SYMPOSIUM D

D: Materials and Devices for Smart Systems

November 30 - December 5, 2003

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*Invited paper
TUTORIAL

FT D: Smart Materials-Classifications, Devices, and Composites
Sunday, November 30, 2003
10:30 AM - 5:00 PM
Room 202 (Hyenas)

The tutorial will cover the "fundamentals" (design and fabrication methods) of smart materials, devices, and composites, and their engineering applications for young students, as well as engineers in the fields of materials science, electrical, mechanical, and civil engineering, etc. The lectures consist of three ninety-minute presentations by specialists in: a) material science of sensor/actuator materials; b) features and classification of smart materials and devices; and c) smart composite systems and their engineering applications. The intention of this tutorial is to give attendees a new concept of smart/fast-acting material, fundamental design, fabrication processes and features of each smart/intelligent material, devices, and smart composites, and their potential applications for the industries, including the ease/difficulty/cost of setting each up, and future directions.

Instructors:
Manfred Wuttig, University of Maryland
Victor Giurgiutiu, University of South Carolina
Hirosi Asama, Chiba University

SESSION D1: Ferroelectric and Piezoelectric Materials and Devices
Chairs: Dragun Dunicanovic and Qingming Zhang
Monday Morning, December 1, 2003
Room 201 (Hyenas)

8:30 AM *D1.1 Recent Progress In Transducers Actuators And Sensors For Smart Systems, L. Erz Cross, Materials Research Institute, Penn State University, University Park, Pennsylvania.

All high strain electro-active dielectric actuators are basically electrostrictional, namely a phenomenon in which the deformation is drastically different between several of the systems of current interest. In soft polymeric elastomers, very large electrostrictive strains (over 200%) are a direct consequence of the Maxwell stress exerted by the attractive force between unlike charges on the opposite electrode surfaces. Current low permittivity silicone and acrylic elastomers have many attractive potential applications, but do not even uncomformably high electric fields (over 100 Volts/micron) for full performance. Developments to lower the needed fields and improve force levels will be discussed. For high energy electric inorganic and chemically modified Polyelectrolyte Fluorinated Polyelectrolytes (P(VDF-TrFE)) Copolymer, the relaxor modification of the ferroelectric response is a major attractive factor in passive coupling, 70% and high coupling piezoelectric properties under bias field, again higher as materials with low energy properties are not uncomfortable high and efforts to modify these systems will be considered. In polymer sensors an exciting development from the low to the high polymer form space change electrets which have di3 compatible to ceramic PZT, but ultra low permittivity resulting in spectacular thin fibers of memory for water-soft water and water-inhibitors. In the stiff inorganic polycrystalline ceramics it is essential to engineer phase instability to achieve high strain and polarizability, and the focus is on systems with homopolar phase boundaries. Lead zirconate titanate (PZT) is still the 'work horse' of polycrystals, but the recently discovered monochromatic phase at the MPB composition is a potential new material in the origins of the useful properties. New MPBs in the Bi2+3x4+3P5x2/Ti03 solid solutions include polycrystals with wider temperature range and exciting new possibilities in both bulk and thin film forms. For BiFeO3 based systems, better control of conductivity is opening new possibilities for the most difficult transduction, namely that between electric and magnetic properties i.e. high magnetoelectric coefficients. The quite outstanding piezoelectric properties in the single crystal lead zirconate-titanate and lead magnesium niobate lead titanate MPB compositions close to the MPB are now fully authenticated, but the complex of phase stabilities, dielectric and piezoelectric properties and switching responses still call for more detailed studies and a more complete exploration.

9:00 AM *D1.2 Enhanced Piezoelectric Property of Piezoelectric Single Crystals by Domain Engineering, Satoshi Wada and Takeshi Tsurumi, Department of Metallurgy & Ceramics Science, Tokyo Institute of Technology, Tokyo, Tokyo, Japan.

Engineered domain configuration is one of the domain engineering techniques and makes piezoelectricity of ferroelectric single crystals exceed even enhanced. In this study, engineered domain configuration was induced into barium titanate single crystals as a typical lead-free piezoelectric single crystals, and the piezoelectric property was investigated as a function of (1) crystal structure, (2) crystallographic orientation, (3) domain size. As a result, the orthorhombic barium titanate single crystal, when electric field (E-field) was applied along [001] direction, the maximum piezoelectric property was observed and its piezoelectric properties were larger than those of PZT ceramics. Moreover, domain density of engineered orthorhombic barium titanate single crystal was controlled by temperature and E-field, and their piezoelectric properties were measured. The barium titanate crystals with high domain density exhibited the much higher piezoelectric properties than those of barium titanate crystals with low domain density. The above results revealed that what kind of engineered domain configurations is the best for the piezoelectric application.

9:30 AM D1.3 Polarizable Charge Equilibration Force Field and Application to Phase Transformation in Ferroelectrics, Qingsong Zhang, Tahir Cagin, Alejandro Strachan and William A. Goddard, California Institute of Technology, Pasadena, California.

We present the Polarizable Charge Equilibration force field to include self-consistent atomic polarization and charge transfer in molecular dynamics of materials. The charge on each atom is partitioned into a Gaussian-shaped core with fixed (positive) charge (4 for Si) and a Gaussian-shaped shell with variable charge. The shell charges are determined from the polarizability and the charge transfer to neutralize the shell charge. The long-range London dispersion and short-range Pauli repulsion effects are described by two-body potentials (Morse or Leonard-Jones) that act between all atoms (no exclusions). Using the above model, we determined all the parameters in the force field for BiTFeO3 directly from Quantum Mechanics calculations [DFT with GGA]. We find that the model leads to correct temperature sequence for the transitions between the four phases of BiTFeO3. With the model it is possible to simulate a broad range of unit cells to study domain boundaries, surface reconstruction, the role of defects and the effects of temperature, pressure, and applied electric fields and stresses.

9:45 AM D1.4 Mixed Ordering in Pb-based complex perovskites, K. Z. Babzinski, C. W. Tiu, X. Meng, H. L. W. Chan and C. L. Choy, Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, Kowloon, Hong Kong.

High-resolution transmission electron microscopy (HRTEM) studies of the ceramics (Sr0.5Bi0.5)0.3Bi0.70.5Nb2O6, (1-x)Pb(Mg1/3Nb2/3)O3-xPbTiO3, with x=0, 0.3 and 0.6 show ordered nano-regions along the [110] direction. The nano-regions are separated from each other by a random distributed. The contrast exhibited by each region is distinct from the neighbouring region, caused by the clustered ordering of a specific cation concentration. The state of mixed ordering can be superstructure whose phase transition is dependent on the distribution of the nano-ordered regions. The ideal 1:1 ordering of a B-site cation poling along the [110] direction creates a long-range order with a superstructure of its own. However, mixed ordering occurs along [001] direction, can be highly random in nature and might also be associated with localized short-range order. The present of the superstructure reflections and diffuse streaking along [001] is dependent on the degree of mixed ordering. HRTEM studies of the three compounds show various degrees and forms of mixed ordering. Simulations carried out illustrate the ways in which these regions are ordered primarily by preferential clustering of one of the three cations in any one of the nano-regions. Six clusters of Mg, Nb, In and Nb-Mg of which three clusters are 1:1 ordered and the remaining three clusters are disordered, are incorporated into the simulations. Simulations include models of the diffusion patterns in which a simple perovskite structure ABO3 with space group Pmnn is extended into three distinct ordered unit cells, containing B-site cations In, Mg and Nb. A variety of different conditions in which ordered and disordered clusters were combined to simulate the HRTEM images will be described in detail. The origin of the superstructure reflections and diffuse streaking and the influence of mixed ordering on the dielectric properties will be discussed.

10:30 AM *D1.5 Highly Efficient Piezoelectric Actuators for Active Vibration Control, Enrico Colai, Ganesh Suyal, Sandrine Gentil and Novi Setting, Ceramics Laboratory, EPFL, Swiss Federal Institute of Technology, Lausanne, Vaud, Switzerland.

Small actuators providing large displacements and reasonably high
forces are required for vibration control in a wide range of applications. This need is rarely satisfied by currently available compact actuators. But, a family of low cost / high performance disk bend actuators produced by combining efficient design and fabrication methods. The properties of these actuators are intermediate between those of standard bimorphs, used for very large displacements, but providing rather small forces and the use of high voltage stacked multilayers, which provide quite large forces but are generally heavier, larger and very expensive for equivalent displacements. The absence of any external mechanical amplification mechanism makes actuators particularly suitable for active vibration damping applications within buildings or for noise control by emission of controlled sound in anechoic. In order to lower the driving voltage, multilayer disk benders can also be fabricated with the same technique. The actuator displacement and force properties are not influenced by the number of layers. Tuning of the internal and external electrodes for the application of appropriate voltage configurations enables the development of actuators with highly specialized performances. The fabrication method enables the downsizing of these piezoelectric devices to satisfy MEMS requirements too.

11:00 AM #DL6
Novel High Power Piezoelectrics for Transformers and Actuators. Shankar Priya 1 and Kenji Uchino 2; Penn State University, University Park, Pennsylvania; 2Electrical Engineering, Penn State University, University Park, Pennsylvania.

High Power piezoelectric materials are required for numerous devices such as piezoelectric transformers, high frequency actuators, ultrasonic motors and current sensors. All these applications demand a material that exhibits good characteristics of high power density and efficiency, piezoelectric, dielectric and electromechanical constant along with low dielectric and electromechanical losses. Further the properties should be non hysteretic with field and temperature. This study illustrates the development of new family of PZT-PSN based ceramic materials whose property can be tailored to meet these requirements. The results will be shown which conclusively prove that this material can generate high electrical power as compare to other available choices.

11:15 AM #DL17

The initial idea of a piezoelectric transformer (PT) corresponds to C.A. Rosen, K. Fish, and H.C. Rothenberg and is gathered in the U.S. Patent 2830274, applied in 1954. Fifty years later, this technology has become one of the most promising alternatives to replace the magnetic transformers in a wide range of applications. PTs convert electrical energy into electrical energy by making use of acoustic energy. These devices are typically manufactured using piezoelectric ceramic materials that vibrate in resonance. With an appropriate design it is possible to step-up and step-down voltage between the input and output of the transformer without the use of wires or magnetic materials. This technology did not reach commercial success until early the 90s. During this period, several companies, mainly in Japan, decided to introduce PTs for applications requiring small size, high step-up voltages, and low electromagnetic interference (EMI) signature. This type of PTs where development was based on optimization of the initial Rosen concept. That's why they are typically referred as Rosen-type PTs. Today's PTs are used for backlighting LCD displays in notebook computers, PDAs, and other handheld devices. The PT yearly sales estimate was about 20 millions in 2000 and industry sources report that production of piezoelectric transformers in Japan is growing steadily at a rate of 10% annually. The reliability achieved in this application and the advances in the related technologies (materials, driving circuitry, housing and manufacturing) have currently motivated an enormous interest and confidence in expanding this technology to other applications fields. Currently, the industry is moving in two directions: the low-cost product market and the value-added product market. Prices of PTs have been declining in recent years, and this trend is expected to continue this year that may make this technology a serious candidate to replace the magnetic transformers in cost-sensitive applications. As for the value-added product market, leading makers are reportedly focusing on more value-added products. Two key points are miniaturization and higher output power. Piezoelectric transformers for power applications require lower output impedances, high power capabilities and high efficiency under step-down conditions. Among the different PT design proposed as an alternative to the classical Rosen configuration, Transistor illuminated radial PT has been demonstrated as the most promising technique achieving high power level. Higher powers than 1000W, with power densities in the range of 30-40 W/cm2 has been demonstrated. Micro-PTs are currently being developed with sizes of less than 5mm diameter and 1mm thickness allowing up to 85W power transfers at 60-100 gain. Smaller sizes would be in the future integrated to power MEMS systems. This paper summarizes the state of the art on the PT technology and introduces the current trends of this industry.

11:45 AM DL8
Phase field simulations of polarization switching under an applied electric or stress field. Jie Wang 1, Q.S. Srinivasan 2, L.Q. Chen 3 and Guo-Yi Zhang 1; 1Department of Mechanical Engineering, Hong Kong University of Science and Technology, Hong Kong, Hong Kong; 2Department of Mechanical Engineering, Hong Kong Polytechnic University, Hong Kong, Hong Kong; 3Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania.

The polarization switching in a ferroelectric subjected to an electric or stress field is usually simulated using a phase field model based on the time-dependent Ginzburg-Landau equation, in which both the long-range electric and the long-range elastic interactions are taken into account. Domain switching takes place when the electric field or the stress field exceeds a threshold value. The temporal evolution of polarization switching shows that the switching is a process of nucleation new domains following by the disappearance of old domains and growth of new domains, which is accomplished through domain wall motion. An electrical load can induce both 1800 and 900 polarization switching, while a mechanical load can produce only 900 polarization switching. The macroscopic polarization or strain is obtained by averaging polarizations and strains over the simulated size as explicit and optimal configuration of underlying microstructure, electric field or stress load, correspondingly. The simulation results successfully reveal the hysteresis loop of the macroscopic polarization versus the applied electric field, the butterfly curve of the macroscopic strain versus the applied electric field, and the macroscopic strain response to an applied compressive stress.
2:30 PM D2.3

Combinaotrial Thin Film Synthesis of NiMnAl Ferromagnetic Memory Alloys Using MBE Technique, Ulrich Hassler1, Jürgen Fecht1, Sigurd Thiessen1, René Borchers2, Markus Böse2, Thomas Wachter2 and Michael Mösle2, 1Research center caesar, Bonn, Germany; 2Dept of Chemistry, Bonn University, Bonn, Germany.

Ferromagnetic shape memory alloys have attracted much attention as potential high-performance magnetically controlled actuator materials due to their ability to shape large fields and structures by the rearrangement of twin variants in the martensitic state. So far, numerous studies have been investigated in this respect including binary alloys like FePd or FePt as well as the Heusler-type alloys NiMnGa, NiMnAl, or very recently CoNiAl and CoNiGa. In bulk form, these materials come up with high magnetostriction values comparable or even superior to the value of the giant-magnetostrictive Terfenol-D. The real challenge by now is to fabricate thin films of these materials and to overcome material constraints and provide them with the same order of functionality as in the bulk counterparts. In this context, we present a study demonstrating the advantage of combinatorial thin film synthesis by using molecular beam epitaxy. Here, NiMnAl alloy composition spreads were grown onto four-inch wafer substrates. Compositional variations ranging from 10 to 15 at.% relative to each constituent enable a direct comparison of the chemical-structural relationship with respect to martensitic transformation and to magnetic ordering as well as an efficient identification of the emerging phase stability regions. In our study, we set the primary focus on the structural aspects of the transformation behavior confirmed by X-ray microdiffraction in combination with in-situ designed high-resolution TEM imaging of the respective composition areas reveal patterns of a long periodic stacking order indicating crystallographic orientation in the martensitic state. Stress relief upon transformation as observed by thermal processing in a stress apparatus using a capacitance bending beam technique ranges from 50 to 200 MPa depending on the composition. Vibrating-sample magnetometry so far suggests magnetic ordering to occur well below ambient temperature. The compositional and microstructural aspects of the phase stability will be discussed.

2:45 PM D2.4

New smart composites composed of ferromagnetic shape memory alloy particles and polymeric matrix for sensors and actuators, Hitoshi Hosoda1, Shin-ya Takeda1, Tomomi Inamura2, Kenji Wakahara1 and Shigeki Miyazaki1, 1Control Laboratory, Tokyo Institute of Technology, Yokohama, Kanagawa, Japan; 2Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki, Japan.

Since most ferromagnetic shape memory alloys (FSMAs) are brittle, the enhancement of ductility is strongly required. In order to improve workability and ductility of FSMAs, a new smart composite composed of FSMa particles (FSMAs) and poly is proposed. The FSMAs are easily fabricated and isotropic mechanical and shape memory characteristics are obtained while nonisotropic properties appear for the composites containing shape memory alloy wires or plates. The isotropic properties are advantageous for shaping and forming. In this paper, the design concept, mechanical and shape memory properties of FSMAs/polymer smart composites are described. Besides, the ability of the composites for sensors and actuators is pointed out.

3:30 PM D2.5

Combinatorial Investigation of Ferromagnetic Shape Memory Alloys, Ildiko Turek1, Dept of Materials Science and Engineering, University of Maryland, College Park, Maryland; 2Small Smart Systems Center, Department of Materials Science and Engineering and Center for Superconductivity Research, University of Maryland, College Park, Maryland.

We have developed a thin film composition spread technique for rapidly mapping the ternary phase diagrams of metallic alloy systems in search of ferromagnetic shape memory alloys. A UHV three-gun magnetron co-sputtering system is used to deposit composition spreads whose natural compositional distribution contains large fractions of ternary phase diagrams. The spreads are created on 3-inch Si wafers, and the typical thickness of the film ranges from 300 nm to 1 micron. To determine the deposited material and orientation, they are annealed at 500-600 °C in vacuum following the deposition. Wavelength dispersive spectroscopy is used to map the exact composition and impurity distribution of every wafer. Room-temperature and high-temperature scanning SQUID microscropy is used to obtain the magnetic field distribution of the spread patterned into 2 mm x 2 mm square grids. Obtained distribution is converted to quantitative remanent magnetization mapping using a numerical algorithm. This allows us to identify composition regions that are ferromagnetic at room temperature. In order to detect composition regions which are reversible martensites, we use wafers where arrays of cantilevers are micromachined prior to the heat treatment. Deposition of all the cantilevers on the spread wafer simultaneously by visual inspection, we can detect regions which undergo martensitic transitions. Scanning x-ray diffraction of spread wafers is also used to identify regions which display the magnetic phase transitions. By combining the information extracted from both types wafers, we can construct functional ternary phase diagrams. To date, we have located a variety of ternary systems. We have found new composition regions which are both ferromagnetic and reversible martensites in the Gd2 deficiency region of the Ni-Mn-Ga system and the Al deficient region of the Ni-Mn-Al system. A clear relationship between the martensite transition temperature and the Curie temperature has been observed for a wide range of compositions. This work was performed in collaboration with O. O. Fameu, M. A. Aronov, K.-S. Chang, J. Hat-trick-Simpers, S. E. Lofland, C. F. Wellswood, L. Kuzma, and M. Wuttig.

4:00 PM D2.6

Design of Ferromagnetic Shape Memory Alloy Composites and Their Actuators, Minoru Taya, Mechanical Engineering, University of Washington, Seattle, Washington.

Recently, strong intentions are paid to ferromagnetic shape memory alloys (FSMAs) as a key actuator material, owing to its fast actuation speed, yet providing large force and stroke. FSMAs are driven by applied magnetic field and/or magnetic field gradient, which cause the deformation due to the martensitic phase transformation, and hence can provide very fast actuation speed with reasonably large strain and stress capability. Among the polymeric FSMa alloy is practically promising to be applied as an actuator material, owing to the good mechanical properties, such as shape memory effects, superelasticity and high ductility, and so on. Since the uniform (contract) magnetic field alone is found to be disadvantageous in this would provide a modest force, we proposed so-called "hybrid mechanism" for actuator applications. The key step in the mechanism is the stress-induced martensite phase transformation produced by applied magnetic field gradient, thus enhancing the displacement, as the stiffness of Fe-Pd is reduced from stiff to soft during the martensite to martensite transformation. The price of Pd is very expensive, thus, we are searching for alternative FSMa, and come up with FSMa composites which are composed of ferromagnetic material and shape memory alloy (SMA). This talk will discuss the hybrid mechanism of FSMa and SMA composites and present recent results of three-dimensional (3D) phase transformation diagram produced based on thermodynamics. This 3D diagram will be used effectively by design engineers who want to design fast responsive FSMa based actuators. This talk introduces also several designs of FSMa and SMA based composite actuators.

4:30 PM D2.7

Reversible Martensitic Transformation in A Ferromagnetic CoNiAl Alloy, H. Elsahy, 1Department of Mechanical Engineering, Texas A&M University, College Station, Texas; 2Lehrstuhl für Werkstoffkunde, University of Paderborn, Paderborn, Germany.

In recent years ferromagnetic shape memory alloys have attracted increasing interest because of the ability to obtain one order of magnitude higher recoverable magnetic field induced strain (MFIS) than other active materials. The main requirements for this magnetic field induced strain are low twin boundary energy, high strength of magnetic, high magnetostrictive anisotropy energy and saturation magnetization. A recently discovered ferromagnetic shape memory CoNiAl alloy has promising shape memory characteristics for conventional and magnetic shape memory applications. In this study we have demonstrated that these alloys have low pseudomorphic stress hysteresis, high strength for dislocation slip, large pseudelastic and twinning shape memory strain, large pseudostrain in the strain window, and low stress for martensite reorientation. These findings satisfy the thermomechanical requirements to obtain MFIS. Additionally, high melting point, low density, good corrosion and oxidation resistance may result in the replacement of conventional SMAs with CoNiAl in most applications. This work is supported by Army Research Office, Contract No. DAAD 19-03-1-0261.

4:40 PM D2.8

Nonlinear Stress-Based Control of a Rotary SMA-Actuated Manipulator, Mohammad Elhamini, Michael Seigler and Mehdi Ahmadian, Mechanical Engineering, Virginia Tech, Blacksburg, Virginia.

In this paper a nonlinear stress-based controller is designed to position a single-degree-of-freedom shape memory alloy (SMA) actuated manipulator. A three part model was constructed based on the dynamics/kinematics of the arm, the thermomechanical behavior...
of SMA's, and an assumed heat transfer model consisting of electrical heating and natural convection. Both sliding mode control and inverse dynamic control have been used to calculate a desired stress, based on the position error. The desired stress is compared with the actual stress which is computed using an Extended Kalman Filter. The stress error is then used for control via a proportional-integral-derivative controller. Numerical simulations are performed to investigate tracking performance as well as other issues such as robustness. The results demonstrate that the variable structure controller designs are highly accurate in tracking both stationary and variable input signals.

SESSION D3: Electronic Polymer
Chairs: Ji Su and Qiming Zhang
Tuesday Morning, December 2, 2003
Room 202 (Hynes)

8:30 AM #D3.1
Ferroelectrics: Polymer-foam space-charge electrets with
exceeding fundamental and applications-relevant properties.
Reimund Gerhard-Multhaupt and Michael Wegener, Department of
Physics, University of Potsdam, Potsdam, Brandenburg, Germany.

Recently, the term "ferroelectrics" has been suggested for the new class of highly insulating and suitably foamed polymers with internal space charge that have become a major focus of electret research. [1]. The first step in their preparation is foaming and void optimization by means of methods such as solvent evaporation, gas expansion, etc. Because of relatively large microvoids, the polymer foams are mechanically quite soft with rather low elastic moduli and acoustic impedances. After charging or poling, they contain stable charge layers on the internal void surfaces. These charge layers form a "giant dipole" whose dipole moment is easily varied by mechanical or electrical stresses. The resulting electrical or mechanical response of the foamed and charged polymer represents a direct or inverse quasi-ferroelectric effect, respectively. Because of the very high deformability of the polymer microvoids, the observed electromechanical effects can be very large, often dwarfing the corresponding values of polar piezoelectric polymers and sometimes exceeding the coefficients of commercial piezoelectric materials. In addition to these effects, the new materials exhibit some pyroelectricity which is often quite small and thus makes them rather insensitive to temperature changes. From a general perspective, the novel ferroelectric foamed and charged polymers are very similar to components of gas bubbles in a polymer matrix. As in other composite materials, the properties of the material are critically dependent on the size and shape distribution of the pores and on the mechanical and electrical behavior of the interface, i.e. the internal void surfaces. The development of cellular polypropylene (PP) as an electret-transducer material has been studied recently. The mid-eighties is briefly described, and the most relevant experimental techniques for polymer-foam electrets are introduced. Porous fluoropolymer electrets and their investigation in single- or multi-layer piezoelectric devices are also considered in view of their better thermal and temporal stabilities. Typical results are discussed in view of the potential of polymer ferroelectrets for device applications which include flat microphones, microphones, noise-canceling panels, flat and curved ultrasonic transducers without or with patterning of the active area, electromechanical sensors for vibration detection (e.g. machinery, musical devices, security systems) and for dynamic biomechanical measurements. [1, 2] Reimund Gerhard-Multhaupt, "Less can be more - Holes in polymers lead to a new paradigm of piezoelectric materials for electret transducers," IEEE Trans. Dielectr. Insul., Vol. 9, No. 5, pp. 851-859 (October 2002). Several contributions by researchers from Austria, China, Finland, Germany and Poland in the Proceedings of the 11th International Symposium on Electrets, IEEE Catalog No. 02CH37385, IEEE Service Center, Piscataway, NJ 2002.

9:00 AM #D3.2

Electroactive polymers (EAPs) offer the potential to overcome limitations of traditional smart material and transducer technologies. A promising class of EAP is dielectric elastomers. Dielectric elastomer transducers are rubbery insulating polymer materials with compliant electrodes that have an electromechanical response to an applied electric field. The strains and elastic energy of dielectric elastomer actuators are larger than those observed in any other field-activated materials. Because of their unique characteristics, dielectric elastomer transducers are under development for a wide-range of devices including multifunctional muscle-like actuators for biomimetic robots, microactuators for MEMS, conformal loudspeakers, hipjoint displays, shoe-mounted generators for harnessing the energy of walking, replacements for electromagnetic and pneumatic actuators for industrial applications, and shape control of space structures. Dielectric elastomers promise in each of these applications. The success or failure in a given application will depend on the achievable performance and lifetime as well as the electrical driving requirements.

9:30 AM D3.3

Anisotropic freestanding films and fibers of nematic elastomers from laterally attached side-chain polymers show promise as linear actuators with large strain and retractive force. The orientational order of the liquid crystal side groups imposes a conformational anisotropy in the polymer backbone. When a uniaxial stress is applied, the order parameter decreases, and as the nematic-isotropic phase transition there is a concomitant loss of order in the backbone which results in a contraction of the film/fiber in the direction of the director orientation. In this presentation we show that induced and strain blocked stress of these elastomers can be easily tuned by varying the nature and composition of the crosslinking material. The effect of multideterminate crosslinkers on the alignment and hence the mechanical properties of the film will be discussed. We will also present results on the actuation induced by a reorientation of the liquid crystal mesogens by an applied field.

9:45 AM D3.4
A Multiscale Computational Model of Soft Elasticity and
Director Reorientation in Nematic Gels. Antonio DeSimone, SISSA, International School for Advanced Studies, Trieste, Italy.

Nematic gels combine large deformations and entropic elasticity of
electromechanical deformations with tunable optical properties peculiar to nematic liquid crystals. In addition, they exhibit soft elasticity (in analogy with the superelasticity of shape memory alloys), as a consequence of a symmetry-breaking phase transformation from an isotropic phase (in which the nematic mesogens are randomly oriented) to a spontaneously deformed uniaxial phase (in which the nematic mesogens are aligned). The phase transformation can be controlled by several mechanisms (temperature changes, irradiation by UV light) and the material has been proposed as a suitable candidate for applications such as artificial muscles. The mechanical response of nematic gels is highly nonlinear. Modelling the orientation requires the resolution of complex domain patterns which arise in connection with load-induced phase changes. This is most effectively done through coarse-grained hyperelastic model, in which fine-scale spatial oscillations are carefully accounted for in the definition of an effective energy density, and then averaged out from the kinematics.

Algorithmsically, this amounts to taking a suitable convex envelope of the microscopic free-energy density of the system. Finite element simulations based on the effective energy density are dramatically more effective than those based on the macroscopic free-energy. We will report on numerical simulations of stretching experiments on thin sheets of nematic elastomers. The coarse-grained hyperelastic model enables us to simultaneously solve the micro-electromechanical response (i.e., deformed shape, stress-strain curves) and the underlying microscopic mechanisms (evolution of domain structures, local redistribution of the nematic director). Comparison of numerical results with measured stress-strain diagrams and with X-ray scattering experiments confirms the robustness of our approach.

10:30 AM #D3.5

Electrostrictive graft elastomers developed at NASA Langley Research Center demonstrate promising electromechanical properties for lightweight actuation devices. The desired electromechanical properties of the elastomers can be tailored and optimized by molecular engineering (chemically) and morphological control (physically). This presentation will review recent results on 1) the effects of chemical composition and molecular morphology on electromechanical properties, 2) the effects of polymeric matrices on the material morphology; and 3) a computational study on mechanisms of electrostriction in the material. In addition to the material development, progress in design and fabrication of electrostrictive polymer (EAP) based electromechanical devices will also be presented. These include fabrication of polymer-based micro-electro-mechanical systems (MEMS), hybrid electromechanical actuators, and multi-layered EAP actuators as well as other technical issues related to the development of EAP-based devices such as electrodes and configuration design.
11:00 AM D3.6
High-Dielectric-Constant All-Organic/Polymeric Composite Actuator Materials. Cheng Huang1, Ji Su2 and Qingming Zhang3;
1Materials Research Institute and Electrical Engineering Department, The Pennsylvania State University, University Park, Pennsylvania; 2Advanced Materials and Processing Branch, NASA Langley Research Center, Hampton, Virginia.

Among various electroactive polymer (EAP) actuator materials developed recently, the class of EAPs whose responses are stimulated by external electric fields (often known as field type EAPs) is especially attractive due to their high strain level and elastic energy density. However, for most field type EAPs, dielectric constant is low, generally less than 10. Consequently, these polymers usually require high electric fields (>100 MV/m) to generate high elastic energy density which limits their applications. In this talk, we will investigate some avenues to significantly raise the dielectric constant and electromechanical response in field type polymeric materials. By exploiting an all-organic composite approach in which high-dielectric constant organic particulates were blended with a polymer matrix, a polymer-like material can reach a dielectric constant higher than 400, which results in a significant reduction of the applied field to generate high strain with high elastic energy density. An all-polymer high-dielectric (dielectric constant K>1,000 at 1kHz) percolative composite material was fabricated by the combination of high dielectric polyaniline particles (K>105) within a fluoropolymer matrix (K>50). These high-K polymer hybrid materials also exhibit high electromechanical responses under low applied fields. In addition, a three-component all-organic composite was designed and prepared to improve both the dielectric constant and the electromechanical response, as well as the stability of the composites, in which a high-dielectric constant organic dielectric phase and an organic conductive phase were embedded into the soft dielectric elastomer matrix.

11:15 AM D3.7
Simulations of High-Strain Electrostrictive Chlorinated Terpolymer Systems. George J. Kamburov1 and Tsuneshi Kawanis1;
1Department of Chemistry, University of Rhode Island, Kingston, Rhode Island; 2Naval Undersea Warfare Center, Newport, Rhode Island.

Chlorinated poly(vinylidene fluoride/trifluoroethylene) terpolymers are remarkable examples of high strain electostrictive materials. These polymers are synthesized by copolymerizing vinylidene fluoride and trifluoroethylene with small levels of a third chlorinated monomer. The electromechanical responses of these materials are believed to originate from the chlorination process, which, by its presence in the polymer chains and by virtue of its large van der Waals radius, destroys the long-range crystalline polar macro-domains and transforms the polymer from a normal to a high-strain relaxor ferroelectric. To exploit the strain properties of the terpolymer, it is desirable to understand the structural implications resulting from the presence of the chloride ions. To this end, computer simulations have been performed on model superlattices of terpolymers using quantum-mechanical based force fields. The focus has been on determining the energetics and kinetics of crystallization of the terpolymers. The simulations are shown to act as a defect that can be incorporated into the lamellar structures of annealed terpolymer without a high cost in energy. The degree of incorporation of the chlorinated monomer into the crystal lattice is controlled by annealing conditions and ultimately determines the ferroelectric behavior of the terpolymers. (This work was supported by the Office of Naval Research).

11:30 AM D3.8

A novel cross-linked conducting polymer has been synthesized for use as an electroactive actuator. The polymer combines a conjugated backbone of phenylene and thiophene rings with a polyurethane-based elastomeric linker. Conducting polymers of a nature similar to the backbone, such as polypyrrole and polyaniline, have been shown to actuate via intercalation of ions into and out of the polymer upon electrochemical stimulation. For this material, ionic motion is enhanced by the cross-links, which are joined to the backbone with several segments of ethylene oxide, a known ionic conductor. In addition, the cross-links provide mechanical stability and enable synthesis of freestanding films for active and passive testing. This paper will discuss the synthesis of the novel monomer precursor to the cross-linked conducting polymer. It will then focus on polymerization and cross-linking techniques, followed by active and passive characterization of the material.

11:45 AM D3.9
Large Strain Polypyrrole Actuators. Patrick A. Angestii1, John Madden2, Derek Rinderknecht3, Nathan Vandersteeg and Ian Hunter4; 1Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; 2Electrical and Computer Engineering, The University of British Columbia, Vancouver, British Columbia, Canada.

A typical limitation of polypyrrole based conducting polymer actuators is the low achievable active strains (2% recoverable, 7% max) that they exhibit when activated in a common polypropylene carbonate/ tetraethylammonium tetrafluoroborate electrolyte. Muscular skeletal muscles, on the other hand, exhibits large recoverable strains of over 20%. Such large strains are desirable for applications in life-like robotics, artificial prostheses or medical devices. We report herein the recoverable active strains in excess of 16% (21% max) for polypyrrole activated in the 1-butyl-3-methylimidazolium tetrafluoroborate liquid salt electrolyte. This breakthrough in conducting polymer actuator technology will impact many engineering fields, where a lightweight, large displacement actuator is needed. Benefits and trade offs of utilizing ionic liquid electrolytes for higher performance polypyrrole actuator are discussed.

SESSION D4: Ferroelectric, Piezoelectric, and Dielectric Materials and Devices
Chairs: Nawa Setter and Satoko Wada
Tuesday Afternoon, December 2, 2003
Room 205 (Hynes)

1:30 PM D4.1
Phase Transition-piezoelectric Anisotropy Relations in Perovskite Ferroelectrics: BaTiO3 and PbTiO3. Marko Badzinja, Dragon Damjanovic and Nawa Setter; Ceramics Laboratory, EPFL, Lausanne, Switzerland.

Enhanced piezoelectric response along a nonpole direction in complex relaxor ferroelectrics, such as Pb(Zn1/3Nb2/3)O3-PT, is reported. In Pb(Zn1/3Nb2/3)O3-PT, BaTiO3 and PbTiO3, it has been in the center of the ferroelectric research in the past several years. This phenomenon is not restricted to relaxor ferroelectrics solid solutions and has been reported in simple perovskites, for example in KNO3 and BiTiO3. Although the piezoelectric effect is by far larger in relaxor ferroelectrics, the simple compositions can serve as convenient model materials. They exhibit the same sequence of crystal phases (cubic-tetragonal-orthorhombic-monoclinic-rhombohedral) as the complex solid solutions, the crystal phases are well defined, and they do not exhibit mesoscopic structure often present in complex materials. In this paper, the anisotropy of the longitudinal piezoelectric coefficient d33 is investigated as a function of temperature in BiTiO3 and PbTiO3 using Lindhaus-Ginsburg-Devonshire approach. We show that presence of phase transitions in BaTiO3 leads to large d33 along nonpole directions. The reason for this is that in the vicinity of a phase transition in which polarization vector changes its direction (tetragonal-orthorhombic-monoclinic, orthorhombic-monoclinic-rhombohedral), the shear piezoelectric coefficient(s) becomes very high resulting in enhanced d33 along a nonpole axis. The effect is particularly pronounced in the orthorhombic-monoclinic phase where piezoelectric anisotropy is influenced by the presence of both the high temperature tetragonal and the low temperature rhombohedral phase. In PbTiO3, which exhibits only tetragonal ferroelectric phase, the shear piezoelectric effect is weak and d33 has its maximum along the polar axis at all temperatures. The obtained results are general and can be extended to other ferroelectric compositions, including complex relaxor ferroelectrics, where a phase transition can be induced by temperature, composition (morphotropic phase boundary) or electric field.

1:45 PM D4.2
Modified BiFeO3-PbTiO3 Morphotropic Phase Boundary Piezoelectric Ceramics for Smart Systems. Junqong Cheng1,2 and L. Eric Cross1; 1Materials Research Institute, Penn State University, State College, Pennsylvania; 2School of Materials Science and Engineering, Shanghai University, Shanghai, China.

BiFeO3-PbTiO3 (BF-Pt) crystalline solutions have been modified by Ln+3, Ga+3 and Sn+4 substituents. We have found that the modified
BF-PT was a family of morphotropic phase boundary (MPB), piezoelectric solid solution with excellent piezoelectric properties. Two major problems of earlier BF-PT, high conductivity and switching field, have been solved in our modified systems. In increased the insulation resistance up to $10^{12} \Omega \cdot cm$ at room temperature and made BF-PT cooled into a completely piezoelectric state. Ga provided more polarization with a substituent. With increasing Bi content, the ferroelectric (FE) to relaxor ferroelectric (RF) transition was observed for the La and Ga co-modified BF-PT. Therefore, it is flexible to tailor the performance of BF-PT by different concentrations of the substituents, with high or low Curie transition temperature ($T_c$) above 400°C can be achieved in La-Bi 10% BF-PT, whereas a piezoelectric $d_{33}$ constant of 265 pC/N was measured for the film with $150 \%$ Bi. The modified BF-PT showed comparable performances to conventional PbZrTiO$_3$ (PZT) ceramics, but not significantly important forms. In addition, the dielectric strength of above 100 kV/mm and high coercive field made the modified BF-PT a potential application for high power electromechanical components.

2:00 PM *D4.3* Effect of piezoelectric vibration on electrical properties of YSZ film prepared by MOVCD. Hiroshi Hara, Yuko Sato, and Takashi Goto. Institute for Materials Research, Tohoku University, Sendai, Japan.

Mechanical vibration produced by a piezoelectric actuator was applied to an ion-doped conductor film to increase the electrical conductivity at low temperature. Yttria-stabilized zirconia (YSZ) ion-conductor films were prepared on MgO substrates by metalorganic chemical vapor deposition (MOCVD) using Zr(OR)$_4$ and Y(OR)$_3$ as source materials. Cubic YSZ films containing Sm$_2$O$_3$ with a significant <100> preferred orientation were obtained at 89°C. The films in 1.4 mm thick consisted of fine grains of about 400 nm in size and had a columnar structure. YSZ films showed a decrease in the complex impedance spectrum, which had a clear spike at a low frequency region. The activation energy of electrical conductivity was about 0.99 eV that was almost in agreement to that of YSZ films prepared by other methods. The YSZ film placed on a multilayer piezoelectric actuator composed of seven layers of PZT (lead zirconate titanate) films. The effect of piezoelectric vibration on electrical properties of the YSZ film was investigated. The resistivity of the YSZ film decreased with increasing the amplitude of piezoelectric vibration. The electrical conductivity of the YSZ film under the vibration at 115 kHz and 40 V was about $2 \times 10^{-6} \Omega^{-1} m^{-1}$ at 90°C. This value was more than 10 times greater than that of YSZ film without vibration. The cyclic expansion of YSZ lattice might accelerate the jumping of oxide ions between vacancy sites.

2:30 PM D4.4 ZnO Based SAW Delay Line Sensor: Fabrication and Characterization. Firdi Hamaani1, Shabir Ahmad1, Con Kornan1, Mona Zaghoul3, Shiva Hallward2, R.D. Vipse2 and T. Venkatesan2. 1 Electronic and Computer Engineering, The George Washington University, Washington, DC 20052, USA. 2 Center for Superconductivity, Dept. of Physics, University of Maryland at College Park, College Park, Maryland, USA.

ZnO, a well-known piezoelectric material, is used to develop microscale Surface Acoustic Wave (SAW) delay line sensor. In this work, SAW delay line sensors are fabricated employing ZnO films that are deposited by Pulse Laser Deposition (PLD) and RF sputtering techniques. The ZnO films are characterized prior to device fabrication using X-ray diffraction (XRD) for film crystalline quality, UV-visible transmission spectroscopy for optical characteristics, and Atomic Force Microscopy (AFM) for surface morphology. Interscattered SAW electrodes producing surface acoustic waves in the hundreds of MHz are developed by photolithography and metalization techniques. SAW delay line sensor device testing, measurement and characteristics on both PLD and RF sputtered ZnO films are presented and compared.

2:45 PM D4.5 Fabrication of lead zirconate titanate thick film disks for micro transducer devices. Takashi Ijima, Shunko Ito and Hirofumi Matsuda, Smart Structure Research Center, AIST, Tsukuba, Japan.

A combination of the preparation techniques for the piezoelectric lead zirconate titanate (PZT) films and the micro machining of Si is considered to be an effective way to fabricate micro electromechanical systems (MEMS), such as piezoelectric micro transducer devices for the electrical and medical fields. To achieve these devices 5-100 µm-thick ZnO films are required. Thin film preparation processes using chemical solutions, like sol-gel, have the advantage of a low firing temperature and dense microstructure despite the low film deposition rate compared with the screen printing process. Therefore, a chemical solution deposition (CSD) process is considered to be an attractive way to ensure compatibility with the Si micro-machining process and to fabricate MEMS devices. In this study, disk shape PZT thick film devices were successfully fabricated. Crack free 5-100 µm-thick Pb$_2$Zr$_{50}$Ti$_{50}$O$_{2}$(PZT) films deposited onto Pt/TiO$_2$/SiO$_2$/Si substrate using a CSD process. A 0.5 M PZT precursor solution was prepared from trihydrolyzed lead acetate, titanium isopropoxide, zirconium n-propoxide, and 2-methoxyethanol as the solvent. The process of spin coating and pyrolysis at 500°C was repeated five times, and then the precursor films were fired at 700°C for 5 min. This sequence was repeated 30 times. Pt top electrode and PZT layer were etched by reactive ion etching (RIE) process with Ar/CH$_2$F$_2$/mixture gas, and 100 µm diameter PZT micro disks were fabricated. The remnant polarization and coercive force of the fabricated disks were measured directly in a vibrating sample measurement (VSM) device and were 13 μC/cm$^2$ and E= 25 kV/mm, respectively. The piezoelectric constant calculation demonstrated that the PZT film was inclusions with PZT had about 220 mV/mm. This means that the ferrite and piezoelectric properties of the micro disks are compatible with that of the bulk PZT ceramics. Investigation of the resonance frequency for the PZT micro disk are undertaken now.

3:30 PM D4.6 Exploration of magneto-electric thin films using superlattice composition spreads. Kuo-Shao Chang, Materials science & engineering, U. of Maryland, College Park, Maryland.

Magnetoelectric materials are attractive due to the coexistence of charge polarization and magnetization. The magnetoelectric effect can be used to induce change in magnetization by applying electric field and induce electric polarization from applied magnetic field. One way to obtain magneto-electric materials is by combining piezoelectric and piezomagnetic materials. Such materials have previously been pursued in bulk composites. We are exploring fabrication of artificial magnetoelectric thin films by creating superlattice structures where piezoelectric materials and piezomagnetic materials are modulated in periods of multiple unit cells. In particular, we fabricate superlattice composition spreads where one end of the spread is a pure piezoelectric material and the other end is a pure piezomagnetic material. This technique allows us to study coupling of the two properties at nanoscale level and 2) systematically investigate magnetization of the two physical properties as a function of magnetic composition which continuously varies across the spread. In order to fabricate a superlattice spread, a series of alternating gradient thickness deposition controlled at a low lattice level is performed for two targets with end compositions using combinatorial pulsed laser deposition. We have thus far fabricated BiFeO$_3$ - CoFe$_2$O$_4$ and PtTiO$_3$- CoFe$_2$O$_4$ spreads. The lattice parameters of these materials are such that they can be grown together in a pseudo hetero-epitaxial manner. Microwave microscopy and scanning SQUID microscopy are used to determine the respective ferroic properties across the spreads. We have used that the composition region of CoFe$_2$O$_4$ phase can often exhibit reasonable dielectric constants and magnetization simultaneously. Thus, this technique allows us to select the composition region and the lagering structure where magnetoelectric effects can be potentially observed in individual samples.


We report a novel precursor suspension method where 65PMN-35PT ceramics and thick films can be processed at lower temperatures. The precursor suspension is made of PMN powders, Ti-isopropoxide, and Pb-acetate in an ethylene glycol solution. The sintering temperature for CoFe$_2$O$_4$ ceramics occurred at 1100°C and good dielectric properties of the PMN ceramics were obtained. The formation temperature for the perovskite phase in thick films occurred at 800°C. However, the sintering temperature remains higher than 800°C and the perovskite phase cannot be stabilized at such temperatures. The PMN powders used in the PMN PT thick film were produced using Mg(OH)$_2$-coated Nb$_2$O$_5$ powders. The size of the core Nb$_2$O$_5$, particles was found to affect the coercing behavior of Mg(OH)$_2$ and the sintering behavior of PMN PT. To improve the sintering of PMN PT thick films, studies involving the control of the solids loading and the dispersion of the particle suspensions will be presented.

It was shown that the addition of strontium in the precursor of lead titanate in ethylene glycol improves the rheological properties of the precursor or sol-gel deposition of thin films. Perovskite phase lead strontium titanate (PST) powders and PST films on Ti substrate were obtained after heat treatment at 450°C. Sintering decreases the tetragonality of PT powders and thin films. Dielectric properties of PST are better than those of lead titanate (PT). Deposition of PST films on Si substrate was also studied. Heat treatment of each layer at 450°C followed by a final 650°C annealing resulted in perovskite PST films with good dielectric and ferroelectric properties. Results of thin films of different thicknesses as well as films with different strontium concentrations will be presented.

4:15 PM D4.9
PZT Thin Film on Silicon Wafer by a Sol-Gel Method for Sensor Applications. Wei-Hong Shih, Zuyun Shen and Wan Y Shih; Materials Science & Engineering, Drexel University, Philadelphia, Pennsylvania.

Piezoelectric unimorph cantilevers have been shown to be excellent sensors for liquid viscosity and density determination, mass detection, in-situ detection of cells, proteins, and specific antigen-antibody binding. In order to fabricate micro/millimeter-scale sensors, we investigate the synthesis of PZT thin films on silicon wafers. Lead acetate, titanium isoproxide, and zirconium propoxide precursors with ethylene glycol as solvent were used to deposit PZT thin films in a clean room condition. Good ferroelectric PZT thin films were obtained with a dielectric constant of 800 and the saturated polarization of 94 μC/cm². By adjusting the precursor concentration, spun-coating speed and time, micron-thick films can be obtained without excessive repeated deposition.

4:30 PM D4.10
Synthesis and Characterization of Ca₁₋ₓSrₓCu₃TiO₉₋₀.₅ thin films for dielectric applications. R. Guzman; Maharaj Singh Tomar and R.E. Melgarro; Department of Physics, University of Puerto Rico, Mayaguez, USA, Puerto Rico.

There is a great deal of interest in Ca₃Cu₃TiO₉₅ system for dielectric properties in microwave applications. In the present work we have studied Ca₁₋ₓSrₓCu₃TiO₉₋₀.₅ for different compositions i.e. for x = 0.0, 0.05, 0.1, 0.3, 0.4, 0.5, 0.7, 0.9, 1.0. The material is synthesized by chemical solution route and thin films were deposited by spin coating. Both powder and thin films were investigated by X-rays, Raman spectroscopy and dielectric spectroscopy. The result indicates stoichiometric films for all compositions and high dielectric values have been achieved.

4:45 PM D4.11
Nanoscale Investigation of polar structure of (1-x) PbMg₀.₃₃Nd₀.₃₃O₋₀.₅PbTiO₃ single crystals. Vladimir Shvartsman; Maciej Wojtasi; Sergey Vakhshurin; and Andrei Khokhlov; 1; Ceramic and Glass Engineering, University of Aveiro, Aveiro, Portugal; 2; Faculty of Chemistry, University of Wroclaw, Wroclaw, Poland; 3; A.F. Ioffe Physico-Technical Institute, St. Petersburg, Russian Federation.

Relaxor ferroelectrics based on Pb(Mg₀.₃₃Nd₀.₃₃)O₋₀.₅PbTiO₃ (PMN) attract significant interest due to their excellent dielectric and piezoelectric properties. The unique properties of relaxor ferroelectric materials are associated with the formation of nano-sized polar regions with a short-range order, while macroscopic ferroelectric order does not develop in the absence of sufficient external electric field. In solid solution between relaxors and "classical" ferroelectrics the gradual transition from relaxor to typical ferroelectric behavior is observed. Even though these compositions were intensively investigated in the past, little attention has been paid to the studies of domain structure and its evolution under applied electric field. The common optimal methods have limited resolution and are appropriate only for the observation of "normal" domains having the sizes of the order of microns. Recently, the PFM (Piezoelectric Force Microscopy) [1] has been successfully applied for the investigation of ferroelectric materials at the nanoscale. The advantages of the PFM are extremely high spatial resolution (down to few nanometers) and high sensitivity to local polarization, which make this method well suitable to study the relaxors. We report here our results of the investigation of local piezoelectric properties of (1-x) PbMg₀.₃₃Nd₀.₃₃O₋₀.₅PbTiO₃ (PMN-PT) single crystals by PFM. Piezoelectric contrast has been observed in 0.35PMN-1.1PT single crystals indicating spatial distribution of polarization and related to the existence of polar clusters. The observed domain structure is found to drastically change with increasing Ti content. In particular, in the composition with x = 0.2 the domain structure already combines both relaxor and ferroelectric features. Finally, in 0.65PMN-0.35 PT only micron-size ferroelectric domains have been observed. The evolution of the polar structures under temperature and external electric field was also investigated. The nature of the observed phenomena is discussed based on the current understanding of the relaxor state in ferroelectrics and possible influence of PFM instrumentation.

SESSION D5: Poster Session: Electroactive Polymer (EAP) 2
Chair: Cheng Hung
Tuesday, December 2, 2003
8:00 PM
Exhibition Hall D (Hyves)

D5.1
Abstract Withdrawn

D5.2

Field-type electroactive polymers (EAPs) are promising for high-performance actuators and artificial muscles due to their high electromechanical conversion efficiency. There are two main classes of field-type EAPs, one is [PVDF-TrFE] based relaxor ferroelectric electroactive polymer developed by Penn State, which has high modulus (~1GPa), but relatively low strain (~5%), and the other is soft dielectric elastomers based on Maxwell stress effect developed by SRI, which has high strain (~100%), but low modulus (~1MPa). When field-type EAPs are applied in biomedical field, higher performance such as high strain, modulus and elastic energy required is especially, for the development of artificial heart. The key issue is that these polymers usually require high electric fields (≥100 MV/m) to generate high elastic energy density which limits their applications. For Maxwell stress (electrostrictive force) based electromechanical materials (MSEAP), both the field induced strain and electromechanical coupling factor are proportional to the ratio of the dielectric constant, K to modulus, Y of the electroactive materials. Hence, high strain and high coupling factor under low electric fields require either a high dielectric constant or a high ratio of K/Y. By optimizing the ratio of K/Y, higher strain can be realized under lower electric field. In this paper, with the combination of the electromechanical properties of hard electroactive ferroelectric polymers and soft dielectric elastomers, three methods will be utilized and demonstrated based on polymer molecular engineering: 1) Improved electromechanical performance from high-dielectric-constant fluoropolymer polar elastomers by electron irradiation or chemical cross linking; 2) Polymer blends or semi-interpenetrating polymer networks (sIPN) based on high-dielectric-constant fluoropolymers and soft dielectric elastomers; 3) Synthesis and characterization of hard ferroelectric/soft dielectric block and graft copolymer elastomers: new dielectric-ferroelectric polymers with large induced strain under low electric field. In these block elastomers, high-dielectric-constant telechelic fluoropolymer hard segments containing reactive terminal groups in opposite chain ends was first synthesized, which can be extended to long chains by polycondensation with telechelic dielectric soft segments.

D5.3

Conducting polymer-based electroactive polymer (EAP) actuators have found numerous applications. Well-defined nanoscale structures are expected to amplify the electrochemical response of EAPs, facilitating larger dimensional changes. Toward this end, efforts are directed to gain control over the microstructures of such materials. Three different norbornene derivatives having electroactive pendant groups were copolymerized with a 70:30norbornene derivative via ring-opening metathesis polymerization. In addition to considering mechanical strength and flexibility, the poly(70:30norbornene) backbone is expected to facilitate ion transport across the bulk material. The cyclic voltammograms of the electrolytized polymer block copolymers displayed redox waves over a broad range of potentials. Processing of EAPs via electrospinning facilitates fabrication of devices having enhanced switching speed of actuation. The morphologies of these block copolymers studied by various microscopic techniques will be also discussed.

D5.4
Structural and Electromechanical Study of Poly(vinylidene fluoride-trifluoroethylene)-Based Composites. Bob Klein; James Rust; and Qiming Zhang; 1 Materials Research Institute, Pennsylvania State University, University Park, Pennsylvania; 2Materials Science and Engineering, Pennsylvania State University, University Park, Pennsylvania.
The PVDF-TrFE copolymer has found wide application in electromechanical devices, due to its ferroelectric properties. Recently, high-energy electron-irradiated PVDF-TrFE copolymer has been shown to produce large electrostrictive strain. Results indicate that the terpolymer made by adding chlorotrifluoroethylene (with varying amounts of trifluoroethylene) to the VDF-TrFE chain can improve upon the irradiated copolymer, with an increase in strain response and reliability and a decrease in processing cost. Through better understanding of the relation between termonomer choice, morphological changes, crystallization effects and the electromechanical properties, the strain and energy density of PVDF-TrFE-based terpolymer can be further optimized. The conformation and morphology changes of the polymer backbone influence formation of the poly(vinylidene fluoride-trifluoroethylene) with small amounts of chlorotrifluoroethylene or chlorotrifluorohyrene were studied by X-ray diffraction, infrared spectroscopy, differential scanning calorimetry, and polarization loops. Results indicate that quenching from a high crystallization temperature to a lower temperature forms a non-polar phase, while cooling has a crystallizing at a lower crystallization temperature produces a more non-polar phase. Essentially, the termonomer disrupts the VDF-TrFE polarization coherency enough that the crystallized phase has conformations with varying degree of polarity, with preference dictated by the thermal history. The effect of the termonomer appears to be due to inclusion. The width of the [100] X-ray peak indicates very thin crystalline regions, and the lamellar thickness is greater than 150 nanometers. If established by a properly chosen crystallization temperature, the crystalline regions can be polarized with applied electric field, or released into a non-polar state heating the crystalline regions, which is a suitable method. The crystallization arrangement also determines the strain response and electromechanical coefficients, which are crucial for electromechanical energy conversion.

D5.5 Device Design and Mechanical Analysis of Conducting Polymer Actuators. Bryan S. Schmid1, Peter Madden1, John Madden1 and Ian Hunter1;Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; Electrical and Computer Engineering, University of British Columbia, Vancouver, British Columbia, Canada.

Conducting polymers, specifically polyurethane, have tremendous potential as actuators. Various device designs using polyurethane as an actuator were theoretically investigated and built for potential advancements in current technology and practice. Two key limitations to using conducting polymers in practical devices include the need for actuation out of a liquid electrolyte solution and the small strains produced by the polymer. Development of a polyurethane trimorph design and various encapsulation techniques were tested as potential solutions to these issues, with the goal of improving upon existing technologies. The trimorph design is composed of two mecanoronic polyurethane electrodes separated by a gel electrolyte and ion-permeable layer. Several encapsulation techniques expanded the environmental conditions under which the actuator could function. This is a significant improvement, as previous designs have been limited to certain environments. The trimorph design and encapsulation techniques are proven, viable solutions for actuator design. Trimorph samples tested in this paper consisted of two 25 µm thick polyurethane sheets, 65 µm thick nylon mesh, and a 0.4 mm thick electrolyte gel. Final trimorph sample dimensions were 15 mm by 30 mm with an average thickness of 280 µm. The trimorph strips demonstrated successful actuation out of a liquid electrolyte, produced forces of 0.2 N and strain curvatures up to 130 °C, while demonstrating a greater than 3 month shelf life.

D5.6 Analysis and Modeling of Electro-Mechanical Coupling In An Electro-Active Polymer-Based Actuator. Thomas A. Bowers1, Neville Hogben1, Patrick Anquetil1, Rachel Zime2 and Ian Hunter3; Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts.

A nonlinear constitutive model is formulated for electro-active polymers (EAP) to describe the energy coupling between electrical and mechanical domains. The polymer is modeled as a multiphase energy storage element with inputs from the electrical and mechanical domain. Using energy conservation methods, the general relationships between stress, strain, voltage, and charge are determined. The solution to thand crystallizing benefits and the device developed fully and compared to a linear model published by Madden and a nonlinear electrochemical model published by Mazzei et al. Additionally, experimental data from a conducting polymer actuator composed of polyurethane are used to validate the electro-mechanical coupling model. It is found that the correlation between the model and experimental data is very good for strains up to 4% and potentials up to 1 V; these within the typical operating range of polyurethane. The model is efficiently simply to allow real-time control while also exceeding Madden’s linear model in its ability to accurately predict polymer behavior in normal operating ranges.

D5.7 Synthesis and Characterization of Sulfated Poly(3,4-(dihydroxythiooxy) Doped Polyurethane Actuators. R. Martinez, Patrick Vel1, Timothy Swanger3 and Ian Hunter2; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts; Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

Conducting, electro-active polymers are very promising materials due to their potential applications in bioelectronics, especially muscle-like actuators. New molecules exhibiting molecular conformational changes are being developed, but films synthesized from these new molecules are often lacking in durability and mechanical robustness compared to Polyurethane. A polyimide dopant can be added to help improve the mechanical properties of the film. However, the new molecular actuator systems are not well understood and the effects of the polyimide dopant on actuator properties unknown. For this reason, Polyurethane (a well-studied electro-active polymer) was deposited in the presence of 0 to 2% (wt sulphated poly(3,4-(dihydroxythiooxy)) (SPHE) to form a robust, electro-active polymer composite. The polyimide presented herein has a high molecular weight (1000 g/mol) and a flexible polymer chain. It replaces the salt typically used to dope the conducting polymer during electropolymerization of the polymer film. The resulting film’s electrical, passive mechanical and active mechanical properties were investigated, and it was determined that through use by an order of magnitude depending on the concentration of SPHE present in the deposition solution. Results have shown that it is possible to tailor the electrical conductivity between 20 S/m and 300 S/m and the elastic modulus between 0.5 GPa through co-deposition of Polyurethane and SPHE. In addition, the active strain can be varied by much as 90% for a given set of electrochemical conditions.

D5.8 High Strain P(VDF-TrFE) based Terpolymer for BioMEMS and Microfluidic Devices. Feng Xin1, Rob Klein2, François Bunte3, Srivas Tallapragada1 and Q. M. Zhang1; The Penn State University, University Park, Pennsylvania; Institut Franco-Allemand de Recherches de Saint-Louis, Saint-Louis, France

BioMEMS and microfluidic devices have gained a lot of attention in recent years due to their emerging applications in biochemical analysis, medical diagnosis, chemical analysis and synthesis, drug discovery and drug delivery, biosensing and biomimetic systems. The materials requirements for bioMEMS are biocompatible, chemically modifiable, easy to fabricate, economic, compilable and smart. Among various materials, the electro polymeric materials can best meet these requirements. Recently, we developed a group of P(VDF-TrFE) based terpolymers which have very high strain level and high energy density. The high strain level and strain energy density are about 7% and 4.5%, and the elastic energy density is around 1.1 J/cm³, which are very attractive for the development of polymer pump, valve and other microfluidic components for all polymer-based biomedical and microfluidic integration systems. The direct positive effects on the entire integration of these microfluidic components using the electroactive terpolymers for bioMEMS, including the multi-layer fabrication, surface modification from hydrophobic to hydrophilic using oxygen plasma etching, and polymer-coated valve and pump.

D5.9 Effects of UV and Gamma Irradiation on the Ferroelectric Behavior of Poly(vinylidene Fluoride-Trifluoroethylene) Copolymers. Luiz Oliveira de Farias1, Cesare Welter2 and Roberto Luiz Moreira2; 1Materials and Nuclear Fuel, Centro de Desenvolvimento da Tecnologia Nuclear, Belo Horizonte, Minas Gerais (Brazil); 2Physics, Universidade Federal de Minas Gerais, Belo Horizonte, Minas Gerais, Brazil.

P(VDF-TrFE) copolymers with 50% of trifluoroethylene were irradiated with gamma and UV rays in order investigate the effects of photodegradation in their ferroelectric properties. Dielectric and calorimetric investigations have confirmed that gamma irradiation provokes the appearance of relaxor ferroelectric features in the copolymer. These induced relaxor properties are thought to be linked to the loss of stability of the ferroelectric domains, provided by interruption of the long-range dipolar interaction. FTIR spectrometry revealed the presence of NH molecules which may take part of gamma induced cross-linking bonds, possibly affecting the ferroelectric domains stability. On the other hand, the UV irradiation does not induce ferroelectric relaxor features on the copolymer. However, it was found that the dielectric loss changes from an Arrhenius to a Vogel-Fulcher-like behavior during the ferroelectric to paraelectric
phase transition, with a decrease in the activation energy when compared to the gamma irradiated one. These results could have direct impact in the electromechanical response of the copolymer.

D5.10 Development of Totally Synthetic Glucose-Responsive Polymer Gel for Use as a Novel Type of Insulin Delivery Device, Akira Masumoto and Kuzumori Kusaka, Graduate School of Engineering, The University of Tokyo, Tokyo, Japan.

Over the past several decades, stimuli-responsive polymer gels have attracted a great deal of research interest. A series of stimuli that includes heat, pH, electric fields and light have been demonstrated to induce abrupt changes in the physical properties of polymer gels. This knowledge led to development of various types of stimuli-responsive, hence "self-regulated" systems so-called "intelligent" materials. Among wide range of their applied fields, applications in the medical field such as the drug delivery systems are of a constant research topic. We attempt to develop a totally synthetic, glucose-responsive polymer gel system, aiming for use in self-regulated insulin delivery system to treat diabetes. As a synthetically available sensor moiety for the blood sugar level, we pay particular attention to the unique ability of phenylboronic acid to form a reversible, covalent bonding with glucose. We have previously reported that a gel composed of N-isopropylacrylamide and 3-acylamidophenylboronic acid exhibits a reversible volume change synchronized with a change in the glucose concentration, through which the sufficiently controlled and pulse-shaped release of insulin was achievable at 38°C in a pH 9.0.

This work is intended to provide a synthetic methodology to optimize the operational condition of the system. The approach involves the use of a newly synthesized phenylboronic acid derivative possessing an appreciably low pKₐ as glucose sensing moiety, as well as the adoption of a different type of main chain structure that exhibits critical solution behavior in the range close to physiological temperature. Evaluations of glucose dependent changes in the swelling degree of the resultant copolymer gels for varied pH and temperatures revealed a markedly improved sensitivity near the physiological conditions. Discussion will be presented in terms of the effect of the modulated copolymer gel structure on the glucose responsive behavior.

SESSION D6: Poster Session: Ferroelectric, Piezo, and Dielectric Materials and Devices
Chair: Feng Xia
Tuesday Evening, December 2, 2013
8:00 PM
Exhibition Hall D (Hyatt)

D6.1 Study of structural ordering in (0.3)Pb(In₀.75Nb₀.25)O₃-(0.7)Pb(Mg₀.5 Nb₀.5)O₃ ceramics by transmission electron microscopy, C. Wu, T. Qi and K. Z. Balsis-Kahal, Department of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, Hong Kong.

Transmission electron microscopy (TEM) studies of the ceramics (0.3)Pb(In₀.75Nb₀.25)O₃-(0.7)Pb(Mg₀.5 Nb₀.5)O₃ (abbreviated as 0.3PIN/0.7PMN) revealed long-range structural order (LRO), short-range order (SRO) and mixed-order (MO). The ceramics, synthesized using mixed-oxide route, have important properties exhibiting negligible slim P-E loop and non-hysteresis electromechanical behaviour at room temperature. TEM observations of the LRO domains and their anisotropic boundaries imaged along <110> and <112> directions show uniform size distribution ranging from 20 to 150nm across. Domains in the proximity of grain boundaries within a grain are several times larger than the domains at the centers of the grains. High-resolution TEM images taken along [001] show clusters of lattice fringes with different contrast. Simulations indicate that the combinations of the three different cations, Mg²⁺, Nb⁵⁺ and Pb⁴⁺, are arranged to form a long-range ordering arrangement in the B-site. The clusters are therefore chemically distinct regions. In addition to the 11-long range order, these clusters could form a mixed structural ordering resulting in nano-scale ordered domains. Mixed ordering is a highly random process and takes place due to the combinations of the various cations present, thus creating a superstructure. Diffuse scattering and streaking were also observed in selected area diffraction patterns along various directions particularly along high order zone axes. The formation of specific mosaic patterns, indicative of short-range ordering, which could partially originate from A-site disorder. In 0.3PIN/0.7PMN, three different combinations of the B-site cations, Mg⁴⁺, Nb⁵⁺ and Pb⁴⁺, exist simultaneously. The electrical changes of the Mg⁴⁺/Nb⁵⁺ pair cannot simply balance in a perovskite structure, although the overall electrical change of the solid solution is neutral.

Such localized order and disorder result in different microdomains with slight misorientations. They give rise to the continuous diffuse scattering between the fundamental Bragg reflections instead of a set of distinct reflections generated by long-range periodic structure. In addition to the LRO, which can also be found in certain other Pb-biased complex perovskite materials, a new mixed state of structural orderings, SRO and cluster order in different scales were observed. This mixed ordering contributes to chemical inhomogeneity, which has implications on the performance. Consequently, the behavior of the ferroelectric relaxor is enhanced, especially affecting the temperature dependence of the dielectric properties.

D6.2 Nanoscale ferroelectric properties of PZN-PT single crystals studied by scanning force microscopy, Igor Bokhon'k, Vladimir Shvartsman and Andrei Khoklin; Department of Ceramics and Glass Engineering, CICECO, University of Aveiro, Aveiro, Portugal.

The nature of the excellent electromechanical properties of ferroelectric single crystals of solid solutions [1-x]Pb(Zn₁/₃Nb₂/₃)O₃-xPbTiO₃ is intensively investigated during last several years. These crystals are expected to replace traditional piezoelectric materials such Pb(Zn₁/₃Ta₁/₃)O₃ in actuators, transducers and smart systems. Recently, the Scanning Force Microscopy has been modified to study the piezoelectric properties at the nanoscale. This new technique, called Piezoresponse Force Microscopy (PFM), was applied for the visualization of domain structure by means of the piezoelectric effect and for the measurements of local piezoelectric coefficients by applying voltages and measuring the corresponding responses. In this work, high-resolution PFM piezoelectric measurements have been performed on [1-x]Pb(Zn₁/₃Nb₂/₃)O₃-xPbTiO₃ (PZN-PT) single crystals of the composition close to the morphotropic (rhombohedral-tetragonal) phase boundary (x=0.05±0.005).

Irregular domains sizes 301±10 nm have been observed on the [001]-oriented surfaces of unpoled samples. On the contrary, [111]-oriented surfaces exhibited normal micro-size regular domains with the domain boundaries directed along allowed crystallographic planes. The existence of nano-scale domains in the [001]-oriented crystals was attributed to the relaxor nature of PZN-PT where small polarization clusters may form under zero-field-cooling (ZFC) conditions. The average size of these polarization clusters is ~10 nm at room temperature as estimated earlier from neutron experiments. It is hypothesized that the presence of the highly polarizable Ti⁴⁺ ions in PZN-PT promotes interaction between clusters, which can then reorient and merge into the micro-size domains upon cooling. These nano-domains can be, in principle, considered as the nuclei of the opposite polarization state that erase the switching process for this particular crystal cut. Local piezoelectric hysteresis has been also performed by PFM on the nanometer scale. Similar switching behavior of [111] and [001] oriented PZN-PT crystals suggests that their superior piezoelectric properties are related to the domain wall motion and is not an intrinsic property of the material. Nanoscale data are complemented with conventional dielectric, ferroelectric and piezoelectric measurements. I. D. La Oramagashvili, J. Tkachuk, Z.-G. Ye, W. Chen, R. Erwin, and J. L. Roberts, Phys. Rev. B 67, 134110 (2003).

D6.3 Off-center Cu⁺⁺ Ions in Ferroelectric Lead Germanate, Michael P. Tschöke, Victor M. Duda and Yuriy D. Krokhin'; solid state physics dept., Dniepropetrovsk national university, Dniepropetrovsk, Ukraine.

New ferroelectric phase transitions off-center impurities may play an especially important role. In the abstract we report the results of electron paramagnetic resonance (EPR) measurements, performed on lead germanate Pb₃GeO₃(OH) (PGO) crystals doped with copper ions. The microstructure of the Cu⁺⁺ EPR spectra shows that paramagnetic ions occupy three structurally equivalent positions of C₃ symmetry coordinated by Ge-OH units. The spectra have been described by spin Hamiltonian with nearly g=2 and hyperfine A=0.5 mmT. The temperature evolution of Cu⁺⁺ spectra have been studied in the interval from 200 to 450 K. On heating the transition line with broadening occurs and move to higher temperatures (C₃) Cu⁺⁺ spectra transform into one broadened line, demonstrating C₃ local symmetry. The data obtained give evidence that Cu⁺⁺ substitution for Pb⁺⁺ host ions in positions of C₃ point symmetry and occupy off-center positions shifted from trigonal lattice point in [001] plane. Thermally activated hopping of Cu⁺⁺ ions between off-center positions motionally averages the low symmetry tetragonal spectra. Since the off-center localization has to induce the electric dipole moments, to confirm this assumption we have investigated the dielectric response of PGO Cu⁺⁺ and revealed the dielectric loss peaks typical for thermally activated relaxation processes. EPR and dielectric data testify for Arrenius-like temperature behaviour of Cu⁺⁺ hopping rate and permit to estimate its parameters ($\tau = e^{-\Delta E/kT}$)}.
Hz, $\Delta \omega = 0.24 \text{ eV})$. The static and dynamic properties of Cu$^{2+}$ centers have been attributed to pseudo Jahn-Teller effect. Influence of the orientational order of Cu$^{2+}$ centers on the PGO properties near ferroelectric phase transition is discussed on the basis of semi-phenomenological approach.

D6.4 Temperature Dependence of Piezoelectricity in Pb$_2$(Bi$_2$Na$_{0.5}$Ti$_{3}$O$_{10}$)O$_3$ (PBN) based single crystals (B=Zn, Mg).

Park Jung Suk$^1$, Park Hye Eun$^1$, Yi Jae Yoon$^1$, Lee Jong Kun$^3$ and Hong Kyo-Sun$^1$.

$^1$School of Materials Science and Engineering, College of Engineering, Seoul National University, Seoul, South Korea.
$^2$Korea Research Institute of Chemical Technology, Daejeon, South Korea.
$^3$Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545, New Mexico.

Dependence of piezoelectricity on temperature in Pb$_2$(Bi$_2$Na$_{0.5}$Ti$_{3}$O$_{10}$)O$_3$ (PBN) based single crystals will be presented. Though ultra-high piezoelectric properties are observed in (001) oriented rhombohedral Pb$_2$(Bi$_2$Na$_{0.5}$Ti$_{3}$O$_{10}$)O$_3$ - PbTiO$_3$ (B=Zn, Mg) crystals (PBN - PT), there are a few limitations to prevent the application of piezoelectric relaxor based single crystals. Most of these problems are related with the temperature stability of piezoelectricity, which decreases the reliable operation of piezoelectric materials. In this study, the tempeature effect on piezoelectricity is evaluated precisely and the modified material to compensate these shortcomings is investigated. The temperature dependence of piezoelectric properties was found to be consistent with the phase transition behavior of $<001>$ oriented crystals. With decreasing the stability of B-field engineered state, the piezoelectric properties of crystals deteriorated. Also, the addition of microwaves with high Te to PBN based crystals lead to stably engineered domain configuration and the piezoelectricity against the temperature.

D6.5 Some Properties of Incommensurably Disordered Rb$_2$ZnCl$_4$ Crystals. Michael P. Trubetsky, solid state physics dept., Dniepropetrovsk national university, Dniepropetrovsk, Ukraine.

Applying of the radioscopical techniques has allowed to achieve the noticeable progress in studying of the incommensurably modulated phases. Just the local nature predetermines the successes of the magnetic resonance methods, since the spatial averaging of structural disorder can strongly reduce the efficiency of the macroscopic experimental methods. In particular, the valuable information on static and dynamic properties of incommensurate systems has been obtained via EPR investigations of Mn$^{2+}$ probe in Rb$_2$ZnCl$_4$ (RZC) crystals. It has been shown that Mn$^{2+}$ centers, substituting for Zn$^{2+}$ ions, are localised in chlorine tetrahedral complexes whose rotations result in modulation of the structure. The EPR data give evidence that Mn$^{2+}$ is a suitable probe, correctly reflecting the properties of the crystal bulk. In the temperature interval of paramagnetic-incommensurate transition point $T_c$ = 304.4 K the EPR spectra of Mn$^{2+}$ ions have been studied for various orientations of the external magnetic field. The singularity spectra, typical for modulated phases, have been observed on cooling below $T_c$. The computer simulations of the singular line shape permit to estimate the critical exponents of the order parameter $\beta = 0.35$ and correlation length $\nu = 0.64$. It has been shown, that just below $T_c$, the line width of central peak is influenced by amplitude fluctuations of the modulation wave whereas the contribution of phase fluctuations dominates in the middle, flat part of the singular spectrum. The values of the critical exponents $\beta$ and $\nu$ confirm the non-classical character of the RZC critical properties corresponding to the universality class of 3d XY Heisenberg systems.

D6.6 Structural and Dielectric Properties of CaCuTi$_{4}$O$_{12}$ Thin Films. Vinay Gupta$^1$, Ram R Das$^2$, Pijush Bhattacharya$^3$, Yuri I. Bryuk$^4$, William Perez$^2$ and Ram S. Kruij$^5$.

$^1$Department of Physics, University of Delhi, Delhi, India.
$^2$Dept. of Physics, University of Puerto Rico, San Juan, Puerto Rico.

Recently, there is a current surge for the enhancement of dielectric permittivity of oxide thin films for various functional devices. CaCuTi$_{4}$O$_{12}$ (CCT) was found to be an interesting material that exhibiting bulk dielectric constant over 100. In this study we have used pulsed-laser-deposition technique to grow CCT thin films on Pt/TiO$_2$/SiO$_2$/Si and LaAlO$_3$ substrates. During the thin film deposition, the substrate temperature was varied in the range of 300-500°C, with fixed oxygen pressure at 200 mTorr. As-grown films are post-annealed at 750°C in order to improve the crystalline quality of the films. X-ray diffraction showed polycrystalline nature of the films. A systematic variation of the grain size with substrate temperature was observed by X-ray micro-diffraction. The temperature dependence of the crystallities was studied by X-ray micro-diffraction. The temperature dependence of the X-ray micro-diffraction suggests that the XRD patterns of the films show a peak at around 750°C, suggesting that the films are fully crystalline at this temperature. The crystallite size was determined from the full width at half maximum (FWHM) of the (111) peak using the Scherrer formula. The crystallite size of the films decreases with increasing substrate temperature, indicating a decrease in the grain size. The temperature dependence of the dielectric constant was studied by measuring the dielectric constant as a function of temperature in the range of 25-200°C. The dielectric constant of the films increases with decreasing temperature, indicating a semiconductor-like behavior. The temperature dependence of the dielectric constant is consistent with the theoretical predictions for the CCT thin films. The dielectric constant of the films was found to be around 1000 at room temperature. The temperature dependence of the dielectric constant was found to be consistent with the theoretical predictions for the CCT thin films. The dielectric constant of the films was found to be around 1000 at room temperature.

D6.7 Structural and dielectric properties of Ca$_{0.7}$ Mg$_{0.3}$Cu$_{0.5}$Ti$_{3}$O$_{12}$. Luis A. Bermudez and Maharaj Singh Tomar, Department of Physics, University of Puerto Rico, Mayaguez, USA, Puerto Rico.

Ca$_{0.7}$ Mg$_{0.3}$Cu$_{0.5}$Ti$_{3}$O$_{12}$ is seen to be a novel dielectric ceramic material for microwave applications due to its high dielectric constant value. This material has been synthesized by chemical route for different compositions and thin films have been deposited by spin coating. X-ray diffraction shows highly stoichiometric films for different compositions. Dielectric measurement indicates high value of dielectric constant, results will be presented.


Despite piezoelectric transformers (PTs) being invented in the late 50s, this technology did not reach commercial success until early the 80s, because the $\Delta \omega$ during this period, several companies, mainly STN and BAX, decided to introduce PT technology for applications requiring small size and low electromagnetic interference (EMI) signature. Since then, PTs have been used as step-up transformers for the CCFL inverter used for backlighting the liquid crystal display of notebook computers and personal digital assistants (PDA). In these applications, PTs provide: i) high voltage gain ratios, ii) high power density - typically about 10W/cm$^3$, iii) high output impedance, iv) high efficiency and v) low EMI. Currently, PT applications for CCFL are limited to 5.8W. In the last decade, the interest in PTs has moved toward a second group of applications beyond CCFL backlighting. Companies in U.S., Japan, and Europe are now investigating the use of PTs for power applications, including battery chargers, linear and compact fluorescent ballasts, DC/DC converter, power supplies and others. In these applications, compared to the CCFL, the requirements include i) step-down transformers, ii) high power transformers, iii) high efficiency power conversion, iv) low output impedance, v) input to output isolation and v) low content of EMI. New topologies of PTs have been proposed to address higher levels of power conversion than those available with the classical Rosen type PTs (typically use for 5.8W with power densities of about 5.1W/cm$^3$). This is the case of the laminated piezoelectric transformers, Transon $\textregistered$, patented and commercialized by Face Electronics. In these transformers power densities of over 40W/cm$^3$ have already been reported for step-down applications. A third group of PTs has been recently proposed by Face Electronics and granted under two ongoing SHB projects for use in the new generation of communication satellite systems as well as space research. Among others, these applications include i) high voltage power supplies for satellites, ii) battery chargers, iii) Traction Wave Transformers amplifiers used for satellite communication, and ii) high voltage igniters for controlling the ignition process of Pulsed Plasma Thrusters used for positioning the new generation of small satellites. These applications are characterized by a combination of high power and high voltage requirements (making them doubly complex), the need for high reliability and, in some cases, the ability to withstand extreme environmental conditions. This paper introduces the ongoing research on space applications for PTs.


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The internal stress distribution in multilayer actuator was analyzed by Finite Element Method (FEM) program. Around the edge of control layer and inter-digital electrodes, the nonuniform electric field generated the stress concentration, which caused the ceramic to crack. To decrease the stress concentration, various internal electrode configurations were presented such as plate-through type, slit-insert type, and non-electrode type. The results showed that the slit-electrode type can decrease the stress concentration of inter-digital type in approximately 1/3.
mechanisms revealed a further dependency of the ferromagnetic hysteresis on the applied thermal annealing. Magnetization of Ni$_5$Mn$_{30}$Ga$_{20}$ thin films sparked interest in this material in a small effort of about 300 ppm limited due to the polycrystalline structure of the film. Financial support provided by the Office of Naval Research (N00014-03-1-0931) is gratefully acknowledged.

9:15 AM D7.3 Theory and Modeling of Gradient Shape Memory Alloy Actuators, Alexander Rayburn1, Victor Rayburn2 and Julia Slasker1
1University of Maryland, College Park, Maryland; 2NIST, Gaithersburg, Maryland; 3Rensselaer Polytechnic Institute, Albany, New York.
A new concept of bending actuation in which the transformation in a SMA active layer proceeds by the movement of phase interfaces or intermediate two-phase zone is presented. The interface movement is determined by gradient of temperature or composition across the thickness of an active layer. The bending of the film is a result of selfstrain in a transformed part of the film. Calculation of the elastic energy of internal stresses show that there is an equilibrium position of interface, which can be shifted by a thermodynamic driving force. Thus, it is possible to obtain a reversible movement of interface by changing temperature. Combining SMA film with top or bottom passive layers of different elastic properties, thickness and misfit it is possible to optimize the actuation deformation. The kinetics of interface movement is quantitatively described by solving a Stefan-type problem with an equilibrium temperature at the interface between phases dependent on interface position. The computational technique has been developed to control dynamics of the actuator through the variation of temperature at the top and bottom of the active layer. The effect of compositional gradient on dynamic actuation is discussed. The work is supported by AFOSR, Grant #F4962001101110.

9:30 AM D7.4 Characterization and Featureization of Re-Pd Shape Memory Thin Films, Yuki Sugimura and Jos日Vlasic1, DEAS, Harvard University, Cambridge, Massachusetts.
Thermally activated shape memory materials such as Ni-Ti alloys are widely used as functional materials in sensors and actuators. However, heat transfer issues in these materials may limit their application in devices that require rapid response. Magnetically driven shape memory effect in select ferromagnetic alloys offers potential for faster response time as well as controllable actuation, expanding the range of application of these materials. Ferromagnetic shape memory alloys such as the Fe-Pd system have been studied in detail in bulk form by a number of researchers. While thin films are more suitable for miniature devices research activities in Fe-Pd thin films have begun only recently. The thermoelastic austenite-to-martensite transformation takes place over a composition range of approximately 28 to 32 atomic percent Pd in bulk Fe-Pd alloys. In recently published papers, Fe-Pd thin films were deposited from alloy targets of specific composition, making it the Pd content and Fe-Pd intermetallics. In this work we present the results from fabrication and characterization of Re-Pd thin films deposited using Fe and Pd elemental targets. Films are produced by dc magnetron sputtering in an UHV chamber equipped with three independent condensable sputter guns. The effect of process parameters and post-deposition thermal treatments on film composition, microstructure and stress are examined by Rutherford backscattering spectroscopy, x-ray diffraction, electron backscatter diffraction and substrate curvature technique.

9:45 AM D7.5 Phase Transformation in Ni-rich Ti-Ni and Ti-rich Ti-Pd Shape Memory Alloys, Masaru Nishida, Materials Science and Engineering, Kumamoto University, Kumamoto, Japan.
New equiatomic Ti-Ni and Ti-Pd alloys undergo thermoelastic martensitic transformation from B2 to B19’ and B19 structures upon cooling, respectively. The former is technologically important materials with their superior shape memory and superelastic properties. The latter is expected to be high temperature shape memory materials, since the transformation temperatures are around 800K. In order to complete the further improvement of both the alloys, various heat treatment have been proposed so far. In the present study, the phase separation processes in Ni-rich Ti-Ni and Ti-rich Ti-Pd alloys are briefly summarized. Subsequently, the mechanism of multiscale martensite transformation in both the alloys are discussed on the basis of thermal analyses and TEM observations. We demonstrate that the martensite transformation in the Ni-rich (Ti)Ni is considered to be a kind of artifact, which strongly depends on heat treatment atmosphere. On the other hand, that in Ti-rich Ti-Pd alloy is closely related to in-situ precipitation of Ti2Pd during the transformation cycles.
10:30 AM D7.6

In this research, we attempted to fabricate the Ti-Ni-Cu shape memory alloys by elemental powders by means of a pulse-current pressure sintering method that can produce high-density sintered compacts in a very short sintering time. We investigated the fabrication conditions of Ti-Ni-Cu alloys and the influence of Cu content in the alloys on the thermal and thermo-mechanical characteristics by experiments. The relative density of the as-sintered compacts was around 95% at any Cu content. The microstructure, tensile properties and thermal mechanical characteristics of the as-sintered compacts were improved greatly by performing a solid-state reaction and a shape memory treatment. The yielding behavior due to the stress-induced martensite in stress-strain curves changed with Cu content, and it became the lowest at some 30% Cu content. The tensile strength and elongation of the alloy were Cu content around 95% were more than 400 MPa and 6%, respectively. The alloys of higher Cu contents showed a superelastic like behavior, and the shape memory characteristics of the alloys were confirmed to be superior. The recovery stress of the alloys was almost the same level of that of the wrought materials. The cyclic deformation behavior of the alloys became stable after 15 cycles.

10:45 AM D7.7
Crack Tip FEIs and Fracture Behavior in a NiTi Shape Memory Alloy Sheet. Wei Tong, Ning Zhang, Chongxin Xie and Hong Tao, Yale University, New Haven, Connecticut.

Shape memory alloys such as NiTi are often used in MEMS and other applications in the field of thin strips. Fatigue failure is one of the important limitations in NiTi shape memory alloy products. We present an experimental investigation on the crack tip deformation fields and fatigue crack growth kinetics in a NiTi thin sheet of 0.25mm thick. The material is 54.8wt% Ni and 45.2wt% Ti with only a trace amount of O, H, and C. The external mechanical and thermal loads are controlled to induce various loads and size of crack tip deformation fields in each load cycle. Experimental results show a positive correlation on the crack tip field characteristics and the fatigue crack growth kinetics will be presented for the NiTi sheet. A micromechanical analysis of the crack tip field will also be given to identify some possible mechanisms on the fatigue damage in NiTi shape memory alloys.

11:00 AM D7.8

Single crystals of Ga$_x$Ni$_{2-x}$Al$_2$ have been synthesized using the modified Bridgman method. The ability to solidify and retain single phase B2 austenite was found to depend not only on the starting composition and growth rate, but also the ability to maintain sufficiently high cooling rates to avoid the precipitation of a Co-rich FCC phase during post-solidification cooling. DSC measurements on the single crystal found the Ms, Mf, As, and Aft to be 35.7, -1.8, 34.1 and 72.9°C, respectively. On subsequent heating the B2 phase was found to partially decompose into a Co-rich phase at temperatures exceeding 39°C, a decomposition temperature of 55°C. The phase B2 phase was tracked by DSC, high temperature powder diffraction, and microstructural observation. Restoration of the crystal to single phase B2 austenite required annealing of the crystal at temperatures above 1125°C.

11:15 AM D7.9
High Transition Temperature Shape Memory Alloys for Micro-actuator Systems. Elizabeth Baldwin and Alfonse Rabiet, Department of Mechanical and Aerospace Engineering, North Carolina State University, Raleigh, North Carolina.

A new generation of thin film shape memory alloy (SMA) for MEMS micro-actuator has been developed, in which film structure and chemistry are optimized, for enhanced transition temperature, high strain capability, and low actuation time. A novel TiNiSLAS process was developed to improve the heat transfer rates. Thin film TiNiSLAS was produced using ion beam assisted deposition (IBAD) technology followed by post processing heat treatment. Shape memory properties of thin film TiNiSLAS and their mechanical properties showed a great improvement over conventional NiTi thin films processed using sputtering technique. This is partly due to their higher transition temperature and more reduced actuation time by improving the heat transfer rates. Furthermore, the service-life of the new thin film SMAs increased by improving their micro structural properties. The desire to introduce this innovative technology to the field of SMA micro-actuators is based on two primary advantages of IBAD process over existing technology used to apply thin film SMAs. First, the chemical composition and grain size of the applied coating can be precisely controlled over a wide range of values. Second, the SMAs cannot be deposited as thin films with a grain size < 5 µm thick with a large grain size, much denser thin films applied with sputter deposition technology. These coatings had a higher interfacial strength and better fatigue resistance than the plasma sprayed coatings. The effect of various processing parameters and post processing heat treatment, on mechanical, and microstructural properties as well as their SMA properties were studied.

11:30 AM D7.10
Crystallography of Ni-Ti SMA in Austenite and Martensite by X-ray Diffraction Study. Misuzu Nogami and Hajime Kyono, Mechanical Engineering, Meiji University, Kawasaki, Kanagawa, Japan.

The crystal structures of the martensite and austenite in Ni-Ti shape memory alloy (SMA) are studied by X-ray diffraction. First, the program that estimates the crystallographic data of an alloy and analyzes its x-ray diffraction pattern is developed on the basis of the theory of the intensity of a particular diffraction peak. The patterns by the program are verified by the comparison with the data of single crystals of Si, Ni, and Ti. Next, we measure the diffraction pattern of Ni-Ti not using powder sample but also wire one by X-ray diffractometer because a wire of Ni-Ti SMA is widely used for application as an actuator and so on. Moreover, the crystal structure should be damaged if powder sample is made by the wire by milling and the curvature of wire surface has the same effect as the aggregate of powder for X-ray scattering. The diffraction pattern of Ni-Ti SMA is measured as the elevated temperature and its crystal structure is austenite phase. This pattern corresponds with the analyzed one from B2 structure by the program. Next, at room temperature the diffraction pattern of Ni-Ti SMA that is martensite is measured. This pattern is compared with the B19 crystal structures presented by R. Onsuka et al., R. F. Hehmann et al., G. M. Michal et al. and Y. Kudo et al. Although the x-ray pattern almost corresponds with that by Kudo, it remains the peak of B2 structure even though the temperature is below the martensitic transformation. The wire shows the shape memory effect. In order to consider the difference of B19 structures by each researcher, the relationship between the unit cell volume and the atomic ratio of Ni and Ti is obtained. The unit cell volume is proportional to the atomic weight percentage of Ti.

11:45 AM D7.11

SMAs are engineering alloys that recover extensive amounts of deformation when subjected to a temperature change. The recovery of deformation is a result of a phase transformation from martensite to austenite, for example, for NITINOL, a very popular SMA, the transformation occurs at 60°C. Actuation is a type of shape memory process that utilizes deformation recovery that is used in smart structural systems. These systems are designed to detect and control structural deformations due to external time varying loads encountered during functional operation. In this paper, the actuating properties of NITINOL are characterized using an analytical, computational, and experimental solution (ACES) methodology. Analytical models are utilized to calculate the deformation under static and dynamic loads. Finite element method (FEM) is used for computational investigations. Optical-electronic holography (OEH) is the experimental method utilized to obtain temperature dependent behavior of NITINOL. As a result of the phase transformation, NITINOL undergoes a stiffness change indicated by a change in the modulus of elasticity from 33 GPa to 73 GPa. Deformations of NITINOL samples subjected to static loads at different temperatures were measured indicating recovery of 85% due to the phase transformation. Addie, amplitudes of vibration were measured as a function of excitation frequency and temperature to determine the effect of these transformations. These show efficiency of Nitinol in development of smart structural systems.

SESSION D8: Electroactive Polymers 3
Chairs: Roy D. Kornbluh and Mohsen Shafipour
Wednesday Afternoon, December 3, 2013
Room 202 (Hynes)
1:30 PM D8.1
Ionic Polymer-Metal Composites as Smart Materials under Subzero Temperature Conditions, Kwan-Jen J. Kim and Jack Paugnette; Mechanical Engineering Department and Nevada Ventures Nanoscience Program, Univ. of Nevada, Reno, Nevada.

This paper presents a description of Ionic Polymer-Metal Composites (IPMCs) as an alternative solution for cold operation actuators. This is because of their capability for actuation with relatively low voltages, durability and capability of operating within the subzero region (T ≤ -40°C). The building blocks of IPMCs are ion-exchange membranes phases changed within the base polymeric material that results in an alteration of the performance of the material in terms of actuator performance. An experimental apparatus is constructed in order to have a controlled temperature environment in which to analyze the material. The results are presented and interpreted to show that there is definite promise for these low temperature polymeric actuators to operate in practical applications. Also, an effective process technique, namely, was attempted to obtain the optimized properties of the base polymeric materials.

2:00 PM D8.2
Hybrid Actuation in Coupled Ionic/Conducting Polymer Devices, Matthew Bennett and Dan Leo; Mechanical Engineering, Virginia Tech, Blacksburg, Virginia.

Ionic polymer membrane actuators represent a relatively new and exciting entry into the field of smart materials. Several key limitations of these transducers have prevented them from experiencing widespread use, however. For example, the bandwidth of these devices is limited by the frequencies by which the mechanical response is observed, at high frequencies by the low elastic modulus of the polymer. In this paper, an overview of the initial results of work with hybrid ionic/conducting polymer actuators is presented. These hybrid actuators are devices that combine the electromechanical coupling of ionic polymer actuators and conducting polymer actuators into one coupled device. Initial results show that these hybrid devices have the potential to offer marked advantages over traditional ionic polymer membrane transducers, including increased stress and strain generation and higher actuation bandwidth. Details of the preparation of these devices and performance metrics are presented and comparisons to baseline materials are made.

2:15 PM D8.3
Temperature-Responsive Polymers with Tailored Onset of Response, Evangelos Minaas and Mindnngs Rocatne; Materials Science & Engineering, Penn State University, University Park, Pennsylvania.

Thermoresponsive materials are central in applications involving chemical sensing and/or stimuldriven actuation. A systematic series of temperature-responsive polymers were synthesized and studied, and the onset of their T-response was tailored by design of the monomer. Their T-response was studied both for their water solutions, and when they were used to coat a surface, hydrogel and phase diagrams were done for the solutions, whereas water contact angle, ellipsometry, and atomic force microscopy were carried out for the embedded gels, as a function of grafting density. A universal dependence of the temperature of response on the monomer composition is found, and the onset of the response can be tailored by design in the range of 5-70°C in water. Model microfluidic devices employing these polymers as T-responsive gates were also realized.

2:30 PM D8.4

Piezoelectric unimorph cantilevers were explored for all-electrical soft-tissue elastic moduli measurements. The elastic moduli of soft tissues were obtained by simple electrical means using a dual electrode design: a driving electrode for force generation and a separate sensing electrode for deformation measurement. Accurate Young's modulus measurements were demonstrated with both indentation and compression tests of model elastic chaps as well as blood vessel plaques. Direct shear modulus measurements were also demonstrated using cantilevers with a L-shaped tip. Potential clinical applications for such a method were studied, namely, the possibility of using this stand-alone instrument for non-invasive detection or diagnosis of diseased tissue. The advantages of piezoelectric unimorph soft-tissue stiffness sensors include simple all-electrical measurements, accurate elastic moduli at very small strains (≤1%), local stiffness measurements that offer potential for tissue imaging. Further miniaturization will allow simple all-electrical soft-tissue stiffness imaging on the micrometer and nanometer scale.

2:45 PM D8.5
Exploration of an Electroactive Polymer as an Actuator for Microrobots, Christian Biedmeier and Wayne Water; Department of Mechanical Engineering, Rochester Institute of Technology, Rochester, New York.

The development of lightweight low power consumption actuators is critical to the development of micro-robots. The Electroactive Polymer (EAP), Nafton N-117, meets these requirements. In the actuation of an EAP, the current does not remain constant over time. A circuit model for current drain versus time to best predict the current behavior has been developed for Nafton N-117. While the material mimics a parallel plate capacitor, it has been found that capacitance plays no role in achieving steady state current levels. This development is critical to understanding and developing the material as a future actuator. This paper discusses the necessary developments required for the EAP actuator to be utilized in microrobotic devices. Specifically, the development of a lightweight reliable electrode for EAP material actuation, the current drain versus time model and equations, and microrobot applications are discussed.

3:30 PM D8.6
Switchable Window Based on Electrochromic(EO) Polymers, Chunye Xu, Liu Liu, Yuan E. Legenksi, Dui Ning and Minzu Tupa; University of Washington, Seattle, Washington.

Switching window technology is a continuously growing field due to its potential for architectural and automotive use. In this research, electrochromic (EC) polymer windows were fabricated to study the effect of temperature on the switching. The performance of the EC polymer windows was assessed using a Au-based counter electrode. Printed circuit board was utilized for carbon-based counter electrode. Lithography and sputtering were used for Au patterned glass counter electrode. Several kinds of polymer gel electrolyte were prepared for separate application. Color change of high contrast ratio of transmission of the window is rapidly obtained when even less than 2V is applied. The reproducibility of color changeable EC polymer windows was estimated by the method of electrochemistry and spectrophotometry.

3:45 PM D8.7
Self-assembly and applications of magnetorheological suspensions in microfluidic devices, Ranjan Hinegroom and Patrick Doyle; Chemical Engineering, MIT, Cambridge, Massachusetts.

Magnetorheological (MR) fluids are suspensions of colloids which acquire dipole moments under application of a magnetic field. Traditionally, these colloids have been used in microscopic applications, such as controllable dampers, where the ability to tune their bulk rheological properties with a magnetic field has been exploited. We have recently shown that the microstructures formed by the colloids in thin gaps can be used to efficiently separate DNA in microfluidic devices (Doyle et al. 2002). Here we investigate the self-assembly of MR fluids in microchannels using Brownian Dynamics simulations and compare our results to microscopic experiments. We study geometries in which the characteristic length scale of the colloidal microstructure is comparable to the channel dimensions. In this regime, we find that the crystal structure deviates from the usual hexagonal lattice commonly seen in static thin gap gaps. Rather, groups of particles interacting through long-range repulsive interactions.

Further fundamental understanding of self-assembly in confined geometries will allow for greater control of the porosity of colloidal matrices used for biomolecule separations in microfluidic devices.

4:00 PM D8.8
In vivo characterization of photoactivating and photothermal polymers, C. Sabey1, M. Moritzzusmann, G. Wirtz2, J. C. H. L. van den Heuvel2, J. E. M. van der Velden3, P. van der Weele4, A. Stroobants5, K. Vincent5, W. N. M. van Blitterswijk6, T. Vanwervelen7, A. J. M. van der Meer8, R. A. J. J. van Puijenbroek9, J. F. van Vliet3, and P. van der Zee1,1


department of 1Chemistry, 2Cell Biology, 3Engineering, 4Economics, 5Mathematics, 6Physics, 7Optics, 8Physics, 9Physics.

In vivo characterization of photoactivating and photothermal polymers
is based on the electrochemical double-layer (ECDL) separation of charges on an electrode from the ionic charges in solution. Briefly, when a short pulse of anodic or cathodic current is biased on or off, the electrodes, it expands or contracts if a voltage is applied between them and a counter electrode. Based on prediction, actuation is due primarily to changes in orbital and bond structure with a secondary contribution arising from double-layer electronic effects. However, the relative contribution and interaction between each of these mechanisms is unclear. We aim to elucidate actuation behavior using Raman spectroscopy (RS) and built a linear actuator from SWNTs. Spectroscopic experiments were carried out using aqueous electrolytes (LiCl, NaCl, KCl, KBr, K2SO4, and CaCl2) to order the clarification of the role of co-ion, if any. The variation of carbon bonding in nanotubes with applied potential was studied by in-situ Raman spectroscopy, because it can detect changes in C-C bond length (d(C-C)), through two of the most prominent bands (radial breathing mode; RBM at ~150 cm^(-1)), and G band at ~1600 cm^(-1)). In addition, the interaction between both the modes varies with the occupation of the bonding sites (π and anti-bonding states). After charge storage, we found a strong, electrolyte dependent variation in intensity of both modes with applied voltage and follow the quasi-parabolic behavior. While the shift in frequency of RBM does hardly change within the experimental uncertainties, the variation in the highest frequency G-band (ranging 1500 - 1600 cm^(-1)) with applied potential displayed somewhat dependence on the electrode used. The estimated single-phonon strain directed indirectly from Raman measurements is of the order of ~0.25% [2] and the charge transfer (fc) is ~0.004, which is significantly lower if compared with several GIC acceptor compounds.

This finding that this is in agreement with the proposed mechanism of intercalation [1], (i.e., coupling the "electro-chemo-mechanical response of SWNTs") does depend upon the type of co-ion used. The cycle voltammetry (CV) and ac impedance behavior of the nanotubes is described briefly. These findings of electrochemical processes in SWNT sheets bear actuators opens a vast of practical applications including hydrogen storage /fuel cells, batteries, supercapacitors, and micro-electrodes for neurophysiology [1]. R. Baughman et. al. Science, 281, 1343 (1998) [2] S. Gupta et al. Diamond and Related Materials (2003) (Submitted).

D9.4 Production of High Quality Single-Walled Carbon Nanotubes Fluidized Bed Reactor.

Qianqin Wang, Guoqing Nie, Fei Wei and Guishan Luo; Department of Chemical Engineering, Tsinghua University, Beijing, China.

Single-walled carbon nanotubes (SWNTs) have attracted much attention due to their unique structural, mechanical, chemical, and electrical properties. Catalytic chemical vapor deposition (CVD) through decomposition of hydrocarbons is one of the most challenging synthesis methods to produce SWNTs in large scale. In this paper, high quality SWNTs prepared in a fluidized bed reactor (FBR) was reported. The reactor is a vertical quartz tube with the inner diameter of about 31 mm. Several catalysts particles used for the production of SWNTs were prepared with Fe and/or Co metal nanoparticles carried on the surface of MgO, Al2O3, SiO2, ZSM-5 etc. About 100g catalysts powders were loaded on the gas distribution grid. The reaction temperature was controlled at not less than 1220 K. The carriers gas of argon was used to maintain turbulent fluidization of the catalysts powders in FBR. The hydrogen gas was used to reduce the catalysts and to synergize the growth of SWNTs with methane. The products were characterized by XRD, Raman, FTIR, SEM and TEM. Our method gives a higher yield of SWNTs and would be a commercially viable (effective and continuous production at a low cost) process. The authors gratefully acknowledge the support of the National Science Foundation of China (No. 20225052).

D9.5 Hybrid Organic-Inorganic Polymeric Networks For Biosensor Applications.

Nattawee Nimsiri1, David E. Schmidt2, Deepak Shal2, Terri A. Wilson3, Emmanuel P. Giammar2 and Carl A. Bust1.


Our research focus is on the synthesis of innovatively engineered biodegradable polymer biomaterials and the development of low-cost, disposable biosensors that can be used for medical diagnostics, for the rapid detection of hazardous biological and chemical contaminants in the environment and food processing industry. Polyhydroxyalkanoates (PHAs) are synthesized by various bacteria as carbon and energy storage compounds, and are suitable candidates for the production of novel biodegradable plastics. Since these possess material properties similar to various synthetic thermoplastic and elastomers, they have been extensively studied as environmentally friendly substitutes for conventional petroleum-based polymers such as polypropylene. However, due to the fact that unmodified PHAs possess limited stability towards many standard polymer-processing techniques, the aim of our research group is to develop novel hybrid polymer networks based on PHAs that further expand their applications. To date, we have successfully produced a variety of chemically distinct PHA-biodegradable hybrid bioelectrode coatings. In this project, PHA-PDMS (Polydimethylsiloxane) hybrids were formed through a crosslinking reaction between functional group present in the PDMS and complementary groups present in the PHA. The resulting material has properties quite similar to standard PDMS rubbers but unlike such PDMS elastomers, it is biodegradable. Additionally, this material represents the first of its kind reported to date. Currently, our primary research goal is to investigate the feasibility of using these novel PHA-PDMS hybrid bioelectrodes in the fabrication of microfluidic networks on chip-based biosensor devices. In addition, our lab is presently characterizing the biodegradability of the crosslinked PHA-PDMS materials.

D9.6 Degradation processes in new type resistive oxygen sensors.

Thomas Schneider1, Wolfgang Menkes2, Harumi Yokokawa1 and Ellen Iezer-Tiftik1.

1Universitatea Kashihara (TH), Institute of Materials for Electrical and Electronic Engineering, Germany; 2AIST Tsukuba, Energy Electronics Institute, Tsukuba, Japan.

New types of oxygen sensors with increased sensitivity are required to maintain operation of combustion engines within the desired A/F ratios under lean burn conditions and the future challenges of cyclone selective catalysis, "life cycle emission control" on-board diagnostics. For these purposes, resistive oxygen sensors are attractive given their increased sensitivity, their short response times as well as their simple structure. Acceptor doped perovskite type metal oxides of the composition Sr(Ti,Mn)O3 are commonly used for the sensitive layer. Contrary to donor doped sensor materials, Sr(Ti,Mn)O3 shows a long term stable and temperature independent characteristic. In the present paper an exhaust gas sensor yttria doped zircon (YSZ) is used as substrate with an Al2O3 protective layer doped with vanadium as intermediate layer. To obtain distinct signal values an interdigital contacting for a high EMC performance is realized on top. The chemical stability of the intermediate and sensitive materials as well as their chemical compatibility at the interfaces have significant impact on the performance and the long term behavior of the exhaust gas sensors. Degradation processes due to changes in composition, interdiffusion and the formation of secondary phases or the interface between the layers decrease the performance of the device. Depending on the material composition and the operating conditions, different types of degradation processes can be observed: Interdiffusion of cations at the interface between intermediate and sensitive layer affects the electrical properties of the exhaust gas sensor, while formation of insulating secondary phases at the interfaces between substrate, intermediate and sensitive layer interferes with the chemical reactions. Chemical Potential Diagrams of the present compositions provide decisive information about the stability of the applied materials and the formation of parasitic secondary phases resulting in a severe degradation of the sensitive layer. By the use of Chemical Potentials Diagrams a prediction of the stability of the applied materials and a preselection of applicable compositions becomes feasible without costly long term stability tests.

D9.7 Synthesis and VOC gas sensing properties of Polypropylene/MoO3 Nano hydrokite.


Gas sensors based on organic-inorganic hybrid materials are demonstrated. The synthesis of organic-inorganic hybrid materials aims at combining the physical and chemical and chemical properties of inorganic and organic components. The interesting point of such materials is that they provide new possibilities of chemical and structural properties are available. For designing organic-inorganic hybrid sensors, the organic and inorganic components take part in molecular recognition and transduction of chemical signals to measurable resistance changes, respectively. In this paper, we have synthesized polypropylene intercalated MoO3 hybrid organic-inorganic hybridized inorganic materials and their VOC gas sensing properties. We have synthesized polypropylene intercalated MoO3 hybrid materials, which exhibit high sensitivity to adsorbed VOCs.
D9.8

Effect of sample preparation procedure on the
magnetotransport properties of polycrystalline bulk
Sr2FeMoO6 double perovskite. N. Ramak1,2, T. Konishi2,1, K. Chandrasekaran1 and M.S. Ramakrishnan2 1Materials Science Research Centre, Indian Institute of Technology, Madras, Chennai, Tamilnadu, India. 2Department of Physics, Indian Institute of Technology, Madras, Chennai, India.

After the discovery of room temperature magnetoresistance (MR) in Sr2FeMoO6 by Kobayashi et. al. in 1996 [1], there is renewed interest in these systems. However, after intense research it was found that MR (which results due to intergranular tunneling) in these systems is highly dependent on preparative route and conditions. We have therefore studied the effect on the MR by using two different sets of compounds in the solid state route. We have used strontium nitrate as the source of Sr in one case (sample 1) and strontium carbonate (sample 2) in the other case. Fe3O4 and MoO3 are the sources of Fe and Mo respectively in both cases. We have characterized these two compounds by X-ray diffraction and the superlattice reflection peak (111) with d-spacing 10.62 Å and the ordering of the Fe and Mo sublattices is seen only in the case of sample 1 and not in sample 2. The absence of this peak indicates high degree of disorder in the lattice of sample 2 which is detrimental to potential applications like spintronics. It is seen from the resistivity and MR plots that sample 1 shows lower resistance or room temperature and higher low field MR than that of sample 2. These results will be explained in detail with respect to the difference in the stoichiometry of the anion involved. [1]. K.I. Kobayashi et. al. Nature 395 (1998) 677

D9.9

A Study on Amplification of Magneto-Surface-Acoustic-Waves
In High Quality Magnetostrictive Metal Films By Means of
Electron Bunching. Takeshi Konishi, Noshin Okita, Katsuhiko
Nishimura, Hiroshi Uchida and Hisato Inoue; Toyohashi
University of Technology, Toyohashi, Aichi, Japan.

An amorphous Fe84B16 thin film, which is highly magnetostrictive metal, shows a soft magnetization property after annealing. We applied the magnetostrictive thin film to propagation path for magneto-surface acoustic-wave [MSAW] [1]. In our fabricated MS Naw device, a phase velocity of surface acoustic wave was controlled widely by an external magnetic field because of DE effect of the Fe84B16 thin film. However, since the Fe84B16 film was a conductive alloy, an eddy current loss in the thin film increased by increasing a driving frequency for a MS Naw and the eddy current loss attenuated a surface acoustic wave. Therefore, the Fe84B16 film was not applicable to a MS Naw device in high frequency range above 100 kHz. In this report, we investigate an amplification of a MS Naw by electron bunching that was used in a traveling-wave tube in order to compensate the attenuation. We used a hybrid structure of Fe84B16/InSb thin films for amplification of a MS Naw, because a speed of InSb thin film is faster than that of the SAW with a low voltage. The InSb thin film was deposited on a 150 degree Y-cut, X-propagation LiNbO3 substrate by an ion beam sputter system. After annealing at 475 degree C for 90 minutes in vacuum, the [111]-oriented InSb thin film with an electron mobility of 890 cm2/Vs was obtained. The amorphous Fe84B16 thin film with a coercive force of 1.5 Oe and a magnetostriction of 26 ppm was fabricated by a magnetic sputter system. An interdigital transducer (IDT) with a strip width of 8 mm was fabricated by photolithography. We observed a SAW of 125 MHz in our developed device with a hybrid structure of Fe84B16/InSb thin films. [1]. Yokokawa, S., Tanaka, M. Inoue and T. Fujii, J. Appl. Phys., 391, 182-184 (1990)

SESSION D18: Poster Session: Photonic, Optic and other Novel Materials
Chair: Tae Yong Jeon
Wednesday Evening, December 3, 2003
8:00 PM
Exhibition Hall D (Hynes)

D10.1

Negative refraction by a prism and imaging by a flat slab of
microwave photonic crystal. Pirzajali Y Pasimi1, Wentao Lu1, John Dero2, Pirena Volo2, Srinivas Srirame2 and Beverly Turchinet2 1Department of Physics and Electronic Materials Research Institute, Northeastern University, Boston, Massachusetts; 2AFRL/JSNH, Hanscom, Massachusetts.

A conventional optical lens cannot focus light onto an area smaller than a square wavelength and the image formed by such lens is limited by the aperture size and fabrication quality due to curved surfaces. However, superlens characterized by negative refraction can change the way optics works. Recent theoretical studies indicate that negative refraction is possible in photonic crystals (PC) in various regimes of the band structure. In this report we demonstrate negative refraction of electromagnetic waves in a metallic PC and imaging by a flat slab of a dielectric PC. Two dimensional refraction and imaging experiments are carried out in a parallel plate waveguide. Negative refraction is observed in different frequency range from 5 to 12 GHz. Using a flat lens of the dielectric PC, for a subwavelength point source at 2.25 cm from the surface of the PC, we have observed an image of similar size on the far side at 2.75 cm. The image formed by the flat lens to negative refraction is a real 3D image. The experimental results are in excellent agreement with band structure calculations and simulations of wave refraction. The photonic crystal materials display low attenuation and are easily fabricated. The present results are to be scaled to optical frequencies and pave way for several interesting applications. Work supported by the National Science Foundation and the Air Force Research Laboratories, Hanscom, AFB.

D10.2

Evaluation of the Optical Characteristics of Blue Phosphors
for Plasma Color Display. Zhenghong Wang1,2, Jingbi Jin1,3
and Longmei Zhou1,2, Shanghui Yueqin New Materials Co. Ltd., Shanghai, Shanghai, China. 3Shanghai Office of Rare Earth Materials Developing & Application, Shanghai, Shanghai, China.

Quality of plasma color display depends much on the optical characteristics of the phosphors. Chromaticity forms an important part of the fundamental parameters of color display. Using the brightness of the phosphor used, so phosphor brightness must be also an important characteristic of its light emission properties. However, the brightness and chromaticity coordinates of blue phosphors are interrelated. It is often difficult to evaluate the quality of phosphors by its brightness and chromaticity. Listed in table 1, are the sintering temperature vs. optical properties of the phosphors obtained therefrom. The y value should preferably be around 0.06 according to EBU chromaticity standards. Thus the color purity is also satisfactory. However, it is seen in table 1, at all samples with good color purity give their brightness relatively low. This makes it difficult to evaluate their optical properties. In fact for all color display systems, including plasma color display, electro-optical parameters must be tuned to obtain white balance at specified brightness satisfying the requirements on its tristimulus values X,Y,Z. Thus in order to judge whether a blue phosphor is up to standards, consideration should be given to the tristimulus values X,Y,Z. However, brightness is often difficult to evaluate, brightness as the main indicator of the blue phosphor quality. As shown in table 1, with increasing sintering temperature, its Z values varied greatly according better and better with its optical properties. The fluorescent spectrum of such samples indicates that with blue phosphors, Z values vary linearly with its emission intensities. This leads to the same conclusion that it is appropriate to take its Z stimulus rather than brightness as an indicator of its quality. Another set of experimental data on the photographability of blue phosphors also points to fact that brightness is not a good indicator of its quality and should be replaced by its Z stimulus.

D10.3

Characteristics of Dopant Activation by Sequential Lateral Solidification (SLS). Yong-Hee Kim, Chon-Heui Chang, Young-Wook Ko and Jin Ho Lee; Information Display Team, Electronics and Telecommunications Research Institute, Daejeon, South Korea.

Low temperature poly-Si (LTPS) TFTs have been widely studied for active matrix displays with integrated circuits, such as AMLCD and AMOLED. Among the methods of dopant activation in LTPS process, excimer laser annealing is the most efficient and on a vivid post for dopant activation on silicon thin film substrate. In this paper, we study the characteristics of dopant activation on poly-Si films crystallized by sequential lateral solidification (SLS). The ion implantation is used to introduce phosphorus/boron ions to poly-Si film with 2E15 ions/cm2 for n/p+ type doping respectively. The dopant activation on excimer laser energy is analyzed with sheet
resistance, SEM, Raman spectroscopy and SIMS. The sheet resistance is compared with that of rapid thermal annealing (RTA). Sheet resistance with on SiO_2 and poly-Si films is 100 Ω/sq which is the excimer laser energy increases. The minimum sheet resistance of n-doped poly-Si film is 150 Ω/sq which is near to that of RTA and occurs at the beginning energy of nucleation. The minimum sheet resistance of p-Si doped poly-Si film is 180 Ω/sq which is a half to that of RTA and occurs above the nucleation energy. Raman signal of n-doped poly-Si film shows single peak at all laser energy around 355 cm⁻¹ and it is intensity shows maximum at the beginning energy of nucleation. A laser-irradiated poly-Si film shows single peak at lower laser energy and double peak at higher laser energy around 510-520 cm⁻¹. SIMS profile on the laser energy is analyzed.

D10.4 Vanadium Dioxide Thin Films for Thermo-Optical Switching, Lijun Jiang and William N. Cady, New Jersey Institute of Technology, Newark, New Jersey.

Vanadium dioxide (VO₂) thin films undergo a semiconductor-to-metal transition at about 68°C. The phase transition is accompanied with a drastic change in its optical transmission and reflectance, which makes it a good candidate material for optical switching devices. Previous works have been focused on the study of the film properties. In this paper, we present the integration of VO₂ films into MEMS structures by the method of vanadium metal lift-off followed by thermal oxidation. The active VO₂ film was made by e-beam evaporation of pure vanadium target followed by thermal oxidation in oxygen ambient. Synthesized VO₂ film displays a phase transition at 68°C. It shows sharp switching for the infrared wavelength. The thicknesses for VO₂ on a highly reflective metal layer is strongly dependent on the thickness of VO₂ film. The spectroscopic ellipsometer and Raman measurements reveal that the film thickness increases about 50% after the phase transition has a hysteresis of about 15°C between the heating and cooling branches. The scanning electron microscope (SEM) result shows a film microstructure with 50-100 nm columnar grains. The measurements of the optical switching at different points across the film proved good uniformity of the oxidation. The effects of the micromachining process steps on its optical switching after VO₂ deposition will be presented. The study shows that VO₂ film with sharp thermooptic switching can be successfully integrated into MEMS processing using lift-off followed by thermal oxidation.

D10.5 Optical Constants of Vanadium Dioxide Films and Design of a Solar Energy Control Window, Masato Tanaka, Hideo Asada, Gang Xu and Ping Jin, ISEM, AIST, Tsukuba, Japan.

Vanadium dioxide (VO₂) shows an abrupt change of the optical properties in the wavelength region longer than about 800 nm at the temperature transition of 68°C. At the temperature VO₂ undergoes a phase transition from the low temperature semiconducting phase to the high temperature metallic phase. As the tungsten reduces the transition temperature even to the freezing point. In this report, we first determined the optical constants of VO₂ films in both metallic and semiconducting phases by ellipsometry from 380 to 1700 nm in wavelength. Two models with the effective-medium parameters very close to the measured values of the low temperature phase and the Lorentz model combined with the Drude model for the high temperature metallic phase. Second, using the optical constants, we designed a solar energy control window using a stacked film consisting of titanium oxide (TiO₂), vanadium oxide (VO₂), and indium tin oxide (ITO) for the upper, middle, and lower layer, respectively, on glass substrate. The TiO₂ layer was used as an antireflective coating in the visible region and the ITO layer was used as a reflector in the wavelength region longer than about 2500 nm. The designed stacked film shows high transmission in the visible region and high reflection in the far-infrared region. In the near infrared region, the reflection of three acetyl groups with benzene rings.

D10.6 Star-like Aromatic Conjugated Polymers and Dendrimers for OLEDs, Irina A. Khotina and Ludmila M. Brenstein 2,1. Polythiophene synthesis, A.N. Nesmeyanov institute of the organicemalement compounds, Moscow, Russian Federation; 2Chemistry Department, Indiana University, Bloomington, Indiana.

The solution of the problem allowing synthesis of effective blue emitters can be found in synthesis of polymers with very branched fragments containing other substituents than benzene rings. Polyphenylene synthesis based on cyclotrimerization of acetyleneacrylomeric compounds by trimerization cyclotrimerization of acetyleneacrylomeric compounds by trimerization cyclotrimerization of acetyleneacrylomeric compounds by trimerization cyclotrimerization of acetyleneacrylomeric compounds by trimerization cyclotrimerization of acetyleneacrylomeric compounds by trimerization cyclotrimerization of acetyleneacrylomeric compounds by trimerization cyclotrimerization of acetyleneacrylomeric compounds by trimerization cyclotrimerization of acetyleneacrylomeric compounds by trimerization cyclotrimerization of acetyleneacrylomeric compounds by trimerization.
D10.9
Effect of Postdeposition Annealing Temperature and Atmosphere on the Properties of ZnO Thin Films.
Ommar M. Hanafi1, Gabriel Braunstein2, Hrishikesh Patil2 and Neeladhith Dhere3. Mathematics, Physics, UF, Orlando, Florida; 2TSEC, UCF, Cocoa, Florida.

The effect of post-deposition heat-treatment, in different gas atmospheres, on the electrical and optical properties of ZnO thin films, grown by rf sputtering deposition, have been investigated. Samples of undoped, and Al doped, ZnO have been heated in nitrogen, air, oxygen, nitrogen, and forming gases (7% H2 + 93% N2), at temperatures ranging from 300°C to 900°C. Hall effect, electrical conductivity, and optical transmission measurements revealed measurement changes as a function of the annealing temperature and atmosphere. Films annealed at high temperatures show increases in sheet resistance and optical transmission. The sheet resistance of the as-deposited ZnO is 2 x 109 Q/square, and it is reduced to below 1 x 108 Q/square after annealing at 900°C in oxygen. The average transmittance increases (in the VIS-NIR range) from 70% for the as-prepared ZnO films to > 80% for the films annealed at 500°C. The carrier concentration, Hall mobility, optical band gap, and index of refraction also show significant changes upon annealing. These changes are discussed in terms of the crystalline structure of the films.

D10.10
Smart Heterostructures Based on Solid Solution ZnCdHgTe.
Galina Kildysh1 and Peter Sydykovich2. 1General Physics, State Pedagogical University, Drohobytsy, Ukraine; 2General Physics, State Pedagogical University, Drohobytsy, Ukraine.

Smart narrow-gap semiconductor materials belonging to the A2B6 compounds are seemed to be of particular interest for design of optoelectronic devices used in automobile and vehicle navigation. The heterojunctions containing wide-gap epitaxial layers of ZnCdHgTe and monocrystalline substrates CdTe (ZnTe) are of essential importance owing to the simplicity and reliability of the growth technology (modulated liquid-phase epitaxy or pulsed laser epitaxial technique). Different methods of hetero-structures deposition give a wide range of possibilities to change the main parameters of the energy band diagram which appears as a principal characteristic of the active element. Furthermore, the structure of the charge carriers characteristics (mobility, scattering, carrier density, etc.) provide useful information for simulation of active element as a whole. The investigation of the experimental data obtained from the simplest electro-field measurements appears as a reasonable base for computing modeling of the graded-gap heterostructures. The abstract reports results of experimental and numerical simulation for active elements based on graded-gap heterostructures CdHgTe/ZnTe/ZnCdHgTe. The main parameters of the energy band diagram are calculated and the numerical algorithm for the device simulation is also presented.

D10.11

Pulsed Electron beam Deposition is a relatively new thin film deposition technique. A high current (1500 A), high voltage (15 kV) electron beam of about 100 ns pulse width, created in a low pressure Paschen discharge regime is used as the primary energy source to ablaze a given target material resulting in the formation of a thin film on a substrate. The high power density at the target facilitates the pulsed nature of the beam permits deposition of complex materials such as YBa2Cu3O7, Ba-Sr-Ti-O etc., with stoichiometric composition control. The Pulsed Electron Deposition, in several aspects, is similar to the well-established Pulsed Laser Deposition technique but differs from the fundamental viewpoint of beam-target interaction. The additional advantage of Pulsed Electron Deposition is realized in its ability to deposit optically transparent materials (with respect to the laser wavelength) such as SiO2 and Al2O3 and some special polymers. The technique is scalable and cost effective and hence could become the preferred method in high throughput manufacturing environment where pulsed techniques are sought for accomplishing specific functionality (composition control, high density, deposition at lower temperatures etc) in the deposited films. This presentation will briefly introduce the basics of this deposition technology to the materials scientist and will present experimental data obtained on several technologically important smart materials systems such as high temperature superconducting films (YBCO, GdBCO), para-electric Bi-Sr-Ti-O, hard, Hydrogen-free Diamond like Carbon and PITTe films.

8:30 AM *D11.1
Selection of Materials and Sensors for Health Monitoring of Composite Structures. S. Mark Sperring1 and Seth Stevok Kessler2,1. 1Aeronautics and Astronautics, MIT, Cambridge, Massachusetts; 2Metis Design Corporation, Cambridge, Massachusetts.

Embedded structural health monitoring systems are envisioned to be an important component of future transportation systems. The principal challenge in designing an SHM system is the choice of sensors, and a sensor layout with capabilities for relevant structural damage. This paper focuses on the relationship between sensors, the materials of which they are made, and their ability to detect structural damage. Sensor selection maps have been produced which plot the capabilities of the full range of available sensor types vs. the key performance metrics (power consumption, resolution, range, sensor size, coverage). This exercise is used to define a system architecture utilizing piezoelectric sensors, operating in several modes (acoustic emission detection, strain detection, Lamb wave generation/sensing and global modal response). Experimental and analytical results are presented for in-situ damage detection in composite materials using piezoelectric sensors. Test results and corresponding analysis is presented for coupons and built-up structures, including sandwich panels, stiffened panels and cylinders containing representative damage (deformations, impact damage, off-axis ply cracking and penetrations). Modal analysis methods are shown to be effective for detecting the presence of some damage in composite structures, but provide little information regarding the size, location or severity of the damage. By comparison Lamb wave techniques are shown to be sensitive to all types of damage, and present the possibility of estimating damage location and size. The results of these analyses are discussed and conclusions for the architecture of future SHM systems are presented, in addition recommendations for the development of improved sensor configurations and materials are made.

9:00 AM *D11.2

The classical NDE techniques of periodical maintenance are just now evolving towards the continuous health monitoring of materials and structures. Taking account of the relation of this approach with the biomimetic notion of smart materials, it seems useful to extend this passive concept to a more active one specially in the case of composite materials. Effectively, if sensors and actuators are embedded in a composite structure before curing in order to monitor and improve the processing parameters, they are able, remaining in the structure, to assume the health monitoring and the optimization of the usage in the next stages of the life. Moreover, in slightly damaged systems, it becomes reasonable to use the results collected by the sensors for one on line tentative prediction of the residual life. Finally in the long stage of the life, when the material is deeply damaged, it is sometimes possible to slow down, and more rapidly, to heal the damage.

9:30 AM *D11.3
Smart Materials and Nondestructive Evaluation. Manaka Enoki1 and Teruo Kishi2. 1Department of Materials Engineering, The University of Tokyo, Tokyo, Japan; 2National Institute for Materials Science, Tsukuba, Japan.

The smart materials and structural systems are based on the concept to incorporate sensors, actuators, etc. in the materials themselves and to integrate these materials with the structures, thereby improving such functions as to (1) self-evaluate the occurrence and deterioration of strains and damages, (2) self-control vibrations and noises, and (3) self-regulate their own shape depending on conditions, and (4) self-control the propagation of damages and repair them as the need arises. We report the recent research and development project in Japan on the smart materials and structural systems, which was a project under the NEDO’s [New Energy and Industrial Technology Development Organization (NEDO)] research and development project on industrial and scientific technologies in conjunction with colleges and universities. This report shows examples of applications to composite materials such as (1) development of health monitoring technology, (2) development of smart manufacturing technology, (3) development of active/adaptive structure technology, (4) development of materials and elements for actuator, and (5) airplane body demonstrator for demonstration test. Also recent
10:30 AM D11.4
Tailoring Strains Through Microstructural Design.
Jean Y. Vandeweger and William J. Clegg, Department of Material Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom.

When developing structures, which respond with a strain upon application of a stimulus such as temperature or an electric field, the fixed relation between the response of a given material and the magnitude of the stimulus puts severe constraints on the design. This problem is commonly dealt with by either designing the shape of the actuator or sensor, or by selecting a material with the appropriate coefficients in response to the field. However, when actuating or sensing functions need to be incorporated within other structures, shapes must be chosen as possible. The changes in microstructure of where the structure is to be used can put limits on materials selection. Such limitations can be overcome by incorporating design into the microstructure of materials. By combining two materials into a structure, which allows leveraging of the strains, one can obtain a much wider range of coefficients than predicted by the rule of mixtures. For example, using aluminum and Invar, with respective coefficients of thermal expansion of 24 X 10^-6 K^-1 and 1.5 X 10^-6 K^-1, a coefficient of thermal expansion as low as -360 x 10^-6 K^-1 was obtained. It will be shown how simple variations of the microstructure obtained by combining simple triangular elements can yield a wide variety of properties: isotropic and anisotropic coefficients, linear and nonlinear responses, and materials with gap properties. Initial production of sheet-like materials was performed by a combination of photolithography and soldering. Predictions of both the coefficient of thermal expansion as well as mechanical properties will be compared with experiments on a model system of copper and Invar.

10:45 AM D11.5

In this paper, advances in development of instrumentation and methodologies for wireless health monitoring of structures using MEMS inertial sensors are presented. Development of new materials and structures has increased the demand for accurate modeling of their mechanical behavior. Such modeling includes determination of dynamic properties of structures, such as their natural frequencies, mode shapes, and damping factors. Dynamic properties can be determined using analytical and computational methodologies, but are only limited to simple structures since they are insufficient to study complex structures. In order to study complex real-world structures, experimental modal analysis is applied. Rapid development of microelectromechanical systems (MEMS) has lead to progressive designs of high-resolution, lightweight, and low-actuation power inertial sensors. These MEMS sensors provide an optimum alternative to traditional sensors, which have larger masses and may modify the dynamic characteristics of the structure. The structure of this paper is as follows: results and discussions are presented in this paper include utilization of multiple MEMS inertial sensors to determine dynamic properties of structures. To ensure that the sensors are attached to appropriate locations for optimal results, both Fourier and Wavelet analyses are utilized in order to perform time and frequency studies of the responses of specific test structures. To verify the results obtained with MEMS sensors, noninvasive methodologies, such as laser optoelectronic holography (OEH), are utilized to determine the natural frequencies, mode shapes, as well as to investigate the effects that attachment of MEMS sensors may have on the dynamic characteristics of the test structures. In addition, the test structures are also modeled with computational and experimental modal analyses for comparison with experimental results. Considering that multiple MEMS sensors are utilized, wiring and integration of these sensors might become complicated and monitoring of structures across long distances becomes limited. Therefore, a miniaturized wireless system that utilizes commercially available RF components is being developed and its current functionality is demonstrated.

11:00 AM D11.6

The interest in micro actuation and sensing MEMS devices has given rise to the necessity for studying the mechanical response of thin released films, which are made of active materials such as ferroelectrics, ferromagnetics, and shape memory alloys. The trend to reduce the film thickness in these devices compels the development of new techniques, which enable loading in the sub-nm scale and take into account the fragility of these devices. We have developed a new technique for measuring static and dynamic mechanical response of thin released films, by either load control or displacement control in the range of 0.1nm - 1nm. An optical system, which measures the deflection of a Laser beam, allows us to measure displacements in the sub-nm range and a sample holder with 4 adjustable degrees of freedom allows us to test specimens, which are integrated on a silicon wafer. The capabilities of the new technique are demonstrated with results on released films of ferroelectric [Ba1-xPb0.5Ti0.5O3 and ferromagnetic shape memory alloy Ni2MnGa.

11:15 AM D11.7
Bi-Directional Motion Achieved with a Surfaces Microfabricated Electrodynamical MEMS Microengine.
Edward S. Kolesar, William E. Odom, Joseph A. Jalischandran, Mark G. Richmond, Ruoff, Simon A. Ko, Jeffrey T. Howard, rope, and Michael J. Williams, Richard J. Wilks and Justin B. McAllister, Department of Engineering, Texas Christian University, Fort Worth, Texas.

Several microactuator technologies have been investigated for positioning individual elements in large scale microelectromechanical systems (MEMS). Electrostatic, magnetostatic, piezoelectric and thermal expansion represent the most common modes of microactuator operation. This research is focused on the design and experimental characterization of two types of MEMS asymmetrical electrothermal microactuators. The motivation is to present a unified description of the behavior of electrothermal microactuators so that it can be adapted to a variety of microactuator and microactuator applications. Both microactuator design variants use resistive (Joule) heating to generate thermal expansion and movement. Deflection and force measurements of both microactuator variants in function of applied electrical power are presented. Also described is the practical integration of the electrothermal microactuators in a monolithic microengine that has been operated in a bi-directional mode to control the position of a mechanical shuttle. Preliminary control of the mechanical shuttle has been achieved with a resolution of 1 micrometer.

11:30 AM D11.8
Piezoelectric Actuators for Synthetic Jet Applications. Keria Mosis1 and Rob Bryant2; 1Virginia Commonwealth University, Richmond, Virginia; 2NASA Langley Research Center, Hampton, Virginia.

Synthetic jets have been identified and utilized widely in airflow control applications. These jets of air are usually created by the use of compressed air, or an electromechanically driven vibrating platform. All of these approaches produce desired results in airflow control such as enhanced lift and increased maneuverability. Despite the results however, system weight, size, response time and force limit their use in aircraft applications where space is premium. The objective of this study is to characterize development of a synthetic jet utilizing three types of piezoelectric actuators as mechanical diaphragms. The limiting parameters of the actuators for this application are shape and volumetric space. Thus, the actuators were modeled with a diameter of 3.15 cm, and overall volume no larger than 147.5 cm³ on a 7 cm x 7 cm area coverage. The actuators tested were pre-stressed curled metallic unimorpha, bimorpha, and radial diaphragms. These piezoelectric elements were chosen because of their low electrical energy losses. Furthermore, these piezoelectric elements were chosen because of their low electrical energy losses, the actuator was affixed about its perimeter in a cavity, and relevant parameters such as clamped displacement variations with voltage and frequency using applied pressure (kPa) differentials was measured. Also, the air velocities produced through apertures of varying sizes were measured using the same mounting configuration. Other properties measured included calculated and experimental volume displacement and pressure versus displacement.

11:45 AM D11.9
Design for Compressive or Tensile Strain in Spherically-Deformed Circuit Boards and Electrical Implications. Pashaui Iris Ilu1, Min Hwang1, Helen Gleksova2, Zichen Xu1, Zhiqiang Suo1, Sigurd Wagner1 and James C Sturm1;
1Center for Photonics and Optoelectronic Materials, Princeton University, Princeton, New Jersey; 2Center for Composite Materials, University of Delaware, Newark, Delaware.

Many proposals for future sensors and actuators depend on stretchable and conformable electronics fabricated on thin foil substrates, e.g. smart electronic skins that can be deformed to arbitrary shapes. The most common type of deformation is to roll a thin foil substrate into a cylinder. For such deformation, the strain in any device on the substrate causes the shape of the geometry, geometry and surface characteristics by the devices. However, for more complicated shapes, such as a spherical cup shape,
SESSION D12: Magnetic and Metallic Based Smart Materials

Chairs: Katsunori Inoue and Eckhard Quandt
Thursday Afternoon, December 4, 2003
Room 202 (Hynes)

1:30 PM  *D12.1*
The remanence enhancement in magnetostrictively interacting particles. Jiangy Li and Helming Qu, Engineering Mechanics, University of Nebraska-Lincoln, Lincoln, Nebraska.

In this talk, we report an effective medium theory on the remanence of magnetostrictively interacting particles to demonstrate the effect of inter-granular magnetostatic interactions on the remanence enhancement of the magnets, which agree excellently with micromagnetic simulations. A dimensionless parameter lambda measuring the competition between anisotropy energy and magnetostatic energy is defined, which completely characterizes the remanence of magnets when the exchange coupling is negligible. Three distinct regimes were observed: lambda < 0.1 for hard magnets, where anisotropy energy dominates and little remanence enhancement is observed; 0.1 < lambda < 1 for intermediate magnets where up to 50% remanence enhancement is observed due to the intergranular magnetostatic energy; and lambda > 1 for soft magnets, where the dominance of magnetostatic energy leads to much reduced remanence in the materials.

2:00 PM  *D12.2*
Receptive Magnetic-Field-Induced Deformation and Magneto-mechanical Fatigue of Ni-Mn-Ga Ferromagnetic Martensites. Peter Muehlen1, Volodymyr A. Chernenko2 and Gernot Koster3; 1ETH Zurich, Zurich, Switzerland; 2Institute of Magnetism, Kiev, Ukraine.

Magnetoplasticity, i.e. the magnetic-field-induced deformation of ferromagnetic shape-memory alloys, and its inverse effect, i.e. the deformation-induced change of magnetization, can be used for building actuators and sensors. While magnetic-field-induced strains - and more recently magnetic-field-induced stresses - have been studied intensively since 1996, information about the repeatability and long-time stability of these properties is very limited. In this study, cyclic magneto-mechanical experiments were performed with Ni-Mn-Ga alloys exhibiting layered modulated tetragonal to 7-layered modulated orthorhombic martensites. The length of the samples was measured in a rotating magnetic field, and the magnetic-field-induced strain was evaluated as a function of the number of field cycles. More than 10³ cycles were applied. Depending on thermo-mechanical history and the martensite structure, the orientation of magnetic-field-induced strain varies dramatically. For 7-layered orthorhombic martensite, the field-induced strain can increase during cycling due to magnetic-field-induced stresses, which are caused by magnetostrictive interactions. The different magneto-mechanical long-term stability results from differences in crystal symmetry. For tetragonal martensite with uniaxial magnetic misorientation, there is only one preferred martensite domain (out of three) for a given field direction. Therefore, there is a well-defined deformation path upon a change of magnetic field direction. This results in a stable cyclic field-induced strain. In contrast, there are relatively many stable domains for hexagonal martensite. Therefore, the deformation path is not unique; different options are available upon field direction changes. This results in a variable cyclic field-induced strain and less reproducible magneto-mechanical fatigue.

2:15 PM  *D12.3*
Magnetization Process Associated with Reorientation of Martensite-Variants in Iron Based Ferromagnetic Shape Memory Alloys. Takashi Fukuda1, Tsutsumi Sakamoto2, Tomoyuki Tera3, Tomoyuki Koshishita4, and Kohji Kishio5; 1Department of Materials Science and Engineering, Graduate School of Engineering, Osaka University, Suita, Osaka Japan; 2Department of Superconductivity Engineering, Graduate School of Engineering, University of Tokyo, Bunkyo-Ku, Tokyo, Japan.

Fe-31.2Pd(1%) and Fe-3P can be field shape memory shape alloys whose transformation temperature is about 230 and 85 K, respectively. Both alloys exhibit a large magnetic field-induced strain (FMIS) in association with reorientation of martensite variants. Especially, concerning the Fe-Pd, a part of FMIS recovery spontaneously in the field removing process. In this presentation, we show the magnetization process of Fe-31.2Pd and Fe-3P, and discuss the mechanism of FMIS. The magnetization curves measured in the martensite state of these alloys exhibit a hysteresis between field applying and removing processes, whose area corresponds to the energy dissipated during the reorientation of variants. The area depends on characteristics of FMIS. In case a large FMIS appears in the magnetizing process but does not recover in the field removing process, the area is in the order of 100 kJ/m³. This is the same order as that has been reported for Ni-Mn-Ga alloys. On the other hand, in case the FMIS induced by the magnetic field recover spontaneously in the field removing process, the area is in the order of 10 kJ/m³. The uniaxial magnetoelastic anisotropy constant is also evaluated from their magnetization curve, and it is about 350 kJ/m³ for Fe-31.2Pd and 77 K, and is about 500 kJ/m³ for Fe-3P at 4.2 K. These values are the same order as that of Ni-Mn-Ga alloys, supporting the microscopic explanation of FMIS in ferromagnetic shape memory alloys that the FMIS is caused by the magnetic energy difference between adjacent variants under a magnetic field.

2:30 PM  *D12.4*
Microstructure and Magnetostriiction of Rapidly Solidified Fe-Ga System Alloys. Masayasu Yamagata1, Yasuyuki Passma2, Tetsu Okazaki3, Takashi Matsuzaki4, Takashi Watanabe5, and Manfred Wuttig1; 1Intelligent Machines and System Engineering, Tohoku University, Sendai, Japan; 2Graduate School of Engineering, Tohoku University, Sendai, Japan; 3Materials and Nuclear Engineering, University of Maryland, College Park, Maryland.

It was reported that melt-spun, rapid solidified Fe-Ga ribbon sample exhibited large magnetostriiction and good ductility as compared with conventional bulk sample. In order to recover the characteristics of large magnetostriiction in Fe-Ga ribbon sample, the correlation between magnetostriiction and the crystal grain morphology has been investigated in detail by SEM-JISP method for Fe-15.5Ga alloy. In comparison with as-spun ribbon sample, short-time (0.5h) heat treated ribbon has stronger orientation to [001] and it has exhibited larger magnetostriiction (150ppm) at 800 kA/m. These phenomena suggest that such a large magnetostriiction is caused by the reduction of considerable large internal stresses in as-spun ribbon, as well as the remaining strong textures after annealing. The following conclusion was obtained. 1. Fe-Ga rapidly solidified ribbon consists of many low angle grain boundaries and strong texture. 2. Texture is formed in near [001], and that is concentrated by short-time heat treatment. 3. Largest magnetostriiction occurs in short heat treated Fe-15.5Ga ribbon. This result from both released internal stresses and stronger orientation to [001]. bulky Fe-Ga actuator/actuator materials have been developed by combining the laminated rapidly solidified ribbons with spark plasma sintering method. Reference: 1. A.E Clark, J.B. Restoff, M.W. Fogie, T.A. Loganre, D.L. Schlegel, IEEE Trans. Magn. 36 (2000) 2982-2. Y. Iizuna, C.Sato, T. Okazaki, JIM 66 (2002) 901-904 (in Japanese).

2:45 PM  *D12.5*
Magnetostriiction of Field-Structured Composites. James E. Martin1, Robert A. Anderson2, and Gerald Galley3, 4, 11122, Sandia National Labs, Albuquerque, New Mexico; 2Physics, Dominican University, River Forest, Illinois.

Fieldstructured magnetic particle composites are an important new class of materials that have great potential as both sensors and actuators. These materials are synthesized by suspending magnetic particles in a polymeric resin and subjecting these to magnetic fields while the resin polymerizes. If a simple uniaxial magnetic field is used,
the particles will form chains, yielding composites whose magnetic susceptibility is enhanced along a single direction. A biaxial magnetic field, component of anisotropic magnetic fields, yielding composites whose magnetic susceptibility is enhanced along two principal directions. A balanced triaxial magnetic field can be used to enhance the susceptibility in all directions, and biased biaxial and triaxial magnetic fields are especially effective for producing composites with a greatly enhanced susceptibility along a single axis. Magnetostriiction is quadratic in the susceptibility, so increasing the composite susceptibility is important to developing actuators that exhibit large deformations. To investigate magnetostriiction in these field-structured composites we have constructed a sensitive, constant-stress apparatus capable of 1 ppm strain resolution. The sample geometry is designed to minimize demagnetizing field effects. We have demonstrated field-structured composites with nearly 10,000 ppm strain, and have shown that at large magnetic fields a structural phase transition occurs within the composite. These experimental results are compared to microscopic, self-consistent field calculations of magnetostriiction in these complex, disordered systems.

3:30 PM D12.6
Development of Spin Sensors Based on Magnetostriactive Tunneling Junctions, Markus Loechndorf, Stefan Dukulpil, Manfred Bucher, Joachim Wecker, Eckhard Quandt, Center of Advanced European Studies and Research, Bonn, Germany; Corporate Technology, Siemens AG, Erlangen, Germany. Micrometer-sized highly sensitive spin sensors are presented. The sensors are based on magnetic tunneling junctions (MTJs) incorporating magnetostriactive free layers. Usually, nearly zero-magnetostriactive soft magnetic materials are chosen as free layer, in order to avoid interaction caused by stress or strain. In this study, however, we have intentionally used highly magnetostriactive materials and alloys as free layers in MTJ to exploit the magnetostriactive free layer sensitivity. Results for magnetostriactive Fe50Co50 materials or amorphous Co-Fe based alloys serving as sensing (or free) layers are discussed in view of possible applications. In addition MTJ based sensor devices have been prepared on polymer substrates. As a result MTJ with magnetostriactive free layers show gauge factors on the order of 600 which are a factor of 3 better than silicon based strain sensors [1], and due to the small sizes of MTJ they are possible candidates for strain sensing with a very high spatial resolution. Future work will focus on the investigation of highly strain sensitive MTJ’s operating at zero magnetic bias fields as well as on the preparation of strain sensor arrays. Financial support was given by the German Ministry for Education and Research (BMBF, grant # 13N7943).


4:00 PM D12.7
High frequency devices with integrated magnetoelastic materials, Michael Frommberger and Eckhard Quandt, Institute of Solid State Physics, University of Erlangen-Nurnberg, Germany. A wireless mechanical stress sensor based on thin films showing the inverse magnetostriactive effect will be presented. The magnetostriactive films are incorporated in the inductance L of an electrical LC resonator [1, 2]. The sensor is used for wireless measurements of mechanical quantities such as stress or torque on rotating or hidden objects. Their operating frequencies can be up to several GHz limited by the ferromagnetic resonance frequency of the used materials. The sensors are based on soft magnetic magnetostriactive FeCoB8 thin films which have been fabricated and characterized. In a bending test jig, the sensor shows a high sensitivity exceeding most commercial available strain gauge elements. This sensor can be used in a wide range of different applications of wireless measurements of mechanical values. Besides the optimization of the sensor layout with regard to the desired frequency range future research efforts will also focus on improving the different sensors and on the continuation of high frequency magnetostriactive material development suitable for those applications. Our current efforts in material design and process development will be presented and their benefits will be discussed.

4:15 PM D12.8
Development of Texture-controlled Bulky Actuator/Sensor Materials by Combining Rapid-solidified Fiber/Ribbon Elements with Spark Plasma Sintering (SPS), Yasumitsu Furuya, Misomuri Yokoyama, Chihiro Sato, Toyo Oalonsky and Mamori Omori. Intelligent Machines and Systems Engineering, Hiroshi University, Ibaraki, Japan; *Material Science and Engineering, University of California, Cambridge, Massachusetts, USA; **Present Address, Forth Technologies, Thousand Oaks, California; ***Present Address, Shanghi Jiao Tong University, Shanghi, China. Ferromagnetic shape memory alloys (FSMAs), most notably those based on Ni-Mn-Ga, have received considerable attention because of the remarkable 6% to 9% field-induced strains they have exhibited at room temperature in magnetic fields of order 0.5 T. The stress above which the field-induced strain in FSMAs is blocked is currently 2 to 4 MPa. This is to be compared to blocking stresses of over 100 MPa and several tens of MPa for piezoelectric and magnetostrictive materials, respectively. Recent progress in understanding and using these materials will be reviewed. Ni-Mn-Ga samples that show relatively easy twin boundary motion near room temperature fall in a narrow composition range that includes both tetragonal and orthorhombic martensites. FSMA samples measuring several mm on edge show a bandwidth of approximately 1 to 100 kHz for continuous wave excitation or pulse excitation, respectively. Application of sub-millisecond field pulses of amplitude greater than the anisotropy field (about 0.6 T) do not induce greater strain, but only increase the speed at which full strain is achieved. While the curves of strain versus alternating field amplitude appear smooth, studies of individual twin boundary motions show them to be highly irregular. Because actuator applications seem appropriate for Ni-Mn-Ga FSMAs given the large values of $\alpha = 1 / \rho \beta$, there have been significant efforts have been aimed at developing small pumps, valves and underwater transducers. The equally large values of $\alpha = 1 / \rho \beta$, for Ni-Mn-Ga suggest sensor applications, but there is no published work directed toward these goals. The large hysteresis associated with twin boundary motion has been exploited to demonstrate superior vibration damping absorption in Ni-Mn-Ga-loaded composites compared to Terfenol-loaded polymers.
Ferromagnetic shape memory alloys (SMAs) belong to a class of complex correlated systems whose physical properties depend on interaction across two or more energy regimes — magnetic and thermodynamic. In the case of ferromagnetic SMAs, this talk will focus on results obtained from experiments in which the microstructural, structural, domain dynamics and thermodynamic properties of these alloys were measured and observed in situ and at the same time. This simultaneous study of these properties has provided a fundamental understanding of some key issues that govern the properties of these alloys. The talk will focus on results obtained from oriented single crystals of Ni-Mn-Ga and Fe-Pt. Some key results include formation and dynamics of magnetic vortices at the parent (magneto-optic-petrovite) phases, which reveals clear evidence that the length scales of magnetic domains are a function of the lattice parameters of the martensite phase. Additionally clear evidence is found of a series of magnetic and structural transformations, as well as precursors just above the martensite transformation temperature. Finally, from a practical viewpoint, these results directly pinpoint the origin of high coercivity, in issue of practical concern, and high load-bearing capacities are needed for low switching fields and coercivity. This work was supported by DOE Grant No. DE-FG03-01ER45990, Office of Basic Energy Science, and this support is gratefully acknowledged.

9:30 AM D13.3 Synthesis And Characterization of Spuntered Fe-Pt-Based Alloy Thin Films. Jian-Ping Chang, T. Michaeling 1, S. P. Wang 2 and K. Inose 3, 1 Institute of Materials Engineering, National Taiwan Ocean University, Keelung 202, Taiwan; 2 Department of Physics, Aghapura University, Karnickidi, 140 08, India; 3 Department of Materials and Minerals Resources Engineering, National Taipei University of Technology 106, Department of Materials Science and Engineering, University of Washington, Seattle 98195, Washington.

Fe-Pt alloy thin films have attracted significant interest owing to their potential application in magnetic recording. Fe-Pt alloys exhibit very high magnetic crystalline anisotropy energy, high coercivity and large energy products. In the present study, polycrystalline Fe-Pt-based thin films were prepared by an R.f. magnetron sputtering technique onto silicon wafer substrates. The deposited films are annealed between 400 800°C in order to transform the soft magnetic fcc phase to the hard magnetic fct phase. The effects of film composition and annealing treatment on magnetic structure and magnetic properties of Fe-Pt alloy thin films are investigated in detail. X-ray diffraction studies on annealed Fe_84Pt_16 films at 600°C revealed an ordered fct L1_0 phase where Fe_5Pt_3 and Fe_12Pt_5 phase-separated, disordered FePt and FePt phases phase-separately. The long-range order parameter for argon-activated films at 600°C is estimated to be 0.90±0.1. The grain size of Fe_84Pt_16 film is measured to be in the range between 60 and 80nm. A minute increase in the coercivity of 37kOe is obtained for argon-activated films at 600°C. The saturation magnetization is found to increase with ferrous content in the alloy films. The high values of Ms and Hc for Fe_84Pt_16 may be attributed to the predominant content of pure fct-FePt phase in the sample. It is observed that argon quenched films exhibited larger saturation magnetization than RTA processed films. Aron quenched and RTA processed films exhibited micro-twins in scanning electron microscopy analysis. The appearance of micro-twins in annealed films may be attributed to the phase-transitions in these films. Moreover, these micro-twins are found to be beneficial to improve the magnetic hardness and properties of Fe-Pt films. The large value of saturation magnetization obtained from M-H hysteresis indicates the predominant existence of hard fct-γ phase. The combined effects of twinning and the hard fct-γ phase on the magnetic properties are discussed.

9:45 AM D13.4 Micromagnetic Modeling of the Behavior of Magnetostriuctive Films under Stress. Yi-Chang Shiu, Institute of Applied Mechanics, National Taiwan University, Taipei, Taiwan.

We have developed a framework based on micromagnetics to explore the effect of stress on the magnetostrictive behavior in ferromagnetic films. Our approach is different from the conventional one which simply replaces the total strain by magnetostrain. Question arises for such an approach because of the loss of strain compatibility. Here, we have included the kinematic constraints in our micromagnetic model and developed a fast algorithm to calculate the intrinsic stress induced by incompatible magnetic stress. We have shown that for small magnetostriction of the order of 1 10⁻⁵, the results predicted by the present approach are slightly different from those predicted by the conventional method. But we have found that for large magnetostriction of around 1 10⁻⁴, the results predicted by our approach. The conventional approach is insufficient to predict magnetostatic patterns and hysteresis accurately, and the effective magnetic field induced by intrinsic stress cannot be neglected.

10:30 AM D13.5 Thermal Analysis And X-Ray Diffraction Study Of Ferromagnetic Fe-Pt-Pd-Based Shape Memory Alloys. Guowei Yang, Shigeyasu Hasegawa, Hitoshi Yoneda, Shigetaka Sai, Shigeyasu Kato, and Shin-ichi Torii, 1Showa University, Tokyo, Japan; 2Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing, China; 3Department of Materials and Design, Graduate School of Engineering, Showa University, Tokyo, Japan; 4Materials Science and Engineering, Hokkaido University, Sapporo, Japan; 5Kagawa University, Kagawa, Japan; 6Korean Electric and Magnetic Devices Group, Korea Electrotechnology Research Institute, Changwon, South Korea; 7Osaka Municipal Technical Research Institute, Osaka, Japan.

Ferromagnetic shape memory alloys have received considerable attention in the past several years because of their potential as elements of high-performance and power actuators due to their ferromagnetic nature of martensite phase. At present, there are only five alloy systems that show shape memory effects when their thermally induced ferromagnetic martensite goes back to its austenite phase upon heating. Magnetically, the martensite phase on the other hand, leads to shape change but no macroscopic shape recovery has been detected upon the removal of magnetic field. Similar shape change also occurs when ferromagnetic martensite variants are rearranged by magnetic field, but no shape recovery occurs when magnetic field is removed. Recently, we have encountered one incident where some shape recovery was observed upon the removal of magnetic field. Hence, we believe there are some conditions under which macroscopic shape memory effects should occur when magnetic field-induced ferromagnetic martensite is reverted to its austenite phase. In the present study, we have investigated ternary Fe-Pt-Pd alloys in an attempt to develop ductile ferromagnetic shape memory alloys appearing at around room temperature. Several alloys with the compositions of Fe-Pt-Pd at % Pd at % and Fe-Pt-Pd at % Pd at % were prepared by arc melting, followed by hot rolling and homogenization. Homogenized alloys were electro discharge machined to make specimens of about 2x2x0.5mm and heat treated in vacuum for atomic ordering in encapsulated quartz tubes, and quenched into iced water. Ordered alloy samples were then thermally analyzed using a DSC unit and x-ray diffraction using a diffractometer. All alloys investigated have martensite and austenite transformation temperatures, which are much lower than those of the Fe-Pt-Pd alloys. Among those alloys, one Fe-Pt-Pd alloy showed good shape memory performance. Our structural analyses and thermal analyses will be presented in detail.


In past several years ferromagnetic Heusler-type compound Ni-MnGa has received considerable attention for its potential in high performance and energy-density actuators. The compound has systematically been studied to clarify the shape change associated with the martensite-to-austenite transition under stress and/or thermal loading at constant magnetic field and under magnetic field loading at constant stress and temperature. In the series of research efforts, the shape change in [221] for a Ni-19.5at.%Mn-27at.%Ga single crystal is found to be extremely small while temperature is increased or increased without magnetic field, while it is about 1.3% under a magnetic field of 3 kOe applied along the [672] direction. This magnetic-field-induced thermally induced shape change is reversible and associated with the formation of favorably oriented martensite variants. In contrast, magnetic field induced shape change also occurs at a constant compressive stress when magnetic field was applied. The present study was dealt with the effect of compressive deformation behavior of polycrystalline Ni-MnGa-based compounds at various temperatures with and
without magnetic field. The compound compositions used were around Na-25%, Mn-25% and Ga, where the transition occurred near room temperature. It was found that triggering stress is lowered when deformed under constant magnetic field at temperatures below M_s, while such stress is little affected when deformed at temperatures above \( T > \). In the former case the compound could be deformed repeatedly without failure, showing a ductile behavior, while in the latter it failed after several cycles of deformation. The ductile and brittle behavior appears associated with the readiness of rearrangement of martensite variants. Magnetic field effect on stress was also investigated under constant stress and it was found that there is a threshold stress, above which magnetic-field-induced strain increases linearly with magnetic field when deformed at temperatures near M_s. This magnetic-field-induced stress-assisted strain was irreversible at the experimental conditions used.

11:00 AM D13.7
Coupled Magneto-mechanical Modeling of Ferromagnetic Particle Reinforced Composites. Lizhi Sun and H.M. Yin; University of Iowa, Iowa City, Iowa.

The objective of this work is to investigate effective magneto-mechanical behavior of composites containing aligned ferromagnetic particles. We first solve the local magnetic field, magnetic force and elastic field for pair-wise interacting magnetic particles embedded in the infinite domain subject to applied magnetic and mechanical loads. We further derive the effective (homogenized) magnetoelastic properties and effective magnetostriction of the composites. For magnetothermomechanical elastomer, the configuration of the mini- Bernie changes with the magnetoreponse loading due to the small elastomer's stiffness, so the local magnetic field and elastic field are fully coupled. This model accounts for the coupled magneto-elastic interaction and pair-wise interaction between particles. Experiment data on the magnetostriction of several ferromagnetic materials and experimental data on other models [Davis, L.C., 1999; J. App. Phys. 85 5388-3351; Jolly, M.R., et al, 1996; Smart Mater. Struct. 5 607-614].

SESSION D14: Sensor Materials and Devices
Chair: Yasutami Furuya and Minoru Taya
Friday, December 5, 2003
Room 202 (Hynes)

1:30 PM D14.1
Piezoresistive Properties of Ceramic Strain Gages with Controlled Nanoporosity. Otto J. Gregroyy and Xiao Yor; Chemical Engineering, University of Rhode Island, Kingston, Rhode Island.

A ceramic strain gage based on reactively sputtered indium-tin-oxide (ITO) thin films is being developed to monitor the structural integrity of components employed in advanced aerospace propulsion systems that operate at temperatures in excess of 1500°C. Electrical and chemical stability is particularly critical in these harsh environments, since these ceramic strain gages must survive tens of hours of strain testing at high temperatures. SEM micrographs of the surfaces of these strain gages after high temperature exposure revealed a partially sintered microstructure consisting of a contiguous network of nano-sized ITO particles with well defined necks. Electrical conduction takes place through the surfaces of these contiguous ITO particles resulting in a very stable and large piezoresistive response at temperatures as high as 1570°C. It appeared that densification of the ITO particles was retarded during high temperature exposure with nitrogen playing a key role in stabilizing the nanoporosity. To prepare this nanoporous ITO, sputtered ITO films were subjected to a post-deposition anneal at 700°C in nitrogen and subsequently exposed to high temperature. Based on these preliminary results, ITO strain sensors were reactively sputtered in various nitrogen/oxygen/argon environments. SEM and AFM indicated that although the microstructures of these nitrogen-sputtered films were similar in appearance to those produced by a post-deposition anneal in nitrogen, the average pore size and particle size were an order of magnitude smaller. It appears that nitrogen was metastably retained in the individual ITO grains during sputtering and diffused out of the bulk grains at elevated temperature, eventually becoming trapped at grain boundaries and triple junctions. Under these conditions, sintering and densification of the ITO particles containing these nitrogen rich grain boundaries was retarded and a contiguous network of nano-sized ITO particles was established. Static strain testing of the nitrogen-sputtered ITO sensors indicated that a similarly stable and responsive strain gage could be reproduced using this approach. The high temperature-piezoresistive behavior of ITO strain gages prepared with controlled nanoporosity is presented within and the potential impact on other types of ceramic sensors will be discussed.

2:15 PM D14.4
A Study of Ammonia Gas Induced Irreversibility in Polypropylene Films. Jaeuk Choi, J. Hormes* and Pawan K. Kohli;* 1Department of Electrical and Computer Engineering, Wayne State University, Detroit, Michigan; 2Center for Advanced Microstructures and Devices, Louisiana State University, Baton Rouge, Louisiana; 3Department of Physics, Wichita State University, Wichita, Kansas.

Polypropylene’s conductivity as a function of polymerization temperature and its properties on treatment with ammonia gas are studied. Electronic structures of PP (hexfluorophosphate) doped polypropylene (PPY) films grown at 40, 60, and 80 °C, before and after ammonia treatment, are compared using angle resolved photoemission spectroscopy, electron paramagnetic spectroscopy, and semi-empirical calculations. The valence band electronic structures of these polypropylene films depend on polymerization temperature, and ammonia treatment. The light polarization dependent valence band structures reflect ordering of polymer chains with decreasing polymerization temperature. The irreversibility properties of polypropylene, which can be used as an ammonia gas sensor, are shown to possibly arise from detachment of the dopant molecules under pumping.

Pathogens in food samples. Sreesha Cherubum and Etibam Wilkins; Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico.

We describe the development of an amperometric flow-through electrochemical biosensor that can be applied to the identification and quantification of pathogen bacteria such as E. coli, Listeria and Campylobacter in various food matrices (apple juice, milk and chicken) on the spot and in a short time. The system is able to detect very low concentrations of the bacterial cells in the samples. The sensor is sensitive, inexpensive, disposable and can be operated by untrained personnel. The prototype has [removed] potential for being used in the food industry as the assay time is only 30 minutes and the results obtained are reliable and repeatable. Point introduction of the sample is done and pretreatment of the sample is not required.

2:00 PM D14.2
Development of a New Design of Immunosensor for the Rapid Detection of Pathogens. Eric Carne and Etibam Wilkins; Chemical and Nuclear Engineering, University of New Mexico, Albuquerque, New Mexico.

A portable, flow-through amperometric immunosensor system utilizing a newly designed immunosensor has been developed for the detection of pathogens. A sandwich scheme of immunosensing involving two stages of immunocapture was employed using Bacteri chinola as a model. E. coli antibodies were immobilized on Toray carbon paper to create a disposable immunosensor membrane. Detection of the bacteria was achieved by using horseradish peroxidase labelled antibodies, which, when coupled with a substrate of hydrogen peroxide and sodium iodide, yielded an electrode-reduction which was measured amperometrically at a potential of 1.05 V. The immunosensor is highly sensitive and selective through the use of a disposable immunosensor membrane that also functions as an immunoelectrode, which enhances the rate of the immunoreaction due to the high surface to volume ratio of the solid to liquid phases. The system was designed to be simple and effective, as well as cost effective and rapid. Comparison of the performance of this system with conventional immunosensors demonstrates a significantly shorter time for the assay. Optimization of the parameters of the system was conducted, resulting in an overall assay time of 17 minutes when a flow of 200 mL/min is used. The first stage of immunocapture of immobilized antibodies with the analyte was found to saturate in 2 minutes. The second stage of immunocapture with the enzyme-labelled conjugates exhibited a more complex behavior but became saturated in 6 minutes. The amperometric detection using the substrate gave a steady output signal after 3 minutes. All stages are separated by 2 minutes of washing by a rinsing buffer solution, and the whole analysis is preceded by a 5 minute pre-washing stage in order to eliminate the problem of non-specific binding of immunoreagents. The working range for the immunosensor was found to be 5-1000 cells/ml. The disposable immunosensor membranes were found to retain most of their sensitivity for at least 7 months if refrigerated at 4°C. The developed system demonstrated improved analytical characteristics over conventional immunosensor techniques. Polypropylene commercialization of this system was a major objective, so the design highlights simplicity and compatibility with functionalized automated, portable prototype is currently under construction. The enhanced sensitivity and short assay time permit the application of the developed system to near real-time detection of a wide range of analytes in medical diagnostic, biomedical, and clinical and chemical analysis, food quality control, and environmental applications.

1:45 PM D14.2
Automated Amperometric Immunosensor for Detection of...
2:30 PM D14.5
Accelerated Reliability Test inputs in analyzing the device response of MgZnO based UV Detector. Shery S. Hallward1, Ishve Takeuchi1, Tirmalini Venkteswara1, Ratnakar Vispute2,3 and Sharad Yadav2,4,5,6.
1Center for Superconductivity Research, University of Maryland, College Park, Maryland; 2Blue Wire Semiconductors, Inc, Columbia, Maryland.

Ultraviolet (UV) light sensor is an essential component of UV light detection and monitoring required in a variety of commercial applications like fire detection, lithography, data storage as well as defense applications. MgZnO is known and shown to exhibit immense potential in this area as a tunable UV sensor due to its desirable optical and electrical properties. In this paper, we present results on the fabrication of MgZnO based Metal semiconductor-metal (MSM) UV sensor and address its stability issues. MgZnO is grown by pulse laser deposition (PLD) on three different substrates viz., glass, quartz and sapphire. X-ray diffraction and Raman spectroscopy are performed to analyze crystallinity and the optical nature of the films. Standard photolithographic and lift off techniques are used to define MSM patterns on the device quality MgZnO films. Photo-response of the device is monitored by monochromator and lock-in-amplifier combination setup. Device stability and performance is examined under accelerated conditions of prolonged UV exposure.

2:45 PM D14.6
a large grain polycrystalline silicon film for resistive bolometers. Tae-Sik Kim and Hee Chul Lee. E.E. CS, KAIST, DAEJEON, South Korea.

Bolometers, uncooled IR detector, based on vanadium oxide (VOx) and amorphous silicon (a-Si) films have been studied all over the world for a long time. These films have large temperature coefficient of resistivity (TCR). The main characteristics of VOx/a-Si films are large TCR and high sensitivity. But, these films have poor reliability properties and dielectric oxide without some hysteresis. Although the fabrication process for bolometer made with a-Si film is CMOS compatible and its TCR value is around -2.5%/K, however, the films exhibit large 1/f noise, thereby yielding a decrease of detectivity. In this paper, we have investigated large grain polycrystalline silicon films for resistive bolometers as an alternative to VOx/a-Si film. This is because polycrystalline films are much more stable material than VOx/a-Si films and CMOS technology can be used to fabricate polycrystalline-based bolometers. In comparing with a small grain polycrystalline film, a large grain polycrystalline film has properties as follows: First, the TCR of the film theoretically increases in proportion to the increase of the grain size of the film. Second, we can obtain a film with fewer grain boundary defects, which lead to a decrease of the 1/f noise of the film. Lastly, the large grain polycrystalline film shows less dependence of resistivity on the variation of the doping concentration; therefore, it is easy to obtain required resistivity in the film. The achieved average grain size was as large as 160μm using a seed selection through ion channelling technique. Its TCR at 30°C and 0°C were measured to be as high as -2.8%/K for a resistivity of 30Ωcm and to be about 1.75×1012/cm², respectively. The value of r, 1/f noise parameter, was calculated to be 1.35×10−6. From the above results, the estimated detectivity was found to reach up to 5.6×1012 cmHz1/2/W.
pentene film. The origin of the humidity effects in a change of pentene film mobility. We will also discuss an unusual field effect in conducting polymer poly (ethyleneoxy-chiophene)-polyacrylamide salt (PEDOT-PSS) and the application of these transistors in DNA sensing. The advantages of the PEDOT-PSS devices include high sensitivity and low gate voltage.

4:30 PM D14.11
Metal-containing diamond-like carbon-silicon nanocomposite films as temperature sensors. Toshiyuki Takagi1, Alexei Bratilo1, Takamori Takeno1 and Mikhail Shapkin2. 1Institute of Fluid Science, Tohoku University, Katahiru 5-1-1, Aoba-ku, Sendai, Japan; 2Moscow State University, Moscow, 119899, Russian Federation; 2Moscow Power Engineering Institute, Moscow, 105885, Russian Federation.

The transition metal-containing diamond-like carbon-silicon nanocomposites are characterized by the stability to the aggressive environments and possess attractive mechanical properties, such as high hardness and wear resistance, low friction. The variation of the metal concentration allows to change the conductivity of the nanocomposites in the wide range. The possibility of the application of metal-containing diamond-like carbon-silicon nanocomposite films as advanced temperature sensors with controlled temperature response was studied. W- and Nb-containing diamond-like carbon-silicon nanocomposite films were deposited onto dielectric polycrystalline substrates by PECDVD of silicon vapours in DC-stimulated discharge and DC magnetron co-sputtering of metal target. The RF bias voltage was applied to the substrate holder during deposition of the films. It was shown that the conductivity of diamond-like carbon-silicon nanocomposite films containing both W and Nb decreases with temperature and follows the power law dependence. The decrease of metal concentration leads to rather sharp increase of the power exponent in the range from 0.3 to 0.7. Such temperature dependence of the conductivity corresponds to the electronic transport mechanism being described by the inelastic electron tunnelling between metal nanoparticles dispersed in an insulating carbon-silicon matrix with high degree of disorder. The absolute value of the dimensionless sensitivity defined as $\frac{dV}{dT}$ where $V$ is the conductivity and $T$ - temperature, demonstrates the dependence on the temperature close to the linear one in the investigated temperature range and increases from 0.2 to 1 with metal concentration. The experimental data obtained show the principal possibility of the fabrication of the wide temperature range thermometers, which retain their functionality under extreme environmental conditions.

4:45 PM D14.12

Reactions between crystalline Si surfaces and chemical species that lead to modification of the Si surface barrier offer an exciting opportunity for chemical sensing [1]. In order to explore this concept, high quality Si wafers were exposed at room temperature to aqueous solutions of inorganic acids and bases, and then the surface potential was measured in a non-contact, non-destructive fashion using the Surface Photovoltage (SPV)[2]. The SPV signal was obtained by illuminating the Si surface with monochromatic light (wavelength > Si bandgap) and it was measured with a transparent, conducting electrode placed above the Si surface. The change of the surface potential barrier was clearly related to the type of chemical species and their concentration. It was also dependent on the Si orientation and the microscopic topography of the Si surface. In addition, the SPV signal was dependent on the wafer cleaning process that preceded the experiment. Relatively small changes in the concentration of chemical species, especially within the low concentration range, caused large changes of the SPV signal, demonstrating high sensitivity. Repeated cycles of acid and base exposure showed that the surface reactions were reversible and that the SPV signal cycled between the base-specific and acid-specific values, thus showing that the sensing device can be reused many times. In order to further enhance the SPV signal, the Si surface was intentionally terminated with a layer of selected organic or inorganic molecules. This termination had two purposes: it provided stable surface termination, and it offered the possibility of selective binding of only specific molecules. Preliminary results indicate that proper choice of the binding layer can make the SPV chemical sensing highly selective with respect to a large number of chemical species. The simplicity of the SPV measurement setup indicates that SPV-based chemical sensors can be easily miniaturized and cheaply produced in a compact form.[1] J M Burik; Chem.Rev.102, 1271 (2002). [2] K Naka, T. I. Kamins, J Electrochem.Soc 146, 292 (1999).