrical characteristics of polymers and investigation of influence of potential analytes on these characteristic is performed. Finally, an automated data analysis is performed. A completely automated set-up providing these procedures, includes an automated dosing station, an electronic multiplexer and a socket board with polymerization cell. The synthesis of polymers and screening of their electrical properties is performed by two- or four-point techniques on the array of 96x4 electrodes situated on the silicon chip. A comparison of measurements performed by the two- and four-point techniques allows one to distinguish between resistance of bulk polymer and contact resistance. As the first application, an influence of non-conductive impurities on dynamic range of gas sensitive chemoresistors is investigated. A simple theory explaining the results is suggested. The developed concept and set-up can be applied for development and optimization of polymeric gas sensors, molecularly-imprinted polymers, enzymatic biosensors, new structures and polymers for organic electronics and in many other fields. The first results were obtained in combinatorial preparation and high-throughput investigation of gas sensors.

9:00 AM JJ4.2
Applications of discrete and gradient compositions in polymer research. Ron Wroczynski[2], Radislav A. Potyrailo[2], Jim Pickett[1] and Malgorzata Rubinsztajn[2]; [1]GE Global Research, schenectady, New York; [2]CCCT, GE Global Research, Niskayuna, New York.

A new general approach for rapid performance screening of polymer compositions is provided. Multiple compositions are generated as one-dimensional libraries in a micro-extruder with step or gradient composition changes in 2 - 10 g of polymer in < 1 min. To accelerate testing, an environmental stress is applied to only local regions, followed by high-sensitivity spatially resolved characterization. We applied our methodology for weathering of arrays of polymeric compositions and provided ranking of polymer/UV absorber compositions equivalent to traditional weathering data while achieved 20 times faster.

9:15 AM JJ4.3

Combinatorial Rheology of Long Chain Branched Polymer Melts. Ronald Larson and Seung Joon Park; Dept of Chem Eng, University of Michigan, Ann Arbor, Michigan.

One of the most important practical polymer characterization problems is the characterization of long chain branch (LCB). Given the low levels of branching one would desire to detect (1 branch per 10,000 backbone carbons), only rheological data show sufficient sensitivity to branching at this level to provide an accurate characterization. However, inferring branching information from rheology has not proved possible so far, due to combinatorial complexity, namely the ill-posed problem of fitting rheological data with a branching model in which there are too many parameters, including the density of branch points, branch lengths, the locations of the branches along the polymer backbone, and the polydispersity of molecular weight. Here we improve a recently developed hierarchical algorithm (Larson, 2001) that predicts the relaxation of general mixtures of the branched polymers, by inclusion of early time fluctuations and other refinements drawn from the theory of Milner and McLeish (1997). We then apply the modified hierarchical algorithm to rheological data for metallocene-catalyzed polyethylene (mPE) and show how, by combining the hierarchical algorithm with a knowledge of the chemical reaction kinetics, information on LCB can be inferred from rheological data of mPEs. The model can also used to design a branching structure necessary to achieve a desired target rheological response, through combinatorial computations that span a wide range of branching structures quickly on the computer using the hierarchical algorithm. Alternatively, by combinatorially mixing an unknown branched specimen with a known, but varying concentration and varying molecular weight linear polymer, a combinatorially large set of data will be generated which can be fitted with the hierarchical model to help overcome the problem of the combinatorial complexity of branching structure. [1] Larson, R. G., Macromolecules, 34, 4556 (2001). [2] Milner, S. T. and McLeish, T. C. B., Macromolecules, 30, 2159 (1997).

9:30 AM JJ4.4

High-Throughput Dynamic Mechanical Measurements of Polymers. Mary Beth Kossuth and Damian A. Hajduk; Symyx Technologies, Santa Clara, California.

The increasing popularity of "combinatorial chemistry" methods as an approach to solving materials issues has brought about a need for non-destructive high-throughput measurement techniques for determining various material properties. We will discuss workflows that have been developed to do this using microscale quantities of materials. One such example is a parallel dynamic mechanical thermal analyzer (PDMTA), which measures the flexural modulus of polymer thin films that have been deposited from solution onto a polyimide membrane. With this technique it is possible to track changes in modulus as a function of temperature, frequency, or time. Simultaneous measurements of 96 samples can be made in the same time it would take to make a single equivalent measurement on a conventional DMTA. Unlike in conventional techniques, it is easy to make replicates for parallel methods, thus improving the reliability of the data. For example, using the PDMTA, we have explored the effect of blending varying amounts of dioctyl phthalate (DOP), a common plasticizer that is selectively soluble in styrene, into narrow polydispersity block copolymers of styrene, methacrylic acid, and butyl acrylate by observing changes in the mechanical characteristics as a function of temperature. Addition of methacrylic acid to the styrene domain reduces the decline in hard block glass transition temperature seen in the equivalent diblock copolymers of styrene and butyl acrylate with increasing DOP content.

9:45 AM JJ4.5

High Throughput Measurements of Epoxy Curing. Dharmaraj Raghavan[1,3], Naomi Eidelman[2], Aaron M. Forster[3] and Alamgir Karim[3]; [1]Chemistry, Howard University, Washington, DC, District of Columbia; [2]ADAF,PRC, NIST, Gaithersburg, Maryland; [3]Polymers Division, NIST, Gaithersburg, Maryland.

The short and long term performance of advanced composites, coatings, and adhesives depends sensitively on the resin curing process. Using gradient high throughput curing and screening techniques, we have studied epoxy curing as a function of both time and temperature. Diglycidyl ether bisphenol A epoxy resin was mixed with fluorescent dye (4 dimethylamino-4-nitrostilbene) and curing agent (2,4,6-tri(dimethyl amino methyl) phenol) and flow coated on glass substrate. A gradient in epoxy curing was created by placing the sample on a temperature gradient stage (50 to 100) ^{o}C for 15, 30, 45, 60, and 180 min intervals . The epoxy film was mapped ex-situ by FTIR-reflectance microscopy (FTIR-RM) and confocal microscopy, in conjunction with Johnson, Kendall, and Roberts (JKR) adhesion test method (contact of hemispherical lens) to provide chemical, physical, and interfacial information on the cured epoxy. FTIR-RM was used to follow chemical conversion of epoxy groups, while confocal microscopy was used to follow the change in fluorescence intensity (emission maximum) of the fluorescent dye related to epoxy network formation, while JKR adhesion test was used to follow the change in epoxy tack, with curing time and temperature. The three techniques were validated by comparing the results obtained using individual epoxy standards. Maps of the combinatorial libraries showed not only distinct curing trends but also allowed visualization of the curing as a function of time and temperature. Good correlation was found in the curing trends obtained with the three techniques. Significant curing was achieved at higher temperatures for short curing times that can be compared to the longer curing times required to achieve similar curing at lower temperatures. We demonstrate a high-throughput approach to map, compare and correlate complementary chemical, physical and adhesive properties of an epoxy resin library undergoing curing by three independent methods: FTIR-RM, confocal microscopy, and JKR adhesion test.

10:30 AM *JJ4.6

Combinatorial Chemistry Methods for Coating Development. Bret Chisholm[1], Radislav Potyrailo[2], James Cawse[2], Christopher Molaison[1], Ronald Shaffer[2], Donald Whisenhunt[2] and Daniel Olson[1]; [1]Performance Coatings Laboratory, GE Global Research Center, Niskayuna, New York; [2]Combinatorial Chemistry Laboratory, GE Global Reseach Center, Niskayuna, New York.

A combinatorial method for the development of organic clear coatings for plastic substrates has been developed. The combinatorial process or combinatorial factory has a throughput on the order of 100 coatings per day and possesses all of the aspects of a conventional combinatorial process such as automated sample preparation, miniaturized samples configured in an array format, high throughput screening of the properties of interest, and computer software developed for data management, storage, and analysis. The combinatorial factory greatly enhanced the rate of organic clear coat development.

11:00 AM JJ4.7

High-Throughput Adhesion Evaluation and Scale-up of Combinatorial Leads of Organic Protective Coatings. Karin Ezbiansky[1], George Medford[1], Hariklia Reitz[1], Radislav A Potyrailo[2], Bret J Chisholm[2], William G Morris[2], James N Cawse[2], William P Flanagan[2], Lamyaa Hassib[2] and Chris A Molaison[2]; [1]GE Silicones, General Electric, Waterford, New York; [2]Global Research Center, General Electric, Schenectady, New York.

Coupling of combinatorial chemistry methods with high-throughput (HT) performance testing and measurements of resulting properties has provided a powerful set of tools for the 10-fold accelerated discovery of new high-performance coating materials for automotive applications. Our approach replaces labor-intensive steps with automated systems for evaluation of adhesion of 8 X 6 arrays of coating elements that are discretely deposited on a single 9 X 12 cm plastic substrate. Performance of coatings is evaluated with respect to their resistance to adhesion loss. This parameter is one primary consideration in end-use automotive applications. Specifically, a temperature, pressure, humidity cycling adhesion test is a key criteria for hardcoat performance on headlamps. Coating leads identified from the combinatorial work have been scaled up and evaluated in the laboratory. The translation of the target candidates to the lab scale as well as initial customer trials will be discussed.

11:15 AM *JJ4.8

Combinatorial Characterization of Heterogeneous Polymer Interfaces. Alfred John Crosby, Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts.

Interactions between surface and near-surface material properties play a critical role in numerous applications ranging from MEMS to packaging tape. In these regions, lateral interfacial heterogeneities often define success or failure, yet most fundamental investigations of interfacial strength, or adhesion, focus on homogeneous interfaces. Adhesion is an interface's resistance to separation. For polymers, this resistance is dictated by: 1) the transfer of stress across an interface, and 2) the dissipation in the near-surface volume. For heterogeneous interfaces, we must not only understand how the interface and bulk properties define adhesion, but also how neighboring phases couple to affect adhesion. In our research, lateral heterogeneities on the micron and nanometer lengths are investigated. Specifically, we determine how the length scale and magnitude of heterogeneities affect the adhesion of polymer interfaces. This topic presents a large, multivariable parameter space that includes: size scale, spatial density, surface chemistry, near-surface mechanical properties, and topography. To efficiently explore these variables over the broad range of polymer/substrate combinations, we rely upon combinatorial methodologies for library preparation, characterization, and analysis. Here, we present our results on the effect of topographical heterogeneities on polymer adhesion. We create two dimensional maps of size scale and spatial density. Our initial results focus on the adhesion of crosslinked polydimethylsiloxane and poly(n-butyl acrylate). We rely upon the theory of Johnson, Kendall, and Roberts (JKR) and the recently introduced combinatorial technique, the Multilens Contact Adhesion Test (MCAT), to quantify the adhesion of our combinatorial heterogeneity maps. In addition to demonstrating the tuning of adhesion with systematic heterogeneities, our results provide insight into the critical length scales for molecular dissipative mechanisms related to adhesion.

11:45 AM JJ4.9

High-Throughput Screening of Colorant Stability in Polymer Formulations. Donald W Whisenhunt, Ronald E Shaffer, Randall L Carter and William Bulsiewicz; Combinatorial Chemistry Lab, General Electric Global Research, Niskayuna, New York.

Commercial polymers are rarely pure; most contain colorants, stabilizer, plasticiers, etc. Determining how the interactions of these components affect the final product can be costly and time consuming to sort out. To solve this problem we developed a high-throughput screen to rapidly gauge the thermal stability of colorants in a polymer formulation and determine how the thermal stability changes in the presence of different additives.

SESSION JJ5: Combinatorial Approach to Polymers
and Biopolymers
Chairs: Olivier Lavastre and Ali R. Mehrabi
Tuesday Afternoon, December 2, 2003
Independence West (Sheraton)

1:30 PM *JJ5.1

Polymer Chemistry the Combinatorial Way. Mark Bradley, Chemistry, Combinatorial Centre, Southampton, United Kingdom.

Combinatorial chemistry has captured the imagination of the pharmaceutical industry and has led to widespread changes in the application and exploitation of synthetic chemistry with respect to drug discovery. However such methods have immense power and application across a broad range of additional areas. In my presentation I will illustrate the breadth of combinatorial methods being developed at Southampton in the areas of library synthesis, screening and analysis. This will include multiple examples fro mthe polymer area ranging from beads produced by suspension/emulsion polymerisation methods to molecular imprinted polymers to random copolymers. A range of innovative HT innovative screens will be described for different polymer based applications. the polymer

2:00 PM JJ5.2

Characterization of Soluble Polymer Supported Organic Molecules by Mass Spectrometry. Christine Enjalbal[1], Frederic Lamaty[1], Patrice Ribiere[1], Stephane Varray[1], Eric Suberchicot[1], Neerja Yadav-Bhatnagar[2], Jean Martinez[1] and Jean-Louis Aubagnac[1]; [1]Chemistry, Universites Montpellier 1 & 2, UMR5810, LAPP, Montpellier, France; [2]Aventis Pharma, Romainville, France.

Liquid-phase chemistry In the case of a soluble polymer supported synthesis,[1] the tuning of the support solubility depending on the solvent offers new opportunities for combinatorial chemistry[2] for two reasons. First, organic syntheses in solution are generally easily translated on a soluble polymer supported substrate. Second, complete automation of the three successive steps of combinatorial chemistry (synthesis, analytical control, and biological test) is approached without releasing the synthesized compound from the support. Among all reported polymers, bifunctional PEG 3400 possessing an average molecular weight centered around 3400 mass units[3] allowed to achieve supported syntheses in high yield. Polyethylene glycol and Mass Spectrometry From an analytical point of view, PEG samples are suitable to conventional spectroscopic methods such as mass spectrometry (ElectroSpray and Matrix Assisted Laser Desorption Ionization) which is not the case for resins used in solid-phase syntheses. Reaction monitoring was thus performed directly on the substituted PEG sample by characterizing the end group structure.[4,5] However, interpretation of the mass spectra was complicated by the fact that, for any detected ion, three unknowns needed to be elucidated: the nature of the ion (protonated or cationized species), the number of ethylene oxide unit to identify the oligomer, and the structure of the end group to characterize the sample. Experimental parameters in both ESI and MALDI techniques were tuned to simplify the recorded data. In ESI mass spectrometry, the addition of alkali metal scavenger to the PEG solutions provided the best mass spectra suitable to automated data processing according to a pass/fail criteria indicating the presence or absence of the expected compound.[6] LC/ESI-MS experiments Liquid chromatography coupled to ESI mass spectrometry is the method of choice to profile mixtures (side-reaction detection, kinetics studies, Mix and Split combinatorial libraries profiling, ...). Chromatographic separation of PEG mixtures was obtained under specific conditions and the subsequent LC/ESI-MS data were acquired.[6] 1. Bayer E.; Mutter M. Nature 237, 512 (1972); Hans H.; Wolfe M. M.; Brenner S.; Janda K. D. Proc. Natl. Acad. Sci. USA, 92, 6419 (1995) ; Gravert D. J.; Janda K. D. Curr. Opin. Chem. Biol. 1, 107 (1997) 2. Sun C. M. Combinatorial Chemistry & High Throughput Screening 2, 299 (1999) 3. Sauvagnat B. ; Kulig K. ; Lamaty F. ; Lazaro R. ; Martinez J. J. Comb. Chem. 2, 134 (2000) 4. Sauvagnat B.; Enjalbal C.; Lamaty F.; Lazaro R.; Martinez J.; Aubagnac J-L. Rapid Commun. Mass Spectrom. 12, 1034 (1998) 5. Thurmer R.; Meisenbach M.; Echner H.; Weiler A.; Al-Qawasmeh R. A.; Voelter W.; Korff U.; Schmitt-Sody W. Rapid Commun. Mass Spectrom. 12, 398 (1998) 6. C. Enjalbal, F. Lamaty, P. Sanchez, E. Suberchicot, P. Ribiere, S. Varray, R. Lazaro, N. Yadav-Bhatnagar, J. Martinez & J-L. Aubagnac Anal. Chem. 75, 175 (2003)

2:15 PM JJ5.3

Combinatorial Strategies for Thin Organic Films by Polyatomic Ion Deposition - From Biomaterials to Conducting Polymers. Luke Hanley[1], Yongsoo Choi[1], Sanja Tepavcevic[1], Andrei Choukourov[2] and Hynek Biederman[2]; [1]Chemistry, MC 111, University of Illinois at Chicago, Chicago, Illinois; [2]Macromolecular Physics, Charles University, Prague, Czech Republic.

Polyatomic ion deposition at ion impact energies below 200 eV is an effective method for the growth of thin organic films on polymer, metal, and semiconductor surfaces [1]. We have previously shown that fluorocarbon and siloxane ions can be employed for the growth and modification of organic thin films on polymer, semiconductor, and metal surfaces. Polyatomic ion beams can also be employed to create chemical gradient thin films by variation of the ion fluence, structure, or kinetic energy across the substrate. We demonstrate here these various combinatorial strategies for eventual application in biomaterials and conducting polymers. Variation of ion fluence can be used to create gradient thin films on surfaces. Mass-selected 50 eV fluorocarbon ion deposition in vacuum is used to create a fluorocarbon gradient film on a polymer substrate [2]. X-ray photoelectron spectroscopy (XPS) shows a continuous change in the surface chemistry from that of the native polymer to a fluorocarbon film. Selection of the ion structure or kinetic energy can also create gradients on surfaces. Mass-selected 5 - 200 eV silazane and allyl amine ions are deposited onto aluminum and silicon substrates to create a variety of amine surfaces. Chemical functionalization prior to XPS analysis permits the unique identification of primary and secondary amine groups. Secondary amine containing films are shown to form at low silazane ion energies whereas the higher ion energies lead to formation of more inorganic, silico-carbo-nitride-like films. Primary amines are produced by allyl amine ions at various energies. Film thicknesses can also be varied by tuning the ion energy or structure, as demonstrated for the deposition two different fluorocarbon ions on H-Si(100) [3]. Finally, neutral beams can be combined with ion beams to create new organic materials, with the ratio of these two reagents controlling film properties. This process, termed surface polymerization by ion assisted deposition (SPIAD), produces films that maintain the chemical structure of the monomer [4]. A polythiophene film is produced here by SPIAD with 100 eV thiophene ions and terthiophene monomers coincident on Si and indium tin oxide (ITO) substrates held under vacuum. XPS observes enhancement in film growth for SPIAD compared with either thiophene ion or terthiophene exposure alone. Polythiophene films grown by both mass-selected and non-mass-selected ions with coincident terthiophene dosing display various fluorescence spectra, depending upon the ion to neutral ratio employed. [1] L. Hanley and S.B. Sinnott, Surf. Sci. 500, 500 (2002). [2] M.B.J. Wijesundara, E. Fuoco, and L. Hanley, Langmuir 17, 5721 (2001). [3] E.R. Fuoco and L. Hanley, J. Appl. Phys. 92, 37 (2002). [4] S. Tepavcevic, Y. Choi, and L. Hanley, J. Amer. Chem. Soc. 125, 2396 (2003).

2:30 PM *JJ5.4

Combinatorial methods and high-throughput experimentation in synthetic polymer chemistry. Ulrich S Schubert, Huiqi Zhang, Stefan Schmatloch, Nico Adams, Berend-Jan de Gans, Michael A.R. Meier and Richard Hoogenboom; Laboratory or Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology, Eindhoven, Netherlands.

Combinatorial and high-throughput methods open new avenues for polymer research, both regarding the understanding of structure-property relationships as well as regarding the selected design of new materials and efficient polymerization processes [1]. Automated synthesizers were successfully utilized for controlled and living polymerizations. This approach was first applied to the living cationic ring opening polymerization (CROP) of 2-oxazoline monomers [2] and to atom-transfer radical polymerization (ATRP) of MMA [3]. For these systems, the reproducibility and comparability with conventional experiments was proven initially. Subsequently, new reaction conditions, catalysts and systematical variations in polymer composition have been studied in detail. During these investigations, procedures for automated sampling and sample preparation for online and offline (kinetic) investigations utilizing GC, GPC and MALDI-TOF-MS were developed in order to gain a better inside into the polymerization processes [2-4]. The automation of kinetic studies improved also the comparability of the obtained results. Moreover, samples could be continuously taken from the polymerization reactions at regular intervals. Finally, the possibility of performing automated parallel emulsion polymerizations was demonstrated yielding similar results as obtained in conventional experiments [5]. Moreover, combinatorial methods for defined spot or film preparation utilizing ink jet printing as well as automated methods for the characterization of thin films, such as plate readers or AFM were investigated [6]. [1] R. Hoogenboom, M.A.R. Meier, U.S. Schubert, Macromol. Rapid Commun. 2003, 24, 15-32; U.S. Schubert, C.S. Kniep, GIT Laboratory Journal Europe 2003, 100-101; R. Hoogenboom, U.S. Schubert, J. Polym. Sci.: Part A: Polym. Chem. 2003, 41, in press. [2] R. Hoogenboom, M.W.M. Fijten, M.A.R. Meier, U.S. Schubert, Macromol. Rapid Commun. 2003, 24, 92-97; R. Hoogenboom, M.W.M. Fijten, C. Braendli, J. Schroer, U.S. Schubert, Macromol. Rapid Commun. 2003, 24, 98-103. [3] H. Zhang, M.W.M. Fijten, R. Reinierkens, R. Hoogenboom, U.S. Schubert, Macromol. Rapid Commun. 2003, 24, 81-86; H. Zhang, M.W.M. Fijten, R. Hoogenboom, U.S. Schubert, ACS Symp. Ser. 2003, 854, 193-205. [4] M.A.R. Meier, U.S. Schubert, Rapid Commun. Mass Spectrom. 2003, 17, 713-716; M.A.R. Meier, R. Hoogenboom, M.W.M. Fijten, M. Schneider, U.S. Schubert, J. Comb. Chem. 2003, in press. [5] D.-J. Voorn, M.W.M. Fijten, J. Meuldijk, U.S. Schubert, A.M. van Herk, Macromol. Rapid Commun. 2003, 24, 320-325. [6] R. Neffati, A. Alexeev, S. Saunin, J.C.M. Brokken-Zijp, D. Wouters, S. Schmatloch, U.S. Schubert, J. Loos, Macromol. Rapid Commun. 2003, 24, 113-117; B.-J. de Gans, U.S. Schubert, Macromol. Rapid Commun. 2003, 24, in press.

3:30 PM *JJ5.5

Polymers for enhanced delivery of bioactives to human tissues: From building blocks to performance screening.

Miroslav Petro, Symyx Technologies, Inc., Santa Clara, California.

It is becoming generally accepted that combinatorial approaches in design, construction and screening of novel compounds and formulations lead to a significant acceleration of material discovery and development process. Polymers are the materials that offer a great opportunity to dial-in a desired set of performance features via a proper combination of various building blocks such as monomer units or polymer chain segments. Formulation of the polymer into its final environment in a combinatorial way results in enhancement of the desired material features even further. Over the last few years at Symyx, we have perfected a variety of parallel polymerization, purification and formulation techniques, supported by rapid automated analyses in combination with a suite of high-throughput protocols for application-related benefit screening, and interconnected via a common software platform. The whole set of tools and procedures is integrated into a robust workflow that serves us in a number of programs targeting discovery and development of novel polymeric materials in a wide range of application areas. In addition to the performance features of the polymeric materials controlled by their chemical, physical and mechanical properties, we can monitor interactions of polymers with a variety of molecules and substrate surfaces. The high-throughput interaction-based procedures were used to screen diverse polymers for their ability to deliver a variety of bioactive molecules to different human tissues from complex biological environments. The presentation will outline our combinatorial approach, from a combination of variety of building blocks, through the screens for molecular properties of resulting polymers and the interaction-based screens for selective delivery of bioactives, up to the identification of the best delivery agents.

4:00 PM JJ5.6

Combinatorial Screening of Cell-Material Interactions.

Newell Washburn, Scott Kennedy, Carl Simon, Mike Weir, Amit Sehgal, Aaron Forster and Eric Amis; NIST, Gaithersburg, Maryland.

Combinatorial and high-throughput techniques are being developed for investigating cellular responses to biomaterials and this talk will compare gradient library with design-of-experiment (DOE) methods. In the gradient library method, cells are seeded on samples prepared with systematic variations in material properties along one or two orthogonal directions. Cellular response to local material parameters is quantified using fluorescence microscopy, assuming each position on the sample represents a discrete experiment. These data are compiled into distributions, which are analyzed using statistical methods. The influence of material parameters on cellular response is characterized in terms of changes in these distributions. Examples of cellular response to polymer crystallinity, blend composition, and surface energy will be presented. DOE methods are used to characterize the interplay between material variables and soluble signaling molecules. Using these methods it is possible to efficiently screen a large number of interacting variables in determining cellular responses. Work on developing response surfaces for in vitro models of inflammation and cartilage repair will be presented.

4:15 PM JJ5.7

Biopolymer Reverse Engineering: Correlating Molecular Structure and Cell Response in a Combinatorial Library of Biodegradable Polymers Using Non-linear Optimization.

Jack R Smith[1,2], Doyle Knight[3], Joachim Kohn[2,1], Khaled Rasheed[4] and Sascha Abramson[2,1]; [1]New Jersey Center for Biomaterials, Piscataway, New Jersey; [2]Chemistry, Rutgers University, Piscataway, New Jersey; [3]Mechanical and Aerospace Engineering, Rutgers University, Piscataway, New Jersey; [4]Computer Science, University of Georgia, Athens, Georgia.

Surrogate modeling of biological response in the presence of biodegradable polymers is an emerging technique for identifying those atomistic or molecular scale properties of biopolymers that are relevant to bioactivity. We have employed Artificial Neural Network (ANN) models in conjunction with a machine learning methodology to predict cell growth of rat and human fibroblasts grown on a library of tyrosine-derived degradable polyarylates, and used the information generated in the analysis to identify molecular descriptors of these polymers that are relevant to cell growth. The library includes experimental cell growth data for rat lung fibroblasts (62 polymers) and human normal foreskin fibroblasts (94 polymers). The surrogate modeling is comprised of four steps. First, an extensive set of 106 molecular and physical-mechanical descriptors are defined for each polymer in the library. The molecular descriptors are calculated using the software package Molecular Operating Environment (MOE). The physical-mechanical descriptors (i.e., glass transition temperature and air-water contact angle) are measured experimentally. Second, a Decision Tree (DT) machine learning routine is used to generate a subset of descriptors (9 and 17, respectively, for the rat and human fibroblasts) from the initial set which have the greatest correlation to cell growth. The DTs are capable of correctly classifying 83% of all polymers using the respective descriptor subsets. Third, a series of ANN models are developed for rat and human fibroblasts using the descriptor subsets and trained on one-half of the polymers selected randomly from the library. Fourth, the ANN models are validated by comparison with the remaining one-half of the polymers. The best ANN model for rat lung fibroblasts achieved a correlation coefficient of 0.87 for the validation set, and evaluation of the leading twenty ANN models indicated that the polymer diameter (the largest value in the petitjean distance matrix), PEOE_VSA+2 (a partial charge summation) and chi1v_C (a carbon connectivity index which gives the sum of distances between carbon atoms) are the critical parameters for predicting cell growth, with diameter being the most significant. The best ANN model for human normal fetal foreskin fibroblasts achieved a correlation coefficient of 0.70 for the validation set, and evaluation of the leading ten ANN models indicated that [number of unsubstituted aromatic C (sp2)], [PEOE_VSA+1]and [PEOE_VSA_POS] (two different partial charge summations) are the critical parameters for predicting cell growth. These results provide strong evidence of the capability of surrogate modeling to predict bioresponse, and pose intriguing questions regarding the critical descriptors affecting cell growth.

4:30 PM *JJ5.8

Formation and Properties of Multivariant Polymer Brushes on Material Surfaces.

Jan Genzer, Tao Wu, Rajendra R Bhat and Michael R Tomlinson; Chemical Engineering, NC State University, Raleigh, North Carolina.

The demands on preparing, processing, and characterizing novel materials and structures and the need for full exploration of the parameter space has recently led to the development of a plethora of new multivariant approaches. In our presentation we will outline several multivariant methodologies that facilitate the preparation and characterization of interfacial properties of macromolecules grafted on flat solid substrates. We will introduce a method for generating polymer assemblies with a gradually increasing position-dependent polymer grafting density. We will document that such a set up can be utilized to probe the "mushroom-to-bush" conformational transition in both neutral polymer brushes [J. Am. Chem. Soc. 124, 9394 (2002)] as well as weak surface-anchored polyelectrolytes. We will also describe a technique leading to the generation of polymer assemblies with a gradually changing molecular weight of the grafted polymers [Macromolecules 36, 3449 (2003)]. A simple extension of the latter approach will facilitate the generation of surface grafted block copolymers with gradually varying compositions [Chem. Comm. No.12, 1350 (2003)]. We will document that by combining the individual gradients, i.e. the grafting density and molecular weight, one can produce complex substrates in which two material properties change independently in two orthogonal directions. We will address the application of such structures for sensing and separation. Finally, we will demonstrate that multivariant polymer brush assemblies represent universal soft material scaffolds that can be utilized in adjusting the spatial distribution of non-polymeric object (such as nanoparticles).

SESSION JJ6: Combinatorial Materials Design and Evaluation

Chairs: Kathryn Beers and Andrew Leach
Tuesday Evening, December 2, 2003
Independence West (Sheraton)

8:00 PM *JJ6.1
Combinatorial Large-Scale Simulation for Catalysts and Materials Design. Momoji Kubo[1], Kotaro Seki[1], Yuki Ito[1], Changho Jung[1], Hitoshi Kurokawa[1], Akira Endou[1], Akira Imamura[2] and Akira Miyamoto[3,1]; [1]Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Sendai, Miyagi, Japan; [2]Department of Mathematics, Faculty of Engineering, Hiroshima Kokusai Gakuin University, Hiroshima, Hiroshima, Japan; [3]New Industry Creation Hatchery Center, Tohoku University, Sendai, Miyagi, Japan.

Recently, we introduce a concept of combinatorial chemistry to computational chemistry for catalysts and materials design, and proposed a new concept called "Combinatorial Computational Chemistry". In this approach, the effects of large number of elements on the properties and functions are systematically calculated using computer simulation techniques in order to predict the best element for required properties and functions [1]. In order to realize the high-throughput screening by the combinatorial computational chemistry approach, the development of the accelerated simulation methods is required. Recently, we succeeded in the development of an accelerated quantum chemical molecular dynamics program "Colors" for the combinatorial computational chemistry, which is more than 5000 times faster than the first-principles molecular dynamics. It indicates that 10 years calculation by the first-principles molecular dynamics can be finished within only one day by our accelerated quantum chemical molecular dynamics program. Moreover, we successfully applied our accelerated quantum chemical molecular dynamics program to large-scale simulation for various catalyst and material systems [2,3]. The validity of some theoretically designed catalysts and materials were confirmed by experiments after our proposal. Hence, we confirmed that our accelerated quantum chemical molecular dynamics program is a very powerful tool to perform the theoretical high-throughput screening of the catalysts and materials. [1] M. Kubo, T. Kubota, C. Jung, K. Seki, S. Takami, N. Koizumi, K. Omata, M. Yamada, and A. Miyamoto, Energy and Fuels, in press. [2] M. Elanany, P. Selvam, T. Yokosuka, S. Takami, M. Kubo, A. Imamura, and A. Miyamoto, J. Phys. Chem. B, 107 (2003) 1518. [3] Y. Luo, P. Selvam, Y. Ito, S. Takami, M. Kubo, A. Imamura, and A. Miyamoto, Organometallics, 22 (2003) 2181.

8:30 PM JJ6.2
Rapid Database Development and Neural Network Modeling of Tensile Properties in Titanium Alloys for Structural Applications. Thomas Searles[1], Sujoy Kar[1], Eunha Lee[1], Jaimie Tiley[2], Gopal Babu Viswanathan[1], Rajarshi Banerjee[1] and Hamish L Fraser[1]; [1]Materials Science and Engineering, The Ohio State University, Columbus, Ohio; [2]Air Force Research Laboratory, Wright Patterson Air Force Base, Dayton, Ohio.

The development of a set of computationally based tools that permit microstructurally-based predictions for the tensile properties of commercially important titanium alloys, such as Ti-6Al-4V, is a valuable step towards the accelerated maturation of materials. This paper will discuss the development of Fuzzy Logic and Neural Network Models based on Bayesian statistics to predict the yield strength, ultimate tensile strength and elongation of Ti-6Al-4V at room temperature. The development of such rules-based models requires the building up of extensive databases which in the present case are microstructurally-based. The steps involved in database development include the varying of microstructures using novel combinatorial approaches to heat-treatments, the use of standardized stereology protocols to rapidly characterize and quantify microstructural features, and mechanical testing of the heat-treated specimens. These databases have been used to train and test the Fuzzy Logic and Neural Network models to predict the tensile properties. In addition, these models have been successfully used to identify the influence of individual microstructural features on the mechanical properties, consequently guiding the efforts towards development of more robust phenomenological models.

8:45 PM JJ6.3
Rapid Chemical and Structural Analysis of Ternary Phase Diagrams with Synchrotron Radiation. Elliot D. Specht[1], A Rar[1,2], G M Pharr[1,2], E P George[1,2], P Zschack[3], H Hong[3] and J Ilavsky[4]; [1]Metals & Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [2]Dept. of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee; [3]Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana-Champaign, Illinois; [4]National Institute of Standards and Technology, Gaithersburg, Maryland.

A technique based on synchrotron radiation provides rapid chemical and structural characterization of ternary alloys over a wide range of composition. The technique is applied to isothermal sections of the Cr-Fe-Ni system grown on Al_2O_3(0001) sapphire substrates by sequential deposition of layers of graded thickness followed by annealing to interdiffuse the elements. An isothermal phase diagram section is characterized in 4 h at a resolution of 2 atomic % by rastering the sample under a focused beam of synchrotron radiation. The diffraction pattern is measured with a CCD detector to identify crystallographic phases and measure texture and lattice parameters while simultaneously measuring the x-ray fluorescence with an energy-dispersive detector to determine elemental composition. Maps of phase composition and lattice parameter as a function of composition for several annealing treatments are found to be consistent with equilibrium values. The technique will be useful in combinatorial materials design. Research sponsored, by the Office of Industrial Technologies, Industrial Materials for the Future Program, under grant number DE-FC07-02ID14251 and by the Division of Materials Sciences and Engineering, U. S. Department of Energy under Contract DE-AC05-00OR22725 with UT-Battelle, LLC. The UNICAT facility at the Advanced Photon Source (APS) is supported by the Univ of Illinois at Urbana-Champaign, Materials Research Laboratory (U.S. DOE, the State of Illinois-IBHE-HECA, and the NSF), the Oak Ridge National Laboratory (U.S. DOE under contract with UT-Battelle LLC), the National Institute of Standards and Technology (U.S. Department of Commerce) and UOP LLC. The APS is supported by the U.S. DOE, Basic Energy Sciences, Office of Science under contract No. W-31-109-ENG-38.

9:00 PM JJ6.4
Combinatorial Evaluation of Personal Care Products. Damian A. Hajduk and Mani Jayaraman; Symyx Technologies, Santa Clara, California.

Multicomponent emulsions are commonly used in the personal care industry for a wide range of beauty care products. Combinatorial preparation and evaluation of these emulsions involves numerous technical challenges, including accurate dispensing and mixing of components with widely varying polarities, viscosities, and target concentrations; small-scale mixing of components to achieve a stable and reproducible particle size distribution; delivery of viscous emulsions to various surfaces; simulation of various aspects of real product application such as rubbing or washing; and evaluation of performance. We will illustrate these challenges by describing the evaluation of novel ternary copolymers proposed as performance enhancing agents for oil-in-water emulsions. Polymer libraries were designed to explore a specified region of the appropriate composition phase diagram, prepared using batch or semicontinuous polymerization, and combined at various concentrations with water, lipophilic material, and surfactants to create model products. For each set of monomer chemistries, nearly 300 unique formulations (representing 24 compositions at four molecular weights and three polymer concentrations) were prepared. After simulated application to model surfaces, system performance was assessed by high throughput TLC or HPLC. More detailed evaluation of selected materials involved measurement of particle size distributions and rheological characteristics. The resulting relationships between these quantities can be used to optimize formulation performance in applications.

9:15 PM JJ6.5
A Combinatorial Chemistry Study of Nucleation. Randall Hay, USAF, WPAFB, Ohio.

Control of nucleation of the equilibrium phase from colloidal materials is very difficult. The nature of nucleation sites and mechanisms for colloidal materials are controversial. Typically nucleation is site-saturated and spherulitic, with a density of 1 nuclei per mm3.

The resultant grain size is much too large for most applications. Typically a grain size less than 0.1 mm is desired, which means at least a 3 order of magnitude increase in nucleation frequency is necessary. The lack of a theory from which spherulitic nucleation density can be predicted makes combinatorial techniques very attractive. Nucleation frequency is a critical technical obstacle to making dense polycrystalline yttrium-aluminum garnet (YAG) fiber. Fine-grained YAG is also necessary to sinter monolithic YAG to high density for such applications as radiant burners and polycrystalline lasers. A combinatorial method was developed to identify dopants that promote profuse nucleation of YAG from colloidal precursors. This method allows large numbers of TEM samples to be rapidly prepared and observed for nuclei density. The concentration and viscosity of colloidal YAG precursors was adjusted so that drops of controlled size formed electron transparent films on nickel TEM grids during drying at room temperature. These precursors were doped with 0.1 to 10 mol% of various oxide forming nitrates. In many cases combinations of two or more dopants were tried. Films were formed from over a hundred different doped precursors and heat-treated for 1h at 900-1100C. Nuclei were counted from TEM micrographs. Dopant levels were screened for anything with more than an order of magnitude increase in nucleation frequency over baseline.

9:30 PM JJ6.6
Heterogeneous design. Structural diagrams of ternary systems. Vasily I. Lutsyk and Vera P. Vorobjeva; Russian Academy of Sciences, Buryat Scientific Center, Ulan-Ude, Russian Federation.

So called structural diagrams were described only for binary systems. Analogous structural diagram may be constructed for a ternary system too, if to accept every its concentration field as a rectangle prism base, and this prism height - as a mass content axis. Topology of phase diagram produces a number of its concentration fields (and a number of crystallization schemes) as x-y projection of all geometrical elements. Sometimes it is more convenient to manipulate a structural diagram in the form of its x-y projection too. In this way a concentration triangle of T-x-y diagram is marked by a set of lines of constant concentration of any phase (combination of phases) and its (their) portions of different origin. The mass of phase reaction products are calculated by matrix algorithms, which give an opportunity to find the origin of every phase and its portion at any temperature within the reaction interval or at the moment of its finishing. Temperature range of reaction is calculated as a response function on the upper and lower boundaries of corresponding phase region. As a result the origin of every microstructural element, having got at the crystallization from the melt of given concentration, is describing by the equations of unruled surfaces and a matrix equation of mass balance. The lines of "constant level" for concentration of given phase, its portions, or some phase combinations are mapping. In total it had got a set of concentrations maps. If to put them one to another, a point of cross-section of these isolines as an initial liquid concentration may be chosen. This liquid crystallization produces the required microstructure elements concentration.

9:45 PM JJ6.7
Management of Combinatorially Acquired Multi-dimensional Data through Object-Oriented Virtual Sample Library.
Shin-ichi Todoroki and Satoru Inoue; Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki, Japan.

Multi-dimensional data management can not be passed by for the researchers who make several measurements on combinatorially integrated samples, especially when they need to examine the correlation among these measurements. In general, the data of each measurement is stored independently in various format, it is very laborious work to pick up correlated data measured at a specific position in the sample. In order to solve this problem, all the data should be stored at one place in common format. For this structuralization and standardization of data, we propose a concept of 'virtual sample library', a container of multi-dimensional data, which are to be accessed in data acquisition, data analysis and data visualization. Virtual sample library models after actual combinatorially integrated sample library. Namely, its logical structure is congruent with the cell structure of the real library. In each cell in the virtual library, references to experimental data (or another references to data) are stored. Thus, the virtual library has a tree-like structure and each experimental data is intuitively accessed by tracing references from the root of the tree. Such kind of structuralization is easily constructed and handled by a framework of object-oriented programming. In order to introduce this concept into the data management of our combinatorial screening system, we wrote a set of software by object-oriented script language called Ruby. This language is free software and has already been used in bioinfomatics and geophysical fluid dynamics because of its simplicity in processing large amount of text and highly structuralized data. Although this system requires object-oriented programming skill and the visualization tools which recognize Ruby's object, an interactive retrieval environment and a client-server system can be easily developed by add-in packages (irb and dRuby). In this presentation, we introduce this concept of object-oriented virtual sample library applied to our combinatorial screening system for developing Er^{3+}-doped transparent glass ceramics. This system includes a parallel annealing furnace for sample preparation and a sequential measurement equipment for fluorescence lifetime.

10:00 PM JJ6.8
Combinatorial Electrodeposition of Ternary Alloys.
Shane D. Beattie and Jeff R. Dahn; Physics, Dalhousie University, Halifax, Nova Scotia, Canada.

It has been shown that composition-spread libraries of binary alloys can be prepared simply, quickly and inexpensively using combinatorial electrodeposition methods [1,2]. Here we will show that a similar method can be used to fabricate composition-spread libraries of ternary alloys. The copper-tin-zinc system will be studied as an example. Approximately 80% of the Cu-Sn-Zn ternary composition space was sampled on a single film. The composition-spread film of ternary alloys is prepared in two steps. A composition-spread film of Sn-Zn binary alloys is deposited first. Galvanostatic deposition is performed in a Hull cell where current density varies as a function of position. Composition of the deposited alloy varies with current density, so a composition-spread range of binary alloys will be deposited along the length of the working electrode. The film is rinsed, rotated 90 degrees and placed in a beaker. A weak solution of copper sulfate is slowly dripped into the beaker. Aqueous Cu ions will exchange with electrodeposited Sn or Zn. The area of film at the bottom of the beaker is exposed to solution longer than the top, so more Cu will exchange. A Cu composition gradient is established along the film, perpendicular to the composition gradient of Sn and Zn. The film is then annealed under Argon at 200°C to encourage homogeneity. References: [1] D. Landolt, Electrochemica Acta, Vol. 39, No. 8/9, pp 1075-1090 (1994) [2] S. D. Beattie and J. R. Dahn, Journal of The Electrochemical Society, July 2003, Volume 150, Issue 7, pp. C457-C460

SESSION JJ7: Sensors and Microfluidics in
Combinatorial Chemistry and Materials
Chairs: Alamgir Karim and Radislav Potyrailo
Wednesday Morning, December 3, 2003
Independence West (Sheraton)

8:30 AM *JJ7.1
Temperature-Dependent Studies of Gas Sensing Materials Using MEMS Microarrays. Steve Semancik[1], Charles Taylor[2], Richard Cavicchi[1], Christopher Montgomery[1] and Zvi Boger[1]; [1]Chemical Science and Technology Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland; [2]Chemistry Department, Pomona College, Claremont, California.

Temperature can have a profound effect on the fabrication, properties and performance of materials. This is certainly the case when one examines various classes of materials for use in solid state chemical sensing, as temperature variations during both fabrication and operation of the devices can alter the inherent characteristics of sensing films, and the ways in which chemical species interact with them. In this presentation we describe MEMS devices called microhotplates which have been developed as low power chemical microsensor platforms at NIST. More specifically, we focus here on multielement arrays of 16 and 36 microhotplates which have been used to efficiently study the processing and performance of multiple, different sensing films in parallel studies. Each $\sim$ 100μm x 100 μm element provides a thermally isolated and individually addressable microsubstrate for depositing and evaluating a sensor material. Temperatures at each element can be rapidly varied ($\sim$ 1 ms) between 20°C to 500°C (or higher), and surface microelectrodes allow electrical characterization of films during and after deposition. Primary examples to be discussed involve localized temperature-dependent deposition of different forms of sensing oxides, such as pure and metal-dosed TiO_2 and SnO_2, by thermally-activated CVD. We illustrate the simultaneous collection of conductometric signals from fabricated array libraries of discrete sensor materials as they are exposed to sequential sets of test analytes. We also show how temperature can be systematically programmed in surveys to acquire response databases which can be pruned to provide critical information on the best materials (composition, microstructure, thickness) and temperatures for recognizing and quantifying target analytes in specific applications (environmental monitoring, planetary exploration, homeland security). We describe the opportunities and challenges one faces in adapting to other technical areas (including areas of nanotechnology) methods similar to those we have employed to efficiently examine sensing microsamples, and indicate the role which on-chip electronics may play in making microarrays into combinatorial research tools for varied types of high throughput studies.

9:00 AM JJ7.2
Sensors for High-throughput Materials Characterization: 24-channel Array of Quartz Crystal Microbalances.
William Morris and Radislav A. Potyrailo; GE Global Research, schenectady, New York.

The success of combinatorial and high-throughput (HT) materials screening programs strongly relies on the availability of analytical instrumentation with adequate capabilities. A system has been developed for applying layers to thickness shear mode (TSM) sensors, also known as quartz crystal microbalances (QCMs). The sensors are arranged as a 6 x 4 array that is compatible with available 24-well plates that can be manipulated with standard robotic equipment. Our sensor system can measure frequencies from 5 MHz to 20 MHz with a noise level of less than 0.1 Hz for a 1 sec acquisition interval. The sensors can be placed in a gas-flow-though cell for studies of vapor-sorption properties, or they can be immersed into a 24-well plate array for studies of materials solubility. The sensor array is connected to the measurement electronics through a multi-conductor cable, enabling the sensors to be operated in a temperature, pressure, or chemical environment, which would otherwise adversely affect the electronic stability. The 24-channel array has been applied to the screening of sensor materials for determination of chlorinated organic solvents at part per billion levels in groundwater wells. The primary screen is the discovery screen where materials are exposed to a single analyte concentration. The secondary screen is the focused evaluation where the best subset of these materials is exposed to analytes and interferences. The tertiary screen involves evaluation of material performance under conditions mimicking the long-term application. Six families of potential sensor materials were examined with rapid downselection by using this approach.

9:15 AM JJ7.3
Combinatorial Study and High Throughput Screening of Transparent Oxygen and Moisture Barrier Films.
Ali R Mehrabi, Jaime Grunlan, Aaron Chavira and Jay Akhave; Avery Research Center, Pasadena, California.

High throughput methods for testing and screening of oxygen and moisture barriers are developed based on opto-chemical sensors. These sensor materials operate based on the change in a certain optical property, such as absorbance and/or fluorescence, due to a chemical reaction. Image processing and pattern recognition methods are also used to screen the diffusion barriers based on their haze and presence of macroscopic defects and pinholes. The results of these measurements for several cases are presented and their advantages and disadvantages are discussed.

9:30 AM *JJ7.4
High Throughput Measurements of Polymer Fluids for Formulations. Kathryn L. Beers, Joao T. Cabral, Howard J. Walls, Alexander I. Norman and Eric J. Amis; Polymers Division, NIST, Gaithersburg, Maryland.

Rapid prototyping of microfluidic handling devices has gained popularity due to the ability to quickly test and modify new design features several times in one day. At the NIST Combinatorial Methods Center (NCMC), we have modified common microfluidic fabrication techniques to extend their use to organic fluids. UV curable adhesives were used to create molded resins with increased solvent resistance. This has allowed the preparation of new types of combinatorial libraries and development of new measurement methods to complement the small sample sizes of these libraries. Most importantly, it can be used to tie together multiple stages of the formulation process, from the synthesis of polymers to the measurement of complex-fluid properties, in small and inexpensive platforms. Our first demonstrations of this technology are in the areas of emulsions and polymer blends. Synthetic variables include molecular weight and copolymer composition. Measurement techniques include light and x-ray scattering and rheology. Milli-fluidic handling and measurements will increase the dimensions of parameter space that are available to accurate and systematic study of polymer solutions. These new capabilities will also enable the generation of new knowledge in the field of polymer formulations, which is presently dominated by empirical knowledge.

10:30 AM *JJ7.5
Discovery of New Fluorescent Materials From Fast Synthesis and Screening of Conjugated Polymers : Precursors of OLED's and chemical sensors. Olivier Lavastre, Illya Illitchev, Gwenaelle Jegou and Pierre Dixneuf; Institut de Chimie, CNRS, Rennes, France.

A diversity of conjugated polymers was prepared in a parallel way from the Pd-catalyzed carbon-carbon coupling reaction between a diversity of dihalogenated and diethynyl monomers. After dilution a simple irradiation of the 96-wells plate with an hand-held UV lamp led to easily discriminate fluorescent and non fluorescent polymers and to visualize the corresponding emission color in solution. 96 film spots were prepared by the slow evaporation of each polymer solutions. Again a simple irradiation of this plate with an hand-held UV lamp led to the visualization of the color emitted by the fluorescent polymers in the solid state.With this fast pre-screening test, only compounds showing the targeted fluorescence properties for OLED's or sensors applications have to be prepared in large scale.

11:00 AM JJ7.6
Massively parallel chip-sized single-bead reactors for high throughput experimentation in catalysis research.
Torsten Zech, Gunilla Bohner, Jens Klein and Stephan A Schunk; hte Aktiengesellschaft, Heidelberg, Germany.

The search for new and better catalysts for chemical processes is to a certain degree still an empirical or intuition guided process. To improve this time consuming and therefore expensive approach of sequential testing in single reactor units throughout the chemical industry developments towards powerful combinatorial and high throughput technologies for application in heterogeneous as well as homogeneous catalysis are undertaken. Especially reaction systems for high throughput screening of heterogeneous catalysts (i.e. more than 100 catalysts/reactors in parallel) which were presented in the past generally suffered from difficulties regarding realistic catalytic materials, efficient automated testing procedures, robotic library handling, adoption of appropriate analysis methods and workflow integration. These challenges were the motivation for us to develop a novel concept for high throughput primary screening in heterogeneous catalysis. Based on the idea of using individual shaped bodies, so-called beads, as catalytic materials of interest, a new parallel reactor type that can accommodate this form of the active component was constructed. This microfabricated "single-bead reactor" contains large numbers of catalytic beads in individual microreaction chambers. Its compact size make it a device that can be easily handled and integrated into an automated screening procedure. The functionality of the chip is multifold: apart from the pure accommodation of the active components, it has an integrated microfluidic system which ensures accessibility of the active components and even reactant distribution over the integrated chip architecture. With the help of computational fluid dynamics calculations it was possible to reach the design goal of a very compact arrangement of reaction chambers together with an intrinsic, scalable method for equal reactant distribution. Therefore, a 384-parallel single-bead reactor could be realized as a chip-based device with an overall size of less than the half of a credit card. Experimental results are given to illustrate the applicability of the new reactor concept in partial hydrogenation and partial oxidation reactions. The single-bead concept has a large impact in terms of flexibility of library preparation. Other than substrate bound libraries a wider range of chemistries can be used for the preparation of active components. An outstanding feature is the application of the so-called "Split & Pool" strategy for the synthesis of vast and diverse catalyst libraries in high throughput discovery programs in heterogeneous catalysis. Especially due to this fruitful combination of a pooled synthesis strategy and a parallel screening methodology, a very efficient automated workflow was established.

11:15 AM JJ7.7
Fiber-Optic Sensor Technology and Combinatorial Chemistry.
Peter - Geissinger and Alan W Schwabacher; Department of Chemistry, University of Wisconsin-Milwaukee, Milwaukee, Wisconsin.

We present a "Fiber-Optic Combinatorial Chemistry" technique that combines our combinatorial synthesis and optical fiber sensor technologies. With our one-dimensional combinatorial chemistry method, we can synthesize libraries of compounds with thousands of members in a linear format, as in the cladding of optical fibers. These compound libraries constitute fluorescent fiber sensor arrays. The location of a particular fluorescent chemosensor along the optical fiber can be determined through the optical time-of-flight technique, in which laser pulses propagating through the fiber core probe through their evanescent fields the fluorescent properties of the library. After excitation with a laser pulse, an excited molecule couples a fluorescence pulse back into the fiber core. This fluorescence pulse is detected at the fiber end and from the time delay between exciting and returning pulse, the location of the emitting molecule is calculated. It is a virtue of our combinatorial synthetic procedure that with the location of a compound on the fiber, its synthetic history is immediately known. Limitations on the spatial resolution of compounds along the fiber due to the excited state lifetimes of the fluorescent marker molecules can be overcome by the use of a second fiber - evanescently coupled to the first one - as an optical delay. With our technique we are in a position of building compound libraries on optical fibers for many different purposes, ranging from the design of new drugs to the fabrication of linear optical fiber sensor arrays for a multitude of sensing tasks, from the screening of medical analytes to the monitoring of pollutants in the environment.

11:30 AM *JJ7.8

High Throughput Flow Cytometric Screening Of Molecular Assemblies For Analysis Of Signaling And Adhesion Pathways, Drug Discovery, And Proteomics. Larry A. Sklar, Joseph Bartsch, Sean M. Biggs, Tione Buranda, Daniel F. Cimino, Bruce S. Edwards, Terry Foutz, Gabriel P. Lopez, Andrea A. Mammoli, Eric R. Prossnitz, Peter Simons, Hy D. Tran, Richard Truesdell, Anna Waller and Susan Young; School of Medicine, University of New Mexico Health Science Center, Albuquerque, New Mexico.

We have developed a flow cytometry system (HyperCyt$^{\text{tm}}$) for the analysis of molecular assemblies and cell responses in cell signaling and adhesion. The system can be applied to cells, particles on which molecular complexes are assembled, and multiplexed analysis of several assays simultaneously. It is also suitable for the generalized analysis of small volumes of cells ("microtechnology") using the myriad of flow cytometric assays. The features of the system include sampling microliter volumes from multiwell plates at throughput rates up 100 endpoint samples per minute, online mixing at rates projected up to 30 samples per minutes using novel microfluidic approaches, and sorting of cells at rates projected up to 10 samples per minute. The analysis of fluidic carryover from sample to sample leads to novel considerations for maintaining throughput in the face of carryover. The assays are adaptable to screening for drug discovery, multiplex approaches suitable for proteomics, and analyzing classes of molecular assemblies in signal transduction. We are currently using these approaches to study the mechanism of assembly and disassembly of signal transduction complexes, conformational differences in G protein coupled receptors induced by full and partial agonists, and discrimination of agonists and antagonists in compound libraries. The addition of microfluidic sample handling to flow cytometry provides a robust discovery tool for approaching the diversity of biological systems and chemical libraries.

SESSION JJ8: Combinatorial Approach to Nanomaterials, Nanocomposites, and Catalysts

Chairs: Toyohiro Chikyow and David Ginley
Wednesday Afternoon, December 3, 2003
Independence West (Sheraton)

1:30 PM *JJ8.1

Development of High Throughput Methods for Polymer Nanocomposite Materials Research. Jeffrey w Gilman[1], Rick D Davis[1], Harris Richard[1], Marc Nyden[1], John R Shields[1], Anthony Bur[2], Walid Awad[1], Takashi Kashiwagi[1], Paul Maupin[3], Paul Trulove[4], Hugh C DeLong[4], Doug Fox[5], Mauro Zammanaro[1,7] and Rick Beyer[6]; [1]NIST, Gaithersburg, Maryland; [2]NIST, Gaithersburg, Maryland; [3]DOE, Germantown, Maryland; [4]AFOSR, Arlington, Virginia; [5]NRL, Washington, District of Columbia; [6]ARL, Aberdeen Proving Ground, Maryland; [7]Univ. of Trieste, Trieste, Italy.

An unprecedented opportunity exists to apply the concepts of High Throughput (HT) science to the study of polymer-nanocomposites (PN). This presentation will discuss the important parameters associated with PN and the HT methods we are developing to evaluate these parameters, for the purpose of obtaining a detailed fundamental understanding of the performance of these materials. The number of important parameters which influence PN properties is large. As a result, literally millions of experiments and measurements are required to provide an understanding of the controlling materials issues. Current methods used to study the flammability and mechanical properties of PN focus on traditional one-at-a-time approaches. The approach we are pursuing focuses on use of the inherent HT capabilities of twin-screw extrusion (TSE) for preparation of compounded polymer samples. To enable a HT workflow with the TSE we have equipped it with on-line sensors capable of nano-scale characterization. We have prepared gradient (composition-spread) polymer samples with continuously varying concentrations of additives using the TSE system. The mechanical properties are evaluated using nanoindentation and the flammability properties are evaluated using flame spread methods.

2:00 PM JJ8.2

Synthesis and Screening of Materials Libraries of Buried Compound Semiconductors by Ion Beam Implantation. Ingo Grosshans, Helmut Karl and Bernd Stritzker; Institut fuer Physik, Universitaet Augsburg, Augsburg, Germany.

In this contribution the synthesis and optical analysis of buried II-VI compound (i.e. CdSe and ZnTe) semiconductor nanocrystals by ion-implantation into thermally grown SiO2 on silicon will be presented. Typically standard ion implantation setups are designed in a way to achieve a laterally homogenous dose distribution of the implanted ion species. In order to get intentional lateral variations of the implanted doses an implanter endstation with computer controlled apertures in front of the wafer was constructed. They cover up in succession parts of a 4-inch wafer, so that a lateral pattern of distinct dose combinations of the successively implanted constituent elements of the buried compound semiconductor can be generated. Continuous or discrete implantation dose pattern are realizable. The materials library described here is a rectangular pattern consisting of a diagonal of 1:1 stoichiometric elements and off-stoichiometric dose ratios in the off-diagonal elements. After implantation the wafer passes through a rapid thermal heat treatment where the implanted material forms buried semiconductor nanocrystals. The photoluminescence spectra of the materials library elements were screened in rapid succession in an optical cryostat into which the whole wafer is mounted and cooled down. The obtained spectra can be compared and key-parameters determined, which control the detailed photoluminescence features. In this contribution will be shown, that slight variations of the dose ratios significantly alter the optical properties and new efficient photoluminescent materials composites and processing parameters can be found. In this way, also other complex interdependencies of physical and chemical parameters in the field of multiple element ion beam implantation can be efficiently synthesized and investigated.

2:15 PM JJ8.3

Nanomechanical properties of compositional spreads possessing novel ferromagnetic shape-memory alloys. Oden L. Warren[1], Antanas Daugela[1], S.A. Syed Asif[1], Dehua Yang[1], Thomas J. Wyrobek[1] and Ichiro Takeuchi[2]; [1]Hysitron, Inc., Minneapolis, Minnesota; [2]University of Maryland, College Park, Maryland.

Recent work involving mapping the functional phase diagram of the combinatorial Ni-Mn-Ga system has demonstrated that the well-known ferromagnetic shape-memory alloy, the Heusler composition Ni2MnGa, lies near the boundary of a large, previously unexplored region of reversible martensites that also are ferromagnetic [1]. Here we present results on mapping nanomechanical properties and acoustic emission activity across compositional spreads possessing novel ferromagnetic shape-memory alloys. The compositional spreads have been extensively characterized using wavelength-dispersive spectroscopy (composition), scanning X-ray microdiffractometry (structure), scanning SQUID microscopy (magnetization), and a method of employing microcantilever arrays to detect martensitic transformations. Our aim is to examine whether the evolution of nanomechanical properties and acoustic emission activity across compositional and structural space can be used as a screening method for differentiating martensitic and austenitic phases at room temperature. [1] I. Takeuchi et al., Nature Mater. 2, 180 (2003).

2:30 PM JJ8.4

Continuous Composition-Spread Approach to the Discovery and Optimization of Metal Catalysts for Carbon Nano-Tube Growth. Hans M. Christen[1], Alex A. Puretzky[1], David B. Geohegan[1], Kalayu G. Belay[1,3], Douglas H. Lowndes[1] and Jane Y. Howe[2]; [1]Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [2]Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee; [3]Department of Physics, Florida A&M University, Tallahassee, Florida.

Efficient catalytic growth of multi- or single-walled carbon nano-tubes using a chemical vapor deposition (CVD) method offers much promise for their high-yield fabrication. The exact mechanisms of catalysis are relatively poorly understood, but strong variations in growth rates are observed with changes in catalyst composition. A continuous composition-spread (CCS) approach offers an efficient route towards the optimization of catalyst composition and allows us to probe a much larger number of metal combinations than possible in single-sample techniques. Here we present a Pulsed-Laser Deposition (PLD) based approach for metal catalyst film deposition (including Fe, Mo, Pt, etc.) in which sub-nanometer thick "wedge-shaped" layers of various metals can be deposited with great accuracy and control. The approach is based on the translation of the substrate behind a slit-shaped aperture through which deposition occurs at precisely pre-determined positions, yielding controlled thickness gradients over cm-scale distances. Simultaneously deposited, much thicker reference layers allow us to accurately determine the actual amount of material deposited for each sample. Catalyst layers deposited on Al-coated Si wafers were then used to obtain dense forests of vertically oriented multi-walled carbon nanotubes (VA-MWNT) using high temperature annealing of the metal catalyst films in flowing Ar/H_2 gas followed by the growth of VA-MWNTs by CVD using C_2H_2 gas. Nano-tube growth rates (and thus catalytic activity) were determined from cross-sectional scanning electron microscopy (SEM) images. In the case of Al/Fe/Mo on Si, the optimized catalyst composition yielded a

VA-MWNT forest with a thickness of 850 μm for a 1-hr growth time. Our results show that for certain combinations of catalyst films, optimization of nano-tube growth requires sub-monolayer control in the deposition of the metallic layers. Research sponsored by the U.S. Department of Energy under contract DE-AC05-00OR22725 with the Oak Ridge National Laboratory, managed by UT-Battelle, LLC

2:45 PM JJ8.5

Nano-Calorimetric Studies of Ultrathin Film Polymers. Azar Alizadeh, Anis B Zribi, Surya P Ganti, Kunal Goray, Pradeep Sharma, Kenneth R Conway and Loucas Tsakalakos; General Electric, Global Research Center, Niskayuna, New York.

Glass transition (Tg) and melting (Tm) temperatures of supported and freestanding ultrathin polymer films have been extensively investigated in the literature using techniques such as ellipsometry, Brillioun scattering, and AFM. Even though these techniques allow for the determination of the location (temperature) of phase transition, they do not provide a direct measurement of heat capacity change. Conventional thermal characterization techniques, such as DSC, don not provide the required sensitivity for ultrathin film and nano-structure characterization. The sensitivity of nano-calorimetric devices (0.1mW-1nW) has been demonstrated to be two-three orders of magnitude better than conventional DSC systems. Moreover, internal time constants on the order of 1 millisecond are readily achievable. In this work, MEMS fabrication technology is used to develop ultra-sensitive thin film differential scanning nano-calorimeters. Design optimization of the nano-calorimeter is achieved by numerical finite element simulation of heat transfer across its various constituents. Glass transition and melting behavior of polystyrene and polyethylene oxide thin films are studied using the nano-calorimeter.

3:30 PM JJ8.6

Combinatorial Approach to Study Phase Behavior of PS - PVME Nanocomposites. Koray Yurekli[1], Alamgir Karim[2], Eric J Amis[2] and Ramanan Krishnamoorti[1]; [1]Chemical Engineering, University of Houston, Houston, Texas; [2]Polymers Division, National Institute of Standards and Technology, Gaithersburg, Maryland.

The influence of nanometer thick, highly anisotropic organically modified layered - silicate (montmorillonite) on the phase behavior of blends of deuterated polystyrene (dPS) and poly(vinyl methyl ether) (PVME) is investigated using a combination of small angle neutron scattering (SANS) and a two - dimensional combinatorial method based on light scattering and corroborated by static cloud - point light scattering. The presence of layered - silicates up to a volume fraction of 0.04 is found to leave the phase diagram essentially unchanged, with the values of the Flory - Huggins interaction parameter at high temperatures being nearly independent of added silicate for blends with layered - silicates. These results are discussed in the context of current theories to understand the thermodynamics of polymer nanocomposites and the influence of confinement on the phase behavior of binary liquids.

3:45 PM JJ8.7

Combinatorial Synthesis of Insoluble Oxide Library from Ultrafine/Nano Particles Suspension using a Drop-on-demand Inkjet Delivery System. Lei Chen[1], Sunxiang Huang[2], Xiaonan Liu[1], Lei Shen[3], Jun Bao[1], Chihui Liu[2], Wenhan Liu[2] and Chen Gao[1,2]; [1]National Synchtron Radiation Lab., University of Science and Technology of China, Hefei, Anhui, China; [2]Department of Physics, University of Science and Technology of China, Hefei, Anhui, China; [3]Department of Chemical Physics, University of Science and Technology of China, Hefei, Anhui, China.

Inkjet printing technique has been widely used in combinatorial synthesis of materials libraries from soluble precursors, e.g. nitrate aqueous solution, polymer solution, etc. In this report, the inkjet printing technique was developed to synthesize the materials libraries from insoluble oxides precursors, such as rare earth oxides, some transition metal oxides and SiO_2, MgO, Al_2O_3, WO_3. These oxides were ground by using high-energy ball miller in the presence of dispersant, binder and wet medium, and formed stable ultrafine/nano particles suspension. The materials libraries were synthesized by jetting the suspension using a combinatorial drop-on-demand inkjet delivery system. Using luminescent materials as model systems, it was established that the technique is very well suited to combinatorial synthesis of insoluble oxides. We believe that this technique could extend the combinatorial synthesis approach.

4:00 PM JJ8.8

Design, Use and Results from Combinatorial Steady-State Reactors for the Optimization of Highly Selective Heterogeneous Catalysts in Liquid Systems. James Lawrence Spivack[1], Jimmy Webb[2], William P Flanagan[1], Cheryl Sabourin[1], Ralph May[3] and Lamyaa Hassib[1]; [1]Combinatorial Chemistry Laboratory, GE Global Research Center, Niskayuna, New York; [2]Cyclics Corporation, Schenectady, New York; [3]Union College, Schenectady, New York.

A reactor was designed, built and successfully operated that allowed the simultaneous running of 96 independent reactions at steady-state. Since the problem involved the attainment of 98% in selectivity from a starting point of 92%, very precise reproducibility in selectivity was required. Because selectivity varies with time in a batch reactor, and since commercial reactors for this process are continuous, continuous reactors operated at steady-state were required. Long-term standard deviation in selectivity of <0.25% was attained. Information feedback from so many reactors allowed study of variation in catalyst composition, liquid retention times, space velocity, temperature and other variables to be accomplished in relatively short time. Comparison between heterogeneous and homogeneous catalysis in the same reactors gave insight into the underlying mechanisms determining activity and selectivity. Results from 200 uL reactors correlated very well with normal laboratory and ultimately pilot plant sizes.

4:15 PM JJ8.9

Application of Combinatorial Methods and High Throughput Screening to Discovery of Non-Pt Catalysts for Hydrocarbon Dehydrogenation. Maureen Lynch Bricker, Adriaan Sachtler, Evgeny T Kolev, John Q Chen, Ralph D Gillespie and Jennifer S Holmgren; Exploratory and Fundamental Research, UOP, LLC, Des Plaines, Illinois.

Introduction In mid 1990's several developments in the materials area made it seem possible that combinatorial tools and methods could be applied to catalyst and materials development (1-3). This paper will report the progress that has been made in applying this approach to finding a non-noble metal system in various dehydrogentaion chemistries. Experimental Using our combinatorial system for lead identification, we have the capability to perform all necessary steps in parallel, including metals impregnation, catalyst heat treatment, high-throughput screening, and informatics. After the impregnation of the metals solution on the supports, the samples were dried and calcined. Reduction was performed in-situ as part of the pretreatment in the reactor testing. Tests were conducted at atmospheric pressure using a set of different conditions, obtaining detailed product analyses using GC. Results and Discussion Screening was done using methylcyclohexane (MCH) dehydrogenation, propane dehydrogenation, and n-heptane (n-C7) aromatization as the probe reactions. The catalyst work started with a quaternary metals system both supported on several supports and unsupported. This work has been extended with other metals and modifiers. All three test methods have been used to develop catalysts for use in the petroleum and petrochemical industries. The paper will detail these results and report the progress that has been made to date. References 1. X.-D. Xiang, X. Sun, G. Briceno, Y. Lou, K.-A. Wang, H. Chang, W.G. Wallace-Freedman, S.-W. Chen, P.G. Schultz, Science, 268 (1995) 1738. 2. E. Danielson, M. Devenney, D.M. Giaquinta, J.H. Golden, R.C. Haushalter, E.W. McFarland, D.M. Poojary, C.M. Reaves, W.H. Weinberg, X.D. Wu, Science, 279 (1998) 837. 3. D.E. Akporiaye, I.M. Dahl, A. Karlsson, R. Wendelbo, Angew. Chem. Int. Ed., 37/5 (1998) 609.

4:30 PM JJ8.10

Combinatorial Discovery of Metal Co-Catalysts for the Carbonylation of Phenol. James L Spivack, James N Cawse, Donald W Whisenhunt, Bruce F Johnson, Kirill V Shalyaev, Jonathan Male, Eric J Pressman, John Ofori, Grigorii Soloveichik, Ben P Patel, Timothy L Chuck, David J Smith, Tracey M Jordan, Michael R Brennan, Richard J Kilmer and Eric D Williams; Combinatorial Chemistry Lab, General Electric Global Research, Niskayuna, New York.

The palladium-catalyzed carbonylation of phenol to form diphenylcarbonate (DPC) requires the presence of a metal co-catalyst to catalyze the reoxidation of palladium from Pd0 to Pd2+ in the presence of oxygen. In this study we utilize a high-throughput screening (HTS) methodology to rapidly study the nature of the co-catalyst with an emphasis on combinations of metal co-catalysts that appear to work in a synergistic manner to increase palladium usage. Critical new developments were made in using a small-scale reactor in diffusion controlled systems. The HTS system is described along with the optimized catalysts packages that were determined. Additionally, the results from HTS were used to better elucidate the mechanism of this potentially important commercial reaction.

4:45 PM JJ8.11

Combinatorial Synthesis and Reactivity Screening of Electro-Oxidation Catalysts. Andrew Campion Hillier and Shrisudersan Jayaraman; Chemical Engineering and Chemistry, Iowa State University, Ames, Iowa.

Combinatorial methods have shown promise in efficiently identifying candidate materials or sample vast regions of composition space in the discovery of heterogeneous catalysts. Two major requirements for the successful application of combinatorial techniques to catalyst discovery include reliable sample fabrication methods to prepare dense combinatorial libraries and the availability of screening tools to probe the spatial reactivity of these samples. In fuel cell electro-oxidation reactions, the poison tolerance of platinum catalyst is improved by addition of metals such as ruthenium, molybdenum, tin or osmium. This results in a vast composition space that must be sampled in order to find the optimum catalyst composition for a given electro-oxidation reaction. Hence, combinatorial methods prove to be a practical option to speed-up the catalyst discovery process. In this talk, we demonstrate a novel method for combinatorial catalyst discovery based on the synthesis and reactivity mapping of catalyst composition gradients. Samples consisting of uniform variations in surface composition of platinum based catalysts (Pt-M1 and Pt-M1-M2, where M1, M2 = Ru, Mo, Sn or Os) are fabricated using a gel-transfer technique which reproduces a concentration gradient of source metal ions in a swollen polymer gel onto a surface composition gradient on a conductive support. The reactivity of the catalyst gradients is tested for the hydrogen oxidation reaction in the presence of CO using an in situ reactivity-mapping tool based on the scanning electrochemical microscope.

SESSION JJ9: Poster Session: Combinatorial and High-Throughput Materials Science

Chairs: Peter Geissinger and Carson Meredith
Wednesday Evening, December 3, 2003
8:00 PM
Exhibition Hall D (Hynes)

JJ9.1

Macroscale Approaches for Control and System Theory Simulation of Dynamic SOFC Operation. Sven Andreas Schaefer, Eric Tabery and Ellen Ivers-Tiffee; Institute of Materials for Electrical Engeneering, University Karlsruhe (TH), Karlsruhe, Germany.

This paper presents an interdisciplinary macroscale modeling approach that is able to combine qualitative expert knowledge with physical relations and measured data. Computational intelligence techniques of systems and control theory [1,2] allow to build a dynamic model of the start up and load cycling of SOFC single cells. The formation of the cathode/electrolyte interface, i.e. microstructural and compositional changes during the first electrical loading of the cell, is crucial to achieve maximum cell performance. The temporal course of the cell voltage and the corresponding anodic and cathodic polarizations shows that with increasing current density, the cell voltage first decreases according to the internal resistance of the cell. Afterwards a significant increase of the cell voltage at a constant current density takes place, which can be attributed to a decreasing polarization resistance of the cathode. The dynamic model describing the internal resistance of the cell includes two types of losses. There are temporal invariant losses and losses irreversibly reduced during startup because of the microstructural changes at the cathode/electrolyte interface[2]. The macroscale modeling approach for this improvement and the way to set the stage to weave this macroscale model into system theory model techniques of dynamic processes [2] is presented. The temporal invariant losses have to be included into the model because their dynamics influences the modeling of the startup. These dynamics can be shown as hysteresis of current/voltage characteristics or as load steps from a low to a high level. After load steps, the cell voltage increases. This is caused by a decrease of the cathodic losses. The paper introduces the startup behavior of SOFC-cathodes. The macroscale modeling of improvement of the interface during startup and the model approach for the dynamic of SOFCs during operation is presented. 1. Schmid et al., Proceedings of Materials Week 2001, Materials Development for Solid Oxide Fuel Cells Using Qualitative Models, CD-ROM (2001). 2. A.Kruegel et al., SOFC VIII, Contol Theory Based Models for Dynamic SOFC Operation, in press.

JJ9.2

Preparation of ternary alloy libraries by means of thick film deposition and interdiffusion: structure of the resulted layer. Andrei Rar[1,2], Eliot D. Specht[2], Harry M. Meyer[2], Mike L. Santella[2], E. P. George[1,2] and George M. Pharr[1,2]; [1]Material Science and Engineering, The University of Tennessee, Knoxville, Tennessee; [2]Metals and Ceramics, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

A method of preparing ternary alloy libraries for combinatorial materials development based on thick film deposition and interdiffusion was studied in these investigations, using the Ni-Fe-Cr ternary system. Specimens were prepared by depositing films onto sapphire substrates with an e-beam evaporation system. After deposition, the layers were interdiffused by annealing at a variety of temperatures and times in a vacuum of approximately 10-5 Pa with and without getter materials. The quality of the resulting specimens was examined using cross sectional SEM with EDS mapping, scanning AES microanalysis, electron microprobe analysis, angular resolved x-ray fluorescence, and XRD. Spatially resolved alloy properties were compared with well-known structural properties by means of rapid XRD mapping with synchrotron radiation. The main problems encountered during sample preparation occurred during annealing. Selection of annealing conditions that could be used to produce good interlayer diffusion without Cr evaporation, Kirkendall voiding formation and chromium oxide formation proved difficult. Despite these problems, an isothermal section of the ternary phase diagram was reasonably well reproduced. Research sponsored by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Industrial Technologies Program, Industrial Materials for the Future, and the Division of Materials Science and Engineering, Office of Basic Energy Sciences, under contract DE-AC05-00OR22725 with UT-Battelle, LLC.

JJ9.3

Materiomics as a New Method for Materials Developments Evolving from Combinatorial Chemistry. Koji Tanaka, Tomoki Akita, Satoshi Ichikawa, Yusuke Yamada, Atsushi Ueda, Hiroshi Shioyama, Kazuyuki Ozakaki, Shingo Tanaka, Masanori Kohyama and Tetsuhiko Kobayashi; Special Division for Green Life Technology, National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka, Japan.

Special Division for Green Life Technology (GLT), National Institute of Advanced Industrial Science and Technology (AIST) is proposing the concept of "materiomics" as a new method for materials developments. Materiomics is the new evolution of combinatorial chemistry and can be defined as the whole study of functional materials. Recently, the fusion of combinatorial chemistry and information technology attracts many researchers. However, there are several problems to resolve such as lack of the structure information of materials when it is applied to complicated functional materials. We believe information of the structure of materials is much important than that of the composition of materials. The final goal of materiomics is to obtain the perfect knowledge for functional materials designs, i.e., we could easily estimate their functions if we chose elements and their structures of material. As a first piece of work of materiomics, we started combining combinatorial chemistry with characterizations by transmission electron microscopy and predictions by theoretical calculations. Combinatorial chemistry covers automatic and/or fast synthesis and testing, whereas characterizations by high-precision analyzers and predictions by theoretical calculations offer deep understandings of the origin of properties. In another word, the former is a statistical and inductive study of the factor of material compositions, and the latter is a pinpoint study of the factor of structures. Both are complementary and offer feedback each other. The process of mateiromics is like a spiral of this iterating feedback to construct high-precision data bases. It can make novel functional materials developments, and constructions of a policy and theory of materials designs realized at the same time. In this presentation we would like to introduce the concept of materiomics and several examples applied to heterogeneous catalysts.

JJ9.4

Combinatorial Catalyst Survey Concerning Proton Exchangemembrane Fuel Cell Technology - As A Part Of "Materiomics". Yusuke Yamada, Atsushi Ueda, Hiroshi Shioyama, Tsutomu Ioroi, Kazuaki Yasuda, Tomoki Akita, Satoshi Ichikawa, Koji Tanaka, Masanori Kohyama and Tetsuhiko Kobayashi; Green Life Technol., AIST, Ikeda, Osaka, Japan.

We show our attempt to combine the surface science and combinatorial survey as targeting the catalysts concerning fuel cell technology. The attempt is one of the methods to realize "materiomics" which is the comprehensive material research based on combinatorial research. Catalyst technologies are indispensable for proton exchange membrane fuel cells (PEMFCs) which are regarded as the low emission and highly efficient energy conversion device in the next generation. We apply the combinatorial survey for the hydrogen production and/or purification catalysts, and anode and cathode catalysts. As for hydrogen production and/or purification catalysts, a series of catalysts consisting of precious metals loaded on various metal oxides is tested for water gas shift reaction, steam reforming of methanol, DME etc. We tested the same catalyst sets for several reactions because we regarded the reaction itself is also a parameter of combinatorial survey. For electrode catalysts, the addition of various metal oxides to platinum loaded on carbon was investigated for both anode and cathode catalysts. TEM observation was performed on a series of catalysts to correlate the structure and catalysis on each reaction.

JJ9.5

Analytical Tem Observations Of Combinatorial Catalyst Libraries For Hydrogen Production -As A Part Of Materiomics. Tomoki Akita, Atsushi Ueda, Yusuke Yamada, Satoshi Ichikawa, Koji Tanaka, Masanori Kohyama and Tetsuhiko Kobayashi; Special Division for Green Life Technology, National Institute of Advanced Industrial Science and Technology, Ikeda, Osaka, Japan.

The combinatorial approach is of great interest as innovation for materials research and development. It has been also applied for the development of heterogeneous catalysts. In usual combinatorial methods, various heterogeneous catalysts are prepared systematically by changing metal species or oxide support, or by changing process conditions. However, in the case of metal/oxide heterogeneous catalysts, there is a possibility that properties are dominated by the structural factors at microscopic scales such as metal-particle sizes or morphology of interfaces or surfaces, as well as the composition or materials factors. Thus, in order to survey various catalysts efficiently, it is quite important to combine the structural observations with the combinatorial survey. This coupling should enable us to find efficiently the dominant factors of catalytic properties. In this study, TEM observation was performed for the catalysts surveyed by combinatorial method, although high-throughput observations did not be carried out at this stage. The catalytic activities for hydrogen production were examined by a combinatorial method. It was found that Pd/MnO_2 showed high activity for the water gas shift reaction. TEM observation was performed for the selected catalysts from libraries. It was found that thin Pd oxide layer about 1-2nm formed on the flat MnO_2 surface in the Pd/MnO_2 catalyst which showed the highest catalytic activity. The Pd oxide were reduced and Pd particles about 2-3nm with narrow size distribution were formed after hydrogen reduction. The structure of Mn oxide support also changed after hydrogen reduction. On the other hand, both Pd particles about 2-3nm and about 10-20nm in diameter on SiO_2 were showed low activity for the water gas shift reaction. Thus, it was concluded that this catalytic activity did not depend on the particle size of metal and the interaction between metal and metal oxide support is important for the catalytic performance.

JJ9.6

Rapid Optical Characterization for Combinatorial Thin Film Materials Research. Charles W. Teplin, Maikel F. A. M. van Hest, M. S. Dabney, L. Gedvillas, B. Keyes, M. Taylor, J. D. Perkins and D. S. Ginley; National Renewable Energy Laboratory, Golden, Colorado.

In order to quickly and non-destructively characterize thin film libraries for our combinatorial research program, we have adapted three principal optical measurement techniques for high throughput. For the UV to near-IR regime, a fiber optic-based system has been developed to allow for simultaneous reflection and transmission measurements. In the infra-red, an Fourier Transform Infra-Red spectrometer has been adapted to allow for rapid data acquisition. Lastly, spectroscopic ellipsometery has been developed for detailed modeling of the dielectric constant as a function of sample composition. This presentation will focus on challenges that we have encountered in the design of these systems, the processing of the large amounts of optical data, and the analysis of specific material systems, including Cr-Ti-N, Cr-Zr-N, and In-Zn-O.

JJ9.7

Combinatorial Synthesis and Screening for Rare Earth Sensitized Fluorescent Organic Chelates in Polymer Matrix. Jianjun Ding[1], Hongfang Jiu[2], Guanqun Zhou[3], Jun Bao[1], Qijing Zhang[2] and Chen Gao[1,3]; [1]National Synchtron Radiation Lab., University of Science and Technology of China, Hefei, Anhui, China; [2]Department of Polymer Science and Engineering, University of Science and Technology of China, Hefei, Anhui, China; [3]Department of Physics, University of Science and Technology of China, Hefei, Anhui, China.

Rare earth (RE)-doped polymethyl methacrylate (PMMA) has a potential application in polymer optical fibers. In this report, a combinatorial approach has been utilized for searching the rare earth organic chelates in PMMA matrix, and their luminescent properties have been studied. The results show that there exist intramolecular and intermolecular energy transfer processes. The variation of the luminescent intensities with the kinds of rare earth organic chelates and their contents were obtained.

JJ9.8

Multiple Image Charge Method for Quantitative Characterization of Dielectric Thin Film Library Using Scanning Tip Microwave Near-field Microscopy. Chen Gao[1,2], Pu Zhang[1], Bo Hu[2] and Wenhan Liu[2]; [1]National Synchtron Radiation Lab., University of Science and Technology of China, Hefei, Anhui, China; [2]Department of Physics, University of Science and Technology of China, Hefei, Anhui, China.

Image charge method has been successfully used in the quantitative characterization of bulk dielectric materials under the approximations of electrostatic and spherical tip. In this paper, we developed a multiple image charge method for the quantitative characterization of dielectric thin film using the scanning tip microwave near-field microscope. With this method, frequency shift of the microscope as the function of the dielectric constant and thickness of film can be computed in an iterative way effectively. We also calculated an entire film/substrate configuration and fitted the results with a simple analytic formula. We believe that this method could promote the high-throughput characterization of dielectric libraries.

JJ9.9

Combinatorial Synthesis and Characterization of Indium-doped Zinc Oxide. Matthew P. Taylor[1], M F A M van Hest[2], C W Teplin[2], M S Dabney[2], J L Alleman[2], P Parilla[2], B To[2], B M Keyes[2], L M Gedvilas[2], D W Readey[1], J D Perkins[2] and D S Ginley[2]; [1]Colorado School of Mines, Golden, Colorado; [2]National Renewable Energy Laboratory, Golden, Colorado.

Amorphous, indium doped zinc oxide (IZO) is a transparent conducting oxide (TCO) of increasing importance for display applications. We report on the application of combinatorial methods to investigate IZO phase space. Compositionally graded IZO thin film libraries were deposited onto 2″x2″ Corning 1737 glass substrates by DC magnetron co-sputtering from ZnO and In_2O_3 targets at ambient temperature. The targets were sputtered in Ar at powers between 3 and 75 watts. The metals composition of the deposited libraries was controlled by the relative sputtering powers and subsequently measured by electron probe micro analysis (EPMA). UV/VIS/NIR ($200-1700$ nm) measurements were performed with a multi-channel fiber-optically-coupled CCD-array-based spectrometer. The infrared ($1.7-25$ μm) reflection and transmission measurements were done with a Fourier Transform Infra-Red (FTIR) spectrometer. The sheet resistance was mapped with a position scanning 4-point probe technique. The indium to zinc ratio varied by roughly a factor of two across individual libraries and the relative indium to zinc sputtering power was adjusted to yield a metals composition range of 5 to 20 atomic% In for Zn. For as-deposited libraries grown at ambient temperature, the resistivity generally decreased with increasing indium concentration and ranged from 20 Ω cm in the indium-poor corner to less than 3x10^{-3} Ω cm in the indium-rich corner. However, along lines of constant composition the resistivity could vary by as much as two orders of magnitude. In one case it was shown to vary from 0.16 to 15 Ω cm along such a line. The results of post-deposition annealing studies will also be presented.

JJ9.10

***Insitu*Photoemission Characterization of $LaFeO_3$ Thin Films Grown on $SrTiO_3$ Substrates by Laser Molecular Beam Epitaxy.** Daisuke Kobayashi[1], Hiroshi Kumigashira[1], Masaharu Oshima[1], Tsuyoshi Ohnishi[2], Mikk Lippmaa[2], Kanta Ono[3], Masashi Kawasaki[4] and Hideomi Koinuma[5]; [1]Applied Chemistry, The University of Tokyo, Tokyo, Japan; [2]Insitute for Solid State Physics, The University of Tokyo, Kashiwa, Japan; [3]Insitute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba, Japan; [4]Institute for Materials Research, Tohoku University, Sendai, Japan; [5]Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

Epitaxial multilayered heterostructures based on perovskite oxides have a great potential for future electronic device applications. For realizing these devices with desired properties, it is important to control the interface and surface structure on an atomic level. In particular, it is indispensable to evaluate the diffusion or segregation of constituent atoms across the heterointerface since the physical properties of a perovskite transition metal oxide is very sensitive to its composition. In this study, we report in-situ photoemission characterization of $LaFeO_3$ thin films grown on wet-etched TiO_2-terminated $SrTiO_3$ (001) substrate with different growth conditions and film thicknesses in order to investigate the segregation or diffusion of Sr atoms at the $LaFeO_3/SrTiO_3$ heterointerface. $LaFeO_3$ thin films with thickness of 8$\sim$40nm were fabricated in a laser molecular beam epitaxy chamber connected to a synchrotron radiation photoemission system at BL-2C of the Photon Factory. The $LaFeO_3$ thin films were deposited on the TiO_2-terminated $SrTiO_3$ (001) substrate at 700C or 950C at an oxygen pressure of 1×10^{-4}Torr. During $LaFeO_3$ thin films growth, we monitored the intensity of specula spot in reflective high energy electron diffraction (RHEED) pattern by $in-situ$. According to the *insitu*RHEED monitoring, the growth mode of $LaFeO_3$ thin film at low temperature (700C) was layer-by-layer growth mode, while step-flow growth mode at high temperature (950C). The fabricated $LaFeO_3$ thin films were moved into the photoemission chamber under ultra high vacuum of 1×10^{-10}Torr. The PES spectra were taken at room temperature and total energy resolution at the photon energy of 500eV is about

200meV. On the photoemission spectra of $LaFeO_3$ thin films grown at 950C with thickness of 8nm, we observed a clear Sr $3d$ signal indicative of existence of substantial Sr atoms on $LaFeO_3$ film surface. The high-resolution spectra of Sr $3d$ core level mainly consist of two components: a sharp peak at binding energy of 132.8eV and relatively broad one with an energy separation of 1.1eV. Detailed analysis of the spectra revealed that the sharp component may originate from the local formation of $La_{1-x}Sr_xFeO_3$, while the broad one emerge as a results of Sr segregation and subsequent recrystallization as Sr oxides (SrO_x) on the surface. The intensity of the Sr $3d$ peak gradually decreases with increasing the film thickness and nearly disappears at 20nm thickness. In constant, we do not observe any indication of existence of the extra Sr atoms on the surface for $LaFeO_3$ thin films grown at 700C (layer-by-layer growth). Furthermore, even after annealing of the $LaFeO_3$ films at 950C, the Sr atoms were not segregated on $LaFeO_3$ film surface, suggesting that Sr segregation depend on the growth mode of $LaFeO_3$ films.

JJ9.11

Mapping of Magnetic Phase Diagrams Using Magneto-Optical Imaging and Compositional Spreads. Leonid A. Bendersky[1], M.J. Turchinskaya[1], A.L. Roytburd[2], K.-S. Chang[2,3] and I. Takeuchi[2,3]; [1]MSEL, NIST, Gaithersburg, Maryland; [2]Materials Science and Engineering Department, University of Maryland, College Park, Maryland; [3]Center for Superconductivity Research, Department of Physics, University of Maryland, College Park, Maryland.

In this paper we present a novel approach for mapping magnetic phases in a composition-temperature space by applying a magneto-optic imaging (MOI) technique to compositional spreads. The MOI allows continuous optical visualization of the location of a magnetic phase in a compositional spread for a given temperature, and the temperature can be varied from room temperature to 10 K. The MOI technique is based on the use of an indicator garnet film (IGF) sensitive to a normal component of a magnetic field from the sample magnetized by an external field. In the case of the compositional spreads, the IGF detects stray fields near edges of the in-plane magnetized combinatorial film. We studied pulsed laser deposited (PLD) 200 nm thick La_{1-x} Ca_x MnO_3 (LCMO) composition spread films on $SrTiO_3$ (STO) substrates, with $0 < x < 1$. A linear composition gradient of the spread was achieved by the mask-controlled deposition of alternating gradient monolayers of $LaMnO_3$ and $CaMnO_3$. The films were characterized by EDS, scanning x-ray and TEM. The ferromagnetic (FM) phase was identified in a composition range of $0 < x < 0.5$ and the temperature range between 210 K and 57 K. A paramagnetic (PM)/ferromagnetic transition curve was found to be below the transition curve determined for bulk LCMO. The onset of paramagnetic/ferromagnetic transition is in a good agreement with results from SQUID measurements. At the cooling rates higher then 10K/min, the PM phase can be completely undercooled and then abruptly transforms into the FM phase during heating. In addition, no FM phase was found at temperatures below 57 K for $0 < x < 0.5$. In conclusion, the presented experiments have demonstrated that the relatively simple MOI technique can be an effective tool for rapid mapping of the magnetic phase diagram, as well as for the real-time, real-space observations of magnetic transitions in thin films.

JJ9.12

Abstract Withdrawn

JJ9.13

Cell Adhesion through a Peptide Concentration Library. Dimitris Stroumpoulis and Matthew Tirrell; Chemical Engineering, University of California Santa Barbara, Santa Barbara, California.

Biomolecular recognition events are very important in designing intelligent biomaterials. Ligands that mimic adhesive components of the extracellular matrix can be synthesized and arranged on a surface in such a way that they target specific cell receptors. In an effort to test promising candidate coating materials we focus on developing a method to create a concentration gradient library. A two dimensional array is constructed on a silicon dioxide surface by micro-contact printing of a polymerized bilayer grid. Two vesicle solutions containing different dye molecules are flown in parallel and at a small separation distance such that a concentration gradient perpendicular to the flow develops. The flow is subsequently stopped so that fusion of the vesicles with the surface can take place and the resulting concentration library is visualized using fluorescence microscopy. The same method is used to investigate the influence of RGD peptide amphiphile concentration on cell function by observing how cell adhesion varies spatially on the surface. In this case RGD peptide amphiphiles are only contained in one of the vesicle solutions under flow, while the other one is composed of pure lipids.

JJ9.14

Combinatorial libraries of semiconductor gas sensors as inorganic electronic noses. Maria A Aronova[1,2], Kao Shuo Chang[2], Ichiro Takeuchi[2,1] and Harry Jabs[3]; [1]Physics, University of Maryland, College Park, Maryland; [2]Material Science and Engineering, University of Maryland, College Park, Maryland; [3]Lynntech Inc., College Station, Texas.

We have fabricated thin-film combinatorial gas sensor libraries based on doped semiconducting SnO2 thin films. Combinatorial pulsed-laser ablation system with a rotatable heater and an automated two dimensional shutter system was used to deposit compositionally varying arrays of 16 sensor elements onto a pre-patterned device electrode configuration. Each element is composed of 50 nm SnO2 doped with different combinations of In2O3, ZnO2, WO3, Pt and Pd. In order to introduce the dopants uniformly in the SnO2 host, individual films were fabricated in a layer-by-layer manner, where dopant layers were deposited after every 0.3 nm of SnO2. Monitoring the change in resistances of the sensors from air to gas allows us to test the performance of the library. Using multiplexing electronics, we have demonstrated detection of chloroform, formaldehyde, and benzene gases at concentrations down to 12.5 ppm through pattern recognition of signals from the arrays of sensors at 200 0C, 300 0C and 400 0C . Each sensor exhibited a different time dependent response pattern for a given gas. The method described allows a fast and relatively inexpensive way of fabricating compact electronic nose devices.

JJ9.15

Automatic Reaction Modeling in Chemical Vapor Depositions Using Multiple Process Simulators. Takahiro Takahashi[1], Kimito Funatsu[2] and Yoshinori Ema[1]; [1]Dept. of Electrical and Electronic Engineering, Shizuoka University, Hamamatsu, Shizuoka, Japan; [2]Dept. of Knowledge-based Information Engineering, Toyohashi University of Technology, Toyohashi, Aichi, Japan.

The identification of appropriate reaction models is very helpful for developing chemical vapor deposition (CVD) processes. Previously we proposed an automatic modeling system of reaction mechanisms for CVD processes by use of both a solver implemented by genetic algorithms and a process simulator, which reproduce deposition profiles (i.e. the film thickness non-uniformities) on substrates. We showed that the system was able to identify the reaction models appropriately from the experimental results. In this work, we improved the reaction modeling systems in order to analyze not only the deposition profiles on the substrates but also deposition shapes of the films on nano- or micro-structured substrates. (e.g. stepcoverage of films deposited on micro-trench) The reaction models, which consist of various deposition species and gas-phase and surface reactions, were determined both quantitatively and qualitatively, based on chemical kinetics ,from these experimental results. Generally speaking, process simulators, which reproduce the deposition shape, have to be implemented by very high-cost algorithms, such as Monte Carlo method. However, we could radically cut down the calculation cost by modeling calculation processes of the simulators and get the appropriate reaction models from the system with practical calculation time. In conclusions, we showed that the system was able to analyze the complex of the experimental results and identified the reaction model appropriately. We also showed that the analysis using the complex of the experimental results improves modeling ability of the system and reliance of the proposed reaction models.

JJ9.16

Combinatorial Ternary Metal Alloying by Ion Beam Sputtering. Parhat Ahmet[1] and Toyohiro Chikyow[1,2]; [1]National Institute for Materials Science, Tsukuba, Ibaraki, Japan; [2]CREST-Japan Science and Technology Corporation, Toyonaka, Osaka, Japan.

We have developed a ternary composition spread thin film fabrication system based on ion beam sputtering and we have applied the system in combinatorial ternary alloying of metals. Composition spread method is an effective method for systematic study of multi-component compounds properties variations with composition variations. In the previous study, we have developed a novel three component composition spread thin film fabrication system using a KrF excimer laser for depositing target materials and we have applied this system in searching new high dielectric materials. Because of the droplet problem in pulse laser deposition when ablating metal targets, the target materials were limited to ceramic materials in our previous composition spread thin film fabrication system. For applying our three component composition spread thin film fabrication method to ternary metal alloy systems, we have developed a new combinatorial thin film fabrication system with an ion beam sputter for sputtering metal target materials. The system has equipped with a rotate-able substrate holder system, a horizontal moving mask system, and a multi-target exchange system and the whole deposition process was controlled by a computer. The new system allows rapid fabrication of ternary metal composition spread thin films. System constructions and obtained results on the ternary metal alloys fabricated by the new deposition system will be presented.

JJ9.17

Combinatorial Approach to Low-melting and Lead-free Glasses. Tomoya Konishi[1], Tetsuo Araki[2], Keishi Nishio[2], Toshio Tsuchiya[2], Shigeru Suehara[1], Shin-ichi Todoroki[1] and Satoru Inoue[1]; [1]Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, Ibaraki, Japan; [2]Department of Materials Science and Technology, Tokyo University of Science, Noda, Chiba, Japan.

Recent development in optical functional devices has discovered new uses for low-melting glasses. For example, they are used as cell walls of plasma displays, and solder to assemble amplification repeaters for submarine fiber optic cables. Low-melting glasses, however, still contain considerable amount of lead oxide in spite of recent interests in environmental protection, because lowering melting temperature, without lead oxide, often increases thermal expansion coefficient and decreases water-resistibility. In this paper, authors will report the combinatorial approach to find lead-free substitutes by borate glasses. A variety of ternary borate glasses were prepared with our combinatorial glass making apparatus including an automatic reagent weighing machine and a multi-sample glass melting furnace. The glass transition temperatures of the samples were measured with a differential thermal analyzer equipped with an automatic sample feeder, and the objective compositions were screened out. Glass-forming compositional regions were newly found in lead-free B_2O_3-TeO_2-RO (R represents an alkaline earth element) ternary systems. The glasses had the softening temperature from 450 to 480 $^{\circ}$C and the thermal expansion coefficient from 100 to 130 $\times 10^{-7}/^{\circ}$C, which are comparable to those of typical PbO-containing glasses. It was also found that addition of fluorides effectively lowered the melting temperature without changing the thermal expansion coefficient.

JJ9.18

Microstructures design in the ternary systems with the only solubility gap. Vasily I. Lutsyk[1,2] and Alexander M. Zyryanov[2]; [1]Russian Academy of Sciences, Buryat Scientific Center, Ulan-Ude, Russian Federation; [2]Buryat State University, Ulan-Ude, Russian Federation.

Heterogeneous materials genotype could be decoded by means of the phase diagrams analysis. With this purpose all its geometrical elements are projecting in the direction of the concentration simplex. As a result the phase regions are divided into the fragments with the phase portions of different origin and a simplex of compositions consists of the concentration fields with the different sets of microstructures. As a phase diagram contains this information in the form that is undeveloped obviously in its geometry, a special technique has been elaborated to manipulate its geometrical model (to cut, to project, to divide etc,) to develop this knowledge. Firstly the contours of the phase regions borders are calculating by means of thermodynamical models, like the Calphad technology. Then they are using to approximate the surfaces as the ruled ones, and with the minimal areas. In this way the software becomes more economical. A ternary diagram with the solubility gap in only one binary system consists of three usual surfaces on the borders of liquid and solid solutions and three ruled surfaces - on the boundaries of three-phase region. All six surfaces were approximated as the ruled ones, which have the minimal areas. Their one-dimensional contours, calculated previously thermodynamically and approximated by polynomials, served as the originating and directing elements for the ruled surfaces construction. The most sophisticated liquidus and solidus surfaces were divided previously into some fragments.

JJ9.19

Electrodeposition of a Combinatorial Library of Binary $Cu_{1-x}Zn_x$ Alloys. Shane D. Beattie and Jeff R. Dahn; Physics, Dalhousie University, Halifax, Nova Scotia, Canada.

Combinatorial methods provide a new paradigm for advancing scientific discovery. Thousands of similar, but unique, materials can be created in a single experiment and then tested for a desired property. Combinatorial methods promise to provide new discoveries "faster, better and cheaper". Combinatorial electrodeposition is a relatively new technique [1-2]. We will describe a simple method for creating a library of binary alloys where composition and structure varies as a function of position, via electrodeposition. We use the copper-zinc system as an example. A composition-spread film of copper-zinc alloys was deposited where atomic percent copper/zinc varies between 30 and 70, representing approximately one third of the copper-zinc phase diagram. X-ray diffraction scans were taken at equal intervals along the film and three phases were identified: Elemental Cu with a solid solution of Zn, $\beta\prime$-CuZn and ϵ-$CuZn_5$. Electrodeposited copper-zinc alloys prepared using combinatorial methods are compared to electrodeposited alloys prepared one at a time in bulk. It will be shown that alloys prepared combinatorially are representative of alloys prepared using traditional one-at-a-time methods. If a technologically significant material is discovered using combinatorial electrodeposition methods it could be easily mass-produced using established large-scale electrodeposition techniques. Our results will show that combinatorial methods via electrodeposition embody, and even extend, the advantages of combinatorial methods: "faster, better, cheaper, simpler and scalable". References: [1] D. Landolt, Electrochemica Acta, Vol. 39, No. 8/9, pp 1075-1090 (1994) [2] S. D. Beattie and J. R. Dahn, Journal of The Electrochemical Society, July 2003, Volume 150, Issue 7, pp. C457-C460

JJ9.20

Ternary Composition Spread Screening of Flux Materials for Single Crystal Growth. Ryota Takahashi[1], Taichi Tanigawa[1], Yukio Yamamoto[2], Yoshiyuki Yonezawa[1,3], Makoto Ohtani[4], Masashi Kawasaki[4], Toyohiro Chikyow[2], Yuji Matsumoto[5] and Hideomi Koinuma[1,2,6]; [1]Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan; [2]National Institute of Material Science, Tsukuba, Japan; [3]Fuji Electric Corporate R&D, Yokosuka, Japan; [4]Institute for Materials Research, Tohoku University, Sendai, Japan; [5]Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, Japan; [6]CREST-Japan Science and Technology corporation, Tokyo, Japan.

Generally, it is laborious and time-consuming to optimize the composition of flux materials in a conventional bulk single crystal growth. A combinatorial technique has been developed for screening flux materials usable for the bulk and thin film single crystal growth. The applicability of this new technique has been verified on the screening of flux composition for the $Bi_4Ti_3O_{12}$ single crystal growth. A combinatorial flux library was fabricated in the form of ternary composition spread films by using a combinatorial pulsed laser deposition method and it was heated into liquid films on a $SrTiO_3$(001) substrate. Then, film precursors were fed by the laser ablation of a mixed oxide target onto the film liquid dissolved in it, and precipitated into single crystalline film at the liquid-substrate interface based on the "Tri-Phase Epitaxy", we reported previously[a)]. As candidate flux materials for ferroelectric $Bi_4Ti_3O_{12}$, we employed the ternary flux library composed of two self fluxes (Bi_2O_3 and $Bi_4Ti_3O_{12}$) and such a third flux component as WO_x, MoO_x etc. A stoichiometric $Bi_4Ti_3O_{12}$ was deposited on this flux library at a temperature presumed to melt the flux. By characterizing the film library with concurrent X-ray, Bi-Ti-Cu-O flux was found appropriate for single crystalline $Bi_4Ti_3O_{12}$ film growth. This Bi-Ti-Cu-O flux was confirmed to be useful for the bulk single crystal growth as well.
[a)] K. S. Yun, et al. Appl. Phys. Lett. 80, 61-63 (2002)

JJ9.21

Development of Scanning Microwave Microscope for High-Throughput Characterization of Dielectric and Conducting Materials at Low Temperatures. Sohei Okazaki[1], Noriaki Okazaki[2], Hidetaka Sugaya[1], Xiaoru Zhao[2], Jun Nishimura[3], Tomoteru Fukumura[3], Masashi Kawasaki[3], Hideomi Koinuma[2,4] and Tetsuya Hasegawa[1,2,5]; [1]Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, Japan; [2]Advanced Materials Laboratories, National Institute for Materials Science, Tsukuba, Japan; [3]Institute for Materials Research, Tohoku University, Sendai, Japan; [4]Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan; [5]Department of Chemistry, Tokyo University, Tokyo, Japan.

Scanning Microwave Microscope (SμM) is a member of SPM family that can map out point-to-point variation of the surface electric properties, such as linear/nonlinear dielectric constant, dielectric loss, and conductance using evanescent microwave. SμM is quite suitable for the rapid characterization of electronics materials and devices, since it enables non-destructive measurement of dielectric properties without any prerequisite sample processing. In this study, we report on the development of SμM designed for low-temperature measurement (LT-SμM). As a resonator probe, we used high-Q $\lambda/4$ coaxial cavity equipped with a probe needle connected to the center conductor. The sensor probe was mounted on the motorized low temperature XYZ stage, which was thermo-regulated by the combination of a liquid-helium circulation and a stage heater. Resonance frequency and quality factor were measured by a network analyzer. Typical resonance frequency and Q-value were 3.0 GHz and 600, respectively. Stage motion and data acquisition were computer-controlled through RS-232C and GP-IB interfaces. The system enables us to evaluate the distributions of frequency shift and 1/Q shift, which are the measures of dielectric constant and dielectric loss, respectively. As a preliminary system performance check, we measured the electric properties of Nd1-xSrxMnO3 composition-spread thin film at room temperature. The measured frequency shift showed broad maximum around x = 0.45, whereas the 1/Q shift had sharp dip around x = 0.49. It is interesting to note that this dip position well coincides with the charge-ordered insulator phase observed at low temperature. More precise low-temperature phase study is now in progress using the LT-SμM system. Detailed results will be shown in the presentation.

JJ9.22

Dynamic mechanical behavior and magnetic properties in NdAlNiCuFe bulk metallic glasses. Bing Chen Wei[1], Wei Huo Li[2], Tai Hua Zhang[1], Yu Feng Sun[1], Yu Ren Wang[1] and Wei Hua Wang[3]; [1]Institute of Mechanics, Chinese Academy of Sciences, Beijing, China; [2]Institute of Material, Shanghai University, Shanghai, China; [3]Institute of Physics, Chinese Academy of Sciences, Beijing, China.

Recently, Nd-TM-Al bulk metallic glasses (BMGs) have been prepared by slow cooling from the melt. Depending on the thermal stability, such alloys can be subdivided into two categories: one class of alloys are iron-free or iron-poor systems, showing a normal thermal stability with Trg near 0.6 and ?ΔTx around 40 K. The other type of alloys is iron-rich systems, which do not exhibit a distinct glass transition prior to crystallization starting at Tx according to constant-rate heating DSC measurements, indicating a low thermal stability of the supercooled liquid. However, an extremely high value of the ratio between the Tx and Tl around 0.9 was observed for such systems, which indicates a rather high stability of the amorphous phase against crystallization. The contradiction between the absence of a distinct glass transition and the extremely high value of Tx/Tl shows that these systems are rather unique within the different families of BMGs. In this work, Nd60Al10Ni10Cu20-xFex (x = 0, 3, 5, 7, 10, 15, 20) cylindrical specimens of 3 mm in diameter were prepared by suction casting method. The effect of Fe addition on the thermal stability and magnetic properties of Nd based BMG were systemically studied by means of DSC, dynamic mechanical thermal analysis (DMTA), and conventional magnetic measurements. All the as-cast cylinders exhibit an XRD pattern typical for an amorphous phase without obvious crystalline reflections. Nd60Al10Ni10Cu20 alloy show an obvious glass transition and supercooled liquid region, followed by two crystallization peaks in the DSC trace. Increasing Fe content leads to the disappearance of endothermic heat flow event due to a glass transition and a complicated exothermic event due to complicated crystallization processes. In order to clarify the thermal stability of the BMGs with different Fe content, DMTA measurements were conducted to reflect the glass transition and phase transition processes. The mechanism of the anomalous thermal stability and the appearance of hard magnetic properties in NdAlNiCuFe system was discussed.

JJ9.23

Materials Discovery Through Large Scale Databases†. Arun Rajagopalan[1], Changwon Suh[1], Xiang Li[1], Vicky Karen[2] and Krishna Rajan[1]; [1]Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York; [2]National Institute of Standards and Technology, Gaithersburg, Maryland.

Large scale crystallographic databases have traditionally been used for retrieving known information. In this paper, we show how one can use such large digital libraries as design tools for materials discovery when the information is integrated with informatics tools. In this presentation, the establishment of patterns of structure - property relationships is shown for high temperature superconducting materials. The potential for establishing databases that are functional and not just phenomenological in nature is demonstrated. †NSF International Materials Institute: Combinatorial Sciences and Materials Informatics Collaboratory (CoSMIC -IMI)

JJ9.24

A Combinatorial Approach to the Development of Neural Networks for the Prediction of Composition/Microstructure/Property Relationships in alpha/beta Ti Alloys. Peter C Collins, Sean Connors, Rajarshi Banerjee and Hamish L Fraser; Materials Science and Engineering, The Ohio State University, Columbus, Ohio.

One approach to the provision of a predictive capability for alpha/beta Ti alloys is to use databases to yield neural networks. The required databases must relate microstructure and properties, but these are not readily available from industry. Consequently, such databases must be generated in a rapid manner. For a given alloy, such as Ti-6Al-4V, this has been accomplished using a Gleeble Thermo-mechanical simulator. However, if variations in alloy composition are to be investigated, it is necessary to make use of alternative combinatorial techniques. This paper describes the application of a new technique for alloy development and database population based on graded compositions produced by laser deposition of elemental blends of powders. Using this technique, alloy variations of Ti-xAl-yV, where 5<x<7 and 3<y<5 and Ti-4Al-xMo-ySn-0.5Si, where 3<x<5 and 1<y<3 (all compositions in wt.%) have been produced using the LENS process. The samples have been upset, and iso-compositional tensile coupons have been cut. These have been heat-treated to produce a wide variation of microstructural features, and subsequently tested in an Electro-thermal Mechanical Test system. Rigorous stereological procedures have been employed to determine quantitatively the microstructural features, and these together with the alloy and phase compositions have been included in neural networks. The capabilities of these networks in predicting alloy properties, optimizing compositions and determining functional dependencies of properties on microstructural features will be demonstrated. This research has been supported by the US AFOSR, Dr. Craig Hartley as Program Manager.

JJ9.25

Data Mining Approach to Ab-initio Prediction of Crystal Structure. Dane Morgan[1], Stefano Curtarolo[1], Gerbrand Ceder[1] and John Rodgers[2]; [1]Department of Materials Science and Engineering, MIT, Cambridge, Massachusetts; [2]Toth Information Systems, Inc., Ottawa, Ontario, Canada.

High-throughput ab-initio computing can lead to novel ways of using computational materials science. Traditionally, ab-initio methods have been used in materials science for detailed studies of specific systems, performing relatively few carefully directed calculations. However, increased speed and reliability have recently made high-throughput ab-initio techniques possible, where tens of thousands of simulations can be performed. In order make optimal use of these large data sets, statistical and data mining approaches must be applied to the ab-initio output. This paper demonstrates how high-throughput and data mining tools can be combined to improve the efficiency of ab-initio crystal structure prediction. A database of over 12,000 structural energies is calculated for a large number of binary alloys. Linear regression methods are then used to derive correlations among these energies. The correlations are in turn used to optimize the process of crystal structure prediction on entirely new alloy systems. It is shown that utilizing correlations derived from the database leads to a practical and efficient algorithm for crystal structure prediction.

JJ9.26

High Throughput Characterizations by Transmission Electron Microscopy for the Combinatorial Samples. Kiyomi Nakajima[1,2], K. Hasegawa[1], T. Tamori[1], T. Hasegawa[1], T. Aoyama[1], H. Koinuma[1,2,3], T. Chikyow[2,3] and P. Ahmet[2]; [1]Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan; [2]COMET-NIMS, National Institute for Materials Science, Tsukuba, Ibaraki, Japan; [3]CREST-JST, Tsukuba, Ibaraki, Japan.

High throughput characterizations using transmission electron microscopy for the combinatorial samples was demonstrated with a support of micro sampling method. In the modern material exploration, the combinatorial synthesis is going to be a major technique in material science. Actually discoveries of new fluorescence materials or ferroelectric materials were demonstrated. Also the combinatorial method can be applied to design super lattices of oxide materials. In this case, interface structures are crucial to exhibit a new functions. As a tool to characterize such interface, the transmission electron microscopy is a post powerful tool. However the problem is the sample preparation from the point of interest in the combinatorial sample. It has been impossible to make thin foils from the points to for the TEM characterization. Recently, an innovative method of the micro sampling was developed and it demonstrates a thin foil fabrication in a accuracy of 20 micron. It seems this method can apply to the combinatorial high throughput characterization. In this presentation, the basic idea of the micro sampling is shown and a few examples of the combinatorial TEM characterization are exhibited such as BaTiO3/SrTiO3 superlattice or LaSrMnO3/SrTiO3 superlattices. With a combination of the image simulations, atomic structures of the interfaces are revealed.

SESSION JJ10: High-Throughput Methods and Instrumentation

Chairs: Oleg Kolosov and Wilhelm Maier
Thursday Morning, December 4, 2003
Independence West (Sheraton)

8:30 AM *JJ10.1

Combinatorial Near Edge X-ray Absorption Fine Structure: Simultaneous Determination of Molecular Orientation and Bond Concentration on Chemically Heterogeneous Surfaces. Daniel Fischer[1], Kirill Effimenko[2] and Jan Genzer[2]; [1]Material Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland; [2]Department of Chemical Engineering, North Carolina State Univeristy, Raleigh, North Carolina.

We show that simultaneous molecular orientation and bond chemistry of planar chemically heterogeneous surfaces can be obtained by combining near edge X-ray absorption fine structure (NEXAFS) spectroscopy and rastering the incident X-ray beam on the specimen. This rastering produces serially two-dimensional NEXAFS images in space and energy revealing information about the chemistry (including bond concentration) and orientation of the surface-bound molecules with sub-millimeter planar spatial resolution and sub-monolayer molecular sensitivity. We call this technique combinatorial NEXAFS. The power of the combinatorial NEXAFS method is illustrated by simultaneously probing the concentration and molecular orientation of semifluorinated (SF) molecules in double SF molecular gradients on flat silica substrates. Other 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. We also envision combinatorial NEXAFS as an insitu probe for catalyst discovery using micro arrays to directly image catalytic chemical activity. Finally, we describe a possible parallel process combinatorial methodology for the production of NEXAFS chemical pictures and reaction kinetics movies of nanostructured materials.

9:00 AM JJ10.2

Imaging Polymer Supported Organic Molecules by Mass Spectrometry Application in Combinatorial Chemistry.

Christine Enjalbal[1], Delphine Maux[1], Robert Combarieu[2], Jean Martinez[1] and Jean-Louis Aubagnac[1]; [1]chemistry, Universites Montpellier 1 & 2, UMR5810, LAPP, Montpellier, France; [2]chemistry, Ecole des Mines de Paris, CEMEF, UMR7635, Sophia Antipolis, France.

Solid-phase Chemistry Organic syntheses are often carried out on insoluble polymeric supports (resins, pins), especially when automated high throughput preparations are required (peptide, combinatorial libraries, ...). The most common resin used in solid-phase syntheses is constituted by polystyrene cross-linked with divinylbenzene and appears like beads (approximately one million beads per gram of resin). Although synthesis and purification steps are facilitated, reaction monitoring presents difficulties. Since the polymeric support is not soluble, an analytical method able to cope with a solid sample is thus required. The direct identification of the anchored molecules must be performed without any chemical treatment. Static-Secondary Ion Mass Spectrometry Mass spectrometry was chosen due to its sensitivity, specificity, speed and analyses automation as required in combinatorial synthetic processes.[1] Among all ionization techniques, only Static-Secondary Ion Mass Spectrometry (S-SIMS) enables the direct desorption of ions from a solid sample into the gas phase by bombardment of the sample by energetic particles. This techniques was therefore investigated to follow polymer supported syntheses. Production of feature ions from the anchored molecules was evidenced, the static mode of the bombardment ensuring little sample degradation. Such ions were produced either by the sole rupture of the covalent bond linking the organic molecule to the support or by multiple bond rupture leading to fragments. Imaging Ions are emitted in S-SIMS from small areas (μm2 range) allowing to analyze only a tiny bit of the polymeric support. Reaction monitoring by S-SIMS can thus be performed on a single resin bead in a non destructrive manner. To increase analysis throughput, mixture of beads were simultaneously characterized through acquisition of an image.[2] The incident energetic beam is rastered on a defined surface including five to six bead. Such strategy was illustrated with different type of mixtures: mixture of components present on the same bead (side-reactions)[3] or mixture of beads issued from pooled batch syntheses[4](for instance Mix and Split combinatorial libraries or pooled beads issued from parallel syntheses). 1. C. Enjalbal, J. Martinez & J-L. Aubagnac, Mass Spectrom. Rev., 19, 139 (2000) 2. J-L. Aubagnac, C. Enjalbal, G. Subra, A. M. Bray, R. Combarieu & J. Martinez J. Mass Spectrom., 33, 1094 (1998) 3. C. Enjalbal, D. Maux, G. Subra, J. Martinez, R. Combarieu & J-L. Aubagnac, Tetrahedron Lett., 40, 6217 (1999) 4. C. Enjalbal, D. Maux, R. Combarieu, J. Martinez and J-L. Aubagnac, J. Comb. Chem., 5, 102-109 (2003).

9:15 AM JJ10.3

Micro X-Ray Fluorescence As A High Throughput Screening Method For Combinatorial Chemistry.

George J Havrilla, Thomasin Miller, Benjamin Warner and Cyndi Wells; Chemistry, Los Alamos National Laboratory, Los Alamos, New Mexico.

The difficult part of combinatorial chemistry is screening the large library of compounds for desired properties of potentially useful molecules. One must either screen each individual reaction (techniques include mass spectrometry or nuclear magnetic resonance) or modify the test substrate so that it produces a faster and more easily detected change such as a change in color. These modifications make the desired properties easy to detect at the expense of making the test case less important, because the colored test substrate may not have the same reactivity as the uncolored desirable substrate. Binding events, such as for pharmaceuticals, also rely on added colored or fluorescent tags. These tags make the binding interaction visible at the expense of perturbing the system, perhaps fatally. Micro X-ray fluorescence (MXRF) eliminates the need for tags, which perturb the molecules in order to detect binding events. MXRF determines the presence and relative amounts of elements heavier than sodium. These elements include sulfur and phosphorus, which are important constituents of proteins (enzymes) and DNA (i.e. gene therapy). Thus, we can screen for intrinsic properties of these important biomolecules. MXRF requires no sample preparation, does not destroy the sample, and can accurately detect very small quantities of the desired element in mixtures using short screening times. We have used a commercially available MXRF to screen combinatorial libraries of oligopeptides bound to 100-micrometer polystyrene bead substrates. A metal is incorporated into the protein sequence for either catalytic activity or binding efficiency. A library of 2500 beads is screened for elemental composition including sulfur, phosphorous, halogens and the target metals. The elemental images indicate which beads have different amounts of metal affinities. Quantification of the metal content can determine which beads and subsequently which oligopeptides are efficient metal binding moieties.

9:30 AM *JJ10.4

A High-resolution Photoemission Spectroscopy System Combined with a Combinatorial Laser Molecular Beam Epitaxy for High-throughput Characterization of Oxide Thin Films.

Hiroshi Kumigashira, Department of Applied Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo, Japan.

Perovskite transition-metal oxide thin-films and superlattices have attracted much attention because of not only the basic scientific interest but also the technological applications, such as tunneling junction devices. Extensive studies on the perovskite oxides films have demonstrated that magnetic and electronic properties of oxides can be controlled through interface effects such as spin exchange, charge transfer, and epitaxial strain. The lack of information about their interface and surface electronic structures, however, does not allow us to fabricate tailored thin films with desired properties. In order to investigate the surface and interface electronic structures of transition metal oxide thin films, we have constructed a high-resolution photoemission spectroscopy (HR-PES) system combined with a combinatorial laser molecular-beam epitaxy (laser MBE) thin film growth system. A photoemission spectrometer GAMMADATA SCIENTA SES-100 was selected for the high-throughput and high energy-resolution photoemission measurements. The system is installed at the high-resolution vacuum-ultraviolet beamline BL-1C or the soft-X-ray undulator beamline BL-2C at the Photon Factory in the High Energy Accelerator Research Organization as an end-station. Total energy resolutions (photon and analyzer) of 6.3 meV and 100 meV were obtained at photon energies of 40 eV (BL-1C) and 600 eV (BL-2C), respectively. Another distinctive feature of this system is the direct connection from the spectrometer to the combinatorial laser MBE chamber. Thin film samples can be transferred quickly into the photoemission chamber without breaking ultra high vacuum. The combinatorial laser MBE system can be used for fabricating combinatorial thin film libraries, i.e. using physical masking during deposition to grow films under different deposition conditions with different compositions or with different thicknesses at different places of a single substrate. Mapping electronic structures can be performed in a single growth-characterization cycle by scanning the synchrotron radiation beam. The capabilities of the system have been demonstrated by in-situ photoemission analysis of (1) $La_{0.6}Sr_{0.4}MnO_3$ thin-film libraries with different growth conditions, (2) the $La_{1-x}Sr_xMnO_3$ and $La_{1-x}Sr_xFeO_3$ thin-film libraries with different compositions, and (3) the $La_{0.6}Sr_{0.4}MnO_3$ thin-film and $La_{0.6}Sr_{0.4}FeO_3$ / $La_{0.6}Sr_{0.4}MnO_3$ superlattice libraries with different thickness.

10:30 AM *JJ10.5

Challenges of Miniaturization in the High Throughput Materials Discovery.

Oleg V Kolosov, Symyx Technologies, Santa Clara, California.

It is almost inevitable that the combinatorial and high throughput materials discovery is directly associated with the miniaturization of the sample size. The minute amount of material created and tested is often 100 to 10,000 smaller than used by traditional synthetic and characterization methods. Small sample size allows one to rapidly study material composition and processing space using small amounts of novel and often expensive materials, as well as to reduce the amount and cost of solvents, energy and space needed for such exploration. At the same time, sample miniaturization presents significant challenges for the development of both high throughput synthetic approaches as well as instruments for characterization. To mention a few, such challenges include higher surface-to-volume ratio, different kinetics of the smaller systems, and absence of averaging over the bigger sample size. The talk presents some advanced solutions to these challenges by Symyx Technologies, Inc. and its Discovery Tools systems that are incorporating a substantial body of the discovery efforts in the areas of polymers, catalysts and electronic materials. The approaches allow to provide relevant and comparable data to the standard laboratory approaches, including synthesis, and chemical and physical properties characterization. The role of adequate sample preparation and instrumentation validation is discussed on the examples of specialty polymers, dispersion formulation discovery workflows and miniature propertiesd sensors.

11:00 AM JJ10.6

Design and testing of a 64 channel combinatorial electrochemical cell for rapid Li-ion battery electrode material characterization.

Michael D. Fleischauer[1], T D Hatchard[1], J M Topple[1] and J R Dahn[2]; [1]Physics, Dalhousie University, Halifax, Nova Scotia, Canada; [2]Physics and Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada.

The field of combinatorial materials science (CMS) is speeding new materials fabrication and characterization efforts. Combinatorial methods have been applied to the search for many advanced materials, including: fuel-cell catalysts, magneto-resistive materials and superconductors [1]. CMS techniques are a natural fit to the search for advanced battery electrode materials, as many of the materials under investigation contain three or more elements [2], and the battery performance is strongly dependent on composition. Dalhousie University has activity in the fields of CMS and Li-ion battery research [3 −9]. This paper describes the design, testing and performance of a high-throughput sixty-four channel combinatorial electrochemical cell used to screen potential Li-ion rechargeable battery electrode materials. Electrochemical measurements determine the charge storage capacity of an electrode material and provide information about phase changes during charging and discharging ("cycling"). Our goal was to design a 64 (eventually 256) channel combinatorial electrochemical cell that was suited for use at a university. Existing combinatorial electrochemical cell designs by Whitacre et. al [10] and Warren et. al [11] do not meet our price or versatility requirements. The cell must be compatible with our sputtering system capable of producing thin films that can map out ternary phase space in a linear and orthogonal fashion [3]. Linear composition gradients are important so that the collected electrochemical data evenly spans the composition range of interest. The electrochemical performance of the combinatorial electrochemical cell was tested by depositing linearly varying amounts of test material on cell plates and arrays of disks and comparing cycling results. This talk will present the comparison results, and demonstrate the power of the combinatorial electrochemical cell by offering glimpses of current investigations. References [1] E.J. Amis et al. MRS Bulletin, 27:295−297, April 2002. [2] O. Mao et al. Electrochem. Solid−State Lett., 2(1):3−5, 1999. [3] J.R. Dahn et al. Chem. Mat. 14(8):3519−3523 2002. [4] T.D. Hatchard et al. Submitted to Thin Solid Films, 2002. [5] A. Bonakdarpour et al. Submitted to Thin Solid Films, 2002. [6] S.D. Beattie and J.R. Dahn. Submitted to J. Electrochem. Soc., 2002. [7] V.K. Cumyn et al. Electrochem. Solid-State Lett. 6(6):E15−E18, 2003. [8] M.D. Fleischauer et al. Submitted to Journal of The Electrochemical Society, January 2003. [9] T.D. Hatchard et al. Electrochem. Solid−State Lett. 6(7):A129−A132, 2003. [10] J. Whitacre et al. 202nd Meeting of The Electrochemical Society, 2002. Talk 149. [11] P.G. Schultz et al. US Patent 6,326,090 B1.

11:15 AM JJ10.7

An overview of combinatorial materials science at Dalhousie University.

Timothy D Hatchard[1], Mike Fleischauer[1], Arman Bonakdarpour[1], Shane D Beattie[1], David Stevens[1] and Jeff R Dahn[1,2]; [1]Physics, Dalhousie University, Halifax, Nova Scotia, Canada; [2]Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada.

The field of combinatorial materials science is speeding new materials fabrication and characterization efforts. Combinatorial methods have been applied to the search for many advanced materials, including: fuel-cell catalysts, magneto-resistive materials and superconductors [1]. Combinatorial materials science techniques are also a natural fit to the search for advanced battery electrode materials, as many of the materials under investigation contain three or more elements [2], and the battery performance is strongly dependent on composition. At Dalhousie, our research focuses mainly on Li-ion battery materials, including anodes, cathodes and electrolytes. Over the past three years, we have been developing combinatorial methods to study these battery components and to speed the discovery of improved materials. Also, being a university lab, cost is a prime factor in all of our research. This presentation will describe the methods that we have developed, including a modified sputtering machine to sputter ternary libraries with linear and orthogonal composition variation [3], a 64-channel combinatorial electrochemical cell [4], a multi-channel micro-potentiostat [5], combinatorial electrodeposition of metal alloy systems [6] and software for data analysis. All of this has been done at a very reasonable cost, which should not be out of reach of many university labs. Currently under development are a 64-channel fuel cell and a method of producing composition gradients in polymer/solid composite electrodes. A description of these activities will also be included, along with some representative results from various projects making use of this equipment. References 1. E.J. Amis, X.D. Xiang, and J.C. Zhao. Combinatorial Materials Science: What's New Since Edison? MRS Bulletin 27 95-297 (April 2002). 2. O. Mao, R.L. Turner, I.A. Courtney, B.D. Fredericksen, M.I. Buckett, L.J. Krause and J.R. Dahn Electrochemical and Solid-State Letters 2 (1) 3-5 (1999). 3. J.R. Dahn, S. Trussler, T.D. Hatchard, A. Bonakdarpour, J.R. Mueller-Neuhaus, K.C. Hewitt and M.D. Fleischauer, Chemistry of Materials, 14(8), (2002) 3519. 4. M.D. Fleischauer, T.D. Hatchard, G.P. Rockwell, J.M. Topple, S. Trussler, S.K. Jericho, M.H. Jericho and J.R. Dahn, submitted to Journal of The Electrochemical Society, January 2003. 5. Vivien K. Cumyn, M.D. Fleischauer, T.D. Hatchard and J.R. Dahn, Electrochem. Solid-State Lett. 6, E15 (2003). 6. S.D. Beattie and J.R. Dahn, J. Electrochem. Soc., 150, C457 (2003).

11:30 AM *JJ10.8

Combinatorial Screening and Characterization of Thermoelectric Oxide Thin Films.

Kenji Itaka[1,2], Quinjiao Wang[1], Hideki Minami[1], Hitoshi Kawaji[1] and Hideomi Koinuma[1,2,3]; [1]Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan; [2]CREST-JST, kawaguchi, Japan; [3]NIMS-COMET, Tsukuba, Japan.

We have developed two kinds of multi-channel thermoelectricity measurement systems of combinatorial thin film libraries. One has ten series of pin-probe type array to measure the Seebeck coefficient and resistance of 10 samples (1.0×7.5 mm^2 each) simultaneously. The other has two heat copper blocks and pads for the wire bonding to measure small (0.3×1.0 mm^2 each) lithography patterned samples. For the validity of these apparatuses, we measured ZnO:Al(Al: 0 to 3%) composition-spread films on a sapphire. The linearity of V-Δ T curves and I-V curves were confirmed, and the highest powerfactor ($=S^2/\rho$) in this library was 0.3 μW/K cm at around 3.0% Al doped ZnO. We also investigate the substitutions effect of the misfitted layer cobalt oxide $Ca_3Co_4O_9$, which was reported to show the highest figure of merit (ZT) in oxide and related materials of perovskite vanadium oxide $LaVO_3$, which are expected to show large thermopower because of its heavy electron mass and multi valence of vanadium ions. We found that Sr- and Cu susbstitution is effecttive for improvement of power factor in the case of $Ca_3Co_4O_9$ and that the polarity of $LaVO_3$ was changed from positive to negative by the change of the substrate from $SrTiO_3$ to $LaAlO_3$. A successful measurement on a composition-spread thin film library indicated that this measurement system accelerates high-speed exploration of thermoelectric materials by combinatorial approach.

SESSION JJ11: Library Design, Fabrication, Data Management, and Informatics

Chairs: Judith Devaney and Bruce Wilson
Thursday Afternoon, December 4, 2003
Independence West (Sheraton)

1:30 PM *JJ11.1

Combinatorial Chemistry and Its Discovery Aspects.

Wilhelm F. Maier, Technische Chemie, University of the Saarland, Saarbruecken-Dudweiler, Saarland, Germany.

The need for new catalysts and materials has never been satisfied by conventional methods. Chemical diversity is much too large to be explored systematically. Combinatorial chemistry applied to the discovery of new materials and catalysts can provide new lead structures, which has been demonstrated by pioneers in the field. We have been engaged in the problems asso-ciated with library design and materials selection and optimization. Two approaches are illus-trated with the search for new CO-oxidation catalysts. The first uses a combination of doping, selection and composition spreads to find and optimize new catalysts. In a second approach, a stochastic method has been used for discovery, followed by an application of evolutionary algorithms. Emissivity corrected IR-thermography as well as spatially resolved mass spec-trometry and gas chromatography have been used for detection of catalytic properties. The presentation covers the library design with the software Plattenbau. The problem of data min-ing and data visualization is illustrated with data from a search for new electrochemical sen-sors materials. The associated combinatorial workflow, including library design and prepara-tion, property testing, data accumulation and data mining is discussed. Literature: J. Scheidtmann, Pierre A. Weiss, Wilhelm F. Maier, Applied Catalysis A: General 2001, 222, 79-89 J. Scheidtmann, J.W. Saalfrank, W.F. Maier, Studies in Surface Science and Catalysis 145, M. Eds. Anpo, M. Onaka, H. Yamashita, Elsevier, Tokyo 2003

2:00 PM JJ11.2
***In* − *silico*Materials Science: A New Strategy for High Throughput Materials Discovery.** Krishna Rajan, Changwon Suh, Arun Rajagopalan and Xiang Li; Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York.

In this presentation we discuss the role of using information sciences and data mining in assessing and discovering structure-property relationships in materials from large and diverse datasets. This approach has now been accepted in the life sciences as "*in* − *silico*" biology and the time has now come to develop a similar strategy in the materials sciences.In order to accomplish this task, one needs to develop the proper tools to support and integrate computational materials science with reliable data. It is shown that by integrating the computational modeling with combinatorial methdologies, one can accelerate materials design and identify new structure-property correlations. NSF International Materials Institute: Combinatorial Sciences and Materials Informatics Collaboratory (CoSMIC-IMI)

2:15 PM JJ11.3
To Data Management and Beyond for Photovoltaic Applications. Brent P Nelson, Daniel Friedman, John Geisz, David Albin, John Benner and Qi Wang; National Center for Photovoltaics, National Renewable Energy Laboratory, Golden, Colorado.

Material science tends to focus around a specific class of materials and devices. After an idea is created, an experiment is postulated, and then materials are grown and devices are fabricated. These materials and devices are characterized using a variety of techniques. Data from these laboratory steps are analyzed, conclusions are formulated, and knowledge is passed on through publications, presentations, and patents. Typically, data are tracked in the area of what is grown and what is measured, but corporate knowledge as to what motivated certain experiments or what was learned from those experiments is often lost. This can be due to many factors including corporate culture, lack of reporting of negative results, and lack of reporting of full data sets. Proper application of informatics must realize that data does not equal to knowledge, but is the foundation for creating knowledge; which is far more useful than mere information. Combinatorial approaches for material growth, device fabrication, and subsequent characterization accelerate experimental throughput. Integrating these systems and their data at all levels ultimately will lead to key knowledge to discover new materials and invent new device structures. We present our early attempts of developing database management schemes for photovoltaic device research at the National Renewable Energy Laboratory that not only critically tracks what was grown and what was measured, but tries to go beyond mere information.

2:30 PM JJ11.4
Data Storage and Evaluation Tools for High Throughput Experimentation Applied to Heterogeneous Catalysis. Wolfgang Strehlau, hte Aktiengesellschaft, Heidelberg, Germany.

Computation is today regarded almost universally as a critical component of high throughput experimentation (HTE), but there is, as yet, no complete solution to the various computational challenges that arise in applying HTE in routine practice. High Throughput Experimentation is the rapid completion of two or more experimental stages in a concerted and integrated fashion. High-throughput experimentation typically comprises four interconnected stages. Expressed as actions, the HTE cycle comprises "Design", "Make", "Test" and "Model" stages and this cycle or spiral applies equally to the discovery and development of drugs, heterogeneous catalysts, or other materials. The "Design" step leverages various computational tools, such as factorial design and other design of experiment ("DOE") protocols, the evaluated results of past rounds of experiments, information already available from other sources, and the insights and intuition of the project team. The catalyst testing profiles defined in the Design stage are typically applied in a parallel reactor system (the "Test" stage). The data relating to and produced by all of these operations are housed in the MatInformatics system. The "Model" stage is, then, coupled closely with the Design stage in application within the next iteration through the HTE cycle. Design of experiment ("DOE") tools support the choice of which experimental points to sample in a complex parameter space. Full coverage of the parameter space defined by just the compositional dimensions of a multi-element inorganic system would require an infinite number of experiments. Thus the practitioner need decide (i) how many experiments to perform; (ii) at what increments each variable is sampled. Based on assumptions about the nature of the experimental space, DOE tools suggest the best coordinates for measurement. If the assumptions are valid, the set of measurements proposed by the DOE tools will then be sufficient to characterize the parameter space. The activity or selectivity of a given heterogeneous catalyst system might vary smoothly with temperature or mixing rate, but vary dramatically, and perhaps discontinuously, with composition or pretreatment conditions. For data evaluation and mathematical modeling as well as search strategies dedicated to reduce the number of data sampling points a variety of different techniques are currently under discussion. These techniques include classical polynomial fitting, linear and non-linear regression analysis, statistical effect analysis, classification trees, partial least squares, stepwise regression analysis, principal component analysis, genetic function approximation, neural networks and genetic algorithms. The presentation illustrates some the design and evaluation tools mentioned above by means of practical examples derived from recent research programs.

2:45 PM JJ11.5
Machine-Learning Models for Combinatorial Materials and Catalyst Discovery. Greg Landrum, Julie Penzotti and Santosh Putta; Rational Discovery LLC, Palo Alto, California.

In order for any model building methodology to be useful in high-throughput materials discovery, it is essential that it be both flexible enough to handle the complexity of the problems at hand and fast enough to not create a bottleneck in the discovery process. Machine-learning techniques satisfy both of these criteria. Whether using statistical techniques or machine-learning methodologies, a good set of descriptors is a pre-requisite for obtaining accurate models which are capable of high computational throughput. The descriptors must capture the essential physics of the problem without requiring overly expensive computations. We have developed an ensemble approach to model building which provides both high accuracy and an estimate of the model's confidence in each prediction. The flexibility and efficiency of our approach have been validated on a number of materials, catalysis, and life-science examples. Here we present the results of applying our methods to several materials-property prediction and catalysis problems. We will also describe our approach to the selection of descriptor sets for these applications.

3:30 PM *JJ11.6
Informatics Needs and Solutions for Supporting High Throughput Research in Catalysis and Material Science. Bruce E Wilson and L. David Rothman; Information Research, The Dow Chemical Company, Midland, Michigan.

Over the past several years, The Dow Chemical Company (Dow) has made a significant investment in high throughput research tools, including both purchased and custom built instruments. These instruments include a very wide range of computer hardware and software, as well as data storage formats. This data is often quite complex, involving: – complex chemical structures (e.g. organometallics), – substances for which no chemical structure can be drawn (e.g. heterogeneous catalysts), – process variables (e.g. temperature, pressure, and feed rate versus time), – conventional analytical methods (e.g. chromatography and spectroscopy), and – data from novel instruments (e.g. a custom built parallel thermal analysis instrument) In this talk, we will present the cultural and technical problems which were identified in our requirements analysis, as well as the approaches we are using to address these problems.

4:00 PM *JJ11.7
Combinatorial Inkjet Technique in Organic Electronics and Optoelectronics. Ghassan E. Jabbour and Yuka Yoshioka; Optical Sciences Center, University of Arizona, Tucson, Arizona.

Due to the many factors that can affect the sheet resistivity of conducting polymers, it difficult to have a rule, such that, when used *apriori* will yield the required resistivity. Significant time and resource savings can be incurred if one resorts to the use of combinatorial techniques. In this talk, we present the use of combinatorial inkjet to modify the sheet resistivity of conducting polymers normally used in organic electronics and optoelectronics. Results of device examples related mainly to light-emitting applications will be shown.

4:30 PM JJ11.8
Combinatorial Materials Development using Gradient Arrays. Sphere Covering Lattice Designs. James N Cawse, GE Global Research, Niskayuna, New York.

Gradient arrays are now common tools in combinatorial chemistry for discovery of new leads to commercial materials. Although the cost per sample has dropped markedly with new high throughput methods, efficient use of experimental resources is still important. Examination of gradient arrays from an informational standpoint suggests that designs which use the concepts of sphere packing and covering will be more efficient than simple gradients. This is especially true in higher dimensional systems.

4:45 PM JJ11.9
Exploratory Immersive Data Mining With Attribute Ordering. Judith Ellen Devaney, NIST, Gaithersburg, Maryland.

We describe an exploratory immersive data mining environment that is based on a museum metaphor. An individual virtual museum is devoted to a single data set and consists of multiple rooms where each room contains multiple representations of an individual view of the dataset. Datasets consist of a fixed number of attributes and possibly a class. Each individual view/room follows an attribute ordering metric such as information gain, or number of outliers. Currently each room contains three types of plots on the walls and a single 3-Dimensional glyph display in the center. Interaction allows the display of statistics. Plots display all of the attributes ordered by the metric for that room. One plot shows the values of the ordering metric for each attribute. Another plot consists of a parallel coordinate plot[3]. A third plot displays the probability density for each attribute with indicators for the median and quartiles. We have developed a Glyph Tool Box [1,5] for creating basic and composite three dimensional glyphs. The Glyph Toolbox has a device independent data format (text) and contains commands for creating glyphs based on this format. The location of the individual glyphs in the three dimensional environment is based upon the values of the first three attributes. Additional attribute values are displayed as properties of the glyphs such as size, color, etc. Attributes that are displayed by the glyphs are determined by the attribute ordering metric. Our immersive environment software is based upon the extensible open source software package DIVERSE [2,4] We present results for multiple data sets. [1] Harry W. Bullen IV, Jessica S. Chang, Alexander V. Harn, Sean P. Kelly, Steven G. Satterfield, Peter M. Ketcham and Judith E. Devaney, A Glyph Toolbox for Immersive Scientific Visualization , October 30, 2002. Available as NISTIR 6924, online at [http://math.nist.gov/mcsd/savg/papers]. [2] DIVERSE, online at [http://diverse.sourceforge.net] [3]A. Inselberg, "The Plane with Parallel Coordinates", The Visual Computer 1, 69-91, 1985. [4] John Kelso, Steven G. Satterfield, Lance E. Arsenault, Peter M. Ketcham and Ronald D. Kriz, DIVERSE: A Framework for Building Extensible and Reconfigurable Device Independent Virtual Environments and Distributed Asynchronous Simulations , Presence: Teleoperators and Virtual Environments, 12 (1) , February 2003. [5]The Glyph Toolbox, online at [http://math.nist.gov/mcsd/savg/software/gtb/].