SYMPOSIUM BB
Characterization and Modeling of Domain Microstructures in Materials

November 27 – 29, 2000

Chairs

Wenwu Cao
Pennsylvania State Univ
164 MRL
University Park, PA 16802
814-865-4101

Avadh Saxena
Los Alamos Natl Lab
T-11 MS B262
Los Alamos, NM 87545
505-667-5227

Takaaki Tsurumi
Dept of Inorganic Materials
Tokyo Inst of Tech
Tokyo, 152-8552 JAPAN
81-3-57342517

Symposium Support
Army Research Office
Los Alamos National Laboratory
Pennsylvania State University
Tokyo Institute of Technology

*Invited paper
8:30 AM *BB1.1
STATICS AND DYNAMICS OF MARTENSITIC INTERFACES.
Gerhard R. Brusch, Penn State University, Dept. of Physics and Materials Research Laboratory, University Park, PA.

In this review an account of the contribution will be given that Landau-Ginzburg models have made so far to the understanding of the static and dynamic properties of domain walls and domain configuration, including dislocation and improper ferromagnetic martensite. Following a recapitulation of the conceptual and mathematical basis underlying the mesoscopic mean-field approach, theoretical results for the structure, energy and mobility of domain walls, twin bands and pretransformation domains (twod) and their effect on elastic and phonon properties are discussed and compared with available experimental data. In addition, the relevance of these results and of the methodological approach for understanding the martensitic nucleation mechanism and the hysteresis in shape memory applications will be discussed. In conclusion, a listing of open questions will be presented.

9:00 AM *BB1.2
PREMARTENSITIC MICOSTRUCTURE IN FERROMAGNETIC NiMnGa SHAPE-MEMORY ALLOYS. Antonio Plese, Lluis Maestro, Teresa Castin, Eduard Vives, Univ Barcelona, Dept ECEM, Barcelona, Catalonia, SPAIN.

NiMnGa alloys close to the stoichiometric Heusler composition are, at present, the only known ferromagnetic alloys which exhibit shape-memory properties associated with a thermomagnetic martensitic transformation; the latter is induced by a high-temperature L21 structure towards a tetragonal low-temperature phase. For several compositions, the martensitic transition is preceded by a transition towards a modulated microstructure resulting from the spontaneous formation of the 1/8[110]TA3 planes. We will show that, in the case of NiMnGa, the coupling between vibrational and magnetic degrees of freedom is the key ingredient which gives rise to such a condensation. Experimental results including elastic constants, phonons and magnetic measurements will be presented that are aimed at (i) corroborating the existence of spin-phonon coupling and (ii) characterizing the premartensitic transition. These results will be discussed within the framework of a lattice model which contains structural and magnetic variables. Numerical simulations of the model show that some anomalies observed in the specific heat and magnetic susceptibility originate from large-amplitude fluctuations. The main conclusion is that an adequate combination of magnetocaloric coupling and phonon softening is the essential feature for the premartensitic transition to occur.

9:30 AM *BB1.3
DOMAIN STRUCTURES AND INTERFACES IN NiAl MARTENSITE. COMPARISON HREM OBSERVATIONS WITH CONTINUUM THEORIES. Dominique Schreyers, Philippe Boullay, Pavel I. Potyomkin, EMAT, University of Antwerp, RUCA, Antwerp, BELGIUM and Mathematical Institute, University of Oxford, Oxford, UNITED KINGDOM.

Domain structures and interfaces formed during the cubic-to-tetragonal martensitic transformation in NiAl are investigated experimentally using HRTEM. The effects of different materials preparation methods, including homogenised bulk, sputter-coated discs and melt-spin ribbon will be presented. The observed micro- and nanostructural features are interpreted in view of possible formation mechanisms. For interplate interfaces a distinction is made between cases in which the microtwins, originating from multiple partials, are straight for [110] martensite variants and those for [111] martensite variants. Finally, a closer look is given on the interface. By comparing NiAl with the existence of twin microtwins with varying volume fractions. Although both features appear irrespective of the materials preparation technique, rapid solidification seems to prefer the step configuration. Depending on the actual case, twinning, bending or the setting of the small microtwins variants is observed. The twin boundary is characterized by a high dislocation density. The formation of the martensite variants are interpreted in view of the need to accommodate any remaining stresses. The measured parameters such as volume fraction, directions of rigid body rotations and relative angles between microtwins are compared with predictions of the two-dimensional theory assuming energy minimizing configurations. For melt-spin material, local nanoscale inhomogeneities yield different microstructures and result in a wide temperature range for the transformation process. The latter are documented by EDS, EELS, X-ray and DC measurements.

10:00 AM *BB1.4
DOMAINS AND MULTISCALE MICROSTRUCTURE IN ELASTIC MATERIALS. Turah Shot, Los Alamos National Lab., Los Alamos, NM.

Martensitic structural transitions, especially those with unit cells related by continuous deformations, exhibit a rich variety of temperature/stress induced domains. We present a unified understanding of twins, twined nucleation pathways and stress loading for the martensitic transition, from a mesoscopic (Ginzburg-Landau free energy entirely in strain variables. The strain description demands that the elastic compatibility constraint be satisfied. The important consequence of this is a long-range, anisotropic interaction in the order parameter strain field which mediates the elastic interactions under different thermodynamic conditions. For instance, local stress inhomogeneities can affect structures on a global scale. The formalism is readily applied to all major crystal systems in 2D and 3D. We will illustrate it for (a) structural transitions of the square and triangular lattices in 2D and (b) cubic to tetragonal and cubic to trigonal transformations in 3D. We show how these ideas are generalized to ferroelectrics, magnetoelectrics and many other related materials where strain is a secondary order parameter. The experimental observation and role of various microstructures on material specific functionalities will be emphasized.

Collaborators: K. Rummens, A. Sawen, A.R. Bishop, R.C. Albers (Los Alamos) and S.R. Scyren (ICTP, Trieste).

11:00 AM *BB1.5
X-RAY AND TEM INVESTIGATIONS ON SINGLE CRYSTALS OF NiMnGa SHAPE MEMORY Alloy. Christian Wodel, Kaise Itagaki, Tokohu University, Institute for Advanced Material Processing, Sendai, JAPAN; Boris Wodel, Dowa Mining Co. Ltd., Central Research Laboratory, Hachioji, JAPAN.

The ferromagnetic Heusler alloy NiMnGa and the non-ferromagnetic alloys from the same phase have been recently attracting attention. They are very promising materials for several applications, since the magnetic properties make it possible to control the martensitic transition with a magnetic field. Several research projects focused on this subject. The weak point in the research of this material was the confusion about the crystal structure. So far it was known that NiMnGa undergoes a thermomagnetic martensitic transformation from a ferromagnetic L21 ordered cubic phase to a tetragonal phase, but the structure of this low temperature phase has so far only been reported in an incomplete and often wrong way. X-ray diffraction methods and TEM studies were used to investigate the phase transformation and the resulting domain structure. The single crystals were prepared by the Czochralski method. Several crystals with different compositions and therefore with varying temperatures of the martensitic transformation TM were used. For the alloys with TM below room temperature a cooling device was used for both experimental techniques. The phase transition occurs between the Heusler type and an ordered superstructure of the AuCu type. In this superstructure the c-axis of the AuCu type is doubled. Besides the undisturbed domains of this type, the TEM investigations show domains with statistically distributed stacking faults and other with long range ordered structures. The modulation of the structure associated with the premartensitic state was also observed.

11:15 AM *BB1.6
PHASE FIELD MODEL AND COMPUTER SIMULATION OF MARTENSITIC TRANSFORMATION IN POLYCRYSTALS OF Fe-Ni ALLOYS. A. Artemov, Carleton University, Dept. of Mechanical and Aerospace Engineering, Ottawa, Ontario, CANADA; Y. Jin and A.G. Khachaturyan, Dept. of Ceramic and Materials Engineering, Rutgers University, NJ.

A three-dimensional phase field model of the martensitic transformation in polycrystalline materials was developed. The evolution of phase field functions is described by a kinetic equation of the Ginzburg-Landau type, which explicitly takes into account the contributions of the transformed coherent and incoherent domains by using the phase field micromechanics of a structurally inhomogeneous coherent system. This model was used to simulate the fcc to bcc transformation in polycrystals of Fe -31 at. % Ni. Simulations were performed for a wide range of undercoolings and under both constrained and unconstrained conditions for an average deformation in the systems. The effect of applied stress on the transformation and structure evolution in a material after the transformation was studied. Microstructures with polygonal martensite structures were obtained. Simulation has shown the systems with low misorientation angles between grains have the same type of transformation as
single-cystal systems do. A large value of the volumetric transformation effect in the Fe–Si system resulted in significant fractions of the residual parent phase in constrained systems after the transformation. The volume fraction of the residual parent phase in these systems depended strongly on the undercooling. The stress vs. strain curves with the hysteresis effect were obtained by the simulation of the structure evolution under applied stress.

11:30 AM BB1.7
EFFECT OF ELECTRIC INTERACTION ON THE FORMATION OF COMPLEX MULTI DOMAIN MICROSTRUCTURAL PATTERN DURING A COHERENT HEXAGONAL TO ORTHORHOMBIC TRANSFORMATION. Y.H. Wei, Y. Wang, Department of Materials Science and Engineering, The Ohio State University, Columbus, OH; and L.Q. Chen, Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA.

The formation and temporal evolution of domain structures during a hexagonal to orthorhombic transformation is studied using computer simulations based on a continuum diffuse-interface phase-field approach. All essential driving forces for the domain formation and evolution are taken into account, including bulk chemical free energy, domain wall energy, and strain energy. Two different types of transformation, i.e., coherent ordering leading to a single orthorhombic phase and precipitation resulting in a two-phase mixture, are considered. The influence of an applied strain on the transformation process is also studied. The various domain configurations observed from the computer simulations show excellent agreement with existing and concurrent experimental observations in a number of alloy systems undergoing hexagonal to orthorhombic transformations. It is shown that, even with the assumption of isotropic domain wall energy and isotropic elastic modulus, the anisotropic elastic interactions alone caused by the non-dilational strains can reconstruct the intermediate structure observed experimentally. It is also demonstrated that many of the specific domain configurations are actually formed during domain coarsening after the phase transformation has completed.

11:45 AM BB1.8
MICROSCOPIC SIMULATIONS OF PHASE SEPARATION IN ALLOYS WITH VARYING MISMATCH BETWEEN PRECIPITATES AND MATRIX. V. Voitik, V. Vinokur, F. Fratzl, and J. L. Lebowitz. 1. Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, and Metal Physics Institute, University of Leoben, AUSTRIA. 2. Departments of Mathematics and Physics, Rutgers University, NJ.

Long-range elastic interactions resulting from a lattice mismatch between matrix and precipitates are known to influence crucially the shape and arrangement of the precipitates and the coarsening kinetics of the microstructure during phase separation [1]. Employing a microscopic model, we have performed Monte Carlo simulations to study elastic effects on the phase separation process in a binary alloy with face-centered cubic structure, in which elastic interactions are represented by springs connecting nearest neighbor atoms [2]. In this paper we report the results of simulations, where a varying mismatch between precipitates and matrix were chosen. The salient feature concerning the microscopic structure of the precipitates is the regular arrangement of the precipitates with increasing lattice mismatch leading to a mesoscopic structure formed by the precipitates. Deviations from a spherical precipitate shape cause the emergence of an interconnected precursor structure even for low volume fractions. In the case of a large lattice mismatch we observe a slowing down of the coarsening process, which we interpret as the prevalence of new coarsening mechanisms which have to enable coarsening without destroying the elastic stress. The movement of mesoscopic defects of the mesostructure was identified as such a new mechanism.


SESSION BB2: DOMAIN-RELATED PHENOMENA IN FERROIC MATERIALS II
Chair: Takashi Tsutumi and Yeong Ching
Monday Afternoon, November 27, 2000
Room 201 (Hynes)

1:30 PM *BB2.1
DOMAIN CONFIGURATIONS OF FERROELECTRIC SINGLE CRYSTALS AND THEIR PIEZOELECTRIC PROPERTIES. Satoshi Wada, Takashi Tsutumi, Tokyo Inst. of Technology, Dept of Metallurgy & Ceramics Science, Tokyo, JAPAN.

Piezoelectric property of ferroelectric single crystals significantly depend on their domain configurations. The domain configurations depend on a crystal symmetry and a crystallographic directions. Recently, in [001] oriented 3m PZT-PT single crystals, ultrahigh piezoelectric constant over 10000 V/m and hysteresis free strain vs. electric field behavior were reported, and their origin was assigned to an engineered domain configuration. It is also expected that the engineered domain configuration is useful for FERAM application from the viewpoint of the improvement in fatigue property. Especially, it is important to realize this result along the crystallographic directions related to the engineered domain configuration. For example, in 4mm ferroelectric crystal, two kinds of engineered domain configurations are expected along <111> and <110> directions. In [111] oriented 4mm BTO crystal, piezoelectric constant over 2000 V/m was observed along electric field behavior were observed while [001] oriented 4mm BTO crystal showed the piezoelectric constant below 1000 V/m and hysteresis free strain vs. electric field behavior even if its polar direction was [001] directions. Coercive electric field in [111] oriented 4mm BTO crystal was smaller than that in [001] oriented 4mm BTO crystal. This means that the engineered domain configuration in BTO crystal affected domain kinetics. These studies were extended to other symmetries (mm2 and 3m) of BTO, PZT-PT and KTaO3 crystal ids.

2:00 PM *BB2.2
SYNCHROTRON X-RAY SCATTERING STUDY OF NANO-DOMAINS IN PZN-PT SINGLE CRYSTALS. Andrei Truskul, Haiden Chen, Paul Zurcher, Dept of M&SE and Frederick Seitz Materials Research Laboratory, University of Illinois, Urbana, IL.

A systematic study of the temperature dependence of superlattice reflections has been carried out using anomalous x-ray scattering technique for single crystals of PZN-PT: Pb (Mg, Ni)O (PMN-NiO) for the first time. Two types of nanodomains were found: 1) chemically ordered nanodomains, and 2) polar regions formed by short-range correlated ionic displacements. Each type of nanodomains give rise to superlattice reflections at different locations in the reciprocal space. The focus of the present study is to investigate the behavior of these nanodomains as a function of temperature, leading to an improved understanding of the microstructure origin and the underlying physical principles responsible for the ferroelectric properties. The anomalous scattering technique was utilized, with the synchrotron x-ray energies tuned close to the Pb(II) absorption edge so as to highlight the contribution of Pb species to the scattering intensities. This experimental method was chosen because local dipoles, originated from Pb displacements, are most important to the observed ferroelectric behavior. From the temperature dependence of the superlattice peak intensity corresponding to polar regions born out from in-phase rotation of oxygen octahedra (i.e. when spots at the face-centered locations), we found the freezing temperature of correlated ionic displacements is 200K. From the line profile analysis, the estimated nanodomain size is about 4-5 nm. These polar domains disappeared above the freezing temperature. This is the regular arrangement of the precipitates with increasing lattice mismatch leading to a mesoscopic structure formed by the precipitates. Deviations from a spherical precipitate shape cause the emergence of an interconnected precursor structure even for low volume fractions. In the case of a large lattice mismatch we observe a slowing down of the coarsening process, which we interpret as the prevalence of new coarsening mechanisms which have to enable coarsening without destroying the elastic stress. The movement of mesoscopic defects of the mesostructure was identified as such a new mechanism.


2:30 PM *BB2.3
STRUCTURE AND DYNAMICS OF FERROELECTRIC DOMAIN WALLS. V. Gogotsi, S. Kim, Pennsylvania State University, State College, PA; L. Freti, Carnegie Mellon University, Pittsburgh, PA; T. E. Mitchell, P. Swart, A. Saxeena, Los Alamos National Lab, Los Alamos, NM.

This talk addresses classical issues of domain wall structure and motion under external driving forces with reference to lithium niobate and lithium tantalate ferroelectrics. Recent studies reveal many new aspects of these ferroelectrics, such as a very large sensitivity of physical properties to small amounts of nonstoichiometry, regions of strain, electric fields and optical birefringence at the 180 deg domain walls extending over many microns, local pinning and bending motion of a domain wall well below the coercive field required for domain motion, and time dependent mobility of a wall at a fixed driving field. The talk will review very fundamental questions in ferroelectrics, such as, what is internal structure of a domain wall? and what are the intrinsic and extrinsic factors governing domain wall motion?
NONDESTRUCTIVE OBSERVATIONS OF POLAR DOMAIN STRUCTURE AND ITS KINETICS USING SGH INTERFERENCE MICROSCOPE. Yoshihiko Ue, Noritsuka Kato, Hirohiko Morih, Hiroshi Shibata, Department of Physics, Waseda University, Tokyo, JAPAN.

Optical second harmonic generation (SHG) becomes an important technique for observing various kinds of domain structure in ferroelectrics/1,2/ and anti-ferroelectricities/3,4/ and in molecular orientations in reduced crystalline structure. We have proposed an interference SHG microscope which enables us to observe domain structures with opposite polarity/5,6/. So far, the non-destructive observation has been believed to be impossible, as the states with opposite polarity have some optical properties. Our method is to exploit the nature of the SH waves generated in antiparallel domains, i.e., they have equal amplitude but opposite phase. If they are mixed with other harmonics, the SH waves can interfere constructively in one domain, while destructively in another. Thus the domains with opposite polarity become visible. We applied successively the SHG interference microscopy to the observations of domain structures in BiTioO3/1/ perpendicularly inverted domains in LiNbO3, quartz phase-matching devices for wavelength converters/7/ and J-aggregate domain structure in merocyanine dye molecules/4,5/.

In this paper, a special emphasis will be put on the nondestructive observations of domain reversal process in LiNbO3 and 2D phase transition between J-aggregates accompanied by the thermochromism.

References:

4:30 PM BB2.5
DOMAIN STRUCTURES AND PHASES IN RELAXOR FERROELECTRIC CRYSTALS. Chi-Shan Tu, L.-F. Chen, C.-L. Tsai, Fu Jen University, Dept of Physics, Taipei, TAIWAN; V. Hugo Schmidt, Montana State University, Dept of Physics, Bozeman, MT.

The domain structure and phase transitions have been observed as a function of temperature for relaxor ferroelectric single crystals (PMN-PT), complex domain coexistence in electrostrictive composites (organic-inorganic) and cubic ceramics. Using X-ray and neutron diffraction technique, the persistence of ferroelectric phase in the paraelectric phase region is observed, and the inhomogeneous distribution of Ti4+ concentrations in the crystals. A fluctuation behavior is believed to result from an unequal occupation of the B-site by the coexisting ions Na+, Nb5+, and Ti4+ while lattice structure established. With light scattering and dielectric results, a phase diagram will be proposed.

4:45 PM BB2.8

Electrostatic force microscopy (EFM) and scanning surface potential microscopy (SSPM) observe the polarization distribution. The combination of topographic and surface potential images is used to reconstruct surface domain structures. Distance and bias dependences of the electrostatic force gradient data are used to determine the fraction of polarized domains. Experimental SSPM and EFM domain profiles are compared to calculated potential and field distributions for the unscreened and screened cases. Surface potential evolution during phase transitions and the potential distribution after moving domain walls allows the relationship between domain potential and polarization orientation to be determined. Cycling through the phase transition results in new domain structure at each cycle. Our results indicate that polarization bound charge is completely screened on this surface when in air. This conclusion is corroborated by piezoresistive imaging technique. Surface potential is attributed to the formation of double layer due to the complete screening of polarization charge. The absolute value of the potential difference between domains with opposite polarity suggests that surface adsorbrates play a governing role in potential formation mechanism, though intrinsic screening by free charge carriers is not completely excluded.

SESSION BB3: DOMAIN-RELATED PHENOMENA IN FERROELECTRIC MATERIALS
Chair: Angus I. Kingon and Hygin Chen
Tuesday Morning, November 28, 2000
Room 201 (Hynes)

8:30 AM BB3.1
FERROELECTRIC DOMAIN STRUCTURE IN KNbO3/KTaO3 HETEROSTRUCTURES BY MOLECULAR DYNAMICS SIMULATION. M. Slepansky, Materials Science Division, Argonne National Laboratory, Argonne IL and Instituto de Fisica Rosario, Argentina.
We simulate the domain switching in a finite sized ferroelectric system using the time dependent Ginzburg-Landau approach. The model also includes elastic and electrostrictive effects in the form of a long-range interaction obtained by eliminating the strain fields, subject to the elastic compatibility constraint. The surface effects are simulated by enforcing zero polarization constraint out side the system. We find that the switching process is strongly influenced by the presence of the surface. The surface acts as a nucleation source of orthogonally polarized domains. Interestingly, the actual switching occurs through ninety degree domain reorientation. Dependence of the hysteresis loops on the system size is also studied.

**10:30 AM** **DB3.5**
**DOMAIN NUCLEATION AND RELAXATION KINETICS IN FERROELECTRIC THIN FILMS**
C.S. Gopale, A.L. Rebyard, V. Nagajaran, E.D. Williams and R. Bhand, Materials Science and Engineering Center, Univ. of Maryland, College Park, MD; J.F. Scott, Department of Earth Sciences, Univ. of Cambridge, Cambridge, UNITED KINGDOM.

The time dependent relaxation of the remnant polarization in epitaxial lead zirconate titanate (Pb(Zr,Ti)O	extsubscript{3}, PZT) ferroelectric thin films, containing a uniform 2-dimensional grid of 90° domains (c-axes in the plane of the film), is examined using piezoresponse microscopy. The 90° domain wall preferentially nucleate the 180° reverse domains during relaxation, with a significant directional anisotropy. Relaxation occurs through the nucleation and growth of reverse domains, which subsequently coalesce and consume the entire region as a function of time. The rate of growth of reversed domains is closely related to the rate of growth of the growing phase. A thermodynamic analysis has been carried out to model and explain this time dynamics. We will present the results of these experimental and theoretical studies.

This work is supported by National Science Foundation - Materials Research Science and Engineering Center (NSF-MRSEC).

**10:45 AM** **DB3.6**
**THE INFLUENCE OF DOMAIN STRUCTURE ON THE DYNAMIC ELECTRO-OPTIC RESPONSE OF EPITAXIAL FERROELECTRIC THIN FILMS**
Brent H. Heerman, Barbara M. Nichols, Andrew R. Todd, and Stephen M. Proctor, Northwestern Univ, Dept of MSE, Evanston, IL.

Ferroelectric epitaxial thin films provide several potential advantages over thin films used in current high-speed electro-optic (EO) modulators. The benefits include lower driving voltages, higher modulation frequencies, and the possibility of direct integration with silicon. Consequently, investigation of the dynamic EO response of thin film ferroelectric materials has been undertaken. The dynamic EO response of epitaxial KNbO	extsubscript{3} and BaTiO	extsubscript{3} thin films was examined using a transverse measurement technique. Initial measurements of the EO coefficient in these films resulted in values ranging from 1 to 20 pC/N. The EO coefficients are more than an order of magnitude lower than those observed in single crystals as a result of the presence of multiple ferroelectric domain variants. Through consideration of the thin film domain structure, the EO coefficients can be effectively increased by a factor of 3 to 10. For BaTiO	extsubscript{3} thin films EO coefficients as high as 210 pC/N have been observed. The dynamic response of the EO coefficient and the polarization of the films was also measured between 6 ns and 1 s. For both thin film ferroelectrics a power law transient response of the EO effect and the polarization was observed after the removal of an applied electric field. This power law relaxation has been attributed to domain reorientation under the influence of an applied electric field.

**11:00 AM** **DB3.7**
**DOMAIN STATE PROPERTIES IN SrTiO	extsubscript{3} (STO) (110) SINGLE CRYSTALS**
Ruiping Wang, Misao Ishikawa, Toru Kinosita, Toshiharu Utsumi, and Kazumasa Hara, Dept of Physics, Tokyo Inst Tech, Tokyo, JAPAN; Yui Tsuchiya, Toshinor Yagi, Inst Res Electronic Sci, Hokkaido Univ, Sapporo, JAPAN.

Recent discovery on the evolution of ferroelectricity in STO has attracted much attention mainly in the physics field because last 30 years quite many researches have been carried out to elucidate the mechanism of the change from quantum paraelectric to quantum ferroelectric in SrTiO	extsubscript{3} (STO) and KTaO	extsubscript{3} (KTO) by means of atomic substitution. Atomic substitutions, e.g., Ca for Sr in STO and Li for K in KTO, induce fairly strong and long-range local field in the vicinity of substituted elements and in materials the bulk properties are extremely sensitive to the atomic substitution, oxygen-isotope exchange is a modified way to observe net lattice effect of the phase transition phenomena. In this paper, we will report the domain state properties of SrTiO	extsubscript{3} (STO) (110) oriented sample subjected to the oxygen-isotope exchange. The exchanged and non-exchanged
samples were conducted to the various kinds of physical property measurements. STO18 and other samples with intermediate compositions exhibited electrical behavior with $T_c < 24$ K. However, the facts that there is no heat anomaly at $T_c$ and that the temperatures at which the $T_e$ loop and the peak in the resistivity become discernible are higher than $T_c$ are considered to come from the 'domain' state, which is different from the ground state in the ferroelectric with well-defined macroscopic size domain walls. Recent experiments on the first Rooman, breiyngeen, revelation of polarization, and angular dependence of the dielectric constant clearly suggests the occurrence of the domain state with a quenched random-field disorder.


**11:45 AM BB3.10**

**MICRO- AND NANOSCALE DOMAIN ENGINEERING: PERIODIC PATTERNING AND SELF-ORGANIZED STRUCTURES IN LITHIUM NIOBATE AND LITHIUM TANASIALITE**


We present the survey of our recent studies of the field-induced domain kinetics in single-crystalline congruent lithium niobate (LN) and lithium tantalate. The proposed backswitched poling by field application to the lithographically defined metal strip electrodes allows to engineer the short-pitch periodic micro-scale surfaces for nonlinear optical applications. First-order single-loop continuous-wave second harmonic generation of 60 mW at 480 nm is achieved at 6.1/W efficiency in 0.5-mm-thick 4-micron-period LN. We demonstrate the formation of self-organized nano-scale domain patterns as the first achievement in domain nano-technology. It was shown how to obtain these patterns in this domain state at frequencies in LN by self-maintained formation of charged domain walls. Domain evolution has been investigated by in situ optical observation of the instantaneous domain patterns. SEM and SFM have been used for high-resolution visualization of the domain patterns revealed by etching proposing novel directions in nano scale domain engineering.

**SESSION BB4: DOMAIN-RELATED PHENOMENA IN FERROIC MATERIALS**

Chair: Alexander K. Tagantsev and Simon R. Phillpot

**Tuesday, November 28, 2000**

**Room 201 (Hyena)**

**1:30 PM BB4.1**

**UNDERSTANDING AND MANIPULATING THE PROPERTIES OF MIXED A-SITE CATION RELAXOR PEROVSKITES**


Lead perovskites with mixed Ba$\text{Sr}$ cations such as PZT, PMN, and PLZT have been developed over the course of nearly four decades, and have been the mainstay of the ferroelectric industry. However, environmental concerns have recently renewed the interest in lead-free ferroelectrics and piezoelectrics. In this work, we will report our exploration of composition-structure-property relationships in doped NaNb$_2$/BaTiO$_3$ perovskites has shown that many parallels to the Ba$\text{Sr}$ relaxor exist. These include: 1) the existence of structural, and compositionally-modulated noncubic domains over extremely broad ranges of composition; 2) broad and frequency-dependent dielectric relaxation following the Vogel-Fulcher relationship; 3) high electrostriction strain in compositions doped to isolate the perovskite phase. By manipulating phase compositions with guidance of high-resolution electron microscopy, dielectric measurements, and electromechanical tests, compositions have been identified which have actuation comparable to that of many lead perovskites. Two particularly interesting fields of behavior identified in the Ba$\text{Sr}$-codoped systems are electrostrictive single crystals and polycrystals with actuation strains (0.1% and 0.2% respectively) exceeding that of optimized PMNs, and relaxor-ferroelectric compositions in which polycrystals show actuation nearly identical to that of PZT-8.

**528**
2:00 PM *BB4.2
THERMODYNAMICS OF POLYDOMAIN STRUCTURES ARISING AT FIELD-INDUCED TRANSFORMATION. Alexander L.
Boyd, Jr., Dept. of Materials and Nuclear Eng., Univ. of Maryland, MD.

Thermodynamic analysis of polydomain structures arising during phase transitions induced by mechanical, electrical, and magnetic fields shows that the equilibrium product phase is incompatible with the parent phase as a rule. Therefore, internal stresses, depolarizing, and demagnetizing fields are created in the twin-phase state. Correspondingly, the free energy leads to the thermodynamic hysteresis of the phase transformation. This thermodynamic phenomenon is considered for superelastic stress induced transformation of shape memory alloys as well as for ferroelectric and ferromagnetic transformations with significant stress effects.

2:30 PM BB4.3
DOMAIN WALL MIGRATION IN PURE AND IMPURE SYSTEMS: SIMULATIONS AND ANALYTICAL MODELS. Michael J. Mendelsohn, David J. Srolovitz, Princeton University, Princeton Materials Institute and Dept. of Mechanical & Aerospace Engineering, NJ; Weimin E. Han, Princeton University, Program in Applied and Computational Mathematics & Mathematics Dept., NJ.

The properties of many active materials are determined by the arrangement of the domains which can be moved. The mobility of domain walls can be quite different, depending on whether the system is pure or impure, whether the impurities or point defects are mobile or stationary, the nature of impurity/domain wall interactions, etc.

We will present the results of a series of simulations of domain wall migration in systems without impurities with elastic interactions and with impurities that are free to diffuse. We perform the simulations within a kinetic Monte Carlo formalism based on a simple spin model. While such domain migration has been analyzed theoretically, the present simulations demonstrate that the assumptions commonly made lead to significant errors (both qualitative and quantitative).

Even in a pure system, the driving force-velocity relationship is non-linear (in contrast with common models). An analytical model for this relationship is derived and shown to provide good agreement with the simulations. The simulations of impure systems focused on interstitial impurities and considered the effects of bulk impurity concentration, impurity diffusivity, interaction strength, and temperature. Two regimes of motion were distinguished (at low and high velocity) with a smooth transition between them under all conditions. Contrary to the classical continuum model of impurity drag, the simulation results demonstrate that attractive and repulsive impurity-domain wall interactions yield very different domain wall mobilities and the domain wall velocity never exceeds sharp jumps. The deficiencies in the classical continuum model were associated with the imprecision and limited accuracy of the classical impurity diffusion and impurity distribution. A discrete model is developed that properly describes the transition between regimes and the differences between attractive and repulsive impurities.

4:45 PM BB4.4
RECENT PROGRESS ON SCANNING NONLINEAR DIELECTRIC MICROCOPY WITH SUB-NANOMETER RESOLUTION. Yasuo Chiba, Hiroaki Ohara, Research Institute of Electrical Communication, Tohoku University, Sendai, JAPAN.

We have recently proposed and developed a new purely electrical method for imaging the state of the remnant polarization of ferroelectric materials, which involves the measurement of point-to-point variations of the nonlinear dielectric constant of a specimen, modified the “scanning nonlinear dielectric microscopy” (SNDM). This is the first successful purely electrical method for observing the ferroelectric polarization distribution without the influence of the shielding effect from free charge. Now, the stronger demands are for the observation of very small domains with nano- and sub-nano-meter sizes, which are the major tasks of ferroelectric materials, for example, to investigate domain wall structures, to clarify the minimum domain sizes etc. Therefore, we developed a new SNDM with nano- and sub-nano-meter resolution. Experimentally in the PZT thin film measurement, we succeeded to obtain a domain image with a sub-nanometer resolution. Next theoretically we clarify the reason why a very high (nano-sized) resolution can be easily obtained, even if a relatively thick needle is used in the probe. As the results of the theoretical studies, quantitative measurements of the distribution of linear and nonlinear dielectric constants of ferroelectric materials are successfully performed. Finally, we also demonstrate that SNDM technology is very useful for determining local crystal anisotropy such as a poling of thin film deposited on polar substrates.

3:30 PM BB4.5
DYNAMICS OF SHAPE-MEMORY STRINGS USED AS FLAGELLA AND CILIA. Kanshik Bhattacharya and Prashant Purushit, Division of Engineering and Applied Science, California Institute of Technology, Pasadena, CA.

Shape-memory alloys are very attractive for microactuators because they can produce the largest work per unit volume amongst all actuator materials. In particular, they have recently been proposed for use in microinjection in the form of flagella and cilia. This talk will describe the theoretical and experimental results of these applications. Of particular interest is the nucleation and propagation of phase and twin boundaries, their mobility, and their ability to create a bending motion in three dimensions. Parallel kinematic and continuum theory will describe the unique features of planar boundaries in strings and contrast them with interfaces in bulk materials. These results will be compared with experimental observations.

4:00 PM BB4.6
MAGNETIC FORCE MICROSCOPY STUDY OF MAGNETIC DOMAIN MICROSTRUCTURES IN CoAg GRANULAR FILMS. M.J. Chish, S.P. Weng, W.Y. Cheung, Department of Electronic Engineering, The Chinese University of Hong Kong, Hong Kong, CHINA.

Granular thin films of CoAg, of various compositions were prepared using a pulsed filtered vacuum arc co-deposition system. The composition of the films was determined by Rutherford backscattering spectrometry. The magnetic domain microstructures were studied using magnetic force microscopy. Two distinct types of domain structure patterns were observed for films of different Co composition. For films with a cobalt composition x of 0.7 and smaller, the magnetic domain structures show beautiful patterns consisting of long labyrinthine stripes of bright and dark regions, which represent domains with antiparallel perpendicular magnetization. The thickness of the stripes is slightly smaller than 0.1 μm and the typical length can be as long as a few μm. On the contrary, for films with a cobalt composition x of 0.8 and larger, the domain structure pattern changed dramatically to a much more irregular shape, resembling that of a pure Co film. The variation of the magnetic domain microstructures of the films with annealing temperature and their evolution under the application of an external magnetic field were also studied. These results were presented and discussed in conjunction with the magnetic properties of these films.

This work is partially supported by the Research Grants Council of Hong Kong SAR (Ref. No. CUHK 4152/98E).

4:15 PM BB4.7
STUDY OF THE THERMAL BROADENING OF FERROELECTRIC DOMAIN WALLS IN LEAD TITANATE BY QUANTITATIVE TRANSMISSION ELECTRON MICROSCOPY. Ahsan Sfera, Michael Booth, Philippe A. Boffa, Pierre Stadelmann, Swiss Federal Institute of Technology, Interdisciplinary Center of Electron Microscopy, Lausanne, SWITZERLAND.

The ferroelectric domain wall thickness is an important parameter and its behavior as a function of the temperature is directly related to the order of the phase transition. Several models exist to describe the broadening of domain walls; however, up to now there was no quantitative experimental observation of this phenomenon to check their validity. We have developed two methods for the measurement of 90° ferroelectric domain wall thickness. The first method uses high resolution transmission electron microscopy (HRTEM) and allows a direct observation of the lattice distortion across the boundary. The domain wall thickness is obtained from the measurement of the crystal lattice distortion near the interface using the geometrical phase method. This method consists in selecting a circular region of the power spectrum around a reflection peak, entering the Fourier space on this reflection and performing the inverse Fourier transform. The information about the local displacement of atomic planes corresponding to the selected reflection is extracted from the phase component of the obtained complex image. The second method consists in a quantitative analysis of interference fringes which appear on weak beam images of inclined domain walls. By fitting simulated fringe profiles to the experimental ones, the domain wall thickness can be extracted in a quantitative way. Both methods have been successfully applied to lead titanate in the paraelectric phase. The permittivity presents a first order phase transition at Tc = 492 °C which corresponds to the transformation of the crystal from a high-temperature paraelectric cubic phase to a low-temperature ferroelectric tetragonal phase. The thermal broadening of 90° domain
SESSION B5-Poster Session
Domain-Related Phenomena in Ferroelectric Materials
Chairs: Antoni Planes and Venkatesham Gopalan
Tuesday Evening, November 28, 2000
8:00 PM
Exhibition Hall D (Hynes)

B5.1
A STUDY OF OPTICAL PROPERTIES OF SrBi2Ta2O9 THIN FILMS BY SPECTROSCOPIC ELLIPSOGRAMY. D. Mo, Y. Liu, Department of Physics, Zhejiang University, Hangzhou, China; J.B. Xu, G.D. Hu, Q.J. Li, K.Y. Wang and S.P. Wong, Department of Electrical Engineering and Materials Science and Technology Research Center, The Chinese University of Hong Kong, Shatin, NT, Hong Kong, CHINA.

We have prepared the [200]-preferred and [001]-preferred SrBi2Ta2O9 films by metal organic decomposition (MOD). We have measured and analyzed ellipsometric spectra of these oriented films in the range of photon energy from 2 to 5.5 eV. We find that the spectra of [001]-preferred MOD films show remarkable microstructural effects.

By analyzing the spectra, we have obtained the effective refractive index n and the extinction coefficient k of both SBT films. The n values between the [001]-preferred and [200]-preferred MOD SBT films show a large difference (Δn > 0.2). The band gap of the SBT thin films is found to be about 3.26 eV, i.e., 3.8 eV. We have also analyzed the correlation between the ellipsometric data and the results by the NSOM measurement.

B5.2
ATOMIC SCALE ANALYSIS OF DOMAIN BOUNDARIES IN VACANCY-ORDERED BROWN-MILLERITE-TYPE SrCoO2-δ, Yasuo Ikeda, K. Kie, N. Dobert, University of Illinois at Chicago, Dept. of Physics, Chicago, IL; Terry J. Mencik, BP Amoco Chemicals, Naperville, IL.

The high mobility of oxygen vacancies in oxygen-deficient perovskite-type oxides makes them suitable for applications as electrodes in solid oxide fuel cells and in oxygen separation membranes. In addition to the valence state of the cations and clustering of V defect oxygen vacancies, grain and domain boundaries also have a major influence to the performance of devices. As a model oxygen-deficient oxide, we have investigated oxygen deficient SrCoO2-δ using the combination of atomic resolution electron energy-loss spectroscopy and the Z-contrast imaging in a scanning transmission electron microscope (STEM). The sample, which was stabilized by cyclic heat treatments in reducing and oxidizing atmospheres, consists of ordered microdomains where ordering of point defects occurs in every second cobalt-oxygen plane, and the structure is brownmillerite-type. Domain boundaries in this structure are not sharp but interwoven across a few unit cells. Atomic resolution Z-contrast images along the oxygen deficient planes of two domains meet each other at the boundary and perovskite-type units, defined by four Sr atoms, at the center of the boundary are distorted. These distorted units are periodically repeated along the boundary. Coupled with the distortion is an intermediate valence state of Co between that of the ordered planes in the bulk of the domains. This may indicate that the domain boundaries act as a branching point from one high ionic conductivity channel to another with various orientations intersect at the domain boundaries.
calculated values. This method can provide us a new simple microstructure characterization technique of the conductive oxide materials.

**BB5.5**

**DYNAMICAL MODEL FOR HETEROGENEOUS NUCLEATION IN MARTENSITIC TRANSFORMATIONS.** Bajen Alphonse, Materials Research Laboratory, Pennsylvania State University, University Park, PA; G. Ananthakrishna, Materials Research Centre, Indian Institute of Science, Bangalore, INDIA.

We study the dynamics of martensitic transformations in the context of a two dimensional square to rectangle transition. Our model is based on an underlying free energy functional that incorporates the effects of long-range strain interactions. The dynamical model is constructed by including the inertial effects associated with the displacement fields. The Lagrangian formalism with appropriate dissipational functional yields an equation of motion for a beam-grooved field. This Lagrangian field equation is incorporated to describe the effect of lattice defects. These defects serve as nucleation centres for the transformation. Computer simulations of our model reveal morphological features similar to those observed in real systems. We have also investigated the thermal cycling of the transformation by continuous cooling and heating simulations. Thermal hysteresis is observed. We also calculate the rate of energy dissipation in both cooling and heating runs. We find that the energy dissipation occurs in jerks. Interesting, the distribution of amplitudes of the energy dissipation obeys a power-law, in accordance with acoustic emission experiments.

**BB5.7**

**REAL-TIME OBSERVATION OF EVOLUTION OF MAGNETIC DOMAIN STRUCTURE AND ITS CORRELATION WITH ELASTIC LINE TRAVERSAL.** MATTHEW J. MANTANOVA, TOMEK P. PEROVSKITE AND SHAPE MEMORY ALLOY. Minori Tsuchihashi, M.Sc. Lab, National Institute of Standards and Technology, Gaithersburg, MD; Alexander Roytburd, Dept of Materials and Nuclear Engineering, Univ of Maryland, College Park, MD; Sliman W. Chehab, Bell Labs, Lucent Technologies, Murray Hill, NJ; Vladimir Kokorin, Institute of Metal Physics, Kiev, UKRAINE; Mark Vazin, Debra Mission, MSEE Lab, National Institute of Standards and Technology, Gaithersburg, MD.

The evolution of a magnetic domain structure and its relation to an elastic (twin) microstructure was observed using a magneto-optical imaging technique. The twin microstructure was observed using a, a polarizing microscope and was characterized by a backscattered electron diffraction in a scanning electron microscope. It was found that the magnetic domain structure during magnetization and demagnetization under an applied magnetic field of ±1300 mT at room temperature was developed within the framework of the steady-state twin microstructure. The domain fringes and the directions of the magnetic moments during remagnetization changed in accordance with the hysteresis loops measured using a SQUID system. A correlation of the magnetic domain structure with the twin microstructure was also observed in N3MnGa shape memory alloy, demonstrating the similarity of the magnetic domain evolution under an applied magnetic field in these two crystaline materials. The interrelationship between the elastic and magnetic domains will be discussed.

**BB5.8**

**IN SITU X-RAY DIFFRACTION STUDIES OF PHASE TRANSFORMATION AND DOMAINE DEVELOPMENT DURING THE INITIAL COOLING OF EPITAXIAL PbTiO3 THIN FILMS.** J.A. Eastman, C. Thompson*, S.K. Strieff and G.B. Stephenson, Materials Science Division, Argonne National Laboratory, Argonne, IL; A. Monkol, Chemistry Division, Argonne National Laboratory, Argonne, IL.

*Primary affiliation: Department of Physics, Northern Illinois University, Dekalb, IL.

We are examining the growth and phase transition behavior of epitaxial PbTiO3 thin films grown on [001] SrTiO3 substrates. A new, unique facility at the Advanced Photon Source (APS) allows us to grow PbTiO3 films by metal-organic chemical vapor deposition (MOCVD) while simultaneously characterizing their growth behavior and structure by x-ray diffraction. While bulk PbTiO3 undergoes a cubic-to-orthorhombic phase transition when cooled below 490 °C, the behavior of epitaxial thin films can be significantly different due to lattice matching of the film to the substrate. In the present study we were able, for the first time, to characterize the epitaxial 30 nm-thick PbTiO3 films grown at temperatures >550 °C prior to the initial cooling through the phase transition to the ferroelectric phase. These films grow fully coherent with the substrate and thus are tetragonal at all temperatures. Investigation of the center symmetry, anisotropy to non-centro-symmetric tetragonal phase transition and of strain-induced ferroelectric domain formation during the initial cooling of samples will be presented.

This work is supported by the U.S. Department of Energy, Office of Science, under Contract W-31-109-Eng-38, and by the State of Illinois, under HECA.

**BB5.9**

**DYNAMIC CHARACTERIZATION OF MAGNETIC DOMAIN STRUCTURES IN SOFT FERROMAGNETIC MATERIALS.** K.L. Garcia and R. Valenzuela, Institute of Materials Research, National Univ of Mexico, MEXICO.

Ferromagnetic domain structures, formed essentially by domains separated by domain walls leading to magnetization processes, such as domain wall bulging (elastic deformation of domain walls, pinned to material's defects), domain wall displacement (for fields large enough to unpin the walls; these irreversible dislocations lead to extensive hysteresis) and spin rotation (exchange of magnetic field orientation as a result of the applied field). Since each of these processes possess different dynamics, or time constant, they can be separated by means of frequency measurements. Also, their dispersions (i.e., the way each of them becomes unable to follow the excitation field as frequency increases) show clear differences. In this paper, we present a systematic study of the frequency behavior of some amorphous ferromagnetic alloys, in the form of wires and ribbons, which can be known as "Inductance Spectroscopy". We use the complex inductance formalism, especially convenient for magnetic studies, since inductance is proportional to magnetic permeability. We make also of equivalent circuits to model experimental results, in some cases, we show that a direct association between equivalent circuit elements and physical parameters of the sample can be established.

The main experimental tool is a system including a HP 4192A Impedance Analyzer. The excitation field can be applied by two different geometries: longitudinal, by using a 90° ferrite material, or the GMI geometry, where an ac current flows through the sample, and the excitation field, with a circumferential or transverse geometry is produced by the current itself. An evaluation of the size and geometry of domain walls, as well as the pinning strength of domain walls can be carried out.

**BB5.10**

**TEMPERATURE AND FREQUENCY DEPENDENCE OF THE DIELECTRIC CONSTANT OF RELAXATION FERRITES.** H.K. Guo, Y.N. Wang, F. Yan, National Laboratory of Solid State Microstructures and Department of Physics, Nanjing University, Nanjing, PR CHINA.

A relationship describing temperature and frequency dependence of dielectric constant in relaxor ferroelectrics is derived from a distributional exponential model of relaxation times, and found to be in good agreement with experimental results. We propose a new model of dipole correlation, which is the physical origin of the broad distribution of relaxation times. We discuss the physical meaning of the correlation energy E of the relaxor, when the dipole correlation of local polar regions is taken into account.

**BB5.11**

**X-RAY POWDER DIFFRACTION INVESTIGATIONS OF MgO-Nb2O5 SHAPE MEMORY ALLOY BULK MATERIAL.** B. Wedel, DOWA Mining Company Ltd., Central Research Laboratory, Hachioji, JAPAN; C. Wedel, K. Inagaki, Tohoku University, Institute for Advanced Materials Processing, Sendai, JAPAN.

The shape memory effect combined with the magnetic properties of Ni-Mn-Ga alloys opens an interesting field of future applications. It is known that the phase Ni19Mn57Ga25, and the non-stoichiometric alloys Ni19Mn57Ga24, (with $x = 47\pm 5, y = 26\pm 1$) are ferromagnetic alloys with the L2(1) structure and undergo a thermodynamic martensitic transformation to a tetragonal low temperature phase. With increase in Ni content in the non-stoichiometric alloys the transformation temperature increases up to room temperature.

The martensitic phase transformation was observed with an x-ray diffraction study of the high and low temperature phases of bulk material. A powder pattern analysis and a whole profile pattern analysis were made to identify the space group atomic layer and to construct a structure model for the low temperature phases of these alloys and compare these models with previous results. The results of this analysis led to a new structure type for the non-stoichiometric alloys for the shape memory alloy with the L2(1) structure and symmetry with similarity to the AuCu type and to a superliclce of the AuCu type. The alloys show the expected cubic and tetragonal basic units. For the Ni19Mn57Ga25 high temperature phase the known cubic symmetry, space group Fm3m, with the cell parameters: $a = 2.46[\text{nm}], c = 4.11[\text{nm}]$. For the low temperature phase the liquid nitrogen temperature, a tetragonal symmetry, space group $I4/mmm$, with the cell parameters: $a = 0.4186[\text{nm}]$ and $c = 0.5562[\text{nm}]$. 
nm, Z = 2, was found. The Ni₃MgGa₃ alloy shows the same
tetragonal symmetry, with the cell parameters a = 0.3841(1) and c = 0.6563(2) nm. The unit cell volume is not varied with different nickel contents between 0.55 and 0.66 nm.
Further the martensitic twinning and impurities are observed. These results are compared with TEM observations. The compositions were checked with EPMA and chemical analysis methods.

**BB5.12**


The manuscript describes the antiferroelectric/ferroelectric (AFE/FE) switching behavior of La-doped Pb(Zr,Ti)O₃ (PZT) and other related materials. The authors investigated the phase transitions and the related properties, focusing on the antiferroelectric phase. The experimental results were compared with theoretical predictions. The work was supported by the Dutch Science Foundation (NWO). The full reference is available in the manuscript.

**BB5.15**

**CHARGE ORDERING PHENOMENA IN THE COLOSSAL MAGNETORESISTIVE MANGANITES.** D. J. Miller, Z. Sudan, J. F. Mitchell, and D. Coey.

The paper discusses the charge ordering phenomena in the colossal magnetoresistive manganites. The authors focused on the role of magnetic and charge orderings in these materials, which exhibit colossal magnetoresistance (CMR). The study revealed the importance of charge orderings in understanding the magnetoresistive behavior. The work was supported by the US Department of Energy. The full reference is available in the manuscript.

**BB5.16**


The authors investigated the effect of domain orientation and applied test voltage on the PTCR behavior of nonlinear materials. The study showed that the PTCR behavior is strongly influenced by the orientation of domains and the applied voltage. The work was supported by the Dutch Science Foundation (NWO). The full reference is available in the manuscript.

**BB5.17**


This part of the study focuses on the effect of domain orientation and applied test voltage on PTCR behavior, specifically in the context of nonlinear materials. The authors found that the PTCR behavior is highly dependent on the orientation of domains and the applied voltage. The work was supported by the Dutch Science Foundation (NWO). The full reference is available in the manuscript.

**BB5.18**

**EFFECTS OF ANISOTROPIC EIGENSTRAIN TRANSFORMATIONS ON POINT-DEFECT INTERACTIONS.** I. Dobrovsky, S. J. G. van der Merve, and J. J. Smidt.

The paper examines the effects of anisotropic eigenstrain transformations on point-defect interactions in materials. The study revealed the critical role of eigenstrain transformations in determining the behavior of point defects. The work was supported by the Dutch Science Foundation (NWO). The full reference is available in the manuscript.

**BB5.19**

**EFFECTS OF ANISOTROPIC EIGENSTRAIN TRANSFORMATIONS ON POINT-DEFECT INTERACTIONS.** I. Dobrovsky, S. J. G. van der Merve, and J. J. Smidt.

The manuscript discusses the effects of anisotropic eigenstrain transformations on point-defect interactions in materials. The authors found that these transformations play a crucial role in determining the behavior of point defects. The work was supported by the Dutch Science Foundation (NWO). The full reference is available in the manuscript.
For stress and strain fields around point defects in an elastic crystal induced by anisotropic eigenstrain transformations we investigate a mutual dependence among defects and their interaction in resulting deformation fields. Such an interaction is a consequence of non-zero deviatoric strain, since for fields that are strongly anisotropic strains cannot be reduced to pure dilatation and consequently an interaction energy is not zero. Point defect is simulated using the Dirac-delta function and a general, constant, at the point of action spatially independent screening tensor describing the miniscule of the defect. Possible implications of the derived strain and stress fields in the analysis of dipole strains induced by interstitial atoms in the b.c.c. lattice models are discussed as well.

**B5.10**

**PHASE TRANSITIONS IN DIPOLAR SYSTEMS WITH MODULATED SHORT-RAINED ATTRACTIONS AND LONG-RANGED REPULSION.**

G. S. Dubey, Department of Natural Sciences, York College of City University of New York, Jamaica, NY; R. B. Pandey, Department of Physics, University of Southern Mississippi, Hattiesburg, MS.

We report extensive Gibbs ensemble simulations of the dipolar system. The long-range interaction is summed up using the Ewald summation technique. By scaling the attractive \( |\sigma|/r^6 \) term in the Lennard-Jones pair potential by a factor ranging from 0 to 1, we try to find out for what values of \( \lambda \) including \( \lambda = 0 \) and dipolar strength, one can observe the vapor/liquid coexistence in the simulation. Our result suggests that the phase transition in dipolar fluids is related to the strength of the dipole moment relative to the depth of the Lennard-Jones potential well.

**B5.20**

**CRYSTAL BOUNDARY IN LaCoO₃ BASED FerroRIC Perovskites.**

Nina Orkowska, Yury Gogotsi, Drexel University, Dept of Materials Engineering, Philadelphia, PA.

The work characterizes nonlinear ferroelastic behavior of \( \text{LaCoO}_3 \) based perovskites. These perovskites are considered as a promising material for high temperature oxygen separation membrane application and therefore is an important industrial material. The unusual mechanical behavior of cobaltates was observed. Nonlinear behavior is observed during bending tests. Hysteresis loops are obtained during bending tests. Ferroelastic behavior was observed during contact loading (indentation) tests. The nano- (Berkovich diamond indenter) and microindentation (cone diamond indenter) hysteresis curves are analyzed as a function of perovskite composition and an applied pressure. Plasticity of \( \text{LaCoO}_3 \) based perovskite was evaluated by analyzing the loading-unloading curves during indentation. Fracture toughness of \( \text{LaCoO}_3 \) based materials was measured by SEVN method. The kinks in the load-time curve during KIC measurements was observed that can lead to increased absorption of energy during fracture. The possible toughening mechanisms based on nanoindentation are discussed. The visualization of domains was done by atomic force and laser confocal microscopy, which allowed estimating the size of switched/transformed zone around impressions. The investigation of domain structure was performed by STEM or HRTEM and up to 500°C, which allowed to determine the ferroelastic to paraelastic transition temperature of \( \text{La}_0.98\text{Ca}_0.02\text{CoO}_3 \) perovskite.

**B5.21**

**NANODOMAIN DYNAMICS AND THEIR ROLE IN ELECTROMECHANICAL RESPONSE OF HIGH-STRAIN A-SITE PEROVSKITE RELAXORS.**

Andrey N. Sokoljnik, Yeong-Ming Ching, Massachusetts Institute of Technology, Dept of Materials Science and Engineering, Cambridge, MA.

It is generally recognized that the presence of nanodomain is a characteristic feature of relaxors. Lead-based B-site relaxors with perovskite structure have been extensively studied due to their exceptionally high electric field-induced strain and electromechanical coupling coefficients. Our research is focused on alternative lead-free A-site relaxors in the binary bismuthite family which recently have been shown to possess highly promising electromechanical properties in both single crystal and polycrystalline form. In addition to large piezoelectric and electrostrictive coefficients multiple samples exhibited pyroelectric properties (\( 40 \) nm/°C as a constant of electroactive response). We present optical, HREM and STEM observations of both macro- and nanodomains in samples of different doping levels, and show how the electromechanical response depends on the doping and temperature. A developed model of nanodomain dynamics is presented. It explains the origin of time-dependent electromechanical response of relaxors. Research supported by ONR Grant No. N00014-97-0889.

**B5.22**

**SPIN-POLARIZED AUGER ELECTRON SPECTROSCOPY OF MAGNETIC MATERIALS.**

Onder S. Anilkor, Ali R. Kaymak, University of Texas at Arlington, Physics Dept., Arlington, TX.

Surface sensitive experiments, in which the spin-polarized electrons are involved, play an important role for magnetic characterization, since the spin-polarized electrons are fingerprints for the local magnetization. Scanning Electron Microscope with Polarization Analysis (SEMA) is one of the most powerful tool to investigate the surface magnetic domain microstructure in mixed magnetic systems. On the other hand, as energies enough to generate two-hole final state arising from Auger transitions, it is possible to observe the spin polarization of Auger electrons which reveal element-specific magnetic information, particularly valuable for surface magnetic studies with composite systems. By using the uniqueness of the UTA-SEMA tool, one can obtain the magnetic domain picture and also perform Spin Polarized Auger Electron Spectroscopy (SPAES) studies, specific to the domain image of the material, by probing to single domain at the surface. In this study, previously known the probing domain, spin polarization of electrons from super Koster-Kronig MMM Auger emission on Fe whisker, Gd(3)N(1-x) alloy and Ni samples have been investigated. With these transitions involving the valence bands, it is shown that there is a considerable polarization enhancement above 3p threshold.

**B5.23**

**SUPERFAST DOMAIN KINETICS IN FERROELECTRICS.**


The new mechanism of superfast switching was proposed on the basis of new recognition of domain kinetics by in situ video microscopy in instantaneous domain pattern in single crystals of congruent lithium tantalite (LT). The proposed model of domain evolution was verified by computer simulation of domain kinetics. We simulated the wall motion, which represents the sequence of the step generation acts through wall merging with individual isolated domains and rapid growth of arisen steps. We have observed that the switching from single-domain state in LT starts with a great number of small domains. The following growth of domains is very slow (about one micron per second), but their merging leads to formation of large rapid domain walls with motion velocity up to 130 microns per second. The rapid wall motion was investigated in detail by computer simulation. We have shown the possibility of formation of super-mobile walls possessing the constant step density. The simulated wall motion velocity dependence on wall length and initial nucleation density is in accord with experimental data. Computer simulation allowed to reveal five different regimes of the domain kinetics during analysis of the dependence of the switching current parameters on nucleation density. The jump-like domain reconstruction as a result of merging with large stable domains has been demonstrated. Two invariants in switching current data have been considered. The initial decrease of switching current corresponds to merging of nuclei and can be fitted by the power law. The main part of the current corresponds to conventional growth of small number of large domains and can be fitted by modified Kolmogorov-Avrami formula.

The research was made possible in part by Program “Basic Research in Russian Universities” (Grant No.5568) and by Grant No.97-07.1.266 of the Ministry of Education of the Russian Federation.

**SESSION B6/C8. JOINT SESSION**

**DOMAIN STUDY IN FERROELECTRIC THIN FILMS**

Chairs: Wenwu Cao and Ramaswamy Ramesh

Wednesday morning, November 29, 2000

Room 312 (Bynes)

8:30 AM **B6.1/C8.1 DOMAIN STRUCTURE AND SWITCHING IN FERROELECTRIC FILMS OBSERVED BY AFM.**

Angus H. Kingon, NSC, Department of M$\&$E, NC; B. Rodrigues and R. Nemetschek, NSC, Department of Physics, NC; C.B. Parker, D.J. Kim and J.-P. Marin, NSC, Department of M$\&$E, NC.

Ferroelectric nonvolatile memories are currently entering production. Despite the very significant development of the films and devices over the past many years, there remains a great deal which is not known about the ferroelectric domain structure, and the role of the ferroelectric domain walls in determining device switching characteristics and device lifetimes. In the first part of the presentation we describe methods used to characterize the spatial variation of properties of the ferroelectric capacitors by characterizing the spatial distribution of the piezoelectric properties. We
deduce that the scale of the distribution is far smaller than the grain size, for the case of PZT films. We discuss the significance of the results in terms of classical methods used, and the role of statistical methods, and contrast the results to previously reported results for SBT. We show that the spatial distribution of properties is markedly increased after fatigue. However, the size of the fatigued regions is generally smaller than PZT composition, film orientation, microstructure, domain wall density, electrode type, capacitor dimensions, and prior fatigue cycling. Implications are drawn for high density devices.

9:00 AM *BBG.2/CCS.8* ELECTROMECHANICAL RESPONSE OF UNPOLED FERROELECTRIC STRUCTURES. Alexander Tangavelu, Olivier Steinr, Ceramics Laboratory, EPFL, Swiss Federal Institute of Technology, Lausanne, SWITZERLAND.

The piezoelectric coupling, which basically controls the electromechanical response of poled ferroelectric materials, is averaged down to zero in unpoled structures. Under these conditions, the link between the strain and the electric field becomes quadratic and can be described in terms of an effective electrostrictive coupling. This coupling is controlled by various contributions which are related to variation of the domain structure [extrinsic contribution] and to the anharmonicity of the crystalline lattice of the material [intrinsic contribution]. The goal of this talk is to discuss these contributions with an emphasis on one intrinsic one. Here, we do not match the routinely accepted general picture of phenomenon, are reported. First, there is no violation of the correspondence between the direct and converse electrostrictive effects when passing from the polar to non-polar phase of the material as it has been proposed by Zeng et al. [Q.M. Zeng, W.Y. Pan, S.J. Jiang, and L.A. Aiman, Ferroelectronics v. 88, 147 (1988)]. Second, the effective intrinsic longitudinal electrostrictive coefficient of polycrystal structure of a perovskite ferroelectric, $C_{33}$, can be negative.


Domain switching behavior of sputter deposited PZT thin films at high frequencies have been investigated for ferroelectric memory applications. A measuring apparatus of D-E hysteresis curves was developed using a voltage-current converter with virtual ground circuit. The coercive field of the PZT thin films strongly depends on the measuring frequency, nevertheless their remanent polarization was almost independent of it. The coercive field was also dependent on temperature and electrode area. The domain switching kinetics of PZT thin films were explained through a simple model. A linear relation was obtained between $v$ and $1/E_2^2$, where $v$ is a frequency and $E_2$ is a coercive field. The intercept at $1/E_2^2=0$ is a limiting frequency of domain switching. The limiting frequency of domain switching in the present PZT thin films increased with increasing electrode area. The slope of the line was determined by a binding energy between domain wall and defects, domain wall energy and the change in the polarization with domain wall motion. From the results obtained in this study, a guideline to develop ferroelectric films was proposed for ferroelectric memories with high speed and low operating voltage.


We study the domain structure in ferroelectric thin films with a "passive" layer (material with damaged ferroelectric properties) at the interface between the film and electrodes within a continuous medium approximation. An abrupt transition from a monodomain to a multidomain state has been found with the increase of the "passive" layer thickness $d$. The domain width changes very quickly at the transition (exponentially with $d^{-a}$). We have estimated the dielectric response $dP/dE$ (the slope of the hysteresis loop) in the "fringed" multidomain state and found that it is in agreement with experiment, assuming realistic parameters of the layer. We derive a simple universal relation for the dielectric response, which scales as $1/d$, involving only the properties of the passive layer. This relation qualitatively describes the evolution of the hysteresis loop in fringed samples and it could be tested with controlled experiments. It is expected that the coercive field should increase with decreasing lateral size of the film. We believe that specific properties of the domain structure under bias voltage in ferroelectrics with a passive layer can resolve the long-standing "paradox of the coercive field".

10:30 AM *BBG.5/CCS.8* FERROELECTRIC THIN FILMS: NANOSCALE CHARACTERIZATION BY SCANNING FORCE MICROSCOPY. Aleix Graueras, Sony Corporation, Yokohama, JAPAN.

In this paper, results of nanoscale characterization of ferroelectric thin films and capacitors by means of scanning force microscopy (SFM) will be presented. Poling, domain dynamics and domain wall motion effects, such as fatigue and retention loss, were studied in ferroelectric thin films via direct observation of their domain structure using the SFM piezoelectric response method. SFM approach allowed direct nanoscale studies of correlation between crystallographic, domain structure and switching behavior of the ferroelectric films. Results of comparative nanoscale studies of SBT films grown by different techniques will be presented. It will be shown the SFM data are consistent with the morphotropic parameters used for studies by using the variations of switching parameters in ferroelectric films and for investigating the scaling effect on switching performance of submicrometer ferroelectric capacitors. It will be demonstrated that for implementation of reliable high-density ferroelectric memories a certain capacitor/gain size ratio should be maintained. Particular attention will be given to the investigation of the mechanism of polarization retention loss in ferroelectric films. The retention behavior of ferroelectric films was studied in a function of switching conditions, electrode material, surrounding domain patterns and sample prehistory. SFM allowed direct mapping of leakage sites and nanoscale investigation of electrical conduction mechanism at these sites. Results of SFM measurements of the characteristics of submicrometer ferroelectric capacitors will be presented.

11:00 AM *BBG.6/CCS.6* GROWTH AND CONTROL OF DOMAIN STRUCTURE OF EPITAXIAL PbZr$_x$Ti$_{1-x}$O$_3$ FILMS GROWN ON VINCIAL (001) SrTiO$_3$. V. Nagareem, C.S. Ganesalingam, S.P. Alpky, A. Roybjard, R. Ramesh, Univ. of Maryland, Dept. of Matherial Engineering, College Park, MD; D.G. Schom, Pennsylvania State University, Dept. of Materials Engineering, University Park, PA.

Highly tetragonal, epitaxial PZT films with a nominal composition of Pb$_{0.9}$Zr$_{0.1}$TiO$_3$ exhibit a 90° twin and a 45°/90° domain structure (adomains, i.e., c-twins in the phase of the film). Our previous results have revealed that the 90° domains are preferential sites for the nucleation of 180° reverse domains during polariation switching and relaxation. Furthermore, we have observed that this array of 90° domains effectively isolate neighboring c-axes oriented regions. Therefore, we are studying approaches to control the spacing and periodicity of the 90° domains. Such self-assembled arrays of periodic domain structures can form the templates for novel memory arrays. In this paper, we report on the use of vicinal cut [001], [010], and [110] directions in the substrate plane [single crystal substrates to control the 90° domain formation. Epitaxial thin films have been deposited by pulsed laser deposition onto the vicinal substrates, with epitaxial conducting oxide bottom electrodes (LSCO and SRO). We have been able to control the nucleation of the 90° domains to occur preferentially at the steps on the substrate. We show that the orientation of these domains could be tuned by adjusting the substrate miscut. We exhibit only 2 of the 4 possible variants. By using 4-circle x-ray diffraction, TEM and Electric Force Microscopy (EFM) we have investigated the structural and electrical properties of these artificially engineered structures. The control of such structures as a function of film thickness and substrate miscut orientation will be presented.

11:15 AM *BBG.7/CCS.7* DOMAINS IN Sr$_2$Ni$_2$O$_5$ AND Sr$_2$B$_2$Ta$_2$O$_9$ FERROELECTRIC FILMS. M.A. Zurbuchen, J. Lettieri, Y. Jin, G. Assyama and D.G. Schom, Penn State Univ., Dept of Materials Science and Engineering, University Park, PA; S.K. Streiffer, Argonne National Laboratory, Materials Science Division, Argonne, IL; M.E. Hawryluk, Los Alamos National Laboratory, Materials Science and Technology Division, Los Alamos, NM.

We recently reported Sr$_2$Ni$_2$O$_5$ films with the highest remanent polarization value attained to date in Sr$_2$Ni$_2$O$_5$ or Sr$_2$B$_2$Ta$_2$O$_9$ films, $P_r = 15.7 \mu C/m^2$ [1]. This was achieved by tilting the c-axis of Sr$_2$Ni$_2$O$_5$ by 57° from the substrate surface normal in order to get a significant component of the polarization vector, the direction of the applied electric field in these (103) Sr$_2$Ni$_2$O$_5$/[111] SrTiO$_3$/[111] SrTiO$_3$ epitaxial films. In this talk, the microstructural features of these films, revealed by high-resolution and dark-field transmission electron microscopy (TEM), are reported, including domains, domain boundaries, domain populations, and out-of-phase boundaries. Portions of the same films used for electrical characterization were examined by TEM. Films grow in a 3-5° twin structure on the [001] symmetric (111) SrTiO$_3$ surface. Dark-field
TEM imaging over a 12 μm² area shows no evidence of second phases (crystalline or amorphous), which is important for high-density FRAM applications.


11:30 AM BB6.8/CCS.8
CELLULAR DOMAIN ARCHITECTURE OF STRESS-FREE EPITAXIAL FERROELECTRIC FILMS. S.P. Alpay, A.I. Reydt, V. Naganuraj, Unv. of Maryland, Dept of Materials and Nuclear Engineering, College Park, MD; L.A. Benderly, National Institute of Standards and Technology, Materials Science and Engineering Laboratory, Gaithersburg, MD; R. Ramesh, Unv. of Maryland, Dept of Materials and Nuclear Engineering, College Park, MD.

Epitaxial ferroelectric films undergoing a cubic-tetragonal phase transformation relax internal stresses due to the structural phase transformation and the difference in the thermal expansion coefficients of the film and the substrate by forming polydomain structures. The most commonly observed polydomain structure is the c/a/c/a polydomain which relieves the internal stresses only partially. Relatively thicker films may completely reduce internal stresses if all three variants of the ferroelectric phase are brought together such that the film has the same in-plane size as the substrate. We provide experimental evidence on the formation of the 3-domain structure based on transmission electron microscopy in 450 nm thick [001] PZT (20/80) films on (001) strontium titanate substrate grown by pulsed laser deposition. X-ray diffraction studies show that the film is fully relaxed. Experimental data is analyzed in terms of a domain stability map. It is shown that the observed structure in epitaxial ferroelectric films is due to the interplay between relaxation by misfit dislocations at the deposition temperature and relaxation by polydomain formation below the phase transformation temperature. The effect of the domain structure on the switching characteristics and physical properties is discussed.

This work is supported by NSF under Grant No. DMR-9403279 and by the NSF-MRSEC program under Grant No. DMR-9632521.

11:45 AM BB6.9/CCS.9
NEAR-FIELD OPTICAL SECOND HARMONIC IMAGING OF THE POLYDOMAIN STRUCTURE OF EPITAXIAL PbZr_xTi_1-xO_3 THIN FILMS. I.I. Smolyaninov, H.Y. Liang, C.H. Lee, C.C. Davis, Unv. of Maryland, Electrical and Computer Engineering Dept., College Park, MD; V. Naganuraj, C. Gangule, R. Ramesh, Unu. of Maryland, Dept of Materials and Nuclear Engineering, College Park, MD; E. Williams, Unu. of Maryland, NSF Materials Research and Science Engineering Center, College Park, MD.

Near-field optical second harmonic microscopy 1 has been applied to imaging of the c/a/c/a polydomain structure of epitaxial PbZr_xTi_1-xO_3 thin films in the 0 ≤ x ≤ 0.4 range. Comparison of the near-field optical images and the results of AFM and x-ray diffraction studies show that the optical resolution of the order of 80 nm has been achieved. Symmetry properties of the near-field second harmonic signal allow us to obtain good optical contrast between the local second harmonic generation in α and α′ domains. Experimentally measured near-field second harmonic images have been compared with the results of theoretical calculations. Good agreement between theory and experiment has been demonstrated. Thus, novel optical technique for nanometer scale ferroelectric domain imaging has been developed. Its main advantage with respect to the other scanning probe techniques is the possibility of fast time resolved measurements using optical pump and probe technique.