

SYMPOSIUM S

Combinatorial and Artificial Intelligence Methods in Materials Science

November 26 – 29, 2001

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SESSION S1: COMBINATORIAL APPROACH TO METAL OXIDE SYSTEMS

Chairs: Ichiro Takeuchi and David S. Ginley
Monday Morning, November 26, 2001
Room 204 (Hynes)

8:30 AM *S1.1

DEVELOPMENT OF COMBINATORIAL PLD-STM SYSTEM FOR QUICK NANO-FABRICATION AND EVALUATION.

Y. Matsumoto^a, T. Ohsawa^b, R. Takahashi^b and H. Koinuma^{a,b,c,d}.
^aMaterials and Structures Laboratory, Tokyo Institute of Technology, JAPAN. ^bFrontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, JAPAN. ^cCOMET, Tsukuba, JAPAN. ^dCREST, Tokyo, JAPAN.

There has been lately a growing interest in nano-science and/or -technology that has made considerable progress in atomically controlled epitaxy and nano-fabrication. Nano-material is new category of materials to be explored for new functions in material science. Thus, the concept of combinatorial technology is also applicable to the exploration of nano-materials. In this paper, we report on development of combinatorial PLD-STM system for quick nano-fabrication and evaluation. In this system, a combinatorial PLD chamber and a surface analysis chamber equipped with LEED and STM are connected through a gate valve. Hence we could transfer a combinatorial nano-materials library fabricated in the chamber to the surface analysis chamber without taking it out in air. The surface electron diffraction pattern and atom-resolved STM image for each pixel in the library can be taken along the direction of sample movement. In order to verify the capability of this combinatorial PLD-STM system, we have investigated atomic-scale surface structure of TiO₂ anatase film as a function of its thickness. The thickness spread (0~20Å) sample was grown on a B site (TiO₂) terminated SrTiO₃(001) substrate and subjected to the measurements of LEED patterns and STM images. With increasing film thickness, one-dimensional structure with four lattice spacing was growing along the [100] and [010], indicating (4×1) surface reconstruction. On this (4×1) reconstructed anatase film surface, Pt could be deposited in the shape of uniform sized nano-particles (~50Å) which were homogeneously dispersed. This kind of information can be effectively used for designing and optimizing surface catalytic reactions.

9:00 AM S1.2

A NOVEL PULSED LASER DEPOSITION TECHNIQUE WITH IN SITU PROCESS DIAGNOSTICS FOR INORGANIC THIN FILM LIBRARY FABRICATION. Peter K. Schenck, Debra L. Kaiser, NIST, Ceramics Division, Gaithersburg, MD; John T. Armstrong, Ryna B. Marinenko, Steven W. Robey, Stephan J. Stranick; NIST, Surface and Microanalysis 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 fine-tuning of the interaction of the two laser plumes. With this diagnostic capability, we are able to control the composition range of the deposited film and the film thickness distribution. Libraries of compositionally-graded Ba_{1-x}Sr_xTiO₃ films, with 0<x<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 wavelength dispersive x-ray spectrometry, and dielectric response by microwave frequency near-field microscopy will also be discussed.

9:15 AM S1.3

FABRICATION OF METAL OXIDE GAS SENSOR LIBRARIES.

Maria A. Aronova, Kao-Shuo Chang, Olugbenga O. Famodu, Ichiro Takeuchi, University of Maryland, College Park, MD; Harry Jabs, Lynntech 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 deposition 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 50 nm SnO₂ doped with different combinations of In₂O₃, ZnO₂, WO₃, Pt and Pd. In order to introduce the dopants uniformly in the SnO₂ host, individual films were fabricated in a layer-by-layer manner, where dopant layers were deposited after every 0.3 nm of SnO₂. 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 NO_x. The libraries/sensor arrays are currently being measured using a multiplexed 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.

9:30 AM S1.4

COMBINATORIAL OPTIMIZATION AND ATOMIC SCALE ANALYSIS OF OXIDE LAYER EPITAXY BY RHEED.

R. Takahashi^d, Y. Matsumoto^b, M. Lippmaa^{c,d}, M. Kawasaki^{c,d,e} and H. Koinuma^{a,b,d,f}, ^aFrontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, JAPAN; ^bMaterials and Structures Laboratory, Tokyo Institute of Technology, JAPAN; ^cDepartment of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama, JAPAN; ^dCOMET, Tsukuba, JAPAN; ^eInstitute for Materials Research, Tohoku University, Sendai, JAPAN; ^fCREST, Tokyo, JAPAN.

We have developed a new combinatorial technique, "Carousel deposition" for quick optimization of oxide layer epitaxy. In this technique, a sequential pulsed laser deposition of eight and more 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 Carousel method. This study has provided us with a new insight into the epitaxial growth unit of complex oxides by the following observation. BaO film deposition was formed 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 remaining areas under in-situ counting of RHEED intensity 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 follow the crystal habit of forming stabler unit cell layer. In other words, the initial growth behavior of BaO can tell us which termination layer covers on the perovskite surface.

9:45 AM S1.5

FABRICATION OF ARTIFICIAL NANO-PARTICLE ARRAYS WITH MODULATED STRUCTURES. C.L. Chen, Y. Lin, T.

Garrett, G.P. Luo, S. Liu, University of Houston, The Texas Center for Superconductivity, Houston, TX.

We have developed a unique technique, the Pulsed Laser Induces Self-Assembly (PLISA), for synthesizing nano-oxide particles and artificial Nano-particle Arrays with Modulated Structures (NAMS). The particle sizes can be controlled from the laser irradiation energy. The NAMS can be obtained from various artificially designed patterns and the modulated periods can be managed from 100 nm to 2000 nm where the particles orderly line up with their sizes from 50 nm to 1000 nm. With this unique technique, we have successfully manipulated various NAMS from different oxides, such as highly ionic conductive (La,Sr)CoO₃, superconductive YBCO, ferroelectric (Ba,Sr)TiO₃, ferromagnetic (La,Ca)MnO₃, and light emitted compound of Y₂O₃ and Al₂O₃, with particle sizes varying from 100 nm and modulated period of about 500 nm separations. Details and their physical properties will be presented in the talks.

10:30 AM *S1.6

COMPOSITION TUNING OF ZnMgO THIN FILMS FOR UV DETECTOR TECHNOLOGY. R.D. Vispute, Ichiro Takeuchi, W.

Yang, Kao Shuo Chang, Maria Aronova, Ravi Bathe, R.P. Sharma, T. Venkatesan, CSR, Dept of Physics, Univ of Maryland, College Park, MD; H. Shen, ARL, Adelphi, MD.

There has been a strong demand for compact solid-state thin film ultraviolet (UV) detectors for UV radiation monitoring. Due to wide (3.0 to 7.9 eV) and tunable band gaps, Zn-Mg-O alloys are ideal for solar blind and UV radiation detectors. Due to excellent thermal, electrical, optical, mechanical properties, and high radiation hardness, Zn_xMg_{1-x}O system offers an opportunity for space applications and high temperature device applications. We have systematically studied thin film growth, band gap engineering, and doping issues in the MgZnO system, and fabricated UV detectors. Growth of thin films of Zn_xMg_{1-x}O alloys has been studied as a function of processing conditions via combinatorial approach in pulsed laser deposition to control the Zn/Mg composition, free carrier concentration, epitaxial quality, surfaces, interfaces, and optical properties. Thermal gradient combinatorial heater was used to grow 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 spectrometry with ion channeling, Hall measurement, UV-visible spectroscopy, and photoluminescence (PL) spectroscopy, device quality films have been achieved with high optical luminescence efficiency. Heterojunction and

Schottky type photodetectors utilizing ZnO/MgZnO heterostructures and refractory metal contacts have been developed and tested for UV detectors. High responsivity of 1000 A/W and fast response of 10%-90% rise and fall time of 10 ns and 1.0 μ s, respectively were achieved. The typical visible rejection was more than four orders of magnitude. Combinatorial approaches for device quality thin film and composition tuning with emphasis towards fabrication of UV detectors will be discussed.

11:00 AM S1.7

CO-DOPING APPROACH FOR P-TYPE ZnO WITH COMPOSITION-SPREAD METHOD. A. Tsukazaki, K. Tamura, Dept. of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama, JAPAN; H. Saito, Electronic Components Laboratories, SHARP Corporation, Tenri, JAPAN; M. Sumiya, S. Fuke, Department of Electrical and Electronic Engineering, Shizuoka University, Hamamatsu, JAPAN; T. Makino, Y. Segawa, Photodynamics Research Center, RIKEN, 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 donor 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 co-doped ZnO film with variable N/Ga ratio using a composition-spread method [4]. ZnO:(Ga,N) composition-spread films were fabricated on lattice matched ScAlMgO₄(0001) substrates by laser MBE equipped with RF-radical source gun. The substrate was heated by a semiconductor laser ($\lambda = 808$ nm) focused on a backside of the susceptor. Local heating of the susceptor 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 a secondary ion mass spectroscopy 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=2 that is considered to be appropriate for *p*-type conduction. 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.

[1] M. Joseph et al., Jpn.J.Appl.Phys. 38, L1205 (1999).

[2] T. Yamamoto et al., Jpn.J.Appl.Phys. 38, L166 (1999).

[3] H. Kawazoe, MRS spring meeting F1.1 (2001).

[4] T. Fukumura et al., Appl.Phys.Lett. 77, 3426 (2000).

11:15 AM S1.8

COMBINATORIAL APPROACHES TO THE DEVELOPMENT OF TRANSPARENT CONDUCTING OXIDES. David Ginley, John Perkins, Jeff Alleman, Joe DelCueto, Xiaonan Li, Tim Coutts, David Young, Philip Parilla, Brian Keyes, Qi Wang, Lynn Gedvilas, NREL, Golden, CO; Renaud Stauber, University of Colorado, Boulder, CO; Davor Balzar, NIST, Boulder, CO.

Transparent conducting oxides (TCOs) are becoming increasingly important for a variety of 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 will present new results on compositional gradient libraries from ZnO:Al 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 stannates are two of the more promising new TCO families because of higher mobilities and higher chemical stabilities. Library analysis has been conducted by automated transmission and reflection from the UV through the NIR to identify the band gap, transmissivity and plasma edge, micro-x-ray 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 S1.9

COMBINATORIAL SYNTHESIS AND CHARACTERIZATION OF ZINC-TIN-OXIDE TRANSPARENT CONDUCTORS. J.D. Perkins, J.A. del Cueto, B.M. Keyes, L.M. Gedvilas, P.A. Parilla, D.S. Ginley, National Renewable Energy Lab., Golden, CO; D. Balzar, National Institute of Science and Technology, Boulder, CO.

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 Cd₂SnO₄ has demonstrated a higher mobility than SnO₂. Extending this idea of blending simple 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 CdO, SnO₂, In₂O₃, Ga₂O₃ and ZnO. 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, Zn₂SnO₄, ZnSnO₃ and SnO₂. Compositionally graded Zn-Sn-O thin film libraries are deposited onto heated glass substrates at 250°C via co-sputtering from separate Zn and Sn containing targets. Compositionally overlapped libraries have been deposited which span the metals stoichiometry range of Zn:Sn from ~ 10:1 to 1:2 and with film thicknesses of 0.5 to 3 μ m. The zinc oxide was RF-sputtered from an ceramic ZnO target while the tin oxide was deposited by reactive magnetron sputtering from a metallic Sn target using either RF- or DC-sputtering in varying argon-oxygen gas mixtures with a constant total pressure of 20 milli Torr. The bulk resistivity, which ranged from 10 to 10⁵ ohm-cm for as-deposited libraries, decreased by several 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 S1.10

COMBINATORIAL MOLECULAR LAYER EPITAXY OF HF BASED PHOSPHOR OXIDES. N. Arai^a, T.W. Kim^a, H. Kubota^a, Y. Matsumoto^b and H. Koinuma^{a,b,c,d}, H. Ofuchi Department of Materials Science and Engineering, Nagoya University, Furo-cho, Nagoya, JAPAN; M. Oshima Department of Applied Chemistry, University of Tokyo, Tokyo, JAPAN. ^aFrontier Collaborative Research Center, Tokyo Institute of Technology, Yokohama, JAPAN. ^bMaterials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, JAPAN. ^cCOMET, Tsukuba, JAPAN. ^dCREST, Tokyo, JAPAN.

Oxide thin film phosphors attract considerable attention from the scientific community because of its possible application in flat panel displays due to the high luminescent characteristics and high lateral resolution. 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 phosphor oxides based on atomic scale material design. Here, we report the systematic screening of Tm-doped MHfO₃ (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 MHfO₃: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 laser molecular beam epitaxy system under in situ monitoring using reflection high-energy electron diffraction (RHEED). Crystal structures and luminescent 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 Sr_{0.3}Ca_{0.7}HfO₃:Tm rather than SrHfO₃:Tm, which was the best in bulk sample. The extended X-ray absorption fine structure (EXAFS) and 4-axis XRD analyses 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 PM *S2.1

PHASE SPREAD ALLOY METHOD FOR COMBINATORIAL CHEMISTRY: APPLICATION TO SUPERCONDUCTIVITY AND OTHER PHYSICAL PHENOMENA. Ivan K. Schuller, 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 very sensitive global 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 and localizing small fractions of particularly interesting compounds which may exhibit desired properties. Work supported by the U.S. Department of Energy.

2:00 PM 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 reflection 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 magneto-optic behavior, including a robust phase near $\text{Co}_{0.4}\text{Mn}_{0.4}\text{Ge}_{0.2}$ with high spin polarization, high T_c and high magneto-optic response. The observed magnetic responses show strong correlation with structural transformations, such that structural ordering and symmetry change can give rise to enhanced magnetic and magneto-optic 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 PM S2.3

COMBINATORIAL INVESTIGATION OF MAGNETIC METALLIC ALLOYS. Olugbenga O. Famodu, Manfred Wuttig, Ichiro Takeuchi, Dept of Materials Engineering, University of Maryland, College Park, MD; Maria Aronova, 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 magnetron guns 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 wafer 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 compositional mapping. A scanning SQUID microscope 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-Cu-Mn-Ga system. Various high-throughput measurement techniques for detecting martensitic 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 PM S2.4

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

Erik B. Svedberg, Rene J.M. van de Veerdonk, Kent J. Howard, Seagate Technology, Materials, Pittsburgh, PA; Lynnette D. Madsen, MS&E, Carnegie Mellon University, Pittsburgh, PA.

Film depositions by ultra high vacuum magnetron sputtering with controlled gradients across the wafer in terms of composition and thickness have allowed (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 models were extracted that incorporated both the dependencies and co-dependencies 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 effect of underlayers was studied. The samples consisted of a set of layers as follows: Ta, $\text{Ru}_x\text{Co}_{1-x}$, CoCr, CoCrPtB. 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, Pt and Ti to the CoCr 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 characterization automation, two CoCr/Pt multilayers consisting of ten bi-layers 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 was varied along with the total thickness.

2:45 PM S2.5

APPLICATION OF COMBINATORIAL METHODS TO STUDIES OF MAGNETISM IN THIN FILMS. Hauyee Chang, Abraham Anapolsky, 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 combinatorial 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 an x-ray circular dichroism microscope will be discussed. Other studies involving the phenomena of exchange bias and magneto-anisotropy will also be presented.

3:30 PM *S2.6

COMBINATORIAL SEARCH FOR TRANSPARENT OXIDE DILUTED MAGNETIC SEMICONDUCTORS. T. Fukumura, M. Kawasaki^a, Inst for Materials Research, Tohoku Univ, JAPAN; Zhengwu Jin, H. Kimura, Y. Yamada, M. Haemori, Dept of Innovative and Engineered Materials, Tokyo Inst of Tech, JAPAN; K. Ando, H. Saito, Natl Inst of Advanced Industrial Science and Technology, JAPAN; T. Nambu, J. Okabayashi, T. Mizokawa, A. Fujimori, Dept of Physics, Univ of Tokyo, JAPAN; K. Inaba, M. Murakami, R. Takahashi, Y. Matsumoto, T. Hasegawa^a, H. Koinuma^{a,b,c}, Materials and Structures Lab, Tokyo Inst of Tech, JAPAN. ^aCOMET. ^bFrontier Collaborative Research Center, Tokyo Inst of Tech. ^cCREST.

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 far above 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 , In_2O_3 , and 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 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-d, p-d, and d-d exchange interactions. Carrying out such high throughput characterizations as scanning SQUID microscope, magneto-optic spectroscopy, and photoelectron spectroscopy for huge numbers of specimens fabricated combinatorially, we discuss the physics of oxide-DMS which should explore applications in information technology.

[1] Y. Matsumoto et al., Science 291, 854 (2001).

[2] Z. Jin et al., Appl. Phys. Lett. 78, 3824 (2001); J. Cryst. Growth, 214/215, 55-58 (2000).

[3] K. Sato and H. Katayama-Yoshida, Jpn. J. Appl. Phys. 39, L555 (2000).

4:00 PM S2.7

HIGH THROUGHPUT CHARACTERIZATION OF MAGNETIC

SEMICONDUCTOR THIN FILMS WITH A SCANNING SQUID MICROSCOPE. X.J. Fan^{a,b}, C.M. Chen^a, M. Murakami^a, R. Takahashi^a, Y. Matsumoto^{a,b}, T. Hasegawa^{a,b}, T. Fukumura^c, M. Kawasaki^c, P. Ahmet^b, T. Chikyow^b, and H. Koinuma^{a,b}, ^aMaterials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, JAPAN; ^bAdvanced Materials Laboratory, National Institute for Materials Science, Tsukuba, JAPAN; ^cInstitute for Materials Research, Tohoku University, Sendai, JAPAN.

Magnetic properties of transition-metal-doped TiO₂, both anatase and rutile in combinatorial thin film form, have been surveyed by means of the Scanning Superconducting-quantum-interference-device Microscope (SSM). As a consequence, we found magnetic domains in Co-doped anatase 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 level from $x = 0$ to about $x = 13\%$. We have also characterized magnetic behavior of combinatorial (Ga,Mn)As films prepared by the ion implantation technique.

4:15 PM S2.8

MAPPING OF PHYSICAL PROPERTIES-COMPOSITION PHASE DIAGRAMS OF COMPLEX MATERIAL SYSTEMS USING CONTINUOUS COMPOSITION MATERIAL CHIPS. Young K. Yoo, Quixen Xue, Hyungchul Lee, Haitao Yang, Gang Wang, Sheng Liu, Xiaodong Xiang, Intematix Co, Moraga, CA; Fred Duewer, XRADIA Inc, Concord, CA; Tsuyoshi Ohnishi, Advanced Materials Lab, Stanford University, Stanford, CA; Yi Dong, Stanford Research Inst, Menlo Park, CA; Yong S. Chu and Derrick C. Mancini, Advanced Photon Source Argonne National Lab, Argonne, 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, ionic radius, etc. We discuss evidence that suggests various electronic phase transitions, such as orbital orderings 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 Ni_{1-x}Fe_x 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. Ohkubo, Y. Matsumoto, M. Ohtani, T. Hasegawa, Ceramics Materials and Structures Laboratory, Tokyo Institute of Technology, Midori-ku, Yokohama, JAPAN; K. Ueno, Central Technology Laboratory, Asahi Kasei Corp, Shizuoka, JAPAN; K. Itaka, AHAMT Parhat, T. Chikyow, COMET-NIMS, Tsukuba, Ibaraki, JAPAN; M. Kawasaki^a, Institute for Materials Research, Tohoku University, Sendai, JAPAN and Department of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama, JAPAN; H. Koinuma^a, Frontier Collaborative Research Center and Ceramics Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, JAPAN and CREST-Japan Science and Technology Corporation. ^aCOMET, Tsukuba, JAPAN.

Ba₂Co₂Fe₁₂O₂₂ (Co₂Y), a family of Y type magnetoplumbite, is a candidate material for thin film inductors operated at GHz as a magnetic core material. Since it has such a complex composition and huge c-axis lattice constant of 43.5Å, there are many growth parameters to be optimized in order to obtain a single phase of Co₂Y thin film. Here, we report on the successful fabrication of Co₂Y thin films by combinatorial pulsed laser deposition technique (C-PLD). The key point was found to be the use of CoO buffer layer to eliminate the second phase of BaFe₂O₄. 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 based on the interface analysis between epitaxial Co₂Y thin film and MgAl₂O₄(111) substrate with the micro-sampling transmission electron microscope (TEM), four circle X-ray diffraction measurements.

4:45 PM S2.10

CHARACTERIZATION OF MAGNETIC AND DIELECTRIC PROPERTIES ON Y-TYPE MAGNETOPLUMBITE EPITAXIAL THIN FILMS FOR HIGH FREQUENCY APPLICATION. K. Ueno, Central Technology Laboratory, ASAHI KASEI CORPORATION,

Fuji, Shizuoka, JAPAN; I. Ohkubo, Y. Matsumoto, N. Okazaki, T. Hasegawa, Ceramics Materials and Structures Laboratory, Tokyo Inst of Technology, Midori-ku, Yokohama, JAPAN; K. Itaka, COMET-NIMS, Tsukuba, Ibaraki, JAPAN; M. Kawasaki^a, Inst for Materials Research, Tohoku Univ, Sendai, JAPAN and Dept of Innovative and Engineered Materials, Tokyo Inst of Tech, Midori-ku, Yokohama, JAPAN; H. Koinuma^a, 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, ^aCOMET, Tsukuba, JAPAN.

Magnetic films for miniaturization of planar inductors operating at GHz frequencies require high resistivity and high resonance frequency. Y type magnetoplumbite Ba₂Co₂Fe₁₂O₂₂ (Co₂Y) is a candidate material to meet such requirements because it has about 10 m 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 DC resistivity of the film was 7.5Ωm. 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 ~1600 Gauss respectively, being close to those of bulk sample. Furthermore, the magnetic micro domain structures 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. Ohkubo et al., to be presented in MRS 2001 Fall meeting.

SESSION S3: COMPOSITION SPREAD TECHNIQUES AND RAPID CHARACTERIZATION

Chairs: Ichiro Takeuchi and Toyohiro Chikyow

Tuesday Morning, November 27, 2001

Room 204 (Hynes)

8:30 AM *S3.1

DEVELOPMENT OF FUNCTIONAL MATERIALS BY A COMPOSITION SPREAD APPROACH. Rainer Cremer, Dieter Neuschuetz, RWTH Aachen, Aachen, GERMANY.

The increasing complexity of modern functional materials leads to the demand of a cost efficient tool for the development of new products. One possible approach to this question is the adaptation of combinatorial methods to the specific requirements of materials industry. These methods, originally developed for the pharmaceutical industry, have recently been applied to the screening of superconductive, magnetoresistant and photoluminescent materials. The principle of these 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 laterally graded 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 apertures. To illustrate the advantages of combinatorial approaches for the development of advanced materials, Ge-Sb-Te based films for rewritable optical data storage as well as multicomponent metastable hardcoatings like (Ti,Al)N, (Ti,Al,Hf)N and Ti-Al-Si-N are discussed: Ge-Sb-Te films were deposited with compositions around the ternary phase Ge₂Sb₂Te₅. The resulting composition-spreads were analyzed by EPMA-mappings, XPS, AES, RHEED and GI-XRD with respect to composition, binding states and structure. The velocity of the phase change was determined using a static tester. (Ti,Al)N, (Ti,Al,Hf)N and Ti-Al-Si-N composition spreads will be discussed with special emphasis on the relations between structure and composition on one hand and oxidation resistance of the ternary and quaternary films on the other hand. The composition of the as-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 homogeneous samples.

9:00 AM S3.2

THIN-FILM METAL ALLOYS FOR MEMS BY COMPOSITIONAL SPREAD DEPOSITION. Ainissa G. Ramirez, Agere Systems-Lucent 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, Pb) from 0 to 5 wt% were generated. In this approach, compositional spreads give rise to an array of alloys with various solute concentrations that were simultaneously synthesized by sputtering, heat-treated by furnace annealing, and characterized with 4-point probe measurements,

nanindentation, 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 applications. This work presents the experiments and measurements.

9:15 AM *S3.3

COMBINATORIAL SYNTHESIS APPROACH FOR OPTIMIZING OXIDE/Si INTERFACE FOR THE FUTURE ULSI.

Toyohiro Chikyow, Parhat Ahmet, Kiyomi Nakajima, Tamami Naruke, COMET National Institute for Material Science, Tsukuba Ibaraki JAPAN, JeongHwan Song, Takashi Koida, Hideomi Koinuma, Tokyo Institute of Technology, Yokohama Kanagawa JAPAN.

A combinatorial synthesis approach was carried out to optimizing 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 limitation. Especially SiO₂ gate oxide becomes a most serious 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 three major factors. Namely they are structure (crystal 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 composition spread 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 microscope is also used to evaluate the dielectric properties. Also in this paper, a few kinds 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. Parhat Ahmet, Toyohiro Chikyow, Comet-NIMS, National Institute for Materials Science, Tsukuba, JAPAN; Takashi Koida, Mamoru Yoshimoto, Hideomi Koinuma, Tokyo Institute of Technology, Yokohama, JAPAN.

SrTiO₃ is one of the most promising candidate of high dielectric materials for further LSI technology because of its extremely high dielectric constant at room temperature and also fairly small 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 exists a low dielectric amorphous layer at the interface besides a few exceptions. For understanding the interface formation and its stability of SrTiO₃ thin films on Si(100) substrate, we have done a systematical study on the interface structures using combinatorial method. A combinatorial PLD with growth temperature gradient system was employed to grow thin films and a high throughput thin foil fabrication system was employed to fabricate thin foils for cross sectional high resolution transmission electron microscope observation. We have observed a SiO₂ interfacial layer and a amorphized 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 amorphized SrTiO₃ layers not only growth temperature dependent but also oxygen partial pressure dependent above the growth temperatures of 600°C. From the growth condition dependences study of the formation of amorphized SrTiO₃ layers and elemental analyze 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. Yasuo 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 characteristic of the dielectric constant of a 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 macroscopic measurement. In particular, for 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 for the precise 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 microscopy¹ and with the ability of in situ observation of SEM images and of material compositions 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 Bi₂Ti₄O₁₁ that have a positive and a negative dielectric temperature coefficient, respectively. 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 quantitative measurement method of temperature coefficient is also reported.

1) Y. Cho, T. Kasahara and K. Fukuda, "Determination of the Temperature Coefficient Distribution of Dielectric Ceramics Using Scanning Photothermal Dielectric Microscopy", J. Am. Ceram. Soc., **82**, (1999)1720.

11:00 AM S3.6

FABRICATION AND RAPID CHARACTERIZATION OF FERROELECTRIC THIN FILM COMPOSITION SPREADS.

Kao-Shuo Chang, Maria Aronova, Olugbenga Famodu, Ichiro Takeuchi, Dept of Materials and Nuclear Engineering, University of Maryland, College Park, MD; Samuel E. Lofland, J. Hattrick-Simpers, Dept of Physics, Rowan University, Glassboro, NJ; L.A. Bendersky, NIST, Gaithersburg, MD; H. Chang, LBNL, Berkeley, CA.

We have developed a compact combinatorial pulsed laser deposition system entirely contained in an eight inch vacuum flange. 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_xSr_{1-x}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 chip. 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_xSr_{1-x}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 Okazaki, Parhat Ahmet, Toyohiro Chikyow, National Inst for Materials Science, Tsukuba, JAPAN; Hiroyuki Odagawa, Tomoteru Fukumura, Yasuo Cho, Masashi Kawasaki, Tohoku Univ, Sendai, JAPAN; Makoto Ohtani, Hideomi Koinuma, Tetsuya Hasegawa, Tokyo Inst of Technology, Yokohama, JAPAN.

High throughput characterization of electric 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 rf / microwave frequency regions has been increasing its importance in the field of communication and information technologies. For this purpose, we have developed a scanning microwave microscope (S μ M) using a lumped constant resonator probe. The probe consists of a commercially available microwave oscillator module (frequency ~ 1.2 GHz) equipped with an electrochemically 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_xSr_{1-x}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 Materials, Tokyo Inst. of Tech., Yokohama,

JAPAN; T. Fukumura, M. Kawasaki^a, Inst. for Materials Research, Tohoku Univ., Sendai, JAPAN; T. Kikuchi, K. Omote, X-ray Research Laboratory, Rigaku Corporation, Tokyo, JAPAN; A. Ohtomo, H. Koinuma^{a,b}, Frontier Collaborative Research Center, Tokyo Inst. of Tech., Yokohama, JAPAN. ^aCombinatorial Material Exploration and Technology, Tsukuba, JAPAN. ^bCREST-Japan Science and Technology, Tokyo, JAPAN.

Combinatorial laser MBE developed by us enables to the integration of epitaxial oxide thin films having various compositions and/or structures on a substrate 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 combinatorial libraries named as concurrent XRD (CXRD) system. This system is a minor modification of a conventional XRD system by employing measures convergent line-focused x-ray source and two-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 parallelly integrated superlattices $[(\text{BaTiO}_3)_m/(\text{SrTiO}_3)_n]$ and the rapid evaluation of both out-of-plane and in-plane lattice constants as a function of composition for a composition-spread $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ film. In addition, this system can be used as a XRD microscopy with a resolution of 0.1 μm as demonstrated by spatial mapping of XRD peak intensity, peak position, and peak full width at half maximum of thin films and patterned devices.

[1] T. Fukumura et al., Appl. Phys. Lett. 77, 3426 (2000).

11:45 AM S3.9

INFRARED CHEMICAL IMAGING: MATERIAL ANALYSIS OF HOT-WIRE CHEMICAL VAPOR DEPOSITED SILICON FOR SOLAR CELL APPLICATIONS. Todd A. Heimer, Edwin J. Heilweil, Optical Technology Division, Physics Laboratory, National Institute of Standards and Technology, Gaithersburg, MD; Qi Wang, National Renewable Energy Laboratory, Golden, CO.

Step-scan FTIR imaging using a 256x256 element InSb infrared camera was applied to the study of silicon thin films deposited on a crystal silicon substrate by the hot-wire CVD technique in a 4x4 element combinatorial sample array. We first describe in detail the approach used to transport the external FTIR beam to image the 21 mm x 21 mm sample in transmission mode and collect spectral images with our camera. Image interferogram acquisition (total acquisition time taking about one hour) and parallel FFT data analysis of eight each sample and reference hypercubes at 16 wavenumber resolution results in several percent absorptions ($\text{OD} \approx 0.02$, clearly discernable above the spectral baseline noise of ca. $\text{OD} \approx 0.005$ rms). The resulting averaged spectra of the 16 different sample elements show clear differences in the amount of Si-H (2000 cm^{-1} absorption) and clustered Si-H (2100 cm^{-1} absorption) content in the deposited films. These observations correlate well with film phase from amorphous- to nano-Si with varying deposition parameters of H_2/SiH_4 ratio and substrate temperatures.

SESSION S4/DD5: JOINT SESSION
COMBINATORIAL APPROACH TO POLYMERS
Chairs: Eric J. Amis and Alamgir Karim
Tuesday Afternoon, November 27, 2001
Constitution B (Sheraton)

1:30 PM *S4.1/DD5.1

AN ELECTRONIC NOSE FROM ARRAYS OF POLYMER COMPOSITE VAPOR SENSORS. Nathan S. Lewis, 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 a chemically reversible, diagnostic pattern of electrical resistance changes upon exposure to different odorants. Such conducting polymer elements are simply prepared and are 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 or hardware-based neural networks for purposes of analyte identification. Principle component analysis has demonstrated that such 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 COPOLYMER THIN FILMS. Alamgir Karim, Archie P. Smith, Jack F. Douglas, Amit Sehgal, Eric J. Amis, Polymers Division, NIST, Gaithersburg, MD.

Surface pattern formation in PS-PMMA 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 L_0 and we attribute this effect to an increase in the surface chain density with h in the outer 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 L_0 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 M . A smooth surface band is observed about a certain E value regardless of h due to non-preferential interaction of both blocks with the substrate surface.

References:

- [1] Physical Review Letters, In press.
- [2] Journal of Polymer Science Part B: Polymer Physics, In press.

2:30 PM *S4.3/DD5.3

INVESTIGATING CRYSTALLIZATION IN THIN POLYMER FILMS USING HIGH THROUGHPUT METHODS. Kathryn L. Beers, Jack F. Douglas, Eric J. Amis and Alamgir Karim, National Institute of Standards and Technology, Polymers Division, Gaithersburg, MD.

The ability to control orientation and morphology in semi-crystalline polymeric 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 polystyrene was studied as a model system due to the comparatively slow rates and high temperatures at which it crystallizes. Preliminary studies on isotactic polystyrene (iPS) confirm the applicability of the method to investigating the kinetics of crystallization as a function of undercooling temperature, T , and film thickness, h . Growth rates, $G(T, h)$ spanning 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 $((T_m - T)/T_m)$ increases along a cross section of the film with uniform h , G passes through a maximum between the glass transition temperature (T_g) and the melt temperature (T_m) as 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 plates, 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.

3:30 PM *S4.4/DD5.4

COMBINATORIAL INVESTIGATION OF THE MECHANICAL PROPERTIES OF NANOSCOPIC POLYMER STRUCTURES. Paul F. Nealey, Heidi Cao, Mark Stoykovich, Kenji Yoshimoto, Department of Chemical Engineering and Center for NanoTechnology, University of Wisconsin, Madison, WI; Leonidas E. Ocola, Agere Systems, Murray Hill, NJ.

As the dimensions of industrial relevant polymeric systems shrink to the length scale of individual molecules, significant new challenges are encountered as the material 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 thermophysical properties are routinely 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 in-plane mechanical properties of patterned polymeric resist is essential to understand, model, and hopefully circumvent this phenomenon. Currently the techniques for applying in-plane forces 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 rinse liquids. Deformation of combinatorial arrays of test structures fabricated from poly(methylmethacrylate) 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 combinatorial arrays. The principal concepts of the test structures, measuring deformation of materials in response to well-defined capillary forces, should be broadly applicable for the determination of in-plane material properties at the nanoscale.

4:00 PM *S4.5/DD5.5

COMBINATORIAL INVESTIGATION OF ADHESION OF POLYMER THIN FILMS. Alfred J. Crosby, Alamgir 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 adhesion at a glassy polymer interface. To facilitate this investigation, we have developed a novel combinatorial technique to characterize polymer adhesion. The technique involves contact and separation of a matrix of spherical caps on a complementary substrate. During the process of contact and separation, we monitor the contact area for each spherical cap and the relative displacement between the spherical caps and the complementary substrate. With these measured quantities, we build upon the theory of Johnson, Kendall, and Roberts (JKR) to quantify the adhesion across the matrix. By varying such parameters as thickness, temperature, and surface energy along the orthogonal axes of the matrix, we use this new technique to efficiently produce quantitative polymer adhesion vs. variable maps. We present results on effects of thickness, temperature, and surface energy on the self-adhesion of polystyrene thin films.

4:30 PM S4.6/DD5.6

COMBINATORIAL LIBRARIES OF BLEND PHASE MORPHOLOGY ON GRADIENT ENERGY SURFACES. Amit Sehgal, Jack F. Douglas, Eric J. Amis, and Alamgir Karim, Polymers Division, NIST, Gaithersburg, MD; Vincent Ferreiro, C.N.R.S., Lab. de Structure et Proprietes de l'Etat Solide (L.S.P.E.S.), Universite des Sciences et Technologies de Lille, Villeneuve d'Ascq, FRANCE.

The presence of an interface in an ultra-thin polymer blend film guides or even significantly alters the phase separation process. Confinement between the air and substrate interfaces and the preferential wetting of specific components at the walls determines the in-plane and the surface directed compositional distribution and the spatial scales. We use a simple method for 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 (H_2O ; $5^\circ - 95^\circ$) and surface energies on a single substrate. Thickness gradients (40 nm to 140 nm) orthogonal to the surface energy axis generate simple, yet powerful, two-dimensional maps to probe how the polymer-substrate interaction acts in concert with the film thickness to influence the scales of phase separation. The morphological evolution of a model LCST (PS-PVME) 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 WETTABILITY ON GRADIENT ENERGY SURFACES. Karen M. Ashley, D. Raghavan, 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 hydrophobic polystyrene (PS) and hydrophilic poly D-lactacid (PDLA) films on chemically modified gradient energy surfaces. Substrate libraries were prepared by immersing Si-H (passivated Si) in Piranha solution (sulfuric acid / hydrogen peroxide / water) at a controlled rate giving a systematic variation of solvent (water and diiodo methane) 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 PDLA coatings on gradient energy surfaces orthogonal to gradients in film thickness were screened for dewetting behavior using automated optical microscopy. Contrasting trends in the wettability of PS and PDLA were visibly apparent as a function of surface energy of the substrate. The number density of polygons of the dewet films was found to obey a power law relationship with both film thickness and substrate surface hydrophilicity as characterized by contact angle studies. The effect on dewetting morphology with molecular weight (above and below entanglement) will be discussed.

SESSION S5: POSTER SESSION

Chair: Haiyee Chang
Tuesday Evening, 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. Ikuo Yanase, Saitama Univ, Dept of Engineering, Saitama, JAPAN; Takugo Ohtaki, Nissei Sangyuu Corp, Tokyo, JAPAN; Mamoru Watanabe, NIMS, Tsukuba, JAPAN.

Application of ceramics powder synthesis through solid and liquid processes to combinatorial chemistry is thought to be much of importance 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 micropipette attached to the arm, measure and mix raw materials. Mixed samples were sucked 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 PSPC 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 robot 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 $La_{1-x}Sr_xCoO_3$ SERIES SYNTHESIZED WITH A COMBINATORIAL PROCESSING. Yoshiaki Takata, Hajime Haneda, Yoshiki Wada, Takefumi Mitsuhashi, Advanced Materials Laboratory, NIMS, Tsukuba, JAPAN; Makoto Ohtani, Tomoteru Fukumura, Masashi Kawasaki, Hideomi Koinuma, Tokyo Institute of Technology, Yokohama, JAPAN.

We evaluated the thermal diffusivity and surface wave frequency for composition-spread thin film $La_{1-x}Sr_xCoO_3$, mono layer $LaCoO_3$ and $SrCoO_3$, and substrate $SrTiO_3(100)$ using transient reflecting grating (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 shows that the change in thermal diffusivity and surface wave frequency has a little anomalous dependence on varied composition ratio (La : Sr) and phase.

S5.3

INVESTIGATION OF GATE INSULATORS TOWARD HIGH PERFORMANCE INVISIBLE ZnO TFT. J. Nishii, S. Takagi, T. Aita, Dept. of Innovative and Engineered Materials, Tokyo Institute of Technology, Yokohama, JAPAN; Y. Ohmaki, S. Kishimoto, Y. Ohno, F. Matsukura, H. Ohno, Research Institute of Electrical Communication, Tohoku University, 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 is the attractive wide band gap semiconductor owing to ultraviolet laser action at 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 would be capable of substituting the other TFT made of a-Si or poly-Si and improving the resolution of the flat

panel display. We have reported on the demonstration of ZnO TFT action grown on glass or plastic substrate [1]. However, the performance is not as high as the commercial one due to 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/Ta/glass substrates with pulsed laser deposition to form bottom gate type TFT's. The size of TFT was the same as a commercial LCD, where the channel length and width were 5 micron and 15 micron, respectively. The TFT mobility was $\sim 1 \text{ cm}^2/\text{V}\cdot\text{s}$ and the on/off ratio was over 10^5 . 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.

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S5.4

COMPUTER-CONTROLLED FABRICATION OF CONCENTRIC MULTILAYERS FOR SYNCHROTRON RADIATIONHARD X-RAY FRESNEL ZONE PLATE. Masato Yasumoto^{1,2}, Shigeharu Tamura^{1,2}, Nagao Kamiyo^{2,3}, Yoshio Suzuki², Mitsuhiro Awaji², Akihisa Takeuchi², Hidekazu Takano², Yoshiki Kohmura⁴, Katsumi Handa⁵. ¹Photonics Research Institute, AIST, Tsukuba, JAPAN. ²Japan Synchrotron Radiation Research Institute(Spring-8), JAPAN. ³Kansai Medical University, JAPAN. ⁴RIKEN Harima Institute, JAPAN. ⁵Ritsumeikan University, JAPAN.

The multilayer 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 multilayer 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 multilayer 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.

S5.5

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

Titanium dioxides(TiO₂: rutile, anatase) provide very useful technological applications such as antifogging/self-cleaning devices with amphiphilic (hydrophilic and oleophilic) surfaces[1] in the chemical photo catalytic activities and the Gratzel solar cell as molecular dye-sensitized electro-chemical devices[2]. But the fundamental mechanism in electron/hole (reduction/oxidation) 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 crystal structures and the adsorbed molecules under UV irradiation using specially designed x-ray system. This system can provide in-plane diffractions from the most surfaces due to a total reflection phenomenon. Also, by simultaneous observations of both the diffraction peaks and widths(FWHMs) using white incident x-rays, we can get very important informations 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 atmospheres of H₂O, CH₃COCH₃, CH₃CH₂OH and CH₃OH, it has been revealed that the only (110) has chemical photocatalytic activities, and that the FWHMs presenting the crystal relaxations show the characteristic responses 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.

[1] R. Wang, K. Hashimoto and A. Fujishima, *Nature(London)* 388,431(1997).

[2] B. O'Regon, M. Gratzel, *Nature(London)* 353,737(1991).

S5.6

INVESTIGATION OF DEEP LEVELS IN n-TYPE Ni-DOPED Si BY A TEMPERATURE DEPENDENCE OF PIEZOELECTRIC PHOTOTHERMAL SIGNALS. S. Sato, A. Ito, T. Ikari, Dept. of Electrical and Electronic Engineering, Miyazaki University, Miyazaki, JAPAN; A. Fukuyama, S. Tada, Dept. of Applied Physics, Miyazaki University, Miyazaki, JAPAN; S. Tanaka, Dept. of Electronics, Fukuoka Institute of Technology, Fukuoka, JAPAN.

Since the performance of silicon(Si) semiconductor devices is greatly influenced by the quality of the substrate, it is very important to know the role of deep lying defect levels in order to produce high quality substrates. We have recently reported that the activation energies, the concentrations and the electron capture cross sections deep defect levels in semi-insulating GaAs such as EL6, EL7 and EL15 were well investigated by the temperature variation of the piezoelectric photothermal(PPT) signals [1]. The great advantage of this technique is that it is a direct monitor of the nonradiative recombination processes that is a major process for the deep 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 has a deep levels induced by nickel (Ni) atoms. Since the Ni level is already well characterized by a usual 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 Si samples from 77 to 298 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 conduction 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 those observed parameters agree well with that reported, we found our proposed experimental methodology is a useful optical characterization technique for deep levels in semiconductors.

1. A. Fukuyama, et al, *J. Appl. Phys*, 89 (2001) 1751.

2. S. Tanaka, et al., *Jpn. J. Appl. Phys*, 35 (1996) 4624.

S5.7

FLASH PHOTOLYSIS OF POLYSTYRENE WITH LASER.

Ma Hongwei, Tang Yongjian, and Cui Baoshun, Gao Wende, Liu Weiming, Wang Shouwen, Chinese Academy of Engineering Physics, Mianyang, Sichuan, PEOPLES REPUBLIC OF CHINA.

This paper describes the flash photolysis of polystyrene with a pulsed Nd-Glass laser (wavelength 1060nm, 10^{-4} s duration, pulse energy 2.5J/shot), that run after Q-switched manner giving 2.5J per pulse at 1060nm and about 10^{-8} s duration. In this experiment a model Finnigan MAT 4510 chromatograph/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 the window on the ion source of the instrument irradiates a sample of polystyrene on the center of the ion volume, so that the polystyrene dissociate, vapor, then the sample injection is achieved. By the fast analyzer of the quart-pole mass spectrometry the sample was scan speedily, 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 Q-switched. Because the pulse duration and the energy effected 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 a laser photolysis. Not only incident energy must be controlled, but also need to prevent the bias induced by randomness with a batch of mass spectrum. The randomness of a laser photolysis mass spectrum of the macromolecular compounds shows the intramolecular energy transfer performance between high vibrational states of a ground electron state. Keywords: polystyrene, laser, flash photolysis, chromatograph/mass spectrometer.

S5.8

PHOTOCHEMICAL NUCLEATION OF COPPER ON POLYIMIDE SURFACE WITH 10NS LASER IRRADIATION. Yasuhiro Ogawa,

Hiroto Tokunaga, Masataka Murahara, The Faculty of Engineering of Tokai University, Kanagawa, JAPAN.

Copper atoms was substituted on the polyimide surface in the presence of copper ion with only 10ns 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 composing plastics and the metal can be combined by chemical methods instead of conventional physical methods, a hybrid material made from both plastics and metal can be produced. Then we have succeeded in substituting copper atoms with dangling bonds of carbon 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 sulfate 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 $32\text{mJ}/\text{cm}^2$ was irradiated

vertically onto the sample. The amount of photo number is 2.5×10^{12} by roughly calculation for dissociating and exciting the copper sulfate solution and the polyimide surface. The dissociated copper atoms form the C-O-Cu bond with active oxygen on the polyimide surface. In this treatment there was no change on the polyimide surface with the naked eye. However, we were able to grow a copper thin film of about $24\mu\text{m}$ after immersing the sample into the electroless plating solution for 15 minutes at 60° . 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 foils peeled off.

SESSION S6: COMBINATORIAL APPROACH TO CATALYSTS AND OTHER MATERIALS

Chair: John M. Newsam
Wednesday Morning, November 28, 2001
Room 204 (Hynes)

8:30 AM *S6.1

COMBINATORIAL CATALYSIS DISCOVERY: SPECIALITY 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 polymeric materials have lagged 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 deconvolution. We report here a process for searching new catalysts for industrially valuable but difficult aryl chlorides coupling transformations. Palladium chlorides possessing phosphinous 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 thiols. ^1H and ^{31}P NMR studies argue that these phosphinous acid ligands in the complexes can be deprotonated to yield electron-rich anionic species, which is anticipated to accelerate the rate-determining oxidative addition of aryl chlorides in the catalytic cycle. Herein, we report the first examples of these isolated air-stable palladium complexes served as efficient catalyst precursors for C-C, C-N, and C-S bond-forming reactions of aryl chlorides.

9:00 AM S6.2

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 new miniaturized, custom-made Teflon-liners that permit accelerated automated workup. A maximum of 150 microlitre 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 microlitre-range, possible evaporation and the reproducibility of dispensed volumes, as well as the homogenization of the reactants will be discussed. 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-direction effects, where we will show that the use of toxic and costly templates can be minimized by using a co-template. [1] K. Choi, D. Gardner, N. Hilbrandt, T. Bein, *Angew. Chem. Int. Ed.*, 38 (1999) 2891.

9:15 AM S6.3

ELECTROSTATIC MANIPULATION OF MICRON SCALE DRY DIELECTRIC MATERIALS. Malinda Tupper, 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 fluorescein powder have been dispensed with this apparatus. Shaped alumina parts, approximately one millimeter square and 50 microns thick have also been manipulated with this apparatus. The technique offers a high-speed method for reproducibly transporting microgram quantities of dry granular material without dissolving the material in a liquid. Such a technique is vital for high throughput screening of compounds such as pharmaceuticals, whose efficacy may be changed by dissolution in a liquid. The method has been used to collect as small as 0.13 micrograms up to 30.5 micrograms of sodium fluorescein, and approximately 7.7 to 145 micrograms of silica spheres were collected. The deviation across ten trials ranged from nine percent for the larger quantities to as high as thirty to forty percent for the smaller quantities. The mechanism for collection and deposition, methods for controlling the amount of material dispensed, and sources of variability will be discussed.

9:30 AM S6.4

COMBINATORIAL EXPLORATION OF ELECTRODE MATERIALS. Kazunori Takada, Kenjiro Fujimoto, Takayoshi Sasaki, Mamoru Watanabe, Advanced Materials Laboratory, National Institute for Materials Science, JAPAN; Satoru Higo, Toho Technical Research, JAPAN; Ikuo Yanase, Faculty of Engineering, Saitama Univ., JAPAN.

Lithium batteries are now widely used in portable electronic equipments. LiCoO_2 is used as a positive electrode material in the battery. Alternatives to LiCoO_2 were under research to reduce the cost and enlarge 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 LiNiO_2 by some additives, or substitutions in LiMn_2O_4 to suppress Jahn-Teller distortion and improve its cyclability. Exploration of such additives or substituents needs a lot of time. We have developed a combinatorial robot system for high throughput synthesis of materials. Here we present a next target, which is a high throughput evaluation system of electrode property. Combinatorial library was prepared automatically by the robot system. 16 samples were synthesized at one time on a platinum plate. Electrochemical evaluation was based on cycle test at a constant current. The current accuracy 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. Multi-channel potentiogalvanostat (PS-08, Toho Technical Research), with a current accuracy of 0.2 nA 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 faced to the sample in electrolyte. The charge-discharge operation was controlled a computer program built on LabVIEW. Constant current was passed between the platinum plate and the counter electrodes, and the voltages between them were acquired by the PC. The combinatorial evaluation will be presented in detail at the meeting.

9:45 AM S6.5

PREPARATION AND CHARACTERIZATION OF ELECTRODE MATERIALS BY COMBINATORIAL PROCESSING. Kenjiro Fujimoto, Kazunori Takada, Akihisa Kajiyama, Takayoshi Sasaki, Mamoru Watanabe, Advanced Materials Laboratory, National Institute for Materials Science, Tsukuba, JAPAN; Ikuo Yanase, Department of Applied Chemistry, Faculty of Engineering, Saitama University, Saitama, JAPAN; Takugo Ohtaki, Nissei 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 weighted and mixed at high speed in a series of various combinations by the system. In this process, sixteen samples were prepared at a time on a Pt pallet $35 \times 35 \times 3\text{mm}$ in size which has 16 - 64 wells. Those samples automatically were recorded in a serial manner on the combinatorial powder X-ray diffractometer ($\text{CrK}\alpha$) 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 $\text{LiCo}_{1-x}\text{Mn}_x\text{O}_2$ ($x=0, 0.1, 0.2$) was synthesized at 1073K for 5 hours in air using LiOH , $\text{Co}(\text{CH}_3\text{COO})_2$ and $\text{Mn}(\text{CH}_3\text{COO})_2$ aqueous solution as raw materials, where the molar ratio $\text{Li}/(\text{Co Mn}) \geq 1.3$ in the mixed solution. The present combinatorial technique could give a reaction map on $\text{Li}_2\text{O}-(\text{Co,Mn})\text{O}_2$ 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.

10:30 AM *S6.6

DEVELOPMENT OF THE COMBINATORIAL GLASS FORMATION TESTER. Satoru Inoue, Shin-ichi Todoroki, Takehisa Matsumoto, National Institute for Materials Science, Advanced Materials Laboratory, Tsukuba, Ibaraki, JAPAN; Takaharu Honda, Tetsuo Araki, Toshio Tsuchiya, Science University of Tokyo, Dept. of Materials Science and Technology, Noda, Chiba, JAPAN.

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 a half an hour heating, the crucibles were taken out from the furnace and moved into the cooling chamber purged 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 crucibles till the placement on the cooling stage was shortened as much as possible, resulting to be 15sec. 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 192 glass samples ($24 \times 8=192$) within a day working time. The speed was roughly 100 times larger than the case of manual operation.

11:00 AM S6.7

RAPID AND QUANTITATIVE DETERMINATION OF CRYSTALLIZATION TENDENCY OF ZINC TELLURITE GLASS MELT BY USING TEMPERATURE-GRADIENT FURNACE. Shin-ichi Todoroki, Matsumoto Takehisa and Satoru Inoue, National Institute for Material 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 ($200\sim 1050^{\circ}\text{C}/40\text{cm}$). A glass capillary tube (ID $1.5\text{ mm}\phi \times$ OD $8\text{ mm}\phi$) is used as a cell of the library. Zinc tellurite melt at 800°C is sucked into the cell by applying a vacuum pressure to the other side of the capillary. Crystallization is observed as a white segment in the library under an appropriate annealing condition. A set of 2D sample array is obtained by preparing several sample libraries with different annealing time. Since this array itself corresponds to 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- TeO_2 system, which has been believed to be 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 thermal hysteresis. For the melt once quenched below the glass transition temperature (T_g) and annealed at above T_g , the Q value becomes larger than that without the quenching. This is because the former glass melt went through the nucleating temperature region located just above T_g . 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.

11:15 AM S6.8

SOLID PHASE SYNTHESIS AND COMBINATORIAL CHEMISTRY OF ORGANIC ELECTRONIC MATERIALS. Christoph Briehn, Oliver Deeg, Marc-Steffen Schiedel, Peter Baeuerle, University of Ulm, Dept of Organic Chemistry II, Ulm, GERMANY.

Material development typically is very tedious and normally done by sequential synthesis and characterization. Very recently, it has been shown that combinatorial approaches in conjunction with high throughput screening represent an effective way to create inorganic material libraries comprising new luminescent phosphors, high temperature superconductors, thin film dielectric materials, and catalysts. We will discuss parallel and combinatorial synthesis of novel organic materials. Firstly, solid phase synthesis of conjugated oligomers, i.e. regularly substituted oligothiophenes, is discussed and the combinatorial synthesis of oligothiophene libraries reported. Secondly, novel reactions have been elaborated to substitute the core of fluorescence and laser dyes which then has been applied to create coumarin libraries in parallel solution phase synthesis. Accelerated parallel testing of the optical and electrochemical properties in both types of libraries give rise to lead structures which are potential

candidates in electronic applications (oligothiophenes) or biolabelling (coumarins), respectively.

SESSION S7: COMBI/AI SESSION:
COMPUTATIONAL STUDIES
Chairs: Luc T. Wille and Momiji Kubo
Wednesday Afternoon, November 28, 2001
Room 204 (Hynes)

1:30 PM *S7.1

PROPOSAL OF NEW CONCEPT "COMBINATORIAL COMPUTATIONAL CHEMISTRY" AND ITS APPLICATION TO CATALYST DESIGN. Akira Miyamoto, Tsuguo Kubota, Kentaro Yoshizawa, Satoshi Sakahara, Kenji Yajima, Rodion Belosludov, Seiichi Takami, Momiji Kubo, Tohoku Univ., Dept. of Materials Chemistry, Sendai, JAPAN.

Recently, computational chemistry gives a great impact on the catalyst and material design. However, computational chemistry is mainly used to elucidate the catalytic mechanism, catalytic activity, and deactivation mechanism in the catalysis field. In addition to the investigation of the mechanism of the well known catalytic reactions at atomic and electronic levels, computational chemistry is expected to have an important role in predicting new catalysts with high activity, high selectivity, and high resistance to poisons. On the other hand, combinatorial chemistry has been developed as an experimental method where it is possible to synthesize hundreds of samples all at once and examine their properties. It is expected to work as a high-throughput screening method even in the catalysis field. In order to realize the prediction of the new catalysts by the computational chemistry, recently we introduced the concept of the combinatorial chemistry to the computational chemistry for catalyst design and proposed a new concept called "Combinatorial Computational Chemistry" [1-3]. In this approach, the effects of large number of metals, supports, and additives on the catalytic activity, selectivity, and resistance to poisons are calculated systematically using computer simulation techniques, in order to predict the best elements for each catalytic reaction. In the present talk, we introduce our successful application of our combinatorial computational chemistry approach to the design of various catalysts including the deNOx catalyst, methanol synthesis catalyst, Fischer-Tropsch catalyst, anode catalyst for fuel cell etc.

[1] K. Yajima, Y. Ueda, H. Tsuruya, T. Kanougi, Y. Oumi, S.S.C. Ammal, S. Takami, M. Kubo, and A. Miyamoto, Appl. Catal. A, 194-195 (2000) 183.

[2] S. Sakahara, K. Yajima, R.V. Belosludov, S. Takami, M. Kubo, and A. Miyamoto, , Appl. Surf. Sci., in press.

[3] R.V. Belosludov, S. Sakahara, K. Yajima, S. Takami, M. Kubo, and A. Miyamoto, Appl. Surf. Sci., in press.

2:00 PM S7.2

DEVELOPMENT OF ACCELERATED QUANTUM CHEMICAL MOLECULAR DYNAMICS PROGRAM FOR COMBINATORIAL COMPUTATIONAL CHEMISTRY. Momiji Kubo, Hitoshi Kurokawa, Tomonori Kusagaya, Minako Ando, Ken Suzuki, Seiichi Takami, Akira Miyamoto, Tohoku Univ., Dept. of Materials Chemistry, Sendai, JAPAN; Akira Imamura, Hiroshima Kokusai Gakuin Univ., Dept. of Mathematics, Hiroshima, JAPAN.

Recently, we introduce the concept of combinatorial chemistry to computational chemistry for catalyst design and proposed a new concept called "Combinatorial Computational Chemistry". In this approach, the effects of large number of metals, supports, and additives on the catalytic activity, selectivity, and resistance to poisons are systematically calculated using computer simulation techniques in order to predict the best element for each catalytic reaction. In order to realize the high-throughput screening by the combinatorial computational chemistry approach, the development of the accelerated simulation methods is required. Recently, we succeeded in the development of an accelerated quantum chemical molecular dynamics program Colors for the combinatorial computational chemistry, which is more than 5000 times faster than the first-principle molecular dynamics [1-3]. It indicates that 10 years calculation by the first-principle molecular dynamics can be finished within only one day by our accelerated quantum chemical molecular dynamics. We successfully applied our accelerated quantum chemical molecular dynamics program to clarify various catalytic reaction dynamics such as deNOx process, methanol synthesis process, polyolefin synthesis, fuel cell system, and so on. Moreover, we confirmed that our accelerated quantum chemical molecular dynamics program enables us to perform the high-throughput screening of the catalysts by using computational chemistry.

[1] Y. Inaba, T. Onozu, S. Takami, M. Kubo, A. Miyamoto, and A. Imamura, Jpn. J. Appl. Phys., 40 (2001) 2991.

[2] H. Takaba, A. Endou, A. Yamada, M. Kubo, K. Teraishi, K.G. Nakamura, K. Ishioka, M. Kitajima, and A. Miyamoto, Jpn. J. Appl.

Phys., 39 (2000) 2744.

[3] A. Yamada, A. Endou, H. Takaba, K. Teraishi, S.S.C. Ammal, M. Kubo, K.G. Nakamura, M. Kitajima, and A. Miyamoto, Jpn. J. Appl. Phys., 38 (1999) 2434.

2:15 PM S7.3

EFFECTS OF ATOMIC ADDITIVES ON COHESION IN STRUCTURAL INTERMETALLICS: A SYSTEMATIC COMPUTATIONAL STUDY. D. Djajaputra, B.R. 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 cohesion 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 TIGHT BINDING PARAMETERS FROM FIRST PRINCIPLES CALCULATIONS USING ADAPTIVE SIMULATED ANNEALING. Anders Froseth, Ragnvald Høier, NTNU, Dept of Physics, Trondheim, NORWAY; Peter Derlet, 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:

R.E. Cohen, M.J. Mehl, and D.A. Papaconstantopoulos, Phys. Rev. B 50, 14 694 (1994)] using Adaptive Simulated Annealing [L. Ingber, "Adaptive Simulated Annealing (ASA)", Global optimization C-code, Caltech Alumni Association, Pasadena, CA (1993). URL <http://www.ingber.com/#ASA-CODE>.

3:15 PM *S7.5

DEVELOPING QSARs FOR MATERIALS SCIENCE. Krishna Rajan, 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 requires the need to integrate both the experimental aspects of combinatorial synthesis with the computational aspects of information based 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 COMPUTATIONALLY 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 machine-learning algorithm to construct predictive models from existing experimental data. These predictive models are used to computationally 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 T_c values for superconductors) and heterogeneous catalysis.

4:00 PM S7.7

FINDING THE MOST STABLE FOUR COMPONENT ALLOYS USING ELECTRONIC STRUCTURE CALCULATIONS. Gisli H. Johannesson, Thomas B. Pedersen, Andrei Ruban, Hans L. Skriver, Karsten W. Jacobsen, and Jens K. Nørskov, Center for Atomic-Scale Materials Physics, Dept of Physics, Technical Univ of Denmark, K. Lyngby, DENMARK.

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 fcc alloys, and the fcc alloys which have the best stability 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 Buelens and Luc T. Wille
Thursday Morning, November 29, 2001
Room 204 (Hynes)

8:30 AM *S8.1

ARTIFICIAL INTELLIGENCE IN MATERIALS SCIENCE; CHALLENGES AND OPPORTUNITIES. John F. 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 information from both actual sensors and virtual sensors is 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 an enabling methodology in fundamental statistical mechanics of 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 Guessasma, Ghislain Montavon, Christian Coddet, LERMPs, Tech Univ of Belfort-Montbeliard, Sevenans, 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 properties and characteristics. 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 been developing over the 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 mechanism of the biological nerve cell. Its purpose is to deal with practical situations that need a decision to be taken or to resolve complex problems by interpolating a behavior. ANN is an implicit model that takes into account the complexity of the problem, but also the interdependency of the parameters and that includes as well the measured error if this latter is known. Moreover, ANN is a model that discovers systematic relationship. The global concept and the protocols to implement (i.e., causal relationships proposal as a physical hypothesis, neuromimetic test 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 S8.3

PARAMETERIZATION OF TRANSIENT DEFECT DYNAMICS MODELS IN CZOCHRALSKI CRYSTAL GROWTH. Talid Sinno and Thomas Frewen, University of Pennsylvania, Dept. of Chemical Engineering, Philadelphia, PA; Erich Dornberger, Robert Hoelzl, and Christian Hoess, Wacker Siltronic AG, Burghausen, GERMANY.

Numerous investigations have attempted to determine quantitatively 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 is used to investigate a transient model for point defect evolution during Czochralski (CZ) crystal growth. Previous attempts at using the CZ system to parameterize point defect properties have relied on quasi-steady state analyses and have not resulted in robust parameterizations. Here, it is shown that a fully transient analysis 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 are 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 S8.4

MATERIALS DEVELOPMENT FOR SOLID OXIDE FUEL CELLS USING QUALITATIVE MODELS. Klaus Schmid, Volker Krebs, Institut für Regelungs- und Steuerungssysteme, Universität Karlsruhe (TH), GERMANY; Helge Schichlein, Albert Krügel, Ellen Ivers-Tiffée, 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 and durability. During sintering of the cathode, a poorly conducting lanthanum zirconate ($\text{La}_2\text{Zr}_2\text{O}_7$) layer may be formed between the lanthanum manganite ($\text{La}_{0.8-x}\text{Sr}_{0.2}$) MnO_3 cathode and the yttrium-stabilized 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 $\text{La}_2\text{Zr}_2\text{O}_7$ 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 materials compositions, operating conditions, electric current, and microstructure. Building a model based on chemical reaction equations fails because 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 by mathematical equations but by linguistic rules. Therefore, it can not be utilized by the conventional modeling techniques of materials science. This work presents an interdisciplinary approach to modeling in materials development by applying control theory and computational intelligence techniques. We use dynamic fuzzy systems to formalize the expert knowledge about the irreversible materials changes in the $\text{La}_2\text{Zr}_2\text{O}_7$ layer. Fuzzy if-then rules represent the dynamic dependency of this layer on the electric current density and operating conditions. The resulting model enables the application of simulations instead of time-consuming experiments. The dynamic behavior of the non-measurable thickness of the

$\text{La}_2\text{Zr}_2\text{O}_7$ 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 *S8.5

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 characterisation of the feasible 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. The same motifs have now been found for polypeptides and bulk glass formers. The global connectivity of the potential energy surface also determines the success or failure of different global optimisation algorithms, and should provide a basis for the design of new methods.

10:45 AM S8.6

DESIGNING CONDUCTING POLYMERS WITH GENETIC ALGORITHMS. Ronaldo Giro, Marcio Cyrillo, Douglas S. Galvao, 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 points of view. As structural disorder is always present in such systems (alloys) 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 factor counting (NFC) technique with genetic algorithms (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 tight-binding hamiltonians. 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 polyaniline chains. This procedure worked 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 S8.7

HEURISTIC METHODS FOR FINDING GROUND-STATES OF ISING MODELS. Hugues J. Lassalle, Luc T. Wille, 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 S8.8

COMBINATION OF EVOLUTIONARY ALGORITHMS AND DENSITY FUNCTIONAL THEORY FOR ATOMIC-SCALE MATERIALS DESIGN. Thomas Bligaard, Gisli Johannesson, Andrei Ruban, Hans Skriver, Karsten Jacobsen, Jens Nørskov, 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 of materials and 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 *S8.9

GLOBAL OPTIMIZATION WITH PARALLEL GENETIC ALGORITHMS - APPLICATION TO COMPLEX SURFACE STRUCTURE DETERMINATION. Michel 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.