SYMPOSIUM S
Combinatorial and Artificial Intelligence Methods in Materials Science

November 26 – 29, 2001

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*Invited paper
SESSION 8: COMBINATORIAL APPROACH TO METAL OXIDE SYSTEMS
Chair: Ichiro Takeuchi and David G. Niley
Monday Morning, November 26, 2001
Room 204 (Hynes)

8:30 AM #8.1.1
DEVELOPMENT OF COMBINATORIAL PLD-STM SYSTEM FOR
QUICK NANO-FABRICATION AND EVALUATION.
Y. Masumoto*, R. Tokuhashi and K. H. Koizumi**
Materials and Structures Laboratory, Tokyo Institute of Technology, JAPAN.
*Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, JAPAN;
**Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, JAPAN.
We have developed a new combinatorial technique, “Curroased deposition” for quick optimization of oxide layer epitaxy. In this technique, sequential pulsed laser deposition of eight different films can be performed in one experiment. Furthermore, in situ diagnostics of surface reaction with reflection high energy electron diffraction (RHEED) enables us to control the film growth on an atomic scale. In addition to some details of the hardware, the initial growth behavior of BaO thin films on SrTiO3(001) is reported to demonstrate a unique applicability of this Curroased method. This study has provided us with a new insight into the epitaxial growth of complex oxides by the following observation. BaO film deposition was performed in layer-by-layer growth on B-site(TiO2) terminated SrTiO3(001) substrate by optimizing the growth conditions on the first few areas of substrate and subsequent BaO layers were grown on the remainder of the surface. In situ measurements of RHEED intensities oscillations. From this one series of experiment we have revealed that the epitaxial growth of BaO thin films is dominated by the chemical interaction between the growing lattice and the underlying atomic layer to forming a unique flake-like or high density compact layer cell structure. In other words, the initial growth behavior of BaO can tell us which termination layer covers on the perovskite surface.

9:00 AM #8.1.2
A NOVEL PULSED LASER DEPOSITION TECHNIQUE WITH IN SITU PROBE TECHNOLOGIES FOR INORGANIC THIN FILM LIBRARY FABRICATION.
Peter K. Schenk, Debra L. Kaiser, NIST; Ceramic Division, Gaithersburg, MD; John T. Armstrong, Ryna B. Maricante, Steven W. Robey, Jeffrey S. Srimack, NIST; Surface and Micromachining Science Division, Gaithersburg, MD.
We have designed and constructed a dual-beam, dual-target pulsed laser deposition system for the fabrication of combinatorial thin film libraries of inorganic materials. The system is equipped with high-speed ICCD imaging and spectroscopy for real-time fines-tuning of the interaction between the two laser plumes. With this diagnostic capability, we are able to control the composition range of the deposited film and the film thickness independently. Libraries of compositionally-degraded Ba0.96Sr0.04TiO3 films with 0<ε<1, have been deposited on Si(100) substrates at room temperature and at 600°C. High throughput mapping of film thickness by spectroscopic reflectometry, film composition by dispersive x-ray spectroscopy, and radiolysis by microwave frequency near-field microscopy will also be discussed.

9:15 AM #8.1.3
FABRICATION OF METAL OXIDE GAS SENSOR LIBRARIES.
Maria A. Aronov, Kao-Shuo Chang, Ollaghen F. Nafady, Ichiro Takeuchi, University of Maryland, College Park, MD; Harry Jabs, LynxTech Inc., College Station, TX.
We have fabricated metal-oxide gas sensor libraries based on SnO2 thin films using a combinatorial pulsed laser deposition system. The system has a rotatable heater and an automated two-dimensional shutter system which allow spatially selective in-situ deposition of films with different compositions anywhere within one inch square. 16 element sensor arrays are deposited at 500°C on sapphire substrates with Au electrode patterns. Each element is composed of 500 nm SnO2 deposited with different combinations of In2O3, ZnO, 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 the layers depositions were deposited after every 0.5 nm of SnO2. As deposited doped SnO2 films show sheet resistance ranging from 100 Ω to 30 MΩ at room temperature. The gases to be sensed include methane and NOx. The libraries/floor sensors are currently being measured using a vacuum system, where changes in the resistance of each element in the presence of various gases are monitored. The goal of the project is two-fold: one is to develop an electronic nose where responses from different elements are used together for pattern recognition. The other is to identify novel compositions with enhanced gas sensitivity, selectivity and electrical stability.

10:30 AM #8.1.6
COMPOSITION TUNING OF Zn-MgO THIN FILMS FOR UV DETECTOR TECHNOLOGY.
R.D. Wagner, Tsuichihi W. Yang, Kao-Shuo Chang, Maria Aronov, Rwei Bathe, R.P. Sherman, T. Venkatesan, CSR, Dept of Physics, Univ of Maryland, College Park, MD; H. Shen, NRL, Adelphi, MD.
There has been a strong demand for compact solid-state thin film detectors for UV radiation monitoring. Due to wide (3.0 e 7.9 eV) and tunable band gaps, Zn-MgO alloys are ideal for both UV and UV radiation detectors. Due to excellent thermal, electrical, mechanical properties, and high radiative hardness, Zn, Mg:O–O system offers an opportunity for space applications and high temperature device applications. We have systematically studied the film growth, band gap engineering, and doping of MgZnO system, and fabricated UV detectors. Growth of thin films of Zn, Mg:O–O alloys has been studied as a function of processing conditions in combinatorial approach in pulsed laser deposition to control the Zn/Mg composition ratios of the films for best material quality, surfaces, interfaces, and optical properties. Thermal gradient combinatorial heating was used to thin film alloys at various temperatures for the rapid prototyping of wide range of compositionally controlled cubic and hexagonal phases. As characterized by x-ray diffraction (θ/2θ, ω, and ϕ), Atomic Force Microscopy, Rutherford Backscattering spectroscopy with ion channeling, Hall measurement, UV-visible spectroscopy, and photoluminescence (PL) spectroscopy, thin films have been achieved with high optical luminescence efficiency. Heterojunction and
Schockley type photodetectors utilizing ZnO/MgZnO heterostructures and refractory metal contacts have been developed and tested for UV detection. High sensitivity of 1000% for 10%–20% rise and fall time of 10 ns and 1.0 μs, respectively were achieved. The typical visible rejection was more than four orders of magnitude. Combinatorial approaches for device quality thin film and composition tuning and emphasis towards fabrication of UV detectors will be discussed.

11:00 AM SL 7.1
CO-DOPING APPROACH FOR P-TYPE ZnO WITH COMPOSITION-SPREAD METHOD. A. Tsukazaki, K. Tamaru, Dept. of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama, JAPAN; H. Sato, Electronic Components Laboratory, Hitachi, JAPAN; M. Yamakawa, K. Takeuchi, M. Sumiya, S. Fuji, Department of Electrical and Electronic Engineering, Shimizu University, Hamamatsu, JAPAN; T. Maki, Y. Segawa, Photodynamics Research Center, IRIKEI, Sendai, JAPAN; H. Koinuma, Frontier Collaborative Research Center, Tokyo Institute of Technology, CREST, and COMET, Yokohama, JAPAN; M. Kawasaki, Institute of Material Research, Tohoku University, and COMET, Sendai, JAPAN.

ZnO has a band gap of 3.37 eV at room temperature, thus it is a potential candidate for ultraviolet optical devices. Recently, a claim of p-type ZnO with co-doping method was reported [1], where Ga and N were used respectively as donors and acceptor as was proposed by first principle calculation [2]. However, the reproducibility is still of debatable issue [3]. Here, we report on a high throughput fabrication of p-type ZnO without a variable composition spread method [1]. The composition spread method was fabricated on lattice matched ScAlMgO4(100) substrates by gas ion beam technique equipped with Ga and N source gun. The substrate was heated by an inductively coupled plasma reactor (A = 800 mm) focused on a backside of the substrate. Local heating of the substrate enabled substrate temperature to have continuously varied gradient with a range of about 100°C on a substrate of 1cm length. The concentrations of N and Ga were determined with secondary ion mass spectrometry to be a logarithmic function and a constant of the growth temperature, respectively. As a result, the composition spread film had a continuously varied N/Ga ratio with a range from 0.5 to 10 including N/Ga of 1,000 to be appropriate for p-type conductivity. We shall discuss the electronic properties of ZnO:Ga: N composition spread films as a function of N/Ga ratio. No p-type conduction was realized for these films at present, contrary to the present report [1]. The other approaches for the reproducible fabrication of p-type ZnO will be presented.

11:15 AM SL 7.8
COMBINATORIAL APPROACHES TO THE DEVELOPMENT OF TRANSPARENT CONDUCTING OXIDES. David Ginley, John Perkins, Jeff Alleman, Joe DelCiceto, Xiongfa Li, Tim Coutts, David Young, Philip Parrill, Brian Keyes, Qi Weng, Lynn Gehlhauser, NREL, Golden, CO; R. Shuster, University of Colorado, Boulder, CO; Davor Balazic, NIST, Boulder, CO.

Transparent conducting oxides (TCOs) are becoming increasingly important for many applications including flat panel displays, thin film photovoltaics, smart windows, and polymer based electronics. Developing new TCOs and optimizing the known ones for specific applications is a daunting task because of the number of parameters that must be optimized uniquely in each case. Combinatorial approaches offer the greatest potential for success. Key is developing the appropriate deposition, analysis and data mining tools to be able to efficiently reach the desired objective. We present new results of compositional gradient libraries of ZnO and ZnO:Ga with and without an active nitrogen source to try and produce p-type ZnO materials and confirm the method of nitrogen incorporation. The nature and extent of p-type doping remains an unanswered question and a controversial question in the literature. Combinatorial approaches can investigate a wide range of phase space and hopefully find the ‘sweet spot’. We will also present work on compositional gradient libraries of ZnSnOx and CdSnOx grown by sputter deposition and chemical vapor deposition respectively. These libraries include two of the more promising new TCO families because of their higher mobility and higher chemical stabilities. Library analysis has been conducted by automated transmission and reflection from the UV through the visible to identify the bandgap, transmission and plasma edge, micro-xray diffraction to identify phase formation as a function of temperature, and direct conductivity for transport data to confirm modeling from the FTIR. Direct information on the phase formation and resultant electro-optical properties has been obtained leading to both an increased understanding of the materials systems and optimized TCOs.

11:30 AM SL 7.9

In recent years the need for improved transparent conducting oxides (TCOs), particularly an increased carrier mobility, has driven the search for better TCOs from tin-oxide and indium-tin-oxide, the established standards, to materials which are compositionally more complex. For example, the spinel CdSnO3 has demonstrated a higher mobility than SnO2. Extending this idea of blending single-metal TCOs in search of improved, and possibly new, TCOs opens up the possibility of ternary, quaternary and possibly even more complex combinations of SnO2, In2O3, SnO and CdO. As a first step towards a combinatorial exploration of this multidimensional phase space, we have investigated the binary tie line from ZnO to SnO2. Even this apparently simple composition spread spans at least four distinct crystalline phases: ZnO, ZnSnO4, Zn2SnO4, and SnO2. Compositional ly graded ZnSnO thin film libraries are deposited onto heated glass substrates at 250°C via co-sputtering from separate Zn and Sn sputtering targets. Compositional overlap libraries have been deposited which span the metal stoichiometry range of ZnSnO2 from ~1.0 to 1.2 and with film thicknesses of 0.5 to 3 μm. The zinc oxide was RF-sputtered from a ceramic ZnO target, while the tin oxide was magnetic RF-sputtered from a metallic Sn target using either RF- or DC-sputtering in varying argon-oxygen gas mixtures with a constant total pressure of 20 milliTorr. The bulk resistivity, which ranged from 10 to 1013 ohm-cm for as-deposited libraries, decreased by a factor of five orders of magnitude upon annealing in N2 X-ray diffraction (XRD) measurements before and after annealing show that annealing also significantly improves the crystallinity and phase development as well. These Zn-Sn-O combinatorial libraries are being further characterized by a variety of combinatorial diagnostics including: UV-VIS-NIR optical transmission and reflection to measure the band gap energy and transparency, FTIR reflectivity to measure the plasma edge which is related to the carrier density; electron microprobe to determine the relative metals stoichiometry; and spatially resolved XRD to look for spatially correlated variations in crystallinity, crystalline-phase, lattice parameters and texture.

11:45 AM SL 7.10
COMBINATORIAL MOLECULAR LAYER EPITAXY OF HF BASED PHOSPHOR OXIDES: N Ar—N, W. Kim, H. Kubota, Y. Misumoto and H. Komura,*—**; H. Ouchi Department of Materials Science and Engineering, Nagoya University, Furo-cho, Nagoya, JAPAN; M. Ohshima Department of Applied Chemistry, University of Tokyo, Tokyo, JAPAN. *Frontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, JAPAN. **Materials and Structures Laboratory, Institute of Industrial Science, University of Tokyo, Tokyo, JAPAN. COMET, Tsukuba, JAPAN. CREST, Tokyo, JAPAN.

Oxide thin film phosphors attract considerable attention from the standpoint of possible applications including flat panel displays due to the high luminescence characteristics and high illumination efficiency. Even though these groups of materials possess such interesting properties, researchers have not been explored these materials yet and there have been few studies on oxide phosphors based on atomic scale material design. Here, we report the systematic screening of Ti-doped MIO3 (M = Sr, Ba and Ca) thin film libraries fabricated not by the conventional precursor (sintering) method but by combinatorial molecular layer epitaxy. A series of MIO3-Tm (M = Sr, Ba and Ca) composition spread films and superlattices (SLs) were quickly fabricated on SrTiO3 (100) substrate by the molecular layer-by-layer growth using combinatorial molecular beam epitaxy system under in situ monitoring using reflection high-energy electron diffraction (RHEED). Crystal structures and luminescence properties of composition spread and SLs films were evaluated by the concurrent X-ray diffractometer (XRD) and cathode luminescence (CL) respectively. CL properties of the films were found strongly dependent on their composition and stacking sequence. The optimal composition for giving the best CL property was found to be Sr2.5Cu1.4H2O4.3Tm rather than Sr2H2O4.3Tm, which was the best in bulk sample. The extended X-ray absorption fine structure (EXAFS) and X-ray XANES suggest that the films have local crystal symmetry, different from the bulk. Such positive effect of stress due to the film-substrate interaction is expected in SLs libraries.
SESSION S2: COMBINATORIAL APPROACH TO MAGNETIC MATERIALS

Chairs: Hideomi Koinuma and Frank Tsui
Monday Afternoon, November 26, 2001
Room 204 (Hynes)

1:30 P.M. S2.1

PHASE SPREAD ALLOY METHOD FOR COMBINATORIAL CHEMISTRY: APPLICATION TO SUPERCONDUCTIVITY AND OTHER PHYSICAL PHENOMENA

Iwai K. Schaller, Physics Department, University of California-San Diego, La Jolla, CA.

I will describe the Phase Spread Alloy Method that we have used for more than 8 years to search for new superconductors, magnetism, corrosion resistant materials and catalysts. This method was combined with novel measurement techniques, which allow discarding large areas of the materials phase diagram that do not contain useful compounds for the particular phenomena being investigated. Thus this method (akin to "finding a needle in a haystack") allows finding characteristic signatures and localizing small fractions of particularly interesting compounds which may exhibit desired properties. Work supported by the U.S. Department of Energy.

2:00 P.M. S2.2

COMBINATORIAL SYNTHESIS AND CHARACTERIZATION OF CoMnGe ALLOYS

Frank Tsui, Dept. of Physics and Astronomy, University of North Carolina, Chapel Hill, NC.

We have employed combinatorial approach to explore molecular beam epitaxy synthesis and characterization of a ternary alloy system, CoMnGe. Structural evolution was studied in situ using scanning electron microscopy for high energy electron diffraction and magnetic properties were probed using magneto-optic imaging and SQUID magnetometry. Growth and properties on several substrate orientations were explored, including 001 and 111. These alloys exhibit a rich variety of magnetic and magnetoelectric behavior, including a robust phase near Co_{1-x}Mn_{x}Ge_{2} with high spin polarization, high Tc, and high magnetic response. The observed magnetic response shows strong correlation with structural transformations, such that structural ordering and symmetry change can give rise to enhanced magnetic and magnetoelectric interactions. The observed magnetism in these alloys and their compatibility with Ge substrates make them potential candidates for spin electronic transport studies and applications.

2:15 P.M. S2.3

COMBINATORIAL INVESTIGATION OF MAGNETIC METALLIC ALLOYS

Igahubugha O. Fumudoh, Joseph B. Witter, Ichiro Takeuchi, Dept. of Materials Engineering, University of Maryland, College Park, MD; Martin Aronov, and F. C. Wellstood, Dept. of Physics, University of Maryland, College Park, MD.

We have developed a combinatorial ultra high vacuum co-sputtering system for exploration of magnetic metallic alloy systems. Three independent magnetor bulk and thin films are placed in a non-confocal geometry, and degree of mixing of materials from individual targets is controlled by adjusting the distance between the heated wafers and the guns. In-situ deposited composition spreads are created on three-inch wafers. Wavelength dispersive spectroscopy and scanning Rutherford backscattering spectroscopy are used to obtain quantitative composition. Scanning SQUID microscopy is used as the primary tool for rapid characterization of magnetic properties. We are currently investigating different regions of phase diagrams of ferromagnetic shape memory alloy systems. We have identified ferromagnetic regions in Ni-Co-Mn system. Various high-throughput measurement techniques for detecting magnetic phase transitions including fabrication of cantilever libraries are being implemented and will be discussed.

This program is funded by the Office of Naval Research.

2:30 P.M. S2.4

COMPOSITIONAL AND THICKNESS GRADIENTS IN MAGNETIC THIN FILMS FOR COMBINATORIAL OPTIMIZATION OF MAGNETIC MEDIA PROPERTIES.

Erik B. Svendsen, Rene J.M. van de Veerdonck, Kent J. Howard, Seagate Technology, Materials, Pittsburgh, PA; Lynnette D. Madsen, MSIP, Carnegie Mellon University, Pittsburgh, PA.

Film deposition by ultra high vacuum magnetron sputtering with controlled gradients across the wafer in terms of composition and thickness is known to provide (i) efficient exploration of a large number of variables, and (ii) the interdependencies between parameters to be studied. Output parameters such as coercivity and squareness of magnetic loops for magnetic media were measured and subsequently modeled to reveal the dependence both of the degradation of the squareness and the thickness of the input parameters. An added bonus to this approach is the tight control maintained on the "fixed" parameters (e.g. temperature and background pressure) through making many samples in a single deposition. To achieve the gradients, six tilted magnetrons were used to deposit the films. In one experimental setup, the Co/TM alloy was used during the deposition. The samples consisted of a number of layers as follows: Ta, Ru, Co_{1-x}, CoCr, CoCr-Pt. In this setup, there seems to be an optimum Ru concentration in the range of 80-85% for achieving a maximum squareness, while the coercivity increases monotonically with the Ru concentration. Hence, it is not possible to maximize both the coercivity and the squareness in the same disc in terms of data. In a second set of samples, the effort was focused on the hard magnetic layer and investigating the effect of the additives Ta, Nb, and Ti to the CoCr-Pt to promote the desired magnetic properties. From the experiments it seems that the combination of Pt and Ta/Ti additives promotes a different growth mode than Pt or the additives alone. Further, to verify the possibility of structural and/or characterization automation, the CoCr-Pt magnetic layers consisting of ten bilayers each were mapped by x-ray diffraction. In the samples, the thickness of each Pt layer was kept constant over the surface of the wafer and the thickness of the CoCr layer varied with the total thickness.

2:45 P.M. S2.5

APPLICATION OF COMBINATORIAL METHODS TO STUDIES OF MAGNETISM IN THIN FILMS

Hae-Young Chang, Abraham Anopolsky, Paul Chu, Lawrence Berkeley National Laboratory, Berkeley, CA; Ichiro Takeuchi, Department of Materials and Nuclear Engineering and Center for Superconductivity Research, University of Maryland, College Park, MD.

There are always needs for better materials. That is also the case for magnetic thin films, which have utilities in fields of immense technological importance. The compositional methods that have served as a means to increase the rate of optimization and discovery of various classes of materials can also be used to effectively study magnetic thin films. We have used the composition spread approach to examine the interactions between ferromagnetism and the shape memory effect. The films are deposited under UHV condition with electron beam evaporation and subsequently measured with a scanning SQUID magnetometer. Analysis of the shape memory effects using optical displacement and x-ray circular dichroism microscope will be discussed. Other studies involving the phenomena of exchange bias and magnetoresistivity will also be presented.

3:30 P.M. S2.6

COMBINATORIAL SEARCH FOR TRANSPARENT OXIDE DILUTED MAGNETIC SEMICONDUCTORS

T. Fukumura, M. Kawasaki, National Material Research Institute, Tohoku University, JAPAN; Zhengwu Jin, H. Kimer, Y. Yamada, M. Hamori, Dept. of Innovative and Engineered Materials, Tokyo Inst of Tech, JAPAN; K. Ando, H. Sato, Nat Inst of Advanced Industrial Science and Technology, JAPAN; T. Namba, J. Yokoyama, T. Masumoto, A. Fujimori, Dept. of Physics, Univ of Tokyo, JAPAN; K. Imai, M. Murakami, R. Takahashi, Y. Matsunou, T. Hasegawa, H. Koinuma, Materials and Structures Lab, Tokyo Inst of Tech, JAPAN. "COMET" Frontier Collaborative Research Center, Tokyo Inst of Tech. "CREST".

Diluted magnetic semiconductors (DMS) attract much interest for developing devices where magnetic, optic, and electronic functionalities are fused. The ferromagnetic Curie temperature of DMS exceeds for room temperature by the discovery of Co-doped TiO_{2} [1]. Including this discovery, we have been searching for DMS oxides combinatorially with choosing transparent wide gap semiconductors ZnO, SnO_{2}, InO, TiO_{2} as hosts and various 3d transition elements as dopants [2]. Mn-doped ZnO and Co-doped ZnO have shown such typical characteristics of DMS as fairly large magnetoresistance and huge magneto-optic properties, respectively. Although theoretical prediction triggered by our experimental work suggests the existence of ferromagnetism in 3d-doped ZnO [3], we find no proof of it so far. Such functionalities should be a consequence of interactions between mobile electrons in continuum states of host compounds and localized spins at the 3d elements. The degree of such interactions is strongly dependent on the character of continuum states (O 2p like valence band, Ti 3d like conduction band, and sp^{3} hybridized conduction bands from s orbitals of Zn, Sn, In) through s-t, p-d, and d-d exchange interactions. Carrying out such high-throughput characterization employing SQUID microscopy, magneto-optic spectroscopy, and photoelectron spectroscopy for huge numbers of samples fabricated combinatorially, we discuss the physics of Oxy-COx-DMS which should explore applications in information technology.


4:00 P.M. S2.7

HIGH THROUGHPUT CHARACTERIZATION OF MAGNETIC

Magnetic properties of transition-metal-doped TiO₂, both in-situ and in-situ in deposition thin films, have been surveyed by means of the Scanning Superconducting-quantum interference device Microscope (SSM). As a consequence, we found magnetic domains in Co-doped manganite without external field, giving a strong evidence for ferromagnetism with finite spontaneous magnetization. From the one-dimensional (1D) and two-dimensional (2D) SSM images, it was revealed that the magnetic moment increases with increasing doping levels from x = 0 to about x = 1.3%. We also characterized magnetic behavior of combinatorial (Ga,Mg)As films prepared by the ion implantation technique.

4:15 PM S2.8 MAPPING OF PHYSICAL PROPERTIES: PHASE DIAGRAMS OF COMPLEX MATERIAL SYSTEMS USING CONTINUOUS COMPOSITION MATERIAL CHIPS. Young K. Yeo, Quien Xue, Hyungchul Lee, Hau-Tieng Yang, Gang Wang, Sheng Liu, Xiaofeng Xiang, Iminia Co, Zhiyao Jiang, XADIA Inc., Concord, CA; Tsujiaki Nishikawa, Advanced Materials Lab, Stanford University, Stanford, CA; Yi Dong, Stanford Research Inst, Menlo Park, CA; Yong C. Chu and Derrick C. Mascarenas, Advanced Photon Source, Argonne National Lab, IL; Robert C. O’Handley, Dept of Materials Science and Engineering Massachusetts Inst of Technology, Cambridge, MA.

High throughput and parallel screening study of complex material systems is described. We focus our discussion to the experimental techniques of epitaxial growth of thin film continuous phase diagrams (CPDs) and mapping their physical properties. As an example, we present the results of mapping optical, electrical, and magnetic properties of manganese oxides as functions of doping concentration, ion radius, etc. We discuss evidence that suggests various electronic phase transitions, such as orbital ordering and smectic phase formation, in this highly correlated electronic system. We will also discuss a different application of CPD to describe the structure-property relation of a traditional materials science in Ni₈₋₆Fe₆ magnetic alloy. New results from other ternary magnetic alloy systems and magnetic semiconductors will be presented.

4:30 PM S2.9 HIGH THROUGHPUT OPTIMIZATION OF Y-TYPE MAGNETOPLUMBITE EPITAXIAL THIN FILM GROWTH BY COMBINATORIAL PULSED LASER DEPOSITION TECHNIQUE. I. Okubo, Y. Mitsutomo, M. Ohtani, T. Hasegawa, Ceramics Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, JAPAN; K. Tono, Central Technology Laboratory, ASAH KASEI Corporation, "COMET", Tsukuba, JAPAN.

Ba₂Co₄Fe₁₂O₧₂ (Co₂Y), a family of Y type magnetoepitaxial, is a candidate material for thin film inducers operated at GHz as a magnetic core material. Since it has such a complex composition and large c-axis lattice constant of 4.5 Å, there are many growth parameters to be considered in order to obtain single phase of Co₂Y thin film. Here, we report on the successful fabrication of Co₂Y thin film by combinatorial pulsed laser deposition technique (CLD). The key point was to use the CoO buffer layer to eliminate the second phase of BaFe₄O₁₂. When single phase epitaxial Co₂Y thin film was deposited at 1100°C the thickness of CoO buffer layer was synthesized to be 900°C by fabricating thickness gradient films and characterizing with the concurrent X-ray diffraction method. The rule of CoO buffer layer is discussed on the introduction analysis by x-ray diffraction analysis of Co₂Y thin film and MgAl₂O₄[111] substrate with the micro-scanning transmission electron microscope (TEM), four circle X-ray diffraction measurements.

4:45 PM S2.10 CHARACTERIZATION OF MAGNETIC AND DIELECTRIC PROPERTIES IN Y-TYPE MAGNETOPLUMBITE EPITAXIAL THIN FILMS AT HIGH FREQUENCY APPLICATION. K. Usui, Central Technology Laboratory, ASAH KASEI CORPORATION, Fuji, Shizuoka, JAPAN; I. Okubo, Y. Mitsutomo, N. Okazaki, T. Hasegawa, Ceramics Materials and Structures Laboratory, Tokyo Inst of Technology, Yokohama, JAPAN; K. Tono, COMET-NIMS, Tsukuba, Ibaraki, JAPAN; M. Kawasaki, "Institute for Materials Research, Tohoku University, Sendai, JAPAN and Dept of Innovative and Engineering Materials, Tokyo Institute of Tech, Midori-ku, Yokohama, JAPAN; H. Koizumi, Frontier Collaborative Research Center and Ceramics Materials and Structures Laboratory Tokyo Inst of Tech, Midori-ku, Yokohama, JAPAN and CREST-Japan Science and Technology Corp, "COMET", Tsukuba, JAPAN.

Magnetic films for miniaturization of planar inducers operating at GHz frequencies require high resistivity and high resonance frequency. Y type magnetoepitaxial Ba₂Co₄Fe₁₂O₧₂ (Co₂Y) is a candidate material to meet such requirements because it has about 10 m Ω cm resistivity and resonance frequency higher than 2 GHz. Since we have succeeded in the fabrication of Co₂Y epitaxial thin film on MgAl₂O₄ substrate by combinatorial pulsed laser deposition technique [1]. We report on the magnetic and dielectric properties of this film. The AC resistivity of the film was 7.5Ω cm. The dielectric constant at 2.4 GHz was measured by a microwave microscope to be 7.5. An easy axis coercive force and saturation magnetization were ~200 Oe and ~1000 Gauss respectively, being close to those of bulk sample. Furthermore, the magnetic micro domain structure of Co₂Y epitaxial thin films were observed by a scanning SQUID microscope. By using these data, the electromagnetic field simulation was performed for a spiral inductor using the Co₂Y film to evaluate its practical applicability [1]. I. Okubo et al., to be presented in MRS 2001 Fall meeting.

SESSION S3: COMPOSITION SPREAD TECHNIQUES AND RAPID CHARACTERIZATION
Chair: Ichiro Takeuchi and Toyohiro Chikyow
Tuesday, November 27, 2001
Room 204 (Hyatt)

8:30 AM S3.1 DEVELOPMENT OF FUNCTIONAL MATERIALS BY A COMPOSITION SPREAD APPROACH. Werner Cramer, Dieter Nechausetz, RWT Anthen, Anthen, GERMANY.

The increasing complexity of modern functional materials leads to the demand of cost efficient tools for the development of new products. One possible approach to this question is the adoption of combinatorial methods to the specific requirements of material industry. These methods, originally developed for the pharmaceutical industry, have recently been applied to the screening of superconductors, magnetic and optoelectronic materials. The principle of this combinatorial approaches is the deposition of large materials libraries in one process combined with fast methods for the determination of the resulting properties. In this paper, the deposition and characterization of layered grinded materials libraries is presented. The films have been deposited by (reactive) magnetron sputtering, using two or three metallic targets at a low angle to the substrate surface as well as a system of sputtering gas. We illustrate the advantages of combinatorial approaches for the development of advanced materials. Ge-Si-Te based films for rewriteable optical data storage as well as multicomponent metal hardcoatings like Ti[AlN] [Ti,AlH]N and Ti-V-Ge-Si-Ti films were deposited with compositions around the ternary phase Ge₅Si₂Te₃. The resulting composition-spreads were analysed by EPMA-mappings, XPS, AES, RHEED and GI-XRD with respect to composition, bonding states and structure. The velocity of the phase change was determined using a static tester. [Ti,AlN] Ti[AlH]N and Ti-Al-Si-N composition spreads will be discussed with special emphasis on the relationship between structure and composition on one hand and oxidation resistance of the ternary and quaternary films on the other hand. The composition of the s-deposited films as well as of the oxidized coatings was determined by EPMA. Fast structural mappings were performed by scanning X-ray diffraction. The results will be compared to those obtained with homogenous samples.

9:00 AM S3.2 THIN-FILM METAL ALLOYS FOR MEMS BY COMPOSITION SPREAD DEPOSITION. Aminan G. Bayer, Agere Systems-Linear Technologies, Applied Materials Research, Murray Hill, NJ.

Gold alloy thin films for microelectromechanical systems (MEMS) devices were combinatorially synthesized by a compositional spread technique and subjected to heat treatments for hardening by precipitation. Using gold as the parent material, a breadth of precipitation structure using solute contents (Co, Sb, Pt) from 0 to 5 % were generated. In this approach, composition spreads give rise to an array of alloys with varying solute concentrations that were simultaneously synthesized by sputtering, heat-treated by furnace annealing, and characterized with 4-point probe measurements.

362
nomenclature, and TEM. In this method, a library of materials can be obtained which give insight into the material's structure-property relationship and can generate films that best suit an application. This work presents the experiments and measurements.

9:15 AM **8.3.3**
COMBINATORIAL SYNTHESIS APPROACH FOR OPTIMIZING OXIDE/Si INTERFACE FOR THE FUTURE ULSI
Toyohiro Chikyow, Parshat Ahmet, Kyonmi Nakajima, Tamami Naruke, COMET National Institute for Material Science, Tsukuba, Ibaraki, JAPAN; Hiroshi Song; Koji Ohama, Tokyo Institute of Technology, Yokohama, Kanagawa, JAPAN.

A combinatorial synthesis approach was carried out to optimize oxide/semiconductor interfaces to understand the origin of the interfacial layer formation. Due to the increasing number of transistors on Large Scale Integrated Circuit (LSI), material which have been used in Field Effect Transistor (FET) is closing to their physical limit. Especially SiO₂ growth in practical problem and a lot of efforts have been made to find new candidates of having higher dielectric property to replace SiO₂. SrTiO₃ is one of attractive oxides because of its higher dielectric constant and a possibility of direct epitaxial growth on Si (100). Actually a few trials of STO growth on Si (100) has been reported and the results showed a great possibility for future ULSI application. However, at the oxide/Si interface, SiO₂ or amorphous layer has been observed and its formation seems inevitable though so many challenging and trials have been reported. To form an ideal and abrupt oxide/Si interface, at first, we must investigate the oxide/semiconductor interfaces systematically to understand the phenomena of the interface from the major factors. Finally they used structure and lattice mismatch, stable chemical bonding (such as charge transfer or electron counting), and thermodynamics (thermal reaction or diffusion of elements). For this purpose, we employ the combinatorial approach. The synthesis method with temperature gradient sample heating system. To characterize the sample, HRTEM with micro-sampling method is used to investigate the interface structure in atomic level. The scanning microwave microscopy is also used to evaluate the dielectric properties. Also in this paper, a few kind of intermediate layers are inserted between oxide/Si interface to obtain a stability of SrTiO₃/Si interface.

9:45 AM **S3.4**
DIFFUSION OF Si IN THE SrTiO₃ THIN FILMS FROM Si (100) SUBSTRATE AND ITS INFLUENCE TO THE SrTiO₃/Si(100) INTERFACE. STRUCTURES INVESTIGATED BY COMBINATORIAL METHOD. Parshat Ahmet, Toyohiro Chikyow, Comet-NIMS, National Institute for Materials Science, Tsukuba, JAPAN; Takashi Kosaka, Masayuki Yoshimoto, Hidetsu Koizumi, Tokyo Institute of Technology, Yokohama, JAPAN.

SrTiO₃ is one of the promising candidate of high dielectric materials for further LSI technology because of its extremely high dielectric constant, low temperature sintering temperature (500°C), and lattice mismatch with Si (100) when it is rotated 45° on Si (100) plane. Although epitaxial growth of SrTiO₃ on Si substrates have been studied extensively, there are always a low dielectric amorphous layer at the oxide/Si interface. In this paper, we investigate the interface formation and its stability of SrTiO₃ thin films on Si(100) substrate, we have done a systematic study on the interface structures using combinatorial method. A combinatorial PDL with growth temperature gradient system was grown on Si films and high throughput thin film fabrication system was employed to fabricate thin film cross section for high resolution transmission electron microscopy observation. We have observed a SiO₂ interfacial layer and a amorphize SrTiO₃ layer for the SrTiO₃ thin films with the growth temperatures above 600°C, while only a SiO₂ interfacial layer was observed for the growth temperatures below 600°C. The observed thickness of the amorphous SrTiO₃ layers not only growth temperature dependence also oxygen flow rate above the growth temperatures of 600°C. From the growth condition dependence study of the formation of amorphized SrTiO₃ layers and elemental analysis by electron energy loss spectroscopy, the origin of the amorphization was concluded as an effect of diffusion of Si from substrate.

10:30 AM **S3.5**
SCANNING ELECTRON-BEAM DIELECTRIC MICROSCOPY FOR THE TEMPERATURE COEFFICIENT DISTRIBUTION OF DIELECTRIC MATERIALS. Yuno Cho, Tohoku Univ, Research Institute of Electrical Communication, Sendai, JAPAN.

A new microscopy for determining the temperature coefficient distribution of dielectric constants was developed using an electron-beam as a heat source. This method is based on the temperature spread of the position of the dielectric constants of an electron-beam irradiated material. Microscopic measurements of the distribution of the temperature coefficients of the dielectric constant provide more precise information for designing the material than that obtained from a microscopic measurement. In particular, the evaluation of combinatorial materials composed of low materials with different dielectric temperature coefficients, a microscopic technique to assess the distribution of the temperature coefficient of the dielectric constant is very effective to give a characterization of the material. In this paper, the results of the studies on scanning electron-beam dielectric microscopy is described, which has a resolution better than that of photothermal dielectric microscopy, and with the ability of Si deposition by material composition by electron probe micro analyzer (EPMA). To demonstrate the usefulness of this technique, we measured the two-dimensional image of a two-phase composite ceramic composed of TiO₂ and Bi₂Fe₁₄O₃ for the temperature coefficient of the dielectric constant. Next, to shorten a measurement time, a new type of SEM for measuring the real time transient response caused by a single pulsed electron-beam is successfully developed. Finally, a data measurement method of temperature coefficient of the dielectric constant is also reported.


11:00 AM **S3.6**
FABRICATION AND RAPID CHARACTERIZATION OF FERROELECTRIC THIN FILM COMPOSITION SPREADS. Kuo-Shiong Chang, Minar Arvosev, Ogihguma Famodu, Ichiro Takeuchi, Dept. of Materials and Nuclear Engineering, University of Maryland, College Park, MD; Crystal Marcink, Dept. of Physics, Rowan University, Glassboro, NJ; L.A. Bendersky, NIST, Gaithersburg, MD; H. Chang, LeBL, Berkeley, CA.

We have developed a compact combinatorial pulsed laser deposition system entirely contained in one inch vacuum chamber. The system allows in-situ fabrication of a variety of composition spreads and libraries with different layout designs. We have fabricated a continuous composition spread of Ba, Sr, TiO₃ using an in-situ atomic layer-by-layer deposition scheme. Scanning x-ray microdiffraction and scanning Rutherford backscattering spectroscopy have been used to confirm the continuous composition change across the spread. Dielectric properties of the spread are characterized by quantitative multi-mode scanning microwave microscopy. The microscope has a variable temperature stage, which allows measurements of the Curie temperature at different compositions. The multi-mode measurement allows frequency dependent dielectric property characterization. We have mapped out the frequency dispersion of dielectric properties of Ba, Sr, TiO₃ as a function of temperature in the GHz range. This program is funded by the National Science Foundation.

11:15 AM **S3.7**
DEVELOPMENT OF SCANNING MICROWAVE MICROSCOPE FOR HIGH-THROUGHPUT CHARACTERIZATION OF COMBINATORIAL DIELECTRIC THIN FILM. Noriaki Okumara, Parshat Ahmet, Toyohiro Chikyow, National Inst for Material Science, Tsukuba, JAPAN; Hiroshi Okonogi, Tomotomi Fujimura, Yuno Cho, Masahko Kuroda, Tohoku Univ, Sendai, JAPAN; Mikoto Okuma, Hidetsu Koizumi, Tetsuya Hasegawa, Tokyo Inst of Technology, Yokohama, JAPAN.

High throughput characterization of dielectric properties such as dielectric constant and loss tangent is highly required for the combinatorial design of dielectric materials. Especially, quantitative evaluation of these properties in the GHz microwave frequency region has been increasing its importance in the field of communication and information technologies. For this purpose, we have developed a scanning microwave microscope [μM] using a lumped constant resonator probe. The probe consists of a commercially available microwave oscillator module (μwave oscillator module with an electromechanically polished tungsten needle and an outer conductor ring. The capacitance between the needle and the ring changes with the dielectric constant of the sample just beneath the needle, which can be detected as a frequency shift of the resonator with high accuracy. The frequency shift measured for various standard bulk samples showed a fairly good agreement with the theoretical values, which guarantees the quantitative evaluation of the bulk dielectric constant. We applied the present system to the characterization of several combinatorial thin film samples, including composition spread Ba,Sr, TiO₃ and succeeded in detecting relative change in the local dielectric constant. Quantitative analysis of the dielectric constant of combinatorial thin films will also be discussed.

11:30 AM **S3.8**
HIGH THROUGHPUT X-RAY DIFFRACTOMETER FOR COMBINATORIAL EPITAXIAL THIN FILMS. M. Ohtani, Dept. of Innovative and Engineered Material, Tokyo Inst of Tech., Yokohama,
Combination of laser and ME developed by us enables the integration of epitaxial oxide thin films having various compositions and structures on substrates with atomic scale precision[1]. X-ray diffraction (XRD) measurement is an indispensable technique for characterizing the epitaxial films; however, the integration on a substrate makes it difficult to be subjected to a conventional x-ray diffractometer. Here, we report on the development of a high-throughput x-ray diffractometer for epitaxial combination libraries named as concurrent XRD (CXR) system. This system is a minor modification of a conventional XRD system by employing many crystal samples. The CXRD system is a true three-dimensional x-ray detector. The CXRD measures a combinatorial library within a few minutes so that the efficiency is increased over 100 times faster than conventional system. We shall show the measurement results of parallelized integrated superlattices [Bi2Te3]/[SeTe2] and the rapid evaluation of both out-of-plane and in-plane lattice constants as a function of composition for a composition-spread Bi, Sb, Se-2, Te3 film. In addition, this system can be used as a XRD microscope with a resolution of 0.1 mm as demonstrated by spatial imaging of XRD peak intensity, peak position, and peak full width at half maximum of thin films and patterned devices.


11:45 AM S3.9 INFRARED CHEMICAL IMAGING: MATERIAL ANALYSIS OF HOT-WALL CVD DEPOSITED SILICON FOR SOLAR CELL APPLICATIONS Todd A. Heimer, Edmund J. Heilweil, Optical Technology Division, California Institute of Technology, Pasadena, CA.

The ability to control orientation and morphology in crystalline polycrystalline thin films has been an elusive goal in both industry and academia for many years. We present methods of accelerating the pace of research in this area by preparing single films in which orthogonal gradients of various parameters influencing crystallization can be established. Isotactic polypropylene (iPS) was studied as a model system due to the comparatively slow rates and high temperatures at which it crystallizes. Preliminary studies on isotactic polypropylene (iPS) confirm the applicability of the method to investigating the kinetics of crystallization as a function of undercooling temperature, T0 and film thickness, H. Growth rates, G(M, h) span temperatures from 130°C to 200°C and film thickness from 20 nm to 200 nm were obtained from 2 to 3 films within a few days. As the degree of undercooling, (T - T0), increases, G passes through a maximum between the glass transition temperature, Tg and the melt temperature, Tm expected based on literature data. G also decreases with h along isothermal cross sections. Changes in crystal morphology were also observed as a function of both T and h. Hexagonal phases, spherulites and dendrites of crystalline iPS were obtained simultaneously on the same film. In order to expand the library of materials and accelerate the pace of data collection, alternative methods of sample preparation and probe techniques are being developed. We will discuss current progress in this area.

SESSION S4/DD5.1 COMBINATORIAL APPROACH TO POLYMERS Chair: Eric J. Amis and Alangir Karim Tuesday Afternoon, November 27, 2001

1:30 PM *S4.1/DD5.1 AN ELECTRONIC NOSE FROM ARRAYS OF POLYMER COMPOSITE VAPOR SENSORS Nathan S. Levin, California Institute of Technology, Division of Chemistry and Chemical Engineering, Pasadena, CA.

A method is described for generating a variety of chemically diverse, broadly responsive, low power vapor sensors. A key to our ability to fabricate chemically diverse sensing elements is the preparation of processable, air stable films of electrically conducting organic polymers. An array of such sensing elements produces chemically reversible, diagnostically pattern electrical resistance changes upon exposure to different odors. Such conducting polymer elements are simply prepared and readily modified chemically to respond to a broad range of analytes. In addition, these sensors yield a fairly rapid, low power, dc electrical signal in response to the vapor of interest, and their signals are readily integrated with software and hardware-based neural networks for purposes of analyte identification. Principle component analysis is used to demonstrate that these sensors can identify and quantify different airborne organic solvents, and can yield information on the components of gas mixtures.

2:00 PM *S4.2/DD5.2 COMBINATORIAL STUDIES OF SURFACE PATTERN FORMATION IN BLOCK COPOLYMERS Alangir Karim, Archdeacon Smith, Jack F. Doughs, Amit Selgal, Eric J. Amis, Polymers Division, NIST, Gaithersburg, MD.

Surface pattern formation in PS/P4MA diblock copolymer films is investigated combinatorially as a function of film thickness, h, molecular mass M and substrate surface energy, E. Smooth films are observed for certain h ranges centered about multiples of the lamellar thickness L0 and we attribute this effect to an increase in the surface chain density with h in the upper brush-like copolymer layer. We also observe stable bicontinuous surface patterns for other h ranges and the average size of these patterns is found to inversely scale with L0 to the -2.5 power. Hole and island patterns occur for h ranges between those of the bicontinuous patterns and the smooth regions and their size similarly decreases with h. A smooth surface band is observed for a certain E value regardless of h due to non-preferential interaction of both blocks with the substrate surface.

References:

2:30 PM *S4.3/DD5.3 INVESTIGATING CRYSTALLIZATION IN THIN POLYMER FILMS USING HIGH THROUGHPUT METHODS Kathryn L. Beers, Jack F. Doughs, Eric J. Amis and Alangir Karim, National Institute of Standards and Technology, Polymers Division, Gaithersburg, MD.

As the dimensions of industrial relevant polymeric systems shrink to the length scale of individual molecules, significant new challenges are encountered as the materials properties become dimension dependent. For amorphous polymeric materials, the characteristic dimensions of individual molecules are on the order of tens of nanometers, and dimension dependent thermodynamic properties are observed for films less than 50 nm thick, and under certain conditions for films as thick as 200 nm. In the realm of advanced lithography, structures are routinely generated with at least one dimension less than 100 nm. An emerging difficulty in fabricating densely packed structures using standard resists and processing protocols is the collapse of the structures during drying due to capillary forces. Determination of the plausible mechanical properties of patterned polymeric resist is essential to understand, model, and hopefully circumvent this phenomenon. Currently the techniques for applying inorganic compounds to deform the nanoscopic polymer structures and measuring the deformation of the structures in response to the applied forces are limited. We report on the design and implementation of test structures with which well-defined in-plane capillary forces were generated during drying of resin liquids. Deformation of combinatorial arrays of test structures fabricated from poly(hydroxyl methyl methacrylate) allowed the determination of the force necessary to collapse the structures, and the extent of deformation of the structures as a
function of the applied forces. In conjunction with appropriate molecular and continuum models, mechanical properties can be extracted using these models. From the test results, the stiffness of the adhesive layer is characterized. 

4:00 PM *S4.5/DD5.5*
COMBINATORIAL INVESTIGATION OF ADHESION OF POLYMER THIN FILMS: Alfred J. Crosby, Ahmigir Karim, Eric J. Amis, NIST, Polymers Division, Gaithersburg, MD.

The adhesion of glassy polymer interfaces is directly dependent upon several parameters including time of contact, temperature, surface energy, and molecular weight. Collectively, these parameters play a dominant role in determining the interfacial strength of a glassy polymer interface due to the enhancement of interfacial strength by molecular diffusion across the interface. This diffusion can lead to molecular entanglements and/or situations where molecular friction greatly augments energy dissipation near the interface, thus enhancing the total work required to separate the interface. In addition to the above parameters, we can investigate the effect of thickness of a polymer film on the adhesion energy. To characterize this adhesion, we have developed a novel combinatorial technique to characterize polymer adhesion. The technique involves coating and separation of a matrix of spherical caps on a complementarily patterned substrate using the polymer. By varying such parameters as thickness, temperature, and surface energy along the orthogonal axes of the matrix, we use this new technique to efficiently perform and characterize polymer adhesion. Future work will focus on the self-assembly of polyethylene thin films.

4:30 PM *S4.6/DD5.6*
COMBINATORIAL LIBRARIES OF BLENDED PHASE MORPHOLOGY ON GRADIENT ENERGY SURFACES. Amit Sehgal, Jack F. Dougha, Eric J. Amis, and Ahmigir Karim, Polymers Division, NIST, Gaithersburg, MD; Vincent Ferreira, C.N.R.S., Lab. de Structure et Proprietes de l’Etat Solide, L.S.P.E.S. (Univ. Sciences et Techniques de Lille, Villeneuve d’Ascq, FRANCE.

The presence of an interface in a ultra-thin polymer blend film is critical for the establishment of a phase-separated morphology. The fluidity of the interfacial layer and the preferential wetting of specific components at the walls determines the in-plane and the surface directed compositional distribution and the final structural evolution. Using chemical modification of chlorosilane self-assembled monolayers (SAMs) on Si surfaces by exposure to a gradient in UV-Ozone radiation to create stable substrates with a range of contact angles (H2O, 3° - 15°) and surface energy gradients (H2O, TCH2COOH), a tunable surface energy gradient from 0.85 to 1.44 mL/m2 orthogonal to the surface was generated, simple, yet powerful, two-dimensional maps to probe how the polymersubstrate interaction acts in concert with the film thickness to influence the scales of phase separations. The optical evolution of model LCST (PS-PVMy) blend was investigated by automated optical microscopy and atomic force microscopy. A non-monotonic change in the lateral scale and surface roughness with surface energy is observed along with the expected systematic increase with thickness. The study was extended to a biocompatible blend of poly(ε-caprolactone) and poly(D,L-lactic acid) for application of the systematic variation in topographical scales to assay cellular response.

4:45 PM *S4.7/DD5.7*
COMBINATORIAL MAPPING OF POLYMER FILM WETTABILITIY ON GRADIENT ENERGY SURFACES. Karen M. Ashley, D. Richard, Polymer Science Division, Department of Chemistry, Howard University, Washington DC; Amit Sehgal, and A. Karim, Polymers Division, Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD.

We demonstrate the use of combinatorial methods for studying dewetting of thin hydrophilic polyurethane (PS) and hydrophobic poly d-lactic acid (PLA) films on chemically modified gradient energy surfaces. Substrate libraries were prepared by immersing SiH (passivated Si) in Piranha solution (sulfuric acid / hydrogen peroxide / water) at a controlled rate giving a systematic variation of solvent (water and dioxane) contact angles across the surface. Additionally, chlorosilane SAMs on Si surfaces were exposed to UV radiation such that a range from hydrophobic to hydrophilic was obtained across the surface (~3 cm). Libraries of thin films of PS or PLA coatings on gradient energy surfaces orthogonal to gradients in film thickness were studied for dewetting behavior using automated optical microscopy. Contrasting trends in the wettabilitity of PS and PLA were visually apparent as a function of surface energy of the substrate. The number density of polygonal dewetted patterns varied with both film thickness and substrate surface hydrophilicity as characterized by contact angle studies. The effect of dewetting morphology with molecular weight (above and below entanglement) will be discussed.

SESSION S5 POSTER SESSION
Chair: Hayase Chang
Tuesday, November 27, 2001
8:00 PM
Exhibition Hall D (Hynes)

S5.1 DEVELOPMENT OF ROBOT SYSTEM AND X-RAY POWDER DIFFRACTION APPARATUS FOR COMBINATORIAL MATERIALS RESEARCH. Isao Yamasaki, Saitama Univ, Dept of Engineering, Saitama, JAPAN; Takao Otsuka, Nisai Sanyo Corp, Tokyo, JAPAN; Masahiro Watanabe, NIMS, Tsukuba, JAPAN.

Application of ceramics powder synthesis through solid and liquid processes to combinatorial chemistry is thought to be much more interesting to expansion of material research field. Combinatorial robot system developed in our laboratory has possibility to synthesize ceramics powder through a liquid process. The robot system has an automatic arm. Automatic microreactor attached to the arm, measure and mix the samples. Mixed powders were sent and carried to a pallet as a sample holder with many holes where the samples were injected. The pallet filled with samples was heated in an electrical furnace. Combinatorial powder XRD equipment with a PSRC counter was developed in this study, which was able to measure a sample for only two minutes, in order to investigate crystalline phases in heated powders. Combinatorial study using robot system to prepare samples and powder X-ray diffraction to investigate crystalline phases in samples was performed. Consequently, the following results were obtained using metal oxide nanoparticle slurries as starting materials. The metal system was able to prepare nanoparticle mixtures with different chemical compositions by removing water from slurries. In addition, the combinatorial powder XRD apparatus was found to be effective for investigating and/or screening a large number of powder samples. From the above results, combinatorial robot system was expected to play an important role in an effective study on a process of crystalline phases changing and/or growth in combinatorial samples with different chemical compositions.

S5.2 ANOMALY OF THERMAL PROPERTIES IN THIN FILMS OF Lu2-xSr,CoO3 SERIES SYNTHESIZED WITH A COMBINATORIAL PROCESSING. Yosuke Takita, Hajime Haraishi, Yoshiki Nishio, Tsukuba, Polymers Division, Materials Research Laboratory, NIMS, Tsukuba, JAPAN; Masahiro Ohtani, Tohoku Fukumura, Masahito Kawai, Hideomi Koizumi, Tokyo Institute of Technology, Yokohama, JAPAN.

We evaluated the thermal diffusivity and surface wave frequency for composition-spread thin film Lu2-xSr,CoO3 mono layer LaCoO3 and SrCoO3 and substrate SrTiO3(100) using transient reflecting gating (TRG) method. The comparison with the change of phase diagrams using x-rays deflection for thin film sample was performed also. The result of our analysis showed that the change in thermal diffusivity and surface wave frequency has a little anomalous dependence on varied composition ratio (Lu : Sr) and phase.

S5.3 INVESTIGATION OF GATE-INSULATORS TOWARDS HIGH PERFORMANCE INVISIBLE ZnO TFT- J. Nakai, S. Takagi, T. Atta, Dept. of Innovative and Engineering Materials, Tokyo Institute of Technology, Yokohama, JAPAN; Y. Ohnuki, S. Shishikura, Y. Ohno, T. Masukura, H. Ohno, Research Institute of Electrical Communication, Tohoku University, Sendai, JAPAN; H. Koizumi, Frontier Collaborative Research Center, Tokyo Institute of Technology, CREST, and COMET, Yokohama, JAPAN; M. Kawasumi, Institute of Material Research, Tohoku University, and COMET, Sendai, JAPAN.

ZnO is the attractive wide band gap semiconductor owing to ultraviolet light action or room temperature. Due to its transparent nature it is useful to realize a transparent thin film transistor (TFT) that is efficient for driving the active matrix liquid crystal display (LCD). The ZnO TFT could be capable of substituting the other TFT made of a-Si or poly-Si and improving the resolution of the first
panel display. We have reported on the demonstration of ZnO TFT action grown on glass or plastic substrate [1]. However, the performance of these substrates is currently limited by the mobile charge in gate insulator and/or the interface trap caused by imperfectness of gate insulator. Here, we report on the investigation of the gate insulator toward high performance ZnO TFT. The ZnO films were deposited on various gate insulators/TiOx/glass substrates with pulsed laser deposition to form bottom gate type TFTs. The size of TFT was the same as a commercial LCD, where the channel length and width were 5 microns and 15 microns, respectively. The TFT mobility was 20 cm²/Vs and the on/off ratio was over 10⁴. The hysteretic behavior of the channel current vs. gate voltage depends strongly on the gate insulator and the fabrication process. In this talk, we shall show the advantage of the combinatorial approach to optimize the TFT performance [1].


5.4 COMPUTER-CONTROLLED FABRICATION OF CONCENTRIC MULTILAYERS FOR SYNCHROTRON RADIATION HARD X-RAY FRESNEL ZONE PLATE: Masato Yamauchi1, Kazuhide Tanimura2, Naoko Kanno3,4, Yoshio Suzuki5, Masahiro Awaji2, Akihisa Takeuchi2, Hidekazu Takano2, Yoshiro Kohmura2, Katsuhiro Honda4, 5.

Physics Research Institute, AIST,Tsukuba, JAPAN.
Japan Synchrotron Radiation Research Institute(SPring-8), JAPAN.
Kanazawa Medical University, JAPAN.
RIKEN Harima Institute, JAPAN.
Ritsumeikan University, JAPAN.

The multiplexer Fresnel zone plate (FZP) is a promising focusing element for synchrotron radiation hard X-ray, which is composed of alternating transparent (Al) layers and opaque layers (Cu) as thin as 100-300 nm. The concentric multiplexer FZP was fabricated onto rotating Au fine wire substrate 50 micron in diameter in a double DC sputtering deposition apparatus. We succeeded in an automatic fabrication of the concentric multiplexer using our developed computer-controlled system. The system automatically controls several simultaneous operations such as the gas pressure control, sputtering power control, shutter control by the input data (focal length, X-ray wavelength, number of layers, etc.) through the process. Therefore, the precise control of deposition rate (0.1-2 nm/s) and absolute thickness improved the X-ray optical element.

5.5 OBSERVATIONS OF TiO₂ SURFACE USING TOTALLY REFLECTED X-RAY IN-PLANE DIFFUSION UNDER UV IRRADIATION. T. Horiuchi, H. Ochi, K. Ishida and K. Matsushige, Kyoto Univ, Dept of Electronic Science and Engineering, Kyoto, JAPAN.

Titanium dioxide(TiO₂, rutile, anatase) provides very useful technological applications such as self-cleaning devices with amphoteric (hydrophilic and oleophilic) surfaces[1]. The chemical photocatalytic activities and the photoreacted solar cell as molecular dye-sensitized electro-chemical devices [2]. But the fundamental mechanism in electronic hole (oxidation/reduction) transferring to the molecules adsorbed on the TiO₂ surfaces under UV irradiation has not been clearly understood yet. Here, in order to clarify this unclear point, we investigated the relationship between the surface structure and the adsorbed molecules under UV irradiation using specially designed x-ray system. This system can produce x-rays from the molecules due to the total reflection phenomenon. Also, by simultaneous observations of both the diffraction peaks and width(FWHM) using white incident x-rays, we can get very important information about the relaxations induced by chemical interaction between the adsorbed molecules and the surface crystallites. From many experiments conducted using (110), (100) and (001) surfaces of substrates and adsorbed molecules under various atmosphere of H₂O, CH₃COCH₃, CH₃CH₂OH and CH₃OH, it has been elucidated that the (110) has the highest photocatalytic activities, and that the FWHMs presenting the crystal relaxations show the characteristic response in terms of kinds of molecules. These results suggested that the chemical photocatalytic reactive processes can be measured directly employing the totally reflected x-ray in-plane diffraction method.


5.6 INVESTIGATION OF DEEP LEVELS IN n-TYPE N-DOPED Si BY A TEMPERATURE DEPENDENCE OF PREELECTRIC PHOTOTHERMAL SIGNALS. S. Sato, A. Ito, T. Ikari, Dept. of Electrical and Electronic Engineering, Miyazaki University, Miyazaki, JAPAN; A. Fukuyama, S. Tsuru, Dept. of Applied Physics, Miyazaki University, Miyazaki, JAPAN; S. Tsuchida, Dept. of Electronics, Fukusuka Institute of Technology, Fukusuka, JAPAN.

Since the performance of silicon (Si) semiconductor devices is greatly improved by the current commercial application of Si, it is very important to know the role of deep lying defect level in order to produce high quality substrates. We have recently reported that the activation energies, the concentrations and the electron capture cross sections of deep defect levels in semiconductors Si wafers such as EL5, EL7 and EL15 were well investigated by the temperature variation of the photothermal transient measurements (PPT) signals [1]. The great advantage of this technique is that it is a direct monitor of the nonradiative recombination processes that are major process over various temperature levels. Therefore, the proposed methodology gives us a new insight for the deep level from the nonradiative electron transition point of view. In this paper, we report on the results for applying our new technique to Si wafers that have a deep levels induced by nickel (Ni) atoms. Since the Ni level is already well characterized by using a DLTS technique [2], a usefulness of the proposed new experimental methodology becomes clear. The temperature variation of PPT signal intensity of n-type Ni-doped and non-doped samples from 77 K to 300 K was measured. The theoretical model was performed for the temperature variation of the PPT signals by using a rate equation for the electrons in the production band and the relevant deep traps. Curve fitting to the experimental results made us to estimate the concentration, activation energy and capture cross section for the Ni deep acceptor. Since these observed parameters agree well with that reported, we found our proposed experimental method is accurate and useful optical characterization technique for deep levels in semiconductors.


5.7 FLASH PHOTOLYSIS OF POLYSTYRENE WITH LASER. Mr.Hongwei, Yangyongjian, and Cui Binshun, Guo Wende, Liu Weiming, Wang Shouswei, Chinese Academy of Engineering Physics, Mianyang, Sichuan, PEOPLE'S REPUBLIC OF CHINA.

This paper describes the flash photolysis of polystyrene with a pulsed Nd:Glass laser (wavelength 1064 nm, 10⁶ W/cm², 10⁻¹₂ sec duration, 2.0 J/sec), the run after Q-switched manner giving 253 ps pulse at 1064 nm and about 10⁻⁶% duration. In this experiment a model Finnigan MAT 4510 chronograph/mass spectrometer is used to detect products speedily in time. The focused laser beam (to a spot size of about 0.5mm in diameter) through a window of the source of the instrument irradiates a sample of polystyrene on the center of the ion oven, so that the polystyrene dissociate, vapor, then the sample injection is achieved. By the fast analyzer of the quadrupole mass spectrometer the mass spectra can be obtained quickly, and a computer processes the received signal and stores the mass spectrum. The mass spectrometric data can be collected in tens seconds after a laser shot. In case of the Q-switched manner the spectrum of the photolysis is simpler than that of without a Q-switched. Because the pulse duration and the energy effect on it. The difference of the relative intensity between the lines and the difference of the product components indicate that the laser photolysis of the macromolecular compounds have some regularity, while have some randomness. We suggested that there are practical limitations on distinguishing macromolecular compounds by laser photolysis. Not only incident energy must be controlled, but also the need to precise the laser pulse must be functioned by randomness with a kind of mass spectrometer. The randomness of a laser photolysis mass spectrum of the macromolecular compound shows the intramolecular energy transfer performance between high vibrational states of a ground electronic state. Keywords: polystyrene laser, flash photolysis, chronograph/mass spectrometer.

5.8 FITOCHEMICAL NUCLEATION OF COPPER ON POLYMIDE SURFACE WITH 10NS LASER IRRADIATION. Yoshihito Ogawa, Hiroto Tokumura, Masayuki Murakura, The Faculty of Engineering of Tokai University, Kashiwa, JAPAN.

Copper atoms was substituted on the polyimide surface in the presence of copper ion with only 1 Each single shot of ArF laser. Polyimide has been widely used for the flexible electronic circuit printed board. However the polyimides have been made by either sticking the copper foil with adhesive agents or heat welding after making the copper foil surface rough. Thus even the printed board of low conductivity might generate high frequency noises due to the difference between copper and adhesive agents. If the atoms conducting plastics and the metal coated copper are a major process for the chemical methods instead of conventional physical methods, an hybrid material made from both plastics and metal can be produced. Then we have succeeded in substituting copper atoms with an electron beam through the medium of oxygen atoms on polyimide surface. In this study we first placed fused silica glass on the photo-oxidized polyimide surface, and poured the sulfuric solution into the gap between the silica glass and the film, forming a thin liquid layer. Then, one shot of circuit patterned ArF laser light having 32mJ/cm² was irradiated.
SESSION 56: COMBINATORIAL APPROACH TO CATALYSTS AND OTHER MATERIALS
Chair: John M. Newman
Wednesday Morning, November 28, 2001
Room 204 (Hynes)

8:30 AM #56.1
COMBINATORIAL CATALYSIS DISCOVERY: SPECIALTY CHEMICAL APPLICATIONS. George Y. Li, DuPont Central Research & Development, Wilmington, DE.

Combinatorial technologies which accelerate the speed and dramatically reduce the cost of new materials and catalyst discovery, have been applied in chemical and materials industries in recent years. Thousands of organic, inorganic and materials catalysts can be rapidly synthesized and quickly screened by combinatorial approaches in a short period of time. However, current combinatorial methodologies for discovery and development of homogeneous catalysts and other applications due to the lack of efficient synthetic and screening methods. We successfully developed useful combinatorial approaches to discover high value industrial catalysts by using combinatorial synthesis and decoupling. We report here a process for searching new catalysts for industrially valuable but difficult aryl chloride coupling transformations. Palladium chlorides possessing phosphonic acid ligands were found to be remarkably active and efficient catalysts in the presence of bases for a variety of cross-coupling reactions of aryl chlorides with arylboronic acids, olefins, amines, and thioles. IC and 31P NMR studies show that these phosphonic acid ligands in the complexes can be deprotonated to yield electron-rich mononuclear species, which in turn, are capable of promoting aryl-aryl bond-forming reactions of aryl chlorides.

9:00 AM #56.2
HIGH THROUGHPUT METHODS IN THE HYDROTHERMAL SYNTHESIS OF MICROPOROUS MATERIALS. Thomas Bein, Norbert Stock, Ludwig Maximilians- Univ, Dept of Chemistry, Munich, GERMANY.

We have developed an automated parallel synthesis methodology that permits the rapid and detailed investigation of hydrothermal systems leading to libraries of microporous materials at the micromole scale, without manipulation of individual samples [1]. Recent advances have led to the use of automated systems that permit accelerated automated workup. A maximum of 150 microtiter solvents per reaction chamber can be employed. The general procedure is as follows: automatic dispensing of reagents into autoclave blocks using a liquid handler, homogenization of the reaction mixture, followed by synthesis, product isolation and automated structure analysis using X-ray diffractometry as well as automated characterization by Raman spectroscopy. Here we describe the application of this technique to the exploration of the aluminophosphate synthesis field. The issues of accurate dispensing of viscous solids in the microtiter-plate, possible evaporation and the reproducibility of dispensed volumes, as well as the homogenization of the reactions will be discussed. The results of the synthesis of microporous aluminophosphates using different templates, template concentrations, and mixed template systems have been investigated. Emphasis is put on the study of cooperative structure-directing effects, where we will show that the use of toxic and costly templates can be minimized by using a cosolvent. [1] K. Choi, D. Gardner, N. Hilbrandt, T. Bein, Angew. Chem. Int. Ed., 38 (1999) 2891.

9:15 AM #56.3
ELECTROSTATIC MANIPULATION OF MICRON SCALE DRY DIELECTRIC MATERIALS. Malinda Tapper, Michael J. Cima, Massachusetts Institute of Technology, Department of Materials Science and Engineering, Cambridge, MA.

An apparatus for dispensing micron-scale dielectric materials has been developed. It is believed that the method may be applicable for transfer of a wide range of dielectric powders as well as small, shaped components. Small silica spheres, approximately 100 microns in diameter, and sodium fluoroaluminate powder coated with the CO-Cu bond with active oxygen on the polycrystalline surface. In this treatment there was no change on the polycrystalline surface with the naked eye. However, we were able to grow a copper thin film of about 20nm after immersing the sample into the electroless plating solution for 15 minutes at 60°C. By washing the sample with an ultrasonic washing machine, the clear image of the circuit pattern appeared only in the exposed area, with the unexposed copper film peaked off.

SESSION 56.4: COMBINATORIAL EXPLORATION OF ELECTRODE MATERIALS. Kazunori Takada, Kenjiro Fujimoto, Takayoshi Sasaki, Masaaki Wasanaka, Advanced Materials Laboratory, National Institute for Materials Science, JAPAN; Saono Higo, Toho Technical Research, JAPAN; Ikuko Yamasaki, Faculty of Engineering, Shinshu University, JAPAN.

Lithium batteries are now widely used in portable electronic equipments. LiCoO₂ is used as a positive electrode material in the battery. Alternatively to LiCoO₂ were under research to reduce the cost and enhance the capacity; however most of candidates do not have enough performance for practical use. There are many trials for improvement, for example the thermal stabilization of LiNiO₂ by some additives, or substitutions in LiMn₂O₄ to suppress John-Deller instability and improve its cyclability. Exploration of suitable dopants or substitutes needs a lot of time. We have developed a combinatorial robotic system for high throughput synthesis of materials. Here we present a next target, which is a high throughput evaluation system of electrode properties. Combinatorial library was prepared automatically by the robotic system. 14 samples were synthesized at one time on a platinum plate. Electrochemical evaluation was based on cycle test at a constant current. The current capacity is very important because of a small quantity of the samples. In addition, all of the samples were electronically connected each other, and hence their working electrode terminals should be grounded together. Multichannel potentiogalvanostat (PS-08, Toho Technical Research), with a current accuracy of 0.2 mA and selectable ground terminal, was used for the system. Potentiogalvanostats were connected with a personal computer via a GPIB interface. The platinum plate was grounded together with 16 working electrode terminals. Each counter electrode was individually fixed to the sample in electrolyte. The charge-discharge operation was controlled a computer program built on LibVIEW. Constant current was passed between the platinum plate and the counter electrodes, and the voltages between them were measured by the PC. The combinatorial evaluation will be presented in detail at the meeting.

9:45 AM #56.5
PREPARATION AND CHARACTERIZATION OF ELECTRODE MATERIALS BY COMBINATORIAL PROCESSING. Kenjiro Fujimoto, Kazunori Takada, Akihisa Kajiyama, Takayoshi Sasaki, Masaaki Wasanaka, Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, JAPAN; Department of Applied Chemistry, Faculty of Engineering, Shinshu University, Saitama, JAPAN; Takako Ohkaki, Nisui Sangyo Corporation, Tokyo, JAPAN.

Electrode materials of Li secondary batteries were prepared using a combinatorial robot system combined with a combinatorial X-ray diffractometer. Raw materials, hydroxides and acetate aqueous solutions were automatically weighed and mixed at highspeed in a series of various combinations by the system. In this process, sixteen samples were prepared at a time on a Pt pellet 3x6x3cm in size that has 16 - 64 wells. These samples automatically were recorded in a serial manner on the combinatorial powder X-ray diffractometer (CRX) with a PSPC detector. Each sample was measured at an angular resolution of 0.02° in two minutes, and the obtained XRD patterns were well fitted to their JCPDS files. The phase LiCoO₂·2MnO₂ (x=0.0, 0.1, 0.2) was synthesized at 1070°C for 5 hours in air using LiOH, Co(II)(CH₃COO)₂ and Mn(CH₃COO)₂ aqueous solution as raw materials, where the molar ratio Li/(CoMn) ≥1.5 in the mixed solution. The present combinatorial technique could give a reaction map on Li₁₋ₓ(CoₓMnₓ)₂O₄ in a day, including the compositional dependency of their lattice constants. Currently, we are applying this methodology to the search on various electrode materials, while we are developing a high throughput screening sensor for electrode materials. Those results will be introduced at the meeting.

367
The combinatorial glass formation tester has been developed to determine the glass forming regions as quickly as possible. The 24 glass batches of about 1g were put into each carbon crucible on a carbon tray and heated in an electric furnace filled with dry nitrogen gas. After about half an hour heating, the crucibles were taken out from the furnace and moved into the cooling chamber pumped with dry nitrogen gas. The tray and the crucibles were moved on to a cooling stage to be cooled down quickly with a water flowing jacket together with nitrogen gas blowing. The time interval after taking out of the crucible till on the cooling stage was shortened as much as possible, resulting to be 1sec. The temperature of the melt in the crucibles was measured with an optical pyrometer to estimate the cooling rate. The top view of the crucibles on the tray was taken with a CCD camera during cooling. The CCD figures were stored on a computer for the judgments of the transparency of the samples in the crucibles to compile a glass forming region. The glass formation tester can manage 24 glass melting tests every 1 hours. In other words, the tester can produce at least 1.92 glass samples ([24 x 8 = 192] within a day working time. The speed was roughly 100 times larger than the case of manual operation.

11:00 AM 50.7
RAPID AND QUANTITATIVE DETERMINATION OF CRYSTALLIZATION TENDENCY OF ZINC TELLURITE GLASS MELT BY USING THERMOGRAVIC ANALYSIS
Shinichi Todoroki, Masatsugu Massumoto, and Satoshi Inose, National Institute for Materials Science, Advanced Materials Laboratory, Tsukuba, JAPAN.

We developed an automatic system in which we can prepare one long piece of glass sample library and anneal it successively under a temperature gradient (2100°C to 40°C). A glass capillary tube (ID 1.5 mm, OD 2.5 mm, 10 cm in length) is used as a cell sample library. Zinc tellurite melt at 800°C is sucked into the cell by applying a vacuum pressure to the other side of the capillary. Crystalization is observed as a white segment in the library under an appropriate annealing condition. A set comprising 2000 glass samples with different annealing time. Since this sample is a T-T-T (Time-Temperature-Transform) diagram, a tangent which touches the crystallized region and pass through the melting temperature at t=0 gives critical cooling rate, Q.

Compositional dependence of Q shows that the minimum of Q is not located at the eutectic point of ZnO-TiO2 system, which has been believed to be the most stable composition on the basis of the known glass forming regions, but is shifted to ZnO-rich region. Considering the high reproducibility of this automated system and the large error bar of previous results, this result is more reliable. We also investigated the dependency of Q on crystal orientation. For the melt obtained by the gradient temperature furnace, a glass transition temperature (Tg) is annealed at above Tg the Q value becomes larger than that without the quenching. This is because the former glass melt went through the nucleating temperature region just past Tg. It is concluded that this automated system makes it easier than ever to examine quantitatively the thermal stability of glass melt having low melting temperature, which is one of the important factors for judging the feasibility of fabricating new glass devices with desired quality.
2:15 PM S7.3
EFFECTS OF ATOMIC ADDITIVES ON COHESION IN STRUCTURAL INTERMETALLICS: A SYSTEMATIC COMPUTATIONAL STUDY. D. Ejigataptra, R.B. Cooper, Dept. of Physics, West Virginia University, Morgantown, WV.

The presence of atomic impurities in intermetallic alloys, e.g. transition metal aluminides such as NiAl, induces a wide range of consequences to its cohesion. Some impurity atoms, e.g. boron, act as a cohesive enhancer which can improve the cohesion substantially, while some other atoms, e.g. oxygen, can destroy the cohesion, even when present in minute concentration. Due to its efficiency, the tight-binding method is a method of choice for studying systematically the effects of atomic impurities on the alloy cohesion. The challenge is to obtain tight-binding parameters that can have comparable accuracy to ab-initio methods. We have developed a method to extract accurate tight-binding parameters directly from a full-potential linear muffin-tin orbital (FP-LMTO) method. These parameters have been used as input to a local Green's function (recursion) calculation. Using this combined method, we systematically study the effects of atomic additives from boron to oxygen.

2:30 PM S7.4
DETERMINATION OF TOTAL ENERGY TIGHTBINDING PARAMETERS FROM FIRST PRINCIPLES CALCULATIONS USING ADAPTIVE SIMULATED ANNEALING. Anders Froseth, Ragnar Hailer, NTNU, Dept of Physics, Trondheim, NORWAY; Peter Deret, Paul Scherrer Institute, Nano-Crystalline Materials Group, Villigen, SWITZERLAND.

Empirical Total Energy Tight Binding (TETB) has proven to be a fast and accurate method for calculating materials properties for various systems, including bulk, surface and amorphous structures. The determination of the tight binding parameters from first-principles results is a multivariate, non-linear optimization problem with multiple local minima. Simulated annealing is an optimization method which is flexible and "guaranteed" to find a global minimum, opposed to classical methods like nonlinear least-squares algorithms. Results are presented from the determination of tight binding parameters for single element materials and binary compounds based on the NRL tight-binding formalism.

References:

3:15 PM S8.5
DEVELOPING QSARs FOR MATERIALS SCIENCE.
Krishna Rujur, Rensselaer Polytechnic Institute, Dept of Materials Science and Engineering, Troy, NY.

The field of combinatorial synthesis and "artificial intelligence" in materials science is still in its infancy. In order to develop an accelerated strategy in the discovery of new materials and processes, it is necesary to integrate both the experimental and the computational aspects of combinatorial synthesis with the computational aspects of information base design of materials. In biology and organic chemistry this has been accomplished by developing "descriptors" which help to specify "quantitative structure activity relationships" at the molecular level. If materials science is to adopt these strategies as well, a similar framework of "QSARs" is required. In this paper we propose to outline some approaches that can lay the foundations for QSARs in materials science applications.

3:45 PM S7.6
THE RATIONAL DISCOVERY FRAMEWORK(TM): A NOVEL TOOL FOR COMpletely GUIDED HIGH-THROUGHPUT DISCOVERY. Greg Landrum, Hugh Genin, Rational Discovery LLC, Palo Alto, CA.

The Rational Discovery Framework(TM) is a novel approach for providing computational guidance in the high-throughput discovery process. The Framework uses a proprietary machines-learning algorithm to construct predictive models from existing experimental data. These predictive models are used to screen the contents of large virtual libraries. A variety of experimental design techniques can be brought to bear on the results of a virtual library screen in order to suggest an optimal set of synthesis candidates for the next round of experimentation. We have demonstrated the power and generality of the Rational Discovery Framework in a series of proofs of concept. Here we present an overview of the Framework as well as the results of studies aimed at developing predictive models for both materials properties (ferromagnetism in ordered and disordered transition-metal alloys; prediction of Tc values for superconductors) and heterogeneous catalysis.

4:00 PM S7.7

We use density functional theory calculations in conjunction with a genetic algorithm to identify the most stable four component alloys. 32 different metals are included in the search and out of around 200,000 possible alloys and structures we find the most stable alloys, the most stable alloy for each metal, and the alloy which gives the best ability to mass density ratio. The approach points to new possibilities of using first principles electronic structure calculations in materials optimization.

SESSION S8: AI METHODS IN MATERIALS SCIENCE
Chairs: Christine Beckens and Luc T. Wille
Thursday Morning, November 29, 2001
Room 204 (Hyatt)

8:30 AM S8.1
ARTIFICIAL INTELLIGENCE IN MATERIALS SCIENCE: CHALLENGES AND OPPORTUNITIES. John P. Maguire, Steven R. LeClair, Air Force Research Lab, Wright-Patterson Air Force Base, OH.

The application of artificial intelligence in materials science offers both opportunity and significant challenge. Short term gains can be made in the area of materials processing through the paradigm of integrating appropriate materials sensors with quite sophisticated materials transformation models (process models) that capture the coupled effects of chemical reactivity and transport phenomena. The integration occurs from both actual sensors and control algorithms interpreted by a decision support hierarchy that manages the process control machinery. This represents a fundamental shift in materials process control philosophy in that the focus is to measure, interpret, and control the structure of the material in-situ during processing rather than the traditional approach of controlling external parameters (pressure, temperature, heat rate, etc.). This presentation will review a number of such systems that have been constructed in our laboratory and highlight the opportunities that exist for transition of this powerful technology into a wide range of applications. The emerging trend of applying artificial intelligence in the area of materials discovery is a major challenge with high risk and the potential for commensurately high return. There has been progress in this area using data mining approaches in the rapid mapping of potentially new phase diagrams. In this talk we will illustrate how AI approaches have also been developed at AFRL as enabling methodology in fundamental material structural and mesoscopic systems. An example of how AI methods enable the accurate simulation of complex mesoscale systems will be presented.

9:00 AM S8.2
ON THE IMPLEMENTATION OF NEURAL NETWORK CONCEPT TO OPTIMIZE THERMAL SPRAY DEPOSITION PROCESS AND DEPOSIT CHARACTERISTICS. Sofiane Guazzesmo, Christian Moret, CEA, LETHEPS, Tech Univ of Belfort-Montbéliard, Stevenens, FRANCE.

Numerous processing parameters, up to fifty, characterize the plasma spray deposition process. A better quality control of the resulting deposits induces a better understanding of their effects on coating formation mechanisms. This derives from three major points, namely to recognize the influencing processing parameters, to be able to quantify accurately the coating properties by managing specific measurement protocols and to establish the different correlation between the operating conditions and the deposit characteristics and the coating formation mechanisms. Numerical models can help to provide such an understanding. From a mathematical point of view, d.c plasma spray deposition process is assimilated to a non-linear problem in regards to its variables (operating parameters, environment, etc.). Explicit modeling have being developed processing past few years to predict either the plasma jet characteristics or the in-flight particles behavior or the particle flattening mechanisms. These models are complex due to their explicit nature and partial since they focus on specific points of the whole process. This paper develops a more global approach
based on an implicit describing of the mechanisms implementing Artificial Neural Networks (ANNs). ANN is a concept that copies the basic mechanisms of the nervous system and can deal with situations that require a decision to be made or to resolve complex problems by integrating a behavior. ANN is an implicit model that takes into account the complexity of the problem, but also the interdependence of the parameters and that includes as well the measured error if this latter is known. Moreover, ANN is a model that discours systemic relationship. The global concept and the protocols to implement (i.e., causal relationships proposal as a global hypotized and scientific interpretation) are presented and developed in the case of the d.c. plasma spray process. An example is then developed.

9:15 AM SS.3
PARAMETERIZATION OF TRANSIENT DEFECT DYNAMICS MODELS IN CZOCHRALSKI CRYSTAL GROWTH. Tadeusz Sienkiewicz and Thomas Freyen, University of Pennsylvania, Dept. of Chemical Engineering and Applied Mechanics, PA, Germany, and Christian Hoess, Wacker Siltronic AG, Burghausen, GERMANY.

Numerous investigations have attempted to determine quantitively the thermophysical properties of native point defects in silicon to generate robust, predictive models for defect evolution and dopant distribution during crystal growth and wafer processing. Despite this effort, even simple point defect models are not yet able to predict point defect transport and aggregation without repeated local parameterizations. A global optimization approach based on the use of both simulated annealing (SA) and gradient-based local optimization has been investigated as a means to parameterize a transient model for point defect evolution during Czochralski (CZ) crystal growth. Previous attempts using a few system and parameter defect properties have relied on quasi-steady state analyses and hence not realized in robust parameterizations. It is shown that a fully transient and local parameterization is required for modeling typical CZ experiments. Lifetime mapping of actual Cz ingots from commercial systems in which the crystal growth rates are continuously varied is used to provide a detailed picture of point defect distributions. The experimental profiles are a surprisingly rich source of point defect thermophysical property information. The response of the point defect distribution to changes in the crystal growth rate is observed to exhibit significant hysteresis, which necessitates a fully transient modeling approach. An analysis of the fluctuation frequencies in the instantaneous pull rate is used to deduce bounds on the transport rates of point defects. Finally, constrained global optimization is used to extract values for point defect transport and reaction properties. A highly adaptive approach is used to reduce the computational expense associated with performing large numbers of two-dimensional, transient simulations.

9:30 AM SS.4
MATERIALS DEVELOPMENT FOR SOLID OXIDE FUEL CELLS USING QUALITATIVE MODELS. Khas Schmid, Volker Krebs, Institut für Regelungs- und Steuerungssysteme, Universität Karlsruhe (TH), GERMANY. Christian Schießl, Thomas Ivers-Tiffé, Institut für Werkstoffe der Elektrotechnik, Universität Karlsruhe (TH), GERMANY.

Solid Oxide Fuel Cells are high temperature electrochemical energy converters. The cathodic polarization contributes a substantial part of the electrical losses. Therefore, the microstructural formation of the cathode/electrolyte interface is crucial for achieving maximum performance in these devices. During sintering of the cathode, a poorly conducting lanthanum zirconate lattice (La2Zr2O7) layer may be formed between the lanthanum manganite (La1-x,6Sr1/3)MnO3 cathode and the yttrium-stabilised zirconia (YSZ) electrolyte. When the cell is operated for the first time, a substantial increase in cell performance is observed. This effect is attributed to the decomposition of the La2Zr2O7 layer under the influence of electric current. To optimize the resulting microstructural formation of the interface, a dynamic model is required that represents the relations between microstructural compositions, operating conditions, electric current, and microstructure. Building a model based on chemical reaction equations, a full picture of the high complexity of the interface reactions. Furthermore, modeling with equivalent circuits would not result in an interpretable model. Nevertheless, there is a great deal of expert knowledge about the reactions at the interface. This knowledge is not given back as for local equations but for linguistic rules. Therefore, it can be utilized by the conventional modeling techniques of materials science. This work presents an interdisciplinary approach to modeling materials development by applying constraint logic theory and computational intelligence techniques. We use dynamic fuzzy systems to formalize the expert knowledge about the irreversible materials changes in the La2Zr2O7 layer. Fuzzy if-then rules represent the dynamic dependency of this layer on the electric current, operating conditions of the resulting model. The application of simulations instead of time-consuming experiments. The dynamic behavior of the non-measurable thickness of the La2Zr2O7 layer is simulated, which allows the optimization of the formation of the cathode/electrolyte interface. As a first result of this optimization a substantial shortening of the duration of the formation process is presented.

10:15 AM SS.5
GLOBAL EXPLORATION OF ENERGY LANDSCAPES. David J. Wales, University Chemical Laboratories, Cambridge, UNITED KINGDOM.

Global analysis of potential energy surfaces, or energy landscapes, provides detailed insight into the structure, dynamics and thermodynamics of systems ranging from clusters to bulk glasses and biomolecules. In small water clusters a complete characterization of the possible rearrangements enables tunnelling splitting patterns to be predicted or explained. Some larger clusters exhibit energy landscapes facilitating efficient relaxation to the global minimum, while others instead support competing morphologies, with separation of time scales for relaxation. These morphologies have now been seen in polypeptides and bulk glass formers. The global connectivity of the potential energy surface also determines the success or failure of different global optimization algorithms, and should provide a basis for the design of new methods.

10:45 AM SS.6
DESIGNING CONDUCTING POLYMERS WITH GENETIC ALGORITHMS. Ronaldo Giro, Marco Cyriilo, Douglas S. Galvão, Applied Physics Department, UNICAMP, Campinas, BRAZIL.

Organic polymers are in general associated to plastics. Until the 1970's their electronic use was mainly as electrical insulators. The discovery of organic conducting polymers opened a new field in materials science due to its large technological potential applications and new fundamental physical phenomena. In the last years the possibility of creating new conducting polymers exploring the concept of copolymerization (different structural monomeric units) has attracted much attention from experimental and theoretical point of view. As structural disorder is always present in such systems (amorphous), theoretical analysis is very difficult due to the necessity of analyzing a huge number of possible structures. In this work we present a new methodology to solve these problems. It combines the use of negative force cooling (NFC) and genetic algorithm (GAs). The NFC technique allows us to obtain the eigenvalues of very large matrices without direct diagonalization. It has been proven very effective in the study of electronic structures of disordered polymeric chains when coupled to real-time heuristics. GAs originated from the studies conducted by John Holland in the 1970's. The metaphor underlying GAs is that of natural evolution. A GA is a search procedure modeled on the mechanics of natural selection. It allows very efficient intelligent searches in huge phase spaces locating optimum solutions with reduced computational effort. In this work we have used NFC coupled to GAs (micro GAs with elitism) in a tight-binding approach in order to obtain optimum composition for highest conductivity of polymeric chains. This procedure is very well for binary and ternary polymeric chains. The methodology is completely general and can be in principle adapted to the design of new materials with pre-specified properties.

11:00 AM SS.7
HEURISTIC METHODS FOR FINDING GROUND STATES OF ISING MODELS. Huges J. Lissalles, Luc T. Ville, Florida Atlantic University, Physics Department, Boca Raton, FL.

We describe the application of simulated annealing and genetic algorithms to determine the ground-state of various classes of Ising models. This problem is relevant to finding equilibrium configurations (at zero Kelvin) of adsorbed monolayers, multi-component alloys, and magnetic systems. Because of the presence of metastable configurations (local minima) the detection of the ground-state (global minimum) is a non-trivial problem, especially in the case of complex interactions or frustrated systems. The speed of convergence is analyzed for various model systems.

11:15 AM SS.8
COMBINATION OF EVOLUTIONARY ALGORITHMS AND DENSITY FUNCTIONAL THEORY FOR ATOMIC-SCALE MATERIALS DESIGN. Thomas Bligand, Gunhild Johansson, Andre Rabin, Hans Schlieker, Karen T. Jacobsen, Jens Nieckel, Center of Atomic-Scale Materials Physics, Department of Physics, Technical University of Denmark, Lyngby, DENMARK.

An evolutionary algorithm is developed for use in combination with standard calculational tools of electronic structure theory. The evolutionary algorithm is used to predict materials which have new interesting properties. Based on an unbiased initial population of materials, the algorithm creates new populations which quickly locates a part of the phase space of material parameters.
yielding interesting material properties. Our special choice of
selection, crossover, mutation and reinsertion operators are
demonstrated to incorporate some of the best qualities of each
operator, while avoiding problems such as premature convergence, and
degeneration of the population quality due to over-mutation.
Application of the algorithm is demonstrated in the conjunction with
density functional theory to discover new alloys and catalysts.

11:30 AM $88.0$
GLOBAL OPTIMIZATION WITH PARALLEL GENETIC
ALGORITHMS: APPLICATION TO COMPLEX SURFACE
STRUCTURE DETERMINATION, Michael A. Van Hove, Lawrence
Berkeley National Laboratory, Berkeley, CA, and Univ of
California-Davis, Davis, CA.

Global optimization is a challenge for many applications. This
presentation will focus on the determination of the atomic structure
(crystallography) of the surface of solid materials, by means of the
technique of low-energy electron diffraction: the positions and
chemical identities of atoms must be determined from a set of
experimental data. No "direct methods" exist to determine complex
structures of this type, so that trial-and-error fitting is the norm. We
have implemented genetic algorithms to tackle this problem: they of
course have much more general validity. Issues to be discussed include:
comparison with simulated annealing; parallelization; asynchronous
operation; islanding; combination with local optimization.