

# SYMPOSIUM R

## Electrically Based Microstructural Characterization III

November 26 – 29, 2001

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\* Invited paper

**8:45 AM \*R1.1**

RECENT DEVELOPMENTS IN THE MODELING AND APPLICATION OF SPATIALLY PERIODIC DIELECTRIC AND MAGNETIC QUASISTATIC SENSORS. Y. Sheiretov and M. Zahn, Massachusetts Institute of Technology, Laboratory for Electromagnetic and Electronic Systems, Cambridge, MA.

Semi-analytical models are used to simulate the response of periodic-field quasistatic sensors. Although it is not typically possible to find analytical expressions that link the physical properties of the material under test to the sensor's two-port transimpedance matrix, it is possible to use Fourier transform methods in combination with collocation point numerical techniques to generate accurate sensor simulations much more efficiently than with the more general finite-element methods, due to the periodic structure of the sensors. The duality between the electroquasistatic and magnetoquasistatic regimes makes it possible to apply the same algorithms to both types of sensors. This paper discusses these modeling techniques and describes the similarities, as well as the principal differences between dielectrometers and magnetometers. Cylindrical geometry models are also developed for both inductive and capacitive sensors. This enables the design of families of circularly symmetric magnetometers and dielectrometers with the "model-based" methodology, which requires close agreement between actual sensor response and simulated response. These kinds of sensors are needed in applications where the components being tested have circular symmetry, e.g. cracks near fasteners, or if it is important to measure the spatial average of an anisotropic property. Although strictly speaking there is no periodicity in cylindrical geometry, it is nonetheless possible to extend the Cartesian geometry models to this case as well. In cases where the current density distribution of a magnetometer is known, it is possible to use simpler and much more efficient simulation techniques, applicable to both the Cartesian and cylindrical geometry sensors. These algorithms are based on highly efficient fast Fourier and fast Hankel transforms (FFT and FHT).

**9:15 AM R1.2**

SCANNING IMPEDANCE MICROSCOPY: FROM IMPEDANCE SPECTRA TO IMPEDANCE IMAGES. Sergei V. Kalinin and Dawn A. Bonnell, Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, PA.

Impedance spectroscopy has long been recognized as one of the major techniques for the characterization of ac transport in materials. The major limitation of this technique is the lack of spatial resolution that precludes the equivalent circuit elements from being unambiguously associated with individual microstructural features. Here we present a novel scanning probe microscopy technique for quantitative imaging of ac and dc transport properties of electrically active interfaces. This technique, referred to as Scanning Impedance Microscopy (SIM), maps the signal phase change caused by an interface. The frequency dependence of the voltage phase shift across the interface yields interface capacitance and resistance. SIM of single interfaces is demonstrated on a SrTiO<sub>3</sub> bicrystal grain boundary. The local interface capacitance and resistance obtained from SIM measurements agrees quantitatively with macroscopic impedance spectroscopy. Superposition of a dc sample bias during SIM probes the C-V characteristics of the interface. When combined with Scanning Surface Potential Microscopy (SSPM), which can be used to determine local I-V characteristics and interface state densities, local transport properties are completely determined. SIM and SSPM of polycrystalline materials are demonstrated on BiFeO<sub>3</sub> ceramics. An excellent agreement between the properties of a single interface determined by SIM and traditional impedance spectra is demonstrated. Therefore, in addition to quantifying local properties this approach provides spatially resolved impedance images of complex microstructures.

**9:30 AM R1.3**

Abstract Withdrawn.

**10:15 AM \*R1.4**

INCENTIVES FOR USING LEIM IN THE INVESTIGATION OF ORGANICALLY COATED ALLOYS. S.R. Taylor, Center for Electrochemical Science and Engineering, University of Virginia, Charlottesville, VA.

Local electrochemical impedance mapping and spectroscopy (LEIM/S) are invaluable tools for the investigation of local electrochemical breakdown events associated with the degradation of organically coated metals. LEIM/S data of coating degradation have revealed a number of events, which if interpreted literally, support a

number of long standing theories, as well as provide new insight into the damage process. Changes in local impedance may be an indication of virtual pores, a long-standing theory for electrolyte entry, while metastability and initial impedance peaks have provided possible evidence of corrosion product formation within the pores and on the substrate. This paper will provide an overview of some of the observed events using LEIM and examine these results in the context of recent analytical and numerical models. Models used to predict the electric field above an equipotential disk electrode have shown that certain experimental observations may be measurement artifact. Experiments to confirm the modeling results will be used to qualify the source of local impedance events.

**10:45 AM R1.5**

ADVANTAGE OF ANTI-STOKES RAMAN SCATTERING EXCITED BY ULTRAVIOLET LASER FOR HIGH-TEMPERATURE MEASUREMENTS. Hirotsuka Fujimori, Masato Kakihana<sup>a</sup>, Koji Ioku, Seishi Goto, Masahiro Yoshimura<sup>a</sup>, Yamaguchi Univ, Dept of Advanced Materials Science and Engineering, Yamaguchi, JAPAN. <sup>a</sup>Tokyo Institute of Technology, Materials and Structures Laboratory, Yokohama, JAPAN.

The extension of Raman scattering from materials at temperatures above 1000°C is an important challenge because structural changes and chemical reactions of various industrial materials and minerals occur in this temperature range. However, the measurable region of temperatures is limited in the conventional Raman spectroscopy using visible region excitation. This can be explained in terms of the fact that it is difficult to detect weak Raman scattering from substances at high temperatures in comparison with an intense continuous background due to thermal emission. Continuous-wave (CW) ultraviolet (UV) Raman spectroscopy is suitable for the measurements at high temperatures, because the UV excitation shifts the Raman scattering to lower wavelength positions away from the intense peak by the thermal emission. We have recently demonstrated that the Raman scattering through UV excitation is eminently well suited to in situ investigation of materials at high temperatures up to 1500°C. By means of UV Raman spectroscopy, we have observed phase transition and soft phonon modes in SrZrO<sub>3</sub>, OH vacancies arising in hydroxyapatite at high temperatures, phase transition of hafnia up to 2085 K, and anharmonic lattice mode in Ca<sub>2</sub>SiO<sub>4</sub>. Here we demonstrate that anti-Stokes Raman scattering is even more suitable for high-temperature measurements following the Boltzmann distribution law and Planck's equation. As compared with Stokes Raman spectra, anti-Stokes spectra were observed with lower thermal emission backgrounds in accordance with Planck's equation. The intensity ratio of anti-Stokes to Stokes scattering approaches to 1 as temperature increases at high temperatures satisfying the Boltzmann distribution law. These results clearly demonstrate the advantage and feasibility of anti-Stokes Raman scattering for elimination of the thermal emission in comparison with Stokes scattering. Such an idea would open up the possibility of new vistas for high-temperature science and technology.

**11:00 AM R1.6**

EVALUATION OF THE DEVELOPMENT OF THE MICROSTRUCTURE OF COMPATIBLE RESTORATION MORTARS FOR HISTORIC MASONRY USING IMPEDANCE SPECTROSCOPY AND DIELECTRIC MEASUREMENTS. Antonia Moropoulou, Georgios Tsangaris, Petros Moundoulas, Eleni Aggelakopoulou, Sofia Anagnostopoulou, National Technical University of Athens, Dept of Chemical Engineering, Section of Materials Science and Engineering, Athens, GREECE.

In the present research work various repair mortars were produced in order to examine their microstructural compatibility with historic mortars by impedance spectroscopy and dielectric measurements. According to the requirements defined by the examination of historic mortars, aerated and hydraulic lime and lime-cement mortars are produced with various ratios of binder - admixtures - aggregates in order to simulate the microstructure of the original mortars. Studies on the development of their microstructure were employed just after the setting and also after twenty-eight days, two and three months of hardening. The evaluation of the performance of the fresh mortars, pastes, is not giving comparable results due to the effect of the water on the results. The results of the applied methods are validated, by simultaneous measurements of Mercury Porosimetry. It is concluded that mortars with lime, lime - pozzolana and hydraulic lime are compatible with the original mortars while at the other hand lime-cement mortars are incompatible to the historic ones. From these results it is concluded that impedance spectroscopy along with dielectric measurements can be used for the evaluation of the development of the microstructure of restoration mortars. These measurements are proved valuable tools, as they are easy to perform and decrease the cost of the evaluation.

**11:15 AM R1.7**

STRUCTURE AND ELECTRONIC PROPERTIES OF DIAMOND-LIKE CARBON AND ITS HEAT-TREATMENT EFFECT. Kazuyuki Takai, Meigo Oga, Hirohiko Sato, Toshiaki Enoki, Tokyo Institute of Technology, Dept. of Chemistry, Tokyo, JAPAN; Yoshimasa Ohki, Matsushita Research Institute Tokyo Inc., Kanagawa, JAPAN; Kazutomo Suenaga, Sumio Iijima, Meijo University, Dept. of Material Science and Engineering, Nagoya, JAPAN.

Compared with the disordered carbon systems based on graphitic structure, little experimental study were performed on the non-graphitic disordered carbon systems, although many of remarkable results were theoretically predicted. Diamond-like carbon (DLC), which is one of the non-graphitic disordered carbon systems, is meta-stable glass state of carbon obtained by quenching the liquid phase of carbon in low pressure. In this study, the structure and the electronic properties on the disordered carbon systems were investigated in the region between non-graphitic structure and graphitic structure by means of heat-treatment of DLC containing about 10% of  $sp^3$ -carbon. Pristine DLC was prepared by laser ablation method, and samples heat-treated at various temperatures were investigated by means of Raman spectroscopy, X-ray diffraction (XRD), electron energy loss spectroscopy (EELS), electrical conductivity, and thermoelectric power. According to Raman spectroscopy and XRD, the disorder nature of the structure is modified from atomic scale  $sp^2 / sp^3$  disorder to disordered  $sp^2$ -domain network by heat-treatment at temperatures 200 – 400°C. Because EELS claims that the ratio  $sp^2 / sp^3$  of the samples are almost 10% independently of heat-treatment temperature, the observed change to the graphitic domain structure is not attributed to the conversion of  $sp^3$ -carbon to  $sp^2$ -carbon. It is rather explained by the migration of the  $sp^3$ -carbon site as the defects by heat-treatment in the meta-stable structure of as-prepared sample, where the homogeneously distributed  $sp^3$ -defects cross-link the hexagonal lattice plane by the major  $sp^2$ -carbon. This structural change increases conductivity and modified the temperature dependence of hopping conduction mechanism at low temperatures associated with the generation of Coulomb gap at  $E_F$ . In the higher heat-treatment-temperature region about 800 – 1100°C, the formation of an infinite percolation path network of the  $sp^2$ -islands induces an insulator-to-metal transition, where the electron transport in the metallic phase is featured by weakly temperature-dependent conductivity with hole carriers.

## SESSION R2: METALS

Chair: Andrew P. Washabaugh  
Monday Afternoon, November 26, 2001  
Room 206 (Hynes)

**1:30 PM \*R2.1**

IMPEDANCE SPECTROSCOPY IN FERROMAGNETIC MATERIALS. Raul Valenzuela, Institute for Materials Research, National University of Mexico, MEXICO.

Impedance spectroscopy (IP) has provided a wealth of information about the structure and conductivity processes of a variety of electric materials (semiconductors, ferroelectrics, ionic conductors, etc.). Ferromagnetic materials are the counterpart of ferroelectrics, so it was natural to explore the possibility of extending IP to their case. In this talk, an overview of the application of the IP methodology to ferro- and ferri-magnetic materials is presented. Some significant changes have to be made in the technique to investigate magnetic polarization (instead of electric polarization): the need of coils (instead of electrodes), and the use of complex inductance formalisms (or complex permeability) instead of impedance, since these are current circuits (instead of voltage circuits). We present some examples of the resolution of magnetization processes in ferrites and amorphous ribbons, such as domain wall movements and spin rotations. An interesting case is Giant Magnetoimpedance in amorphous ferromagnetic wires, where the ac current flows through the sample, and the presence of a dc magnetic field severely decreases the impedance response.

**2:00 PM \*R2.2**

PERIODIC FIELD EDDY CURRENT SENSORS. Neil J. Goldfine, Vladimir Zilberstein, Yanko Sheiretov, Andrew Washabaugh, JENTEK Sensors, Inc., Waltham, MA.

Recent advances in periodic field eddy current sensors and sensor arrays provide new capabilities for materials characterization, process quality control, defect detection, and characterization of magnetic and conducting materials. The sensors have been designed with a primary winding that can be accurately modeled, which permits, in many cases, absolute property measurements (such as electrical

conductivity, magnetic permeability, coating thickness, and sensor lift-off) with only calibration in air, without calibration standards. Arrays of sensing elements can be distributed around the primary winding to permit high-resolution imaging of the material properties. For sensitivity to bulk property variations in metals, giant magnetoresistive (GMR) elements can also be used in combination with a low frequency, or even DC, excitation. In addition, linear and circular arrays can be surface-mounted for on-line fatigue monitoring and early stage crack detection and crack growth monitoring. This paper will provide an overview of periodic field eddy current sensors and discuss several representative applications. These will include: 1) characterization of as-manufactured and aged metallic coatings on superalloy substrates using multiple frequency measurements, 2) characterization of process-affected zones, such as cold-working on aluminum and alpha case formation on titanium, 3) detection, characterization, and imaging of cracks and subsurface inclusions in titanium, 4) continuous monitoring of fatigue tests on aluminum alloy test articles, and 5) the use of GMR based sensors for property measurements and hidden crack detection in thick metals (e.g., up to 10 mm in aluminum, copper, and austenitic stainless steel).

**2:30 PM R2.3**

DAMAGE DETECTABILITY ON ALUMINUM ALLOY PANELS UNDER COMPOSITE PATCHING BY VARIOUS NDT TECHNIQUES. Antonia Moropoulou, Niki Kouloubi, Nicolas P. Avdelidis, Paraskevi Pantazopoulou, National Technical University of Athens, Dept. of Chemical Engineering, Section of Materials Science and Engineering, Athens, GREECE; Zaira P. Marioli-Riga, Hellenic Aerospace Industry, Dept. of Research and Development, Composite Materials and Processes Laboratory, Schimatari, GREECE.

Composite patching method is widely applied for repair cases of metallic aircraft structures due to more efficient performance than conventional repairs. However, the detection of structures integrity under patch, during the service life of aircraft, by non-destructive means is considered of great importance. In the present study, different NDT techniques such as active infrared thermography, eddy currents and electrical impedance spectroscopy, were applied for the detection of simulated artificially introduced damages - notches, on the surface of aluminum aircraft skin panels, Al 2024-T3, under composite patching (carbon reinforced laminates). The detection sensitivity of each technique was investigated based on the relation between thickness of composite patch and specific parameters of each method aiming at the development of a reliable, for this purpose, quality inspection technique.

**3:15 PM R2.4**

AN AB INITIO INVESTIGATION ON THE EFFECTS OF IMPURITY IN ALUMINUM GRAIN BOUNDARY. Guang-Hong Lu, Tomoyuki Tamura, Ryoichi Yamamoto, Inst. of Industrial Science, Univ. of Tokyo, Tokyo, JAPAN; Masanori Kohyama, The National Institute of Advanced Industrial Science and Technology (AIST), KANSAI Center, Osaka, JAPAN.

Recently it has been experimentally found that Na, Ca and S have the embrittling effect on Al alloys. As for Si, it is reported that the precipitated Si promotes the nucleation and growth of the voids of the Al conductor films for LSI use. Therefore ab initio pseudopotential calculations based on density functional theory (DFT) with local density approximation (LDA) were carried out to investigate the effects of these impurities in the Al grain boundary. Results show that the charge density decreases significantly near the substituted Na or Ca atom, which means the formation of the weak bonding region between Al-Na or Al-Ca atom at the boundary and between grains. Such weak bond regions may act as the origin of the crack or the preferential path of the cracks under stress. The impurity-promoted embrittlement mechanism by Na and Ca's segregation is one kind of 'decohesion model'[1]. For the case of Si segregation, the charge density is much higher around Si atom. There forms a stronger directional metallic-covalent character mixing bond between Al and Si atom. The bond should have localized, rigid and directional characters, and thus prevent the rearrangement of atoms, such as sliding under stress. The mechanism of embrittlement by Si segregation can be classified as the 'bond mobility model'[2]. As for S case, the charge density increases between S and one of neighbouring Al atoms, and decreases between S and other neighbouring Al atoms. It is possible that these bonds becomes weaker than the former Al-Al bond. Therefore it can't be decided that the mechanism of the embrittlement by S segregation is classified into the 'bond mobility model' or 'decohesion model'. [1] W. Losch, Acta Metallurgica 27 (1979) 1885 [2] R. Haydock, J. Phys. C: Solid State Phys. 14 (1981) 3807.

**3:30 PM R2.5**

EFFECT OF GRAIN BOUNDARIES AND INDENTATION LOAD ON THE ELECTRICAL PROPERTIES OF NICKEL BASE

**SUPERALLOYS.** Kimberly Pinkos, Celestina Laboy, Rosario A. Gerhardt, School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA.

Non-destructive testing methods are important in aerospace applications for detecting and monitoring the effect that defects have on a material's performance. The existence of a grain boundary or extended deformation in a gas turbine blade presents the hazard of failure at lower temperatures than expected. Material and service costs for replacement of a part are expensive and therefore, it is preferred that the blades and vanes be cast as single crystals. However, it is not always possible to grow single crystals large enough for all applications or prevent extended plastic deformation. We have used impedance spectroscopy to evaluate the effect of the presence of grain boundaries and plastic deformation, as caused by hardness indentation, on the electrical response of several commercial nickel base superalloys at room temperature. These alloys consist of a mostly nickel matrix that contains small precipitates of intermetallic phases such as Ni<sub>3</sub>Al or Ni<sub>3</sub>Ti (often referred to as gamma prime). The gamma prime is the reinforcing phase. In some cases, additional additives cause carbides to precipitate at the grain boundaries between the primary grains or the grain boundary region is found to be devoid of the reinforcing gamma prime. Measurements were made as point contacts so that data could be tracked from point to point. Results indicate that the grain boundaries tend to have higher conductivities than the individual grains in most cases. It is speculated that this is due to the boundary regions having a different compositional profile than the center of the grains. Hardness indentation, on the other hand, had a more dramatic effect, by causing the magnitude of the imaginary impedance to change in size as well as position. X-ray diffraction and microscopy data will be included as supporting evidence for the effects discussed.

**3:45 PM R2.6**

**DETECTION OF COMPOSITIONAL FLUCTUATIONS IN HIGH TEMPERATURE EXPOSED WASPALOY.** Xiaodong Zou, Tariq Makram, Rosario A. Gerhardt, Georgia Institute of Technology, School of Materials Science and Engineering, Atlanta, GA.

Waspaloy is a nickel base superalloy used in aircraft engines. When this alloy is placed in service, it is subjected to long term exposure at high temperatures, which can cause the reinforcing gamma prime precipitate population to fluctuate. The population fluctuates as a result of coarsening, dissolution or reprecipitation. Samples exposed to 1200 degrees Fahrenheit for times ranging from 0-12626 hours were characterized using impedance spectroscopy, x-ray diffraction, quantitative stereology and hardness measurements. Two important parameters were derived from the impedance measurements: (1) the imaginary admittance peak magnitude ( $Y''_{max}$ ) and (2) the associated relaxation frequency ( $f_{max}$ ). As the distribution, shape and size of the precipitates change with exposure time, these two parameters were also found to vary. The fluctuations in the two electrical parameters were mirrored by similar fluctuations in hardness. In addition to the changes in the precipitate geometry, lattice constant changes detected by analyzing the x-ray diffraction data suggest that there are compositional shifts in the matrix as well as the gamma prime precipitates. Furthermore, the preferred orientation of the precipitates can also be seen to change with exposure time. In conclusion, our results demonstrate that electrical measurements can be used to detect changes in the gamma prime population of Waspaloy in a non-destructive way. The electrical results were correlated with hardness, x-ray diffraction and microstructural analysis.

**4:00 PM R2.7**

**PHASE TRANSFORMATION HYSTERESIS IN A PLUTONIUM ALLOY SYSTEM.** Jeffery J. Haslam, Mark A. Wall, David L. Johnson, Adam J. Schwartz, University of California, Lawrence Livermore National Laboratory, Livermore, CA.

An examination of phase transformation at sub-ambient temperatures in a plutonium alloy system was studied by electrical resistivity techniques. This system is characterized by a large difference in the electrical resistivity between the delta (FCC) and alpha' (monoclinic) phases. The phase transformation involves a 20 volume percent decrease in density during cooling along with a >30 percent change in electrical resistivity. Although the entire microstructure does not usually transform, substantial changes in properties can be observed. A large hysteresis in the forward and reverse transformation is believed to be associated with the large density change during the transformation. This hysteresis is being studied by electrical resistivity along with optical and transmission electron microscopy to better understand and model the phase transformation behavior in this material system. To facilitate comparison of data from electrical resistivity measurements and microscopy, a 2.8 mm diameter disk sample size is being used. The sample can be used for electrical resistivity measurements of the phase transformation and then

examined by microscopy techniques to observe the microstructure produced during the transformation. A calibration of the resistance measurement for this sample size has been performed using a computational approach to model the electrical resistivity. Tests with aluminum samples were successful in validating the approach. Optical and TEM observations have indicated that lenticular type phases are formed during the transformation of the plutonium alloy. This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

SESSION R3: POSTER SESSION  
Monday Evening, November 26, 2001  
8:00 PM  
Exhibition Hall D (Hynes)

**R3.1**

**FORMATION OF DIFFUSION PHOTOVOLTAGE IN NANOSCALED MATERIALS.** V. Duzhko and Th. Dittrich, Technische Universität München, Physik Department E16, Garching, GERMANY; V. Kytin and V. Timoshenko, M.V. Lomonosov Moscow University, Physics Department, Moscow, RUSSIA.

Photovoltage phenomena in porous TiO<sub>2</sub>, porous Si, poly(p-phenylene vinylene) and PZT are investigated by the transient photovoltage technique. A strong retardation of photovoltage transients after short pulse excitation is observed. Concentration gradients, non-equal diffusion coefficients of excess electrons and holes and huge Maxwell relaxation times as reasons for independent separation of excess electrons and holes are discussed. The correlation of the photovoltage maximum with dc conductivity, i.e. Maxwell relaxation time has been shown in porous TiO<sub>2</sub> and porous Si. The generality of the diffusion photovoltage phenomenon for nanoscaled materials is discussed.

**R3.2**

**INVESTIGATION OF MAGNETIC PROPERTIES OF PERMALLOY AND PERMALLOY/COPPER/PERMALLOY THIN FILMS USING THE PLANAR HALL EFFECT.** Marius Volmer, Transilvania Univ, Physics Dept, Brasov, ROMANIA; Jenica Neamtu, Institute for Electrical Engineering and Advanced Research, Bucharest, ROMANIA.

We have used the planar Hall effect (PHE) and the in-plane magnetoresistance effect (IP-MR) in order to investigate magnetic properties like the coercive field and the perpendicular anisotropy of NiFe (Permalloy) and NiFe/Cu/NiFe thin films. We have related these properties with the structure of the films investigated with AFM. We measured the field dependence of the PHE at fixed angles and the angular dependence of the PHE at various fixed fields applied in a plane lying perpendicular to the surface of the film. We applied to these measurements some corrections obtained from the field dependence of the IP-MR. We used the PHE as an indicator of the interaction between the magnetic layers and fitting the angular dependence we extract a value of the perpendicular anisotropy field. The fitting was made using the Stoner-Wohlfarth model for an array of 4x4 magnetic domains. For our multilayers a magnetic field of about 5 to 6 kOe was required for saturation in the out of plane configuration, which is less than predicted from the shape anisotropy. We show that such a reduction of the saturation field leads to a roughness effect in agreement with AFM measurements. For multilayers with the NiFe layer thinner than 5 nm we found a decrease of the Hall resistivity and the IP-MR effect was very small. This degradation of the magnetic properties is characteristic for evaporated thin NiFe layers that present a very rough surface. This is because the percolation occurs at NiFe thickness of about 2 nm when the samples are deposited onto oxidized Si substrates.

**R3.3**

**MICROSTRUCTURAL CHARACTERIZATION OF Al-Nd-Cu TERNARY ALLOY FILMS BY USING 4-PROBE METHOD.** Shinji Takayama, Hosei University, Dept of Systems and Control Engineering, Koganei, Tokyo, JAPAN.

Microelectronic conductor lines with low resistivity and high thermal stability have received a high attention for the application of advanced TFT-LCD. For this purpose, Al<sub>100-x</sub>RE<sub>x</sub> (RE=rare-earth-elements, X = 3-5at%) alloy systems have recently been developed and already used in part for practical application. To improve their thermal stability and resistivity further, we have currently investigated the effects of adding transition metal elements to Al-rare-earth-binary alloy (Al-RE) films on microstructures and resistivities during annealing. In this report, subsequent works were conducted by adding Cu to Al-Nd alloy films and investigating the change of microstructures and resistivities during annealing by using 4-probe method. Al<sub>100-x</sub>(Nd<sub>1-y</sub>Cu<sub>y</sub>)<sub>x</sub> (X = 3 - 6, y = 0.4 - 0.9) alloy

films with 400 nm thick were deposited on a 7059 glass substrate by using a DC magnetron sputtering apparatus. Both X-ray diffraction measurements and TEM observation showed that all the as-made structures of present ternary alloy systems mainly consisted of highly supersaturated solid solutions of the Al phase, having very fine grains less than 100 nm in size. All high values of resistivities of as-made samples decrease sharply above 250°C, associating with the segregation of metallic compounds of Al-RE and RE-Cu in the Al matrix (mostly at the grain boundaries of Al). These resistivities approach the values for pure Al with a further annealing up to 450°C as a result of a large grain growth of Al matrix. The apparent activation energy  $E_a$  of Al grain growth and precipitation of metallic compounds were obtained by using a Kissinger-like method where the resistivities were measured as a function of the heating rate. They were 0.7 - 1.1 eV. It should note that no growth of hillocks and whiskers were found on the film surfaces for all above Al-Nd-Cu samples after annealed at 450°C. Al<sub>97</sub>Nd<sub>1</sub>Cu<sub>2</sub> film samples annealed at 450°C showed a very low resistivity of 4  $\mu\Omega\text{cm}$ .

### R3.4 CHARGE-BASED DEEP LEVEL TRANSIENT SPECTROSCOPY OF SEMICONDUCTING AND INSULATING MATERIALS.

V.I. Polyakov, A.I. Rukovishnikov, N.M. Rossukanyi, Institute of Radio Engineering & Electronics, RAS, Moscow, RUSSIA; B. Druz, Veeco Instrument Inc., NY.

In this work, we have demonstrated the opportunity of the charge-based deep level transient spectroscopy (Q-DLTS) for characterization of the structures based on wide bandgap semiconducting and insulating materials such as diamond and aluminium oxide. Using our Q-DLTS method with rate window scanning [V.I. Polyakov, et al, Mat. Res. Soc. Symp. Proc., v. 442 (1997) 687], we obtained information about concentration, activation energies, capture cross-sections and locations of the native and extrinsic electrical active defects - trapping centers (TC). In comparison with widely used capacitance-based deep level transient spectroscopy, Q-DLTS give one possibility to investigate the structures in which a capacitance does not depend on the charge state of the surface and bulk traps. For this reason the Q-DLTS was applied for study of undoped and slightly doped diamond and manufactured by Veeco company aluminium oxide films. Charging transient spectroscopy was made by the computerizing system ASEC-03 in which charge sensitivity - 2000q, where q is the electron charge;  $\log(N_t/N) = -7$ , where  $N_t$  is the concentration of the trapping centers,  $N$  is the concentration of the noncompensated shallow impurities; and range of the rate window from 1 microsecond to 200 seconds. The Q-DLTS spectra, I-V and C-V characteristics obtained on ASEC-03 system also, were analyzed and parameters of the TC were determined. The results are discussed in comparison with data available in the literature. This work was supported by Grant No of the 01-02-16046 of the Russian Foundation of Fundamental Research.

### R3.5 ADMITTANCE SPECTROSCOPY OF Si/Si<sub>1-x</sub>Ge<sub>x</sub> NANOSTRUCTURES WITH P-TYPE AND N-TYPE DOPING.

K.A. Slinker, F.S. Flack, D.E. Savage, P. Rugheimer, M.A. Eriksson, M.G. Lagally, University of Wisconsin-Madison, Madison, WI; Y. Zhao, Keithley Instruments, Cleveland, OH.

Self-assembling quantum dots (QDs) are of interest both in fundamental condensed matter physics as artificial atoms and in many technological applications such as photodetectors and lasers. In particular, they are known to create strong traps for charge carriers with a trap strength tunable by varying the dot growth parameters. QDs based on the Si/SiGe system offer the additional prospect of integration into Si-based devices. Since most of the band offset in SiGe heterostructures is located in the valence band, SiGe QDs grown on Si are efficient hole traps. The properties of electrons in arrays of SiGe QDs are less well understood although they may induce strong perturbations in carrier transport in QD-based devices as well as create the potential for devices that exploit the resulting electron confinement. To address this potential, we use admittance spectroscopy to study self-assembled SiGe quantum dots embedded in p-type Schottky diodes 400 nm from the front contact and 100 nm from a highly doped (p<sup>+</sup>) substrate. Admittance spectroscopy provides information on energy levels of confined states. We examine QD ensembles in a wide variety of sizes and distributions grown by both MBE and UHV-CVD. The hole activation energies are shown to vary with QD composition and size, with typical energies of order 100 meV. Electrons can be trapped in and near the QDs because of Coulomb attraction to the trapped holes or because the Si around the QDs is strained. We show qualitative band diagrams of this potential electron confinement. We contrast the results we obtain on p-type Schottky diodes with similar structures with n-type doping, focusing on the electrons confined to regions surrounding the dots.

### R3.6 ELECTRICALLY ACTIVE DEEP DEFECTS IN ScN. Florentina Perjeru, Xuewen Bai and Martin E. Kordesch, Department of Physics and Astronomy, Ohio University, Athens, OH.

ScN is a material that has seen an increasing number of publications in recent years, mostly due to clarification of its nature (semiconductor with indirect band gap of 0.9 eV and direct band gap of 2.2 eV). Most of the research has been done on structural characterization and band gap measurements. Several studies on ohmic contacts and heterojunctions have been recently published as well. In this study we report the first results of the investigation of deep electrically active levels in asymmetrically n-ScN/p-Si diodes using deep level transient spectroscopy. Depending upon the method of deposition of ScN onto Si, defects with different activation energies are found. In material grown by plasma assisted physical vapor deposition (PAPVD) an electronic trap with activation energy  $E_C-E_T = 0.52$  eV is found to have a higher concentration closer to the ScN/Si interface. In material grown by rf-sputtering, an electronic trap as well is found, situated at approximately  $E_C-E_T = 0.90$  eV. Details on sample fabrication, experimental results and data analysis will be presented and discussed.

### R3.7 INFLUENCE OF SUBSTRATE ANNEALING TEMPERATURE UPON DEEP LEVELS IN N-TYPE 4H-SiC. Martin E. Kordesch, Florentina Perjeru, Department of Physics and Astronomy, Ohio University, Athens, OH; R.L. Woodin, Extreme Devices, Austin, TX.

Electrically active deep levels in N implanted n-type 4H-SiC samples have been investigated as a function of substrate annealing temperature. Ni Schottky barriers on SiC material, as grown and annealed at 400°C, 700°C and 900°C in air, have been used for deep level transient spectroscopy analysis. The results suggest that electrically active defects exist in the material, and have a dependence upon the annealing temperature of the substrate before junction formation. For example, for the as-grown material, the defect situated at  $E_C-E_T = 0.33$ eV anneals out if the sample is heated at 400°C, while the defect due to N sitting at C or Si lattice ( $E_C-E_T = 0.19-0.23$  eV) persists for temperatures up to 900°C. A hole trap ( $E_T-E_V = 0.14$ eV) is present only in the material annealed at 900°C, suggesting a relation with the relaxation of the structure after implantation effects are annealed. Several defects that have not been reported by other groups have similar behavior ( $E_C-E_T = 0.41$ eV and 0.50 eV). Detailed discussion of the experiment and results will be presented.

### R3.8 LOW TEMPERATURE OHMIC CONTACT FORMATION OF Ni<sub>2</sub>Si ON N-TYPE 4H-SiC AND 6H-SiC. Abdalla M. Elsamadicy<sup>a</sup>, D. Ila<sup>a</sup>,

R. Zimmerman<sup>a</sup>, M.A. George<sup>b</sup>, J.K. Hirvonen<sup>c</sup>, J.D. Demaree<sup>c</sup>, <sup>a</sup>Center for Irradiation of Materials, Alabama A&M University, Normal, AL; <sup>b</sup>University of Alabama-Huntsville, Huntsville, AL; <sup>c</sup>WMRD, U.S. Army Research Lab., APG, MD.

Nickel Silicide (Ni<sub>2</sub>Si) is investigated as possible ohmic contact to heavily nitrogen doped n-type 4H-SiC and 6H-SiC. Nickel Silicide was deposited via electron gun with various thicknesses on both Si and C faces of the SiC substrates. The (Ni<sub>2</sub>Si) contacts were formed at room temperature as well as at elevated temperatures. The Electric Force Microscopy (EFM) and Surface Potential (SP) imaging were used to map the electrostatic potential on the sample surface. Contact resistivities and I-V characteristics were measured at temperatures between Room Temperature and 527K. To investigate the electric properties, I-V characteristics were studied and used to estimate the specific contact resistance for the samples at each annealing temperature. Both Rutherford Backscattering Spectroscopy (RBS) and Auger Electron Spectroscopy (AES) were used for depth profiling of the (Ni<sub>2</sub>Si), Si, and C. X-ray Photoemission Spectroscopy (XPS) was used to study the chemical structure of the (Ni<sub>2</sub>Si)/SiC interface. Acknowledgment Research sponsored in part by the NASA-Alabama Space Grant Consortium, Ctr. for Irradiation of Materials of Alabama A&M University.

### R3.9 ELECTRICAL PROPERTIES AND LAYER STRUCTURE OF HEAT-TREATED POLYPARAPHENYLENE (PPP). Tatsuo Nakazawa, Kyoichi Oshida, Kozo Osawa, Nagano Nat'l College of Technology, Dept of Electronics and Computer Sci, Nagano, JAPAN; Morinobu Endo, Shinshu Univ, Dept of Electrical and Electronic Engineering, Nagano, JAPAN.

Polyparaphenylene (PPP) is one of the expective materials for many applications such as cathode electrodes for the lithium ion secondary batteries. In this study, a relation between heat treatment temperature and the resultant PPP powder resistivity was discussed. Moreover, a layer structure of heat treated PPP was investigated by means of a transmission electron microscope (TEM) observation

combined with a digital image processing technique. PPP powders, which were synthesized by Kovacic method, were heat treated in pure argon flow at the temperature of 700 to 900°C in 1 hour. The crashed powder, amount of about 80 mg, was charged in an apparatus with a small volume sample chamber (inner diameter of 6mm). The chamber wall is made by the insulating material, so that the sample powder and metal electrodes are contacted only upper and bottom ends of cylinder. Voltage across the sample was measured under a condition of constant applied current of 100 mA and up to 65 MPa pressure by compressed air. The volume change of the sample was measured using a dial gauge to determine the packing density at each applied pressure. The resistivity of the powder under pressure was drastically dropped, more than 2 orders, after 800°C treatment compared to that of the 700°C treated one. Relative small change of resistivity was observed after 900°C treatment. The layer structure, however, grew gradually by the elevation of heated temperature. It is thought that the edge condition of the PPP powder have influence significantly on the resistivity. Detail features of the layer structure were extracted from TEM images by means of the digital image processing.

### R3.10

**CYCLING BEHAVIOR OF LITHIUM MANGANESE OXIDE THIN FILMS PREPARED BY A SOL-GEL METHOD FOR LITHIUM SECONDARY BATTERIES.** Jong-Hyuk Park, Hunjoon Jung, Jinyoung Kim, Hyun-Seok Jung, Min Park, Kugsun Hong, and Seung-Ki Joo, School of Materials Science and Engineering, Seoul National University, Seoul, KOREA.

Thin film fabrication process of the spinel phase  $\text{LiMn}_2\text{O}_4$  was developed and the electrochemical characteristics of  $\text{LiMn}_2\text{O}_4$  thin films were investigated for rechargeable thin film lithium batteries.  $\text{LiMn}_2\text{O}_4$  thin films were prepared by a sol-gel method using spin-coating and annealing processes. Li-acetate and Mn-acetate were chosen as source materials, pure ethanol as solvents and diethanolamine (DEA) as stabilizer. After drying at 300°C, the thin films were annealed at several temperatures. The thin films were tested as cathodes in 4 V lithium cells. The charge-discharge characteristics and the cycling behavior of Li / 1M  $\text{LiClO}_4$ -PC electrolyte /  $\text{LiMn}_2\text{O}_4$  cells revealed that  $\text{LiMn}_2\text{O}_4$  electrode annealed at higher temperatures showed a high initial capacity. However, the rate of capacity fading during cycling decreased as the annealing temperature decreased. Particularly the capacity of the cells annealed at 500°C slightly increased during cycling. The increased crystallinity of  $\text{LiMn}_2\text{O}_4$  thin film after cycling is evidenced by the sharper (111) XRD peak.

### R3.11

**OPTIMIZATION OF IONIC CONDUCTION IN THE AURIVILLIUS SYSTEM USING D-OPTIMAL EXPERIMENTAL DESIGN.** Chris Say, Alfred University, Alfred, NY; John Pierce, Viral Modi, Scott Speakman, Mike Haluska, David Earl, Scott Misture.

A D-optimal design space of the  $(\text{Bi}_{2-x}\text{Pb}_x)(\text{Sr}_{2-y}\text{Ba}_y)\text{Nb}_2(\text{Al}_{1-z}\text{Ga}_z)\text{O}_{11.5}$  Aurivillius structure will be quantified using a full quadratic model. The linear concentration effects of Al-Ga, Ba-Sr, Pb-Bi, the quadratic concentration effects of  $(\text{Al-Ga})_2$ ,  $(\text{Ba-Sr})_2$ ,  $(\text{Pb-Bi})_2$ , and the interaction concentration effects of all combinations of the linear parameters will be quantified. The materials listed above will be synthesized using the acetate solution method and/or via solid state synthesis. The ionic conductivities will be understood by impedance spectroscopy and galvanic cell measurements; impedance spectroscopy measures the overall conductivity whereas the galvanic cell determines the amount of ionic versus electronic conductivity. As a result of this research the influence of cation substitutions and interactions on ionic conductivity will be understood using a statistically designed mathematical model.

### R3.12

**DEFECT MECHANISM IN  $\text{PbSnF}_4$  FAST-ION CONDUCTOR.** Georges Dénès, and M. Cecilia Madamba, Concordia University, Department of Chemistry and Biochemistry, Laboratory of Solid State Chemistry and Mössbauer Spectroscopy, Laboratories for Inorganic Materials, Montreal, Québec, CANADA.

$\text{PbSnF}_4$  is the highest performance fluoride-ion conductor. Among the  $\text{MF}_2$  fluorides, the highest fluoride-ion conductivity is found those crystallizing in the fluorite-type structure. This has been attributed to the presence of a large number of  $[\text{F}_8]$  cubes, where  $[\ ]$  is a metal ion vacancy, the other half of the  $\text{F}_8$  being  $\text{MF}_8$ , i.e. they have a metal ion in their center. The high fluoride-ion mobility in fluorite-type  $\text{MF}_2$  has been explained by the opportunity to form a large number of Frenkel defects, whereby a fluoride ion leaves its normal crystallographic site and goes in interstitial position inside a  $[\text{F}_8]$  cube. However, one of us showed earlier that this mechanism does not explain: (i) why the fluoride ion conductivity of  $\beta\text{-PbF}_2$  is much higher than that of  $\text{BaF}_2$ , even though there is much more room for  $\text{F}^-$  interstitials in the latter, and (ii) why the conductivity of  $\text{MSnF}_4$

(M = Pb and Ba) is three orders of magnitude than that of the corresponding  $\text{MF}_2$ , even though there is no  $[\text{F}_8]$  cubes in the  $\text{MSnF}_4$  structure. In the present work, we have analyzed the opportunities for fluoride ion motion in  $\text{MSnF}_4$  and the role of soft shell  $\text{Pb}^{2+}$  and covalently bonded Sn(II) in these structures, in terms of creation partial occupancy of fluoride ions over several sites.

### R3.13

**EFFECTS OF GRAIN SIZE DISTRIBUTION ON COLE-COLE PLOTS OF POLYCRYSTALLINE SPINELS.** M.P. Gutiérrez-Amador and R. Valenzuela, Institute for Materials Research, National University of México, MEXICO.

Impedance Spectroscopy of spinels such as Ni-Zn ferrites and Mn-Zn ferrites has shown that the grain boundary resistance is larger than the grain (bulk) resistance [1,2] which allows the possibility of a resolution of both contributions to the total complex impedance. In this contribution, an investigation of the effects of different grain size distribution (GSD) on the complex impedance plane (Cole-Cole plots) is presented. We used samples of  $\text{Zn}_x\text{Ni}_{(1-x)}\text{Fe}_2\text{O}_3$  ferrites prepared by coprecipitation methods and then submitted to various thermal treatments to modify their grain size distribution. Their dielectric properties were measured in the temperature range 25-200°C and in the frequency range of 5Hz-13MHz. Clear differences were observed on the form of the impedance spectra. Samples with a narrow GSD showed two well resolved semicircles corresponding to grain (high frequencies) and grain boundaries (low frequencies) response. As the extent of the GSD increased, semicircles exhibited a deformation and eventually became unresolved. These results are a clear evidence of the correlation between the electric time constant and GSD. [1] A. Peláiz-Barranco, M.P. Gutiérrez-Amador, A. Huanosta and R. Valenzuela. Appl. Phys. Lett. 73 (1988) 2039. [2] H.F. Cheng. J. Appl. Phys. 56 (1984) 1831.

### R3.14

**OXYGEN-ION DIFFUSION AND IONIC CONDUCTIVITY IN  $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_x$ .** Akihiko Yamaji, Kenji Tojyu and Tadaharu Adachi, Department of Mechanical Engineering, Tokyo Institute of Technology, Meguroku, Tokyo, JAPAN.

Brownmillerite ( $\text{Ca}_2\text{Al}_2\text{O}_5\text{-Ca}_2\text{Fe}_2\text{O}_5$ ) solid solution) structure can be regarded as an oxygen-ion deficient perovskite structure. Because of high proportion of the oxygen vacancies in the structure, this material could be a candidate of fast oxide-ion conductor. Goodenough et al. indeed observed a first-order transition to a fast oxide-ion conductor at 930°C for  $\text{Ba}_2\text{In}_2\text{O}_5$  which adapts brownmillerite structure at ambient temperature. In the present study, we investigated the ion conductivity and the oxygen ion diffusion in  $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_x$  system. The oxygen diffusion coefficients for  $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_x$  ( $x=0$  to 0.3) ceramics were determined from an isotope-gas exchange measurement using the stable isotope  $^{18}\text{O}$  as a tracer between 570°C and 1000°C. The abrupt changes in the diffusion coefficients are observed at 790°C in  $\text{Ba}_2\text{In}_{2-x}\text{Ga}_x\text{O}_x$ . This change is caused by the phase transition from orthorhombic to the cubic phase. The diffusion coefficients at a high temperature region above 790°C is given by  $D=7.04 \times 10^{-4} \exp(-82.72\text{kJ/RT})\text{cm}^2/\text{sec}$  and below 790°C the those are given by  $D=1.17 \times 10^{-4} \exp(-76.61\text{kJ/RT})\text{cm}^2/\text{sec}$ . We can compare measured diffusion coefficients with those obtained from the ion conductivity measured values. The activation energy is almost same, but the diffusion coefficients from Nernst-Einstein equation are slightly larger than those obtained from the diffusion experiments. This difference will be discussed considering the transport number and the oxygen-ion carrier density.

### R3.15

**COMPUTER SIMULATION AND MEASUREMENT ON THE MICROSTRUCTURE AND THE MICROWAVE PROPERTIES IN  $(\text{Mg,Ca})\text{TiO}_3$  DIELECTRIC CERAMICS.** Hyuna Hwang, Jae-Hwan Park, Yoonho Kim, Materials Science & Technology Div, Korea Institute of Science and Technology, Seoul, KOREA.

Electromagnetic simulation of  $(\text{Mg,Ca})\text{TiO}_3$  dielectric ceramics was compared to the measurement with a network analyzer using the cavity resonator method which has been used for determining microwave quality factor. Scattering matrix  $S_{21}$  obtained from the network analyzer was compared to the  $S_{21}$  obtained from the simulation. From electric field distribution, the dominant resonant  $\text{TE}_{015}$  mode could be easily determined. The effects of the pore and the conductive inclusion inside the dielectric were investigated. Quality factor decreased with the pore and the second phase in the dielectrics. The decrease of quality factor is more significant when dielectric have conductive inclusions inside the dielectric.

### R3.16

**EFFECT OF B-SITE CATION ORDERING ON THE MICROWAVE DIELECTRIC PROPERTIES OF BARIUM NIOBATE AND TANTALATE COMPLEX PEROVSKITE CERAMICS.**

Dielectric ceramics based on  $Ba(B_{1/3}B_{2/3})O_3$  complex perovskites where  $B = Mg, Zn$  and  $B' = Ta$  and  $Nb$  are extensively used in microwave passive electronics owing to their low dielectric loss. Below the frequency of the fundamental optical phonon modes, the major mechanism of dielectric loss in these ceramics is attributed to the two-phonon difference absorption. Due to the small energy of the incident photon in the microwave range, absorption occurs close to the lines of degeneracy of the phonon branches in the Brillouin zone. A high temperature order-disorder transition in  $Ba(B_{1/3}B_{2/3})O_3$  from low to high crystal symmetry increases the number of degeneracies of the phonon modes. This in turn increases the dielectric loss due to increased probability of the photon absorption. Thus, in order to obtain low-loss ceramics, it is crucial to preserve a high degree of B-site cation ordering during the sintering process. This can be done by lowering the sintering temperature below the temperature of the order-disorder phase transition. By using this approach, we succeeded in obtaining several complex perovskite ceramics with exceptionally low dielectric loss; e.g.,  $Ba(Mg_{1/3}Ta_{2/3})O_3$  with  $Q \times f = 280$  THz,  $Ba(Mg_{1/3}Nb_{2/3})O_3$  with  $Q \times f = 160$  THz, and  $Ba(Ni_{1/3}Ta_{2/3})O_3$  with  $Q \times f = 80$  THz.

### R3.17

SCALING EFFECTS IN  $Al_{72}Mn_{22}Si_6$  QUASICRYSTALS DEDUCED FROM PRESSURE AND TEMPERATURE DEPENDENCE OF THE RESISTANCE. John K. Vassiliou, Edwin A. Simons, Department of Physics, Villanova University, Villanova, PA; Jens W. Otto, Joint Research Center for the European Commission, Brussels, BELGIUM.

X-ray diffraction and resistivity measurements on the  $Al_{72}Mn_{22}Si_6$  rapidly quenched alloy are reported. The x-ray pattern shows that the alloy is essentially single phase, with a little mixture of unreacted Al. The peaks can be indexed using icosahedral vectors in the six dimensional space  $Z^6$ . The resistance of thin ribbons of  $Al_{72}Mn_{22}Si_6$  quasicrystals has been measured as a function of temperature between 1.4 and 300 K at fixed pressures in the range 0 to 15 Kbar. Below 40 K, the resistance increases with decreasing temperature, and below 14 K, the conductivity varies as  $T^{1/2}$ . This result is in agreement with the scaling and localization models in which spatial disorder and electron-electron correlation effects determine the electronic transport properties of the material. The value of the magnetoresistance measured at 60 KGauss and 0.34 K agrees qualitatively with the predictions of the above models. The pressure dependence of the correlation gap  $\Delta$  and the resistivity  $\rho$  suggests that the system is in the strong coupling limit.

### R3.18

STUDY OF THE VARIATION OF THE MAJORITY AND MINORITY CARRIERS DENSITIES WITH THE TEMPERATURE IN NANO-STRUCTURED Si-SiO<sub>2</sub> USING THE PHOTO-GRATING TECHNIQUE. Yury Posada, Luis F. Fonseca, Oscar Resto, S. Zvi Weisz, Dept of Physics, University of Puerto Rico, San Juan, PR; Isaac Balberg, The Racah Institute of Physics, The Hebrew University, Jerusalem, ISRAEL.

We have measured the temperature dependencies for the two carriers mobility-life time products, the  $(\mu)_n$  and  $(\mu)_p$ , and the light intensity exponents,  $\gamma$  and  $S$ , in nano-structured Si-SiO<sub>2</sub> of two co-sputtered samples with a silicon concentration of 42 and 81-volume%, and Si particles average sizes of 7 and 36 nm respectively. Measurements were made for a temperature range from 215 to 325°K. The diffusion length for these samples showed to rise with the increase of the temperature, and the same behavior is found for the photoconductivity and the dark conductivity. These measurements are used to obtain conclusions about the nano-crystalline silicon electrical transport properties and the corresponding electron energy configuration.

SESSION R4: SEMICONDUCTORS  
Chair: Mohammad A. Alim  
Tuesday Morning, November 27, 2001  
Room 206 (Hynes)

### 9:00 AM \*R4.1

RELIABILITY IMPROVEMENT AND YIELD ENHANCEMENT OF GaAs CHIP THROUGH MATERIAL CHARACTERIZATION AS DEPLOYED IN PROCESS ENGINEERING. Kanti Prasad, A. Saini, V. Srinivasan, University of Massachusetts, Lowell, MA; Kim Conway, J. Mason, B. Murphy, Alpha Industries, Woburn, MA.

University of Massachusetts, Lowell is carrying out innovative experiments to improve the reliability of GaAs chips such as  
●Experiments to improve gate oxide integrity. ●Metal to polycide

contact resistance measurements. ●Material formation over polycide in platinum processing. ●Intermetal dielectric capacitance measurements to improve reliability. ●Dopant impurity distributions across channel, source and drain in GaAs MESFETS. The preliminary results are quite encouraging and will be reported at the conference. The project is sponsored by the Alpha Industries, Woburn, MA.

### 9:30 AM R4.2

ANALYSIS OF ION IMPLANTATION DAMAGE IN SILICON WAFERS BY A CONTACTLESS MICROWAVE DIAGNOSTIC. R.K. Ahrenkiel, Measurement and Characterization, National Renewable Energy Laboratory, Golden, CO; B. Lojek, ATMEL Corp, Colorado Springs, CO.

Because rapid thermal annealing (RTA) of ion implantation damage is required to maintain the integrity of submicron integrated circuit devices, a quick, efficient, and contactless diagnostic of the implantation damage is highly desirable. This is desirable in both research and production environments. A contactless measurement technique has been recently applied to this problem that uses a deeply penetrating low-frequency microwave probe frequency operating at 424 MHz. Here, we will demonstrate the use of this ultra-high frequency resonance-coupled photoconductive decay (RCPCD) technique, which, when combined with tunable optical excitation source, enables us to map the radiation damage in boron and arsenic-implanted silicon wafers. The surface-recombination contribution to lifetime is eliminated by the growth of a thermal oxide on the silicon wafers. We quantify the damage by mapping the minority-carrier lifetime as a function of optical penetration depth. We scan the optical nm and compare the near surface lifetime ( $1/\alpha(711 \text{ nm}) \sim 2 \mu\text{m}$ ) with the bulk lifetime. The lifetime is fairly independent of excitation wavelength for the as-grown, oxidized wafers with typical values larger than 50  $\mu\text{s}$ . After ion implantation with either arsenic or boron, the near-surface (711 nm) lifetime drops more than two orders of magnitude because of recombination at implantation-produced defects. After implantation, the shorter wavelength (711 nm) lifetime drops to less than 0.4  $\mu\text{s}$ . Plotting the lifetime vs. absorption depth shows a steep drop in lifetime when  $1/\alpha < 60 \mu\text{m}$  for implanted samples. However, the lifetimes again become independent of excitation wavelength for well-annealed samples, and are equal to the pre-implanted lifetimes in some cases. In this work, we quickly and efficiently compared the effectiveness of various RTA processes by the RCPCD diagnostic.

### 10:15 AM R4.3

DETERMINATION OF SURFACE SPACE CHARGE DENSITY ON SEMICONDUCTOR FROM DISPLACEMENT CURRENT-VOLTAGE CURVE USING A SCANNING VIBRATING PROBE. Yutaka Majima, Tomohiko Masuda, Setsuri Uehara, Atsushi Okuda, Mitsumasa Iwamoto, Tokyo Institute of Technology, Dept. of Physical Electronics, Tokyo, JAPAN.

A determination method of the local surface space charge density in thin films on semiconductor surfaces is described. In this method, the displacement current and the tunneling current flow periodically in accordance with the perpendicular vibration of the probe of the scanning tunneling microscopy (STM). The external circuit current is separated into the mean displacement current and the mean tunneling current by using the two-phase lock-in amplifier [1]. The displacement current-probe voltage curve of a p-type silicon with a native oxide layer was measured in a vacuum ( $< 3 \times 10^{-9}$  torr). The displacement current-voltage curve has been analyzed taking into account surface space charge density. The theoretical displacement current-voltage curve has been fitted to the measurement in order to obtain both the local surface space charge density and the local carrier concentration of the semiconductor, and the theory is in good agreement with the measurement in both voltage regions where the majority carriers are accumulated and depleted. We also demonstrate a simple determination method of both the surface space charge density and the surface potential difference of thin films from flat-band conditions in the displacement current-voltage curve. This simple method is useful for determining the local surface space charge density of ultra-thin films such as organic thin films.

1. Y. Majima, Y. Oyama, M. Iwamoto Phys. Rev. B, 62, 1971-1977 (2000).

### 10:30 AM R4.4

CONDUCTANCE-TRANSIENT THREE-DIMENSIONAL PROFILING OF DISORDERED INDUCED GAP STATES ON METAL-INSULATOR-SEMICONDUCTOR STRUCTURES. Helena Castán, Salvador Dueñas, Juan Barbolla, Universidad de Valladolid, Dept. Electricidad y Electrónica, Valladolid, SPAIN; Ignacio Mártil, Germán González-Díaz, Universidad Complutense, Dept. Electricidad y Electrónica, Madrid, SPAIN.

Metal-insulator-semiconductor (MIS) structures fabricated on III-V semiconductors to be used in field-effect transistors present some

problems related to insulator-semiconductor interface quality. So, these structures must be carefully characterized and standard electrical measurements, as Capacitance-Voltage and Deep-Level-Transient-Spectroscopy (DLTS) are usual tools to do it. However, these techniques do not provide information about the defect spatial distribution. In the last years we have proved that Conductance Transient (G-t) measurements provide quantitative information about the disordered induced gap states (DIGS). In fact, from the experimental conductance transients we can obtain the DIGS state density as a function of the spatial distance to the interface and of the energy position in the bandgap. Up till now we have only used this technique in order to compare the interface quality of several sets of samples by complementing DLTS results. So, we have only recorded and processed room temperature-constant frequency (typically 200 KHz) conductance transients. In this work we report for the first time the DIGS spatial and energetical distribution obtained by recording conductance transients at several temperatures (ranging from 77 to 300 K) and several frequencies (ranging from 100 Hz to 200 KHz). These measurements allow us to obtain a three-dimensional defect map of Al/SiN<sub>x</sub>:H/InP structures. We obtained variations of 0.5 eV in energy and 40 Å in depth. The InP substrates are (100) oriented undoped wafers with carrier concentration of 5x10<sup>15</sup> cm<sup>-3</sup>. The insulator layer is a 500 Å-thick SiN<sub>x</sub>:H film obtained by means of electron cyclotron resonance plasma enhanced chemical vapour deposition (ECR-CVD). A nitrogen plasma cleaning was carried out just before insulator deposition. Once the cleaning process was finished, the insulator deposition was carried out by using N<sub>2</sub> and pure SiH<sub>4</sub> gases. The substrate temperature during the plasma cleaning and deposition process was kept constant at 200°C.

#### 10:45 AM R4.5

SUBSURFACE DOPANT OBSERVATION ON THE Si(100)2x1:H SURFACE BY SCANNING TUNNELING MICROSCOPY: EXPERIMENTAL AND THEORETICAL INVESTIGATION. Lequn Liu, Jixin Yu and J.W. Lyding, Beckman Institute for Advanced Science and Technology, University of Illinois, Urbana, IL.

The lack of surface states within the band gap of the perfect Si(100)2x1:H surface opens the way to scanning tunneling microscopy (STM) studies of dopant atom sites in Si(100). The N and P type dopant induced features were observed in filled state images and empty state images of STM. The donor (Arsenic) induced feature shows as a protrusion in both the filled state image and empty state images, while the acceptor (Boron) induced feature appears as a hillock in the filled state image but depression in the empty state image. The bias dependence, depth dependence and dopant concentration dependence of the dopant induced features were investigated in detail. Based on the scattering theory, the numerical calculation was performed to achieve fundamental understanding about this issue. The calculation results were in agreement with the experimental observations. The potential application of this study for 3D dopant profiling with STM on both P and N type samples is discussed, and the optimal scanning condition is also suggested.

#### 11:00 AM R4.6

CAPACITANCE SPECTROSCOPY OF N-I-N AND P-I-P GaAs SANDWICH STRUCTURES WITH NANOSCALE AS CLUSTERS IN THE I-LAYERS. V.V. Chaldyshev, P.N. Brunkov, A.V. Chernigovskii, A. Moskalenko, S.G. Konnikov, Ioffe Institute, St. Petersburg, RUSSIA; V.V. Preobrazhenskii, M.A. Putyato, B.R. Semyagin, Institute of Semiconductor Physics, Novosibirsk, RUSSIA.

Accumulation of electrons and holes in GaAs layers, that contained As clusters and were sandwiched between n- and p-type buffer GaAs layers, was revealed by capacitance-voltage measurements. As a result of majority-carrier accumulation, expansive depletion regions are formed in the adjoining buffer layers. Simulation of the capacitance-voltage characteristics, based on a numerical solution of the Poisson equation, shows that the accumulated charge density is  $\sim 1 \cdot 10^{12}$  cm<sup>-2</sup>, which is comparable with the concentration of As nanoclusters determined by transmission electron microscopy. The levels where the electrons or holes are accumulated lie close but above the GaAs midgap. A strong difference in the emission rates of the accumulated electrons and holes has been revealed.

#### 11:15 AM R4.7

DISPLACEMENT CURRENT STAIRCASE DUE TO COULOMB BLOCKADE. Kouhei Nagano<sup>a</sup>, Atsushi Okuda<sup>a</sup>, Yutaka Majima<sup>a,b</sup>; <sup>a</sup>Tokyo Institute of Technology, Dept. of Physical Electronics, <sup>b</sup>Organization and Function, PRESTO, Japan Science and Technology Corporation (JST), Tokyo, JAPAN.

Displacement current staircase due to Coulomb blockade in displacement current-voltage curves has been measured in a two-junction system with probe of vibrating scanning tunneling microscope (STM)/colloidal Au nanoparticles/vacuum/Si structure, taken with a low temperature at 72 K. In this measurement, the

distance between the colloidal Au nanoparticles (ca. 8 nm in diameter) on tungsten (W) probe and Si surface is changed sinusoidally, and is adjusted as small as some few nm at which Coulomb blockade condition changes periodically with the vibration of the scanning probe. Both displacement current and tunneling current flow periodically in external circuit with applying dc. probe voltage and are separated by using a two-phase lock-in amplifier. The displacement current staircase due to Coulomb blockade is analyzed by taking into account a simple analytic expression for the displacement current in a voltage-biased two-junction system in which the ratio of tunneling resistances change with the vibration. The theoretical displacement current staircases are in good agreement with the measurement. The change in number of quantum electrons on nanoparticles by vibration of the scanning probe can be determined by fitting the theoretical displacement current staircase due to Coulomb blockade with the experimental results.

#### 11:30 AM R4.8

MICROWAVE TRANSIENT PHOTOCONDUCTIVITY IN POROUS SEMICONDUCTORS. Horia-Eugen Porteanu, Elisaveta Konstantinova<sup>a</sup>, Vladimir Kytin<sup>a</sup>, Victor Timoshenko<sup>a</sup>, Thomas Dittrich, and Frederick Foch, T.U. München, Physik-Department E16, Garching, GERMANY. <sup>a</sup>Perm address: Lomonosov State University, Moscow, RUSSIA.

The advanced method of transient microwave photoconductivity (AMTTP), introduced by Grabtchak and Cocivera [1] offers a complete view of the change in time of both, the real and imaginary part of the dielectric constant. We used this method to study special aspects of conductivity in porous anatase (TiO<sub>2</sub>) and porous silicon under pulsed UV light excitation (337 nm, 5 ns, 0.3 mJ). Porous anatase (average diameter of nanoparticles about 16 nm) shows a strong photodielectric effect. The photoelectrons are trapped instantaneously in defects. Trapped excess electrons form oscillators driven by the microwave field at 35 GHz, what is below their resonance frequency. This leads macroscopically to an increase of the dielectric constant. The decay time for mesoporous Si is shorter than in bulk Si due to spatial confinement of the carriers. The sign of the change of the dielectric constant in porous silicon depends on the size of the nanoparticles. Big silicon nanoparticles (5-10 nm) allow a quasifree motion of the excess carriers (oscillator with quasi zero resonance frequency) resulting in a decrease of the dielectric constant. On the other hand, the decay time increase for much smaller nanoparticles (nanoporous silicon) because of retardation by trapping and the dielectric constant increases. [1] S. Grabtchak, M. Cocivera, Phys. Rev. **B** 50, 18219 (1994).

#### SESSION R5: MICROELECTRONICS

Chair: Gyeong Man Choi

Tuesday Afternoon, November 27, 2001

Room 206 (Hynes)

#### 1:30 PM \*R5.1

INVESTIGATION OF Pt/Si/CeO<sub>2</sub>/Pt SYSTEM BY IMPEDANCE SPECTROSCOPY. Darja Kek<sup>a,c</sup>, Jyrki Lappalainen<sup>b,c</sup> and Harry L. Tuller<sup>c</sup>, <sup>a</sup>Jozef Stefan Institute, Ljubljana, SLOVENIA; <sup>b</sup>Microelectronics Laboratory, University of Oulu, FINLAND; <sup>c</sup>Department of Material Science and Engineering, MIT, Cambridge, MA.

Epitaxial growth of dielectric layers on silicon substrates has attracted a great deal of recent interest given their potential applicability in the fabrication of high quality silicon-on-insulator (SOI) structures, high density capacitor devices, and stable buffer layers between silicon and other materials. Cerium dioxide (CeO<sub>2</sub>) appears to be a particularly attractive candidate, given its high dielectric constant and its compatibility with Si. To date, measurements of the electrical properties of CeO<sub>2</sub> films on Si have been limited to room temperature. In this study, thin films of CeO<sub>2</sub> were prepared by in situ pulsed laser deposition (PLD) on n-type (100) silicon substrates, with varied deposition conditions. Impedance measurements were performed from room temperature to 350°C. Impedance spectroscopy enabled us to characterize the electrical signature of the Pt/Si interface independent from that of the CeO<sub>2</sub> film. It was found to contribute insignificantly above approximately 50°C. The conductivity of the CeO<sub>2</sub> film was found to be thermally activated with activation energy of  $\sim 0.45$ eV, while the magnitude of conductivity was strongly dependent on the deposition parameters. We discuss these results in the relation to the potential use of CeO<sub>2</sub> as a dielectric film on silicon devices.

#### 2:00 PM R5.2

DIRECT OBSERVATION OF CURRENT CROWDING AROUND FABRICATED DEFECTS IN METAL LINES. R. Yongsunthorn, A. Stanishevsky, J. McCoy, E.D. Williams, Physics Department, University of Maryland, College Park, MD.



The spatial variation of current density in metal lines with model void defects fabricated using Focused-ion Beam (FIB) milling has been imaged using Magnetic Force Microscopy (MFM). The model defects were designed to systematically simulate the natural void shapes that occur in electromigration failure of current-carrying metal lines. Deconvolution and analysis of the resulting MFM signal allows us to deduce the current density variation near such defects and thus better understand the role of current crowding on electromigration-induced void evolution. The measured current crowding manifests itself in the form of atypical asymmetry in the MFM signal around such defects. The extent of the crowding is greatly dependent upon the defect geometry, with the absolute defect length having greater influence than the width. At current densities of  $5 \times 10^5$  A/cm<sup>2</sup>, an asymmetry in the MFM signal is clearly visible around defects, such as  $(1 \times 1) \mu\text{m}^2$  and  $(0.5 \times 0.5) \mu\text{m}^2$  notches and  $(1 \times 9) \mu\text{m}^2$  slanted slits, at the edge of a  $10 \mu\text{m}$  wide line. Comparison to calculations suggests that the asymmetry is due to highly localized current crowding, e.g. with 70% of the current displaced by the  $(1 \times 1) \mu\text{m}^2$  notch localized to within  $1 \mu\text{m}$  of the notch. (This work has been supported by the NSF-Materials Research Science and Engineering Center under grant NSF-DMR-00-80008.)

### 2:15 PM R5.3

DETERMINATION OF INCREASED RESISTIVITY IN SMALL DIMENSIONS: EXPERIMENTAL METHODS AND ANALYSIS. John Sanchez, Advanced Micro Devices, Sunnyvale, CA.

Integrated circuit metallization interconnects of small dimension show an increased resistivity as thickness and width decrease. Determination of conduction electron scattering factors such as interface character, adjacent materials, grain boundaries, mechanical stress and impurity levels requires very accurate knowledge of properties such as grain size, roughness and especially conductor cross-section. Experimental results of resistivity calculations for advanced Cu-based interconnect structures to less than 0.10 micron in width are described. Analytical methods utilizing the electrical area methodology are compared to standard high resolution electron microscopic techniques. Results indicate the electrical area method provides a more accurate description of dimension-dependent resistivity in Cu interconnects than traditional microscopic techniques. The proper scaling of size-dependent resistivity is shown to require two (orthogonal) dimensions such as aspect ratio and line width. Projections of Cu interconnect resistivities for future circuit technologies are provided.

### 2:30 PM R5.4

ELECTRICAL AND STRUCTURAL INVESTIGATION OF THE EFFECTS OF VIA-CONDUCTOR GEOMETRY IN THE ELECTROMIGRATION OF Al:Cu. R. Leon, D. Vu, A.S. Johnson, R. Ruiz, J. Okuno, J. Uribe and G. Hather, Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA; J.R. Lloyd, IBM Research Division, Thomas J. Watson Research Center, Yorktown Heights, NY.

Electromigration (EM) experiments conducted using two types of via/plug to conductor alignment indicate a geometrical dependence of electromigration failure in Al:Cu conductors. The resistance vs time curves show distinctive steps when the alignment is parallel. This is explained by a successive loss of conductivity through the tungsten plug (0.5 microns wide) due to void formation at the W/Al:Cu interface. These changes in electrical properties are correlated with microstructure using cross-sectional micrographs in the two different via geometries. In the perpendicular via/conductor arrangement, resistance increases by smaller and closely spaced steps. EM experiments without vias, found that the conductor lifetime under high temperature and current stressing increases by at least an order of magnitude. Kinetic studies at four temperatures between 180-2406°C found activation energies to be  $1.0 \pm 0.1$ eV. Results from EM experiments performed at different current densities will also be presented.

### 3:15 PM R5.5

REFRACTORY THIN-FILM METALLIZATIONS WITH CONTROLLED ELECTRICAL RESISTIVITY AND STRESS. Ilan Golecki and Margaret Eagan, Honeywell International Inc. (formerly AlliedSignal Inc.), Corporate Materials Laboratory, Morristown, NJ.

Refractory metals, such as rhodium and iridium, intrinsically possess high electrical conductivity, and their chemical inertness enables their use at relatively high temperatures in microelectronics. However, due to the high Young's modulus of these materials, a residual tensile stress of hundreds of MPa and higher is measured in evaporated thin films. New data is presented, demonstrating control over both the magnitude and the sign of the residual stress in such refractory thin films on oxidized Si substrates. These thin-film materials are formed

by means of ion-beam-enhanced physical vapor deposition. The electrical resistivity and stress are determined by controlling the substrate temperature, deposition rate and ion beam parameters. Thicker films are achieved in this manner, including films with near-zero residual stress.

### 3:30 PM R5.6

SURFACE ROUGHNESS AND SURFACE INDUCED RESISTIVITY OF THIN GOLD FILMS ON MICA. Raul C. Munoz, Departamento de Fisica, Facultad de Ciencias Fisicas y Matematicas, Universidad de Chile; German Kremer y Luis Moraga, Departamento de Fisica, Facultad de Ciencias, Universidad de Chile; Guillermo Vidal y Claudio Arenas, Departamento de Ingenieria Electrica, Facultad de Ciencias Fisicas y Matematicas, Universidad de Chile, Santiago, CHILE. \*Work funded by FONDECYT 1010481.

We report measurements of the surface topography of a 70 nm gold film deposited on mica preheated to 300°C in UHV performed with a Scanning Tunneling Microscope (STM). From these measurements we determine the rms amplitude and the lateral correlation length characterizing the average height-height autocorrelation function on a nanometric scale. We also report a method of analyzing thin film resistivity data that departs sharply from the traditional method of parameter fitting. This new method allows the determination of the resistivity and mean free path characterizing the bulk from the measured thin film resistivity by means of a new iteration procedure, that uses as input data the roughness parameters experimentally determined with the STM, and any of the available quantum transport theories, without adjustable parameters. We examine the resistivity data reported by Sambles et al. [Philos. Trans. R. Soc. London, Ser. A304 (1982) 365] for gold films deposited on mica under similar substrate temperature and similar speed of evaporation. The remarkable outcome is that any of the quantum transport theories available, the modified theory of Sheng, Xing and Wang [Munoz et al., J. Phys.: Condens. Matter 11 (1999) L299], the theory of Trivedi and Aschroft [Phys. Rev. B38 (1988) 12298], and the theory of Tesanovic et al. [Phys. Rev. Lett. 57 (1986) 2760], describe approximately both the temperature as well as the thickness dependence of the resistivity data without any adjustable parameter. Another surprise is the fact that the parameters characterizing the bulk—assumed to be independent of thickness for many decades—turn out to be thickness dependent, and that the quantum reflectivity characterizing electron-surface scattering turns out not to be a constant, but it depends on the angle between the momentum of the incoming electron and the normal to the surface.

### 3:45 PM R5.7

MICROSTRUCTURAL CHARACTERIZATION OF THIN Cr-Si COMPOSITE FILMS BY TEMPERATURE COEFFICIENT OF RESISTANCE MEASUREMENTS AND CONDUCTIVE ATOMIC FORCE MICROSCOPE. Fan Wu, Medtronic, Inc, Microelectronic Center, Tempe, AZ; James E. Morris, State Univ of New York at Binghamton, Dept of Electrical Engineering, Binghamton, NY.

Thin Cr-Si films with thicknesses between 8 and 40 nm were deposited by reactive sputtering onto SiO<sub>2</sub> on Si(100) substrates. Sheet resistance ( $R_s$ ) and temperature coefficient of resistance (TCR) of the films were measured using van der Pauw method.  $R_s$  and TCR data show that the  $R_s$  of the Cr-Si films can be changed from several hundred  $\Omega/\text{sq}$  to several hundred  $\text{k}\Omega/\text{sq}$  and the TCR of the films can be changed from -4000 ppm/C to 300 ppm/C. The negative TCR corresponds to a linear  $\log(R) \sim 1/T$  relationship and the positive TCR corresponds to a linear  $\log(R) \sim T$  relationship. The negative TCR suggests that the deposited films consist of chromium grains (possible containing some dissolved silicon) dispersed in a matrix of silicon. The physical separation of the metallic particles leads to a high resistivity as well as to a large negative TCR, since electron must be thermally activated in order to across the gaps between the particles. The slopes of the  $\log(R) \sim 1/T$  curves indicates that the activation energy varies from 0.003 eV to 0.31 eV, which depends on the composition and the microstructure of the films. After the films were annealed in an inert ambient, some of the silicon reacts at the surface of the metal particles and reduce the gaps between particles, which leads to a more positive TCR. Conductive atomic force microscope was used to analyze the composition and microstructure of the thin Cr-Si films and confirms the results postulated from the electrical characterizations.

### 4:00 PM R5.8

INVESTIGATION OF TRAPPING IN ULTRATHIN METAL OXIDES BY TRANSIENT PHOTOVOLTAGE TECHNIQUE. V. Duzhko and Th. Dittrich, Technische Universität München, Physik Department E16, Garching, GERMANY; V. Kytin, M.V. Lomonosov Moscow University, Physics Department, Moscow, RUSSIA; J. Rappich, Hahn-Meitner-Institut, Abt. Silizium Photovoltaik, Berlin, GERMANY.

Ultrathin TiO<sub>2</sub> layers are used as a model system to investigate transport properties of the basic spatial unit of porous TiO<sub>2</sub>. Injection of electrons into the Ti substrate and trapping of holes in the TiO<sub>2</sub> layer during illumination lead to the photovoltage. The relaxation of trapped charge was investigated by the transient photovoltage technique. The decay of the photovoltage was associated with spatially dependent recombination of charge carriers (low temperatures) and with hole detrapping and recombination at the metal side (high temperatures). The trap distribution is calculated from the intensity dependence of the activation energy of the detrapping time. The application of the transient photovoltage method to other metal oxides for the investigation of trap parameters is discussed.

#### SESSION R6: MICROWAVE AND OPTICAL PROPERTIES

Chair: Rosario A. Gerhardt  
Tuesday Evening, November 27, 2001  
Room 206 (Hynes)

##### 8:00 PM \*R6.1

DEPTH PROFILING ELECTROCERAMICS WITH SPECTROSCOPIC ELLIPSOMETRY. S. Trolier-McKinstry, B.J. Gibbons<sup>a</sup>, M. Biegalski and D.G. Schlom, MS&E Dept. and Materials Research Institute, Penn State University, University Park, PA. <sup>a</sup>Los Alamos National Lab, Los Alamos, NM.

Spectroscopic ellipsometry can be used to non-destructively depth profile the microstructure and composition of bulk and thin film samples with a depth resolution that is frequently on the Angstrom scale. Several examples will be given on how spectroscopic ellipsometry can be used in the characterization of electroceramics, including: 1. Monitoring dc electric field induced degradation in barium titanate and strontium titanate-based capacitors 2. Tracking oxidation/reduction processes at the surface of yttrium barium copper oxide superconducting films, and 3. Characterizing the optical properties and band gaps for members of the bismuth pyrochlore family of dielectrics. To augment the experimental data, calculations on the sensitivity of the technique to changes in the surface chemistry and microstructure will be presented.

##### 8:30 PM \*R6.2

MEASUREMENTS OF BIREFRINGENCE IN SINGLE GRAIN BOUNDARIES OF PTCR BARIUM TITANATE CERAMICS ABOVE THE CURIE POINT. Makoto Kuwabara, Kouichi Hamamoto, Univ of Tokyo, Dept of Material Engineering, Tokyo, JAPAN.

Measurements of birefringence in single grain boundaries of barium titanate above the Curie point have been carried out using a polarizing microscope equipped with a high sensitivity CCD camera under various electric fields. Single grain boundaries that exhibited normal type and saw-tooth type of PTCR characteristics were used to be examined, which were formed in thin semiconducting barium titanate ceramic bars with a diameter of 10-20 μm. The birefringence in the grain bulk was extinct above the Curie point (T<sub>c</sub>), but in the vicinity of the grain boundaries transmitted light due to birefringence could be detected up to the temperature giving a maximum resistivity in their PTCR characteristics. Moreover, it has been confirmed that the magnitude of the birefringence is increased with increasing electric field and decreased with increasing temperature (above T<sub>c</sub>). The observed birefringence clearly demonstrates that spontaneous polarization, associated with strain partly induced by an applied field, in the vicinity of a grain boundary can still exist above T<sub>c</sub>. Based on the results obtained the mechanism of the PTCR effect in semiconducting barium titanate ceramics may be interpreted by a charge compensation model by spontaneous polarization at grain boundaries. We cannot explain the obtained results by the Heywang model, which has been widely accepted as one that can most adequately explain the PTCR effect in barium titanate ceramics.

##### 9:00 PM R6.3

DIELECTRIC PROPERTIES OF CAPACITOR MATERIALS IN THE OPTICAL FREQUENCY RANGE. Michael D. Biegalski, and Susan Trolier-McKinstry, Materials Science and Engineering Department and Materials Research Institute, Pennsylvania State University, University Park, PA.

The optical properties and band gaps of capacitor materials are important for a number of reasons including assessing the viability of candidate materials for gate dielectrics in semiconductors, identifying the electric components of the polarizability, and monitoring degradation processes. This paper reports the high frequency dielectric function of several gate dielectric candidates in the near UV to near IR range as determined by spectroscopic ellipsometry. Spectroscopic ellipsometry (SE) is a non-destructive light reflection tool. SE data

were acquired for oxidized and reduced Fe-doped SrTiO<sub>3</sub>, oxidized and reduced BaTiO<sub>3</sub>, bismuth pyrochlore dielectrics and several gate oxide candidates. In Bi<sub>2</sub>Zn<sub>2/3</sub>Nb<sub>4/3</sub>O<sub>7</sub> and Bi<sub>1.5</sub>Zn<sub>1.0</sub>Nb<sub>1.5</sub>O<sub>7</sub> the optical band gap was found to be approximately 3.05eV and changed only slightly with different compositions. The refractive index at 500nm was found to be 2.63 for Bi<sub>2</sub>Zn<sub>2/3</sub>Nb<sub>4/3</sub>O<sub>7</sub> and 2.72 for Bi<sub>1.5</sub>Zn<sub>1.0</sub>Nb<sub>1.5</sub>O<sub>7</sub>. In GdScO<sub>3</sub> the band gap was found to be between 5.1 and 5.4eV. Spectroscopic ellipsometry can also be utilized to determine changes in the depth profile due to changes in the dielectric function. In this work dielectric materials, primarily strontium titanate, were examined to determine their changes during DC electric field induced degradation. The changes due to degradation were found to be detectable by ellipsometry in the optical frequency range. However detection is complicated by presence of surface roughness.

##### 9:15 PM R6.4

EFFECT OF THERMAL OXIDE ON CRYSTALLIZATION OF THE ANODIC Ta<sub>2</sub>O<sub>5</sub> FILM. Yuri Pozdeev-Freeman, Vishay-Sprague, Sanford, ME; Alexander Gladkikh, Tel Aviv University, Ramat Aviv, ISRAEL.

Amorphous Ta<sub>2</sub>O<sub>5</sub> film with the thickness of 30-100 nm is employed as the dielectric in MOM and MOS capacitors. The advantage of this film versus other dielectrics is a combination of high dielectric permeability and high electrical strength. The direct current leakage (DCL) in the Ta<sub>2</sub>O<sub>5</sub> film is usually attributed to electron transport via different type of defects: impurity atoms, oxygen vacancies, crystalline inclusion, etc. Gradual DCL increase under the strong electrical field and elevated temperatures may be caused by crystalline inclusions growth in the amorphous matrix of the anodic oxide film. In this paper we give the results of SEM and TEM studies of the crystallization process in anodic Ta<sub>2</sub>O<sub>5</sub> film in comparison with the current-voltage (I-V) measurements at different stages of the crystallization process. Two different modes of crystallization were detected depending on the original state of the tantalum surface prior to its anodization. The first "soft" crystallization corresponds to thin (3-5 nm) natural surface oxide. It comprises the growth of narrow crystalline peaks at the Ta/Ta<sub>2</sub>O<sub>5</sub> interface without any disruption of the amorphous matrix. The I-V characteristics in this case gradually shift up with the time. The second "rough" crystallization corresponds to the original thermal oxide layer on the Ta surface (10 nm and above). In this case large oxide polycrystals grow up through the broken amorphous matrix of the anodic film, causing "shortage" of the dielectric. Aborting of the crystallization was shown to be possible using short heating of the Ta/Ta<sub>2</sub>O<sub>5</sub> sandwiches which cuts crystalline inclusions grown into the amorphous matrix of the anodic Ta<sub>2</sub>O<sub>5</sub> film from the Ta surface, and provides low and stable DCL values. The effect of ordering and crystallization on the mechanism of electron transport via amorphous Ta<sub>2</sub>O<sub>5</sub> film is also under the discussion.

##### 9:30 PM R6.5

RADIO-FREQUENCY IMPEDANCE ANALYSIS OF ANODIC TANTALUM PENTOXIDE THIN FILMS. S. Dueñas, H. Castán, J. Barboña, Universidad de Valladolid, ETSI Telecomunicación, Dept. Electricidad y Electrónica, Valladolid, SPAIN; R.R. Kola, P.A. Sullivan, Bell Laboratories, Lucent Technologies, Murray Hill, NJ.

In previous works we presented a fabrication method of thermally stable anodic Ta<sub>2</sub>O<sub>5</sub> MIM capacitors. We investigated the influence of different technological parameters on the capacitor performances. We studied the conduction mechanisms in our dielectric films. Modified and standard Poole-Frenkel effects appear as the main conduction mechanisms responsible for conduction in the capacitors. Finally, we observed by Transmission Electron Microscopy (TEM) and Auger Electron Spectroscopy (AES) that Ta<sub>2</sub>O<sub>5</sub> films actually consist of two layers: the lower one, just over the precursor, containing nitrogen and the upper one with no nitrogen content. Recently, we observed the existence of conductance transients for different conditions of voltage bias amplitude, frequency and temperature. We obtain supplementary information on the physical nature of anodic tantalum pentoxide thin films. Several relaxation mechanisms occur in the dielectric. At frequencies in the range of 100 KHz cathodic pulse bias induce relaxation processes related to the molecule orientation inside the dielectric. Moreover, the electric field produce displacements in interface charged traps that gives place to the slowest component of the conductance transients. That must be related to some absorption peak occurring at frequencies close to 100 KHz. Relaxation processes occurring at these frequencies are typically related to the orientation of dipoles caused by the applied electric field. In this work we extend this study up to 3 GHz by using for the first time the Radio-Frequency Impedance Analysis Technique. That allows extracting new results on the physical properties of the dielectric films. Ion resonance mechanisms appear as a peak in  $\epsilon''(\omega)$  at frequencies in the range of 1 GHz. Moreover, we have set up an electrical characterization technique to directly measure the dispersion curve of the dielectric permittivity from DC to 3 GHz. The main results and conclusions will be presented at the Symposium.

**9:45 PM R6.6**

IMPROVEMENT OF CHARACTERISTICS IN HIGHLY RELIABLE THIN FILM DIODE WITH ANODIC TANTALUM PENTOXIDE BY LOW TEMPERATURE ANNEALING CONDITIONS. Chan Jae Lee, Sung Jei Hong, Yong Hoon Kim, Sung Kyu Park, Min Gi Kwak, Won Keun Kim, Jeong In Han, Korea Electronics Technology Institute, PyungTack, KyungGi, KOREA, MA; Myung Jae Lee, Kwan Soo Chung, Kyung-Hee University, Dept of Electronics Engineering, Suwon, Kyunggi, KOREA.

In this study, we developed novel thin film diode (TFD) with high reliability and good electrical properties for switching device in active-matrix liquid crystal displays (AM-LCDs). The TFD device was consist of Ta bottom electrode, Ta<sub>2</sub>O<sub>5</sub> insulating layer, and top electrode, respectively. After etch stop layer Ta<sub>2</sub>O<sub>5</sub> was deposited on glass substrate by RF magnetron sputter, bottom electrode was sequentially deposited on the etch stop layer. High quality tantalum pentoxide, Ta<sub>2</sub>O<sub>5</sub> was obtained by anodization method in 1.0wt% aqueous ammonium tartrate solution with a silicon counter electrode. Ti or Cr was used as top electrode. Annealing was done with two kinds of conditions at low temperature below 350°C. One was post annealing for 2 hours in vacuum after TFD device fabricated, and the other was that for 1hour after each layer formed. We measured the electrical properties of TFD device and analyzed interface and composition with depth. The fabricated TFD device had good electrical properties: perfect current-voltage symmetry characteristics, low leakage currents < 10<sup>-7</sup> A/cm<sup>2</sup> at 2 MV, high breakdown voltage 5 MV/cm, and low threshold voltage. After annealing of both conditions, symmetry characteristics and reliability were improved. In case of annealing after each layer formed, threshold voltage was lower than post annealing. Microscopic images and depth profiling of the interface between metals and insulator were analyzed before and after annealing. According to these results and energy band, we investigated the conduction mechanism of the TFD device.

**10:00 PM R6.7**

LOW-TEMPERATURE SINTERING AND MICROWAVE PROPERTIES IN (Ba<sub>0.5</sub>Pb<sub>0.5</sub>)Nd<sub>2</sub>Ti<sub>5</sub>O<sub>14</sub> CERAMICS. Jae-Hwan Park, Yoonho Kim, Korea Institute of Science and Technology, Material Science and Engineering Division, Seoul, KOREA.

Low temperature sintering and microwave properties were studied in (Ba<sub>0.5</sub>Pb<sub>0.5</sub>)Nd<sub>2</sub>Ti<sub>5</sub>O<sub>14</sub> with borosilicate glass system. When 2-3 wt% of borosilicate glass was added, sinterability greatly increased and microwave properties enhanced. When sintered at 950°C with 3 wt% of glass, the quality factor and temperature coefficient of resonant frequency maintained its original values of 4500 and 10 ppm/°C, respectively, while the dielectric constant lowered to 75 from its original value of 90.

SESSION R7: POLYMERS, LIQUID CRYSTALS,  
BATTERIES, AND GAS SENSORS  
Chair: Rosario A. Gerhardt  
Wednesday Morning, November 28, 2001  
Room 206 (Hynes)

**8:30 AM R7.1**

APPLICATION OF A BUFFERING LAYER FOR DIELECTRIC MEASUREMENT OF ULTRA-THIN POLYMER FILMS. C.K. Chiang, Wataru Sakai Polymer Division, National Institute of Standards and Technology, Gaithersburg, MD.

The dielectric electrical characterization for thin polymer films is not only of fundamental interest, but also of critical importance to their electronic application. To have a well-defined geometric factor, conventional dielectric constant measurement technique uses parallel plate method. It is often depositing a metal electrode onto the thin film directly. This MPM structure is simple and reliable. However, increasingly, the direct metal deposition method became undesirable due to the decreasing of the thickness of the film. We have attempted applying a buffer layer on top of the thin-film to adjust its electrical characterization to a convenient level. The dielectric data of the combined layered thin-film was measured with suitable instrument. The dielectric of the thin-film was interpreted. Layered samples with structures AB, ABA and ABC have been discussed, where A, and C were buffering layers. We have attempted to extend the sample film B down to nano-meter range.

**8:45 AM R7.2**

THE STRUCTURE AND ELECTRICAL PROPERTIES OF POLYANILINE. Runqing Ou, Robert Samuels, Georgia Institute of Technology, School of Chemical Engineering, Atlanta, GA; Rosario A. Gerhardt, Georgia Institute of Technology, School of Materials Science Engineering, Atlanta, GA.

Polyaniline films have been spin coated and cast from N, N-Dimethylpropylene urea (DMPU) solution and stretched to different draw ratios. The anisotropic structure of the films was studied by x-ray diffraction and a modified waveguide technique. The electrical properties were studied by 3D impedance spectroscopy. X-ray diffraction shows that PANI films processed from DMPU solution are noncrystalline and that stretching does not cause crystallization to occur. The PANI films become partially crystalline when they are doped by HCl. The impedance of spin coated and HCl-doped PANI films was measured in the film plane and through the film thickness as a function of doping level. This is the first time the in-plane impedance of polyaniline is reported. A Debye-like conductivity relaxation was observed for the HCl-doped PANI samples. The relaxation shifts to higher frequency as the doping level is increased. The conductivity shows a dramatic increase at low doping levels and levels off at higher doping levels. The in-plane conductivity is over three orders of magnitude higher than the through-plane conductivity. The significance of the results is discussed in relation to the planarity index determined by the three dimensional refractive indices obtained from the modified waveguide technique. Comparison of stretched and unstretched films will also be made.

**9:00 AM R7.3**

FT-IR SPECTRA OF Li(Al<sub>x</sub>Co<sub>1-x</sub>)O<sub>2</sub> (x=0.1-0.5). Wanjun Hao, Chang Li, Gang Chen, Jilin Univ, Dept of Material Science, Changchun, CHINA.

We report the FT-IR spectra from a new cathode material, Li(Al<sub>x</sub>Co<sub>1-x</sub>)O<sub>2</sub> (x=0.1-0.5) which is used in rechargeable lithium batteries. We found out four peaks at 556 cm<sup>-1</sup>, 601cm<sup>-1</sup>, 1438 cm<sup>-1</sup>, 1498 cm<sup>-1</sup> in the spectra. Two peaks at 556 cm<sup>-1</sup> and 601cm<sup>-1</sup> can be assigned to A<sub>2u</sub> and E<sub>u</sub> vibration modes, respectively. Detailed explanation for the other two new peaks at 1438 cm<sup>-1</sup> and 1498 cm<sup>-1</sup> is unclear. With the increasing of Al concentration, all peak positions remain unchanged, but a relative change in the intensity of A<sub>2u</sub> and E<sub>2u</sub> peaks occurs. These four peaks can be regarded as the characteristic peaks of Li(Al<sub>x</sub>Co<sub>1-x</sub>)O<sub>2</sub>'s FT-IR spectra.

**9:15 AM \*R7.4**

INFLUENCE OF CONFINEMENT ON MOLECULAR REORIENTATIONAL DYNAMICS OF LIQUID CRYSTALS: BROADBAND DIELECTRIC SPECTROSCOPY INVESTIGATIONS. Fouad M. Aliev, Department of Physics, University of Puerto Rico, San Juan, PR.

Broad band dielectric spectroscopy has been applied for investigations of the dynamic behavior of liquid crystals (LCs) -5CB and 8CB - confined in porous matrices with random pores as well as in parallel cylindrical pores. The confinement strongly influences the dynamical behavior of LCs and has resulted in qualitative changes in their properties. We observed deep supercooling of LC in random pores (pore size 10 nm) up to 160 degrees below the bulk crystallization temperature. The relaxation times of the process due to the molecular rotation in deeply supercooled state are slower than at the temperatures corresponding to nematic phase by a factor of 106. This slowing down is accompanied by anomalous broadening of both the dielectric spectra and the relaxation time distribution functions. For LC confined in cylindrical pores we have investigated the influence of boundary conditions axial (planar) and homeotropic on the pore walls, as well as the thickness of the surface layer, on relaxation processes. Homeotropic boundary conditions allow the investigations of the librational mode in 5CB and 8CB. We found that the dynamics of the librational mode is different from the behavior observed in investigations of relaxation due to reorientation of molecules around their short axis. The interpretation of the temperature dependencies of relaxation times and of the dielectric strength of the librational mode needs the involvement of the temperature dependence of orientational order parameter. Layers of different thickness were formed on the pore walls as a result of controlled impregnation of porous matrices with 8CB from solutions of different LC concentration. The process due to rotation of molecules around their short axis with single relaxation time observed for bulk 8CB is replaced by process with a distribution of relaxation times in thin layers. The main relaxation process broadens with decreasing of thickness of the layers.

**10:15 AM R7.5**

RELATION BETWEEN HEAT-TREATMENT TEMPERATURE AND CHARACTERISTICS OF POLYPARAPHENYLENE(PPP)-BASED CARBON MATERIALS FOR LITHIUM ION SECONDARY BATTERIES. Kozo Osawa, Kyoichi Oshida, Tatsuo Nakazawa, Nagano National College of Technology, Dept of Electronics and Computer Science, Nagano, JAPAN; Morinobu Endo, Shinshu Univ, Dept of Electrical and Electronic Engineering, Nagano, JAPAN.

Non-graphitizing carbons are useful materials for the negative

electrode of Li ion secondary batteries, since a large amount of Li ion can be held in gaps between crystallites of the carbon. PPP-based carbon is a kind of non-graphitizing carbons and it is known that many Li ions are taken into PPP-based carbon. Electric charge capacity in the 2nd cycle for the Li ion secondary battery with the PPP electrode, which is heat-treated at a temperature around 700°C, is beyond 400mAh/g, and the resistivity is about 50 ohm-cm. Resistivities become 0.25 and 0.07 ohm-cm after heat-treated at 800 and 900°C, respectively. On the other hand, electric charge capacity decrease using these PPP. The layer in PPP is developing gradually with the increase of the heat-treatment temperature from 700 to 900°C, from the analysis of the TEM images. In this paper, we study the relation between heat-treatment temperature and battery characteristics of charge and discharge capacity of Li ion secondary batteries using PPP-based carbon, especially in the range between 650 to 750°C. The effect of the chemical conformational change at temperature around 700°C on the characteristic is also investigated.

#### 10:30 AM R7.6

A NEW SERIES OF ANODE MATERIALS  $\text{Li}(\text{V}_{1-x}\text{M}_x)\text{MoO}_6$  FOR USE IN RECHARGEABLE Li-ION BATTERIES. Chien-Yuan Wang, Ru-Shi Liu, Department of Chemistry, National Taiwan University, Taipei, Taiwan, PR CHINA; Shu-Fen Hu, National Nano Device Laboratory, Hsinchu, Taiwan, PR CHINA; Ling-Yun Jang, Jyh-Fu Lee, Synchrotron Radiation Research Center, Hsinchu, Taiwan, PR CHINA.

The lithiated transition metal oxides,  $\text{Li}(\text{V}_{1-x}\text{M}_x)\text{MoO}_6$  ( $\text{M} = \text{Fe}$ ,  $0 < x < 0.5$ ), have been synthesized by solid state reaction. This is the first report of this series of compounds to be studied as anode materials. The structural properties of the synthesized products have been studied by means of X-ray diffraction (XRD), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), X-ray absorption near edge structure (XANES), extended X-ray absorption fine structure (EXAFS) and high-resolution transmission electron microscopy (HRTEM). The electrochemical characteristics of the prepared electrodes assembled in coin cells together with lithium metal foil anodes were also investigated in terms of half-cell performance as well as cyclic voltammetry. It is observed that the electrodes exhibit a discharge plateau at 1.5-1.7 V and can deliver capacities of about 140 mAh/g at C/10 rate while still retaining the ability to be discharged and recharged through at least 30 cycles, indicating that the layered structure remains stable during cycling.

#### 10:45 AM \*R7.7

ELECTROCHEMICAL POROSIMETRY. Hyun-Kon Song, Kun-Hong Lee, Pohang University of Science and Technology (POSTECH), Dept of Chemical Engineering, Pohang, SOUTH KOREA.

Porous structure is omnipresent in Nature. It is the basic structure of life and universe. It can provide large surface area in a space-saving way. Therefore, characterization of porous structure is the essential step for the understanding of energy and material transport. "Porous" electrode is also a common denominator for the energy technology of the 21st century: battery, fuel cell and supercapacitor. Microstructure of porous materials has been investigated by various analytical methods. Previous methods, however, are non in situ techniques for the electrochemical energy applications, so that measured pores or surfaces may not be identical to those accessible to electrolyte ions in real applications. Therefore, it has been extremely difficult to correlate the microstructure of porous electrodes with electrochemical behavior of energy storage devices. We have developed a novel analytical method, electrochemical porosimetry, based on electrochemical impedance spectroscopy technique. The electrochemical porosimetry can provide the in situ geometric information meaningful in electrochemical systems for a wide spectrum of porous materials. It can also be used as a nondestructive probe sensing the microstructure of porous electrodes in real devices. The electrochemical porosimetry is an important advancement to the understanding of the microstructure-performance correlation of porous electrodes and provides a powerful tool for the optimum design of electrochemical devices.

#### 11:15 AM R7.8

IN-SITU CONDUCTIVITY AND HALL EFFECT CHARACTERIZATION OF TUNGSTEN OXIDE THIN FILMS. S.C. Moulzolf, D.J. Frankel, R.J. Lad, Laboratory for Surface Science & Technology, University of Maine, Orono, ME.

Tungsten oxide thin films are useful materials for chemiresistive and impedance based gas sensors. The selectivity of these sensors is strongly dependent on surface chemistry, but the electrical transport behavior is also very important in dictating sensing response characteristics, which in turn are very dependent on film microstructure. To study electronic properties of well-defined film microstructures, we have constructed a 4-point conductivity and Hall

effect apparatus and have attached it to a multi-chamber ultra-high vacuum thin film synthesis and characterization system. Measurements can be performed over a range of temperatures in vacuum immediately after film deposition or in controlled gas environments up to atmospheric pressure. A variety of  $\text{WO}_3$  thin film structures (<300 nm thickness) were created on r-sapphire and c-sapphire substrates using low-rate rf magnetron sputter deposition. The specific microstructures, as characterized by RHEED, XRD, and STM, are dependent on deposition parameters including Ar/ $\text{O}_2$  plasma composition, substrate temperature, rate, and substrate type. Tetragonal, monoclinic, and hexagonal  $\text{WO}_3$  phases were produced and all three phases exhibited different electrical behavior versus temperature. The conductivity measurements indicate that  $\text{WO}_3$  becomes substoichiometric following heating in vacuum with transport dominated by oxygen vacancy induced states. Post deposition annealing in oxidizing atmospheres decreases the vacancy population and other defect states become important. Hall effect data show that the  $\text{WO}_3$  films have very low mobility and the temperature dependent mobility behavior is consistent with polaron hopping conduction being dominant.

#### 11:30 AM R7.9

ORDER-DISORDER TRANSFORMATIONS OF AURIVILLIUS-TYPE CERAMIC OXIDES. S.A. Speakman, M.S. Haluska, V.B. Modi, S.T. Misture, Alfred University, NYS College of Ceramics, Alfred, NY.

In-situ diffraction and impedance spectroscopy are used to study phases with an Aurivillius crystal structure and a compositional variant of  $\text{Bi}_2\text{O}_2 \bullet \text{A}^{3+}_{n-1}\text{B}^{4+}_n\text{O}_{3n+1}$ . These materials exhibit potential as oxygen ion conductors in electrochemical devices such as fuel cells. In the Aurivillius crystal structure, the A and B site cations reside in perovskite-type layers sandwiched between bismuth oxide layers. These sites can accommodate a variety of cations. A-site cations included in this study are Bi, Sr, Ba, and La; B-site cations include Ti, Nb, Al, Ga, and In, amongst others. Oxygen vacancies can be introduced by inclusion of divalent cations on the A site and trivalent cations on the B site. Most often, at room temperature these vacancies are ordered and thus not highly mobile. Some of these phases then have a transformation temperature above which these oxygen vacancies become disordered and mobile; such is the case for  $\text{BaBi}_4\text{Ti}_3\text{ScO}_{14.5}$  and  $\text{BaBi}_4\text{Ti}_3\text{InO}_{14.5}$ , which become fast ion conductors. In-situ X-ray diffraction is used to study these order-disorder transformations. Using a custom designed X-ray furnace, which minimizes sample displacement, Rietveld analysis of the disordered crystal structures is possible. Unlike many brownmillerites or the parent Aurivillius phase-  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ , which undergo orthorhombic to tetragonal transformations, many of the Aurivillius phases studied undergo tetragonal to tetragonal transformations. Lattice water may also play a significant role in the behavior of these materials. The structural aspects of the transformation are correlated to changes in ionic conductivity. The crystal structures thus derived are also used to build computer simulations, which are subsequently used to predict the structure and transformation temperatures of other compositions.

#### 11:45 AM R7.10

COMPLEX IMPEDANCE MEASUREMENTS OF THE NEW FLUORIDE-ION CONDUCTOR  $\text{CaSn}_2\text{F}_6$ . Michael F. Bell, Georges Dénès, and Zhimeng Zhu, Concordia Univ, Dept of Chemistry and Biochemistry, Laboratory of Solid State Chemistry and Mössbauer Spectroscopy, Laboratories for Inorganic Materials, Montreal, Québec, CANADA.

The highest performance fluoride-ion conductors are usually derived from the fluorite-type structure, and most of them contain a covalently bonded weak metal (Sn(II), Pb(II), Tl(I)) or a semi-metal Bi(III)), that has a stereoactive lone pair of electrons (non-bonded electron pair occupying a hybrid orbital). The  $\text{PbF}_2/\text{SnF}_2$  system contain many of these, namely  $\text{PbSnF}_4$  and the  $\text{Pb}_{1-x}\text{Sn}_x\text{F}_2$  solid solution. We have also studied  $\text{BaSnF}_4$ , another fast-ion conductor. Recently, we isolated a new material,  $\text{CaSn}_2\text{F}_6$ , the first Ca/Sn(II) fluoride.  $\text{CaSn}_2\text{F}_6$  is prepared by precipitation from aqueous solutions of calcium nitrate and tin(II) fluoride, however, its preparation in the form of a pure material requires a detailed knowledge of the reaction system and a fine control of the reaction parameters. The material is crystalline. Complex impedance measurements were carried out versus temperature and showed its fluoride-ion conductivity is similar to that of  $\text{SnF}_2$ . Measurements versus temperature show that it decomposes at ca. 250°C to give a system, the conductivity of which is dominated by  $\text{SnF}_2$ . X-ray diffraction show that  $\text{SnF}_2$  was formed. No calcium-containing phase was observed, therefore, amorphous calcium fluoride was probably also formed.

**1:30 PM R8.1**

**MICROSTRUCTURE AND ELECTRICAL PROPERTIES OF DENSE LASER ABLATED  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  ON YSZ.**

Ramanan Ganeshanathan, Siu-Wai Chan, Columbia University, Dept of Applied Physics and Applied Math - Materials Science Program, New York, NY; Nan Yao, Princeton University, Princeton Materials Institute, Princeton, NJ.

The impedance response and microstructure were studied for dense  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  oxygen cathodes prepared by laser ablation for solid oxide fuel cells, under varying temperature conditions (300-800°C) and oxygen partial pressure ( $1\text{-}10^{-13}$ ). Two types of cathodes, stoichiometric un-doped lanthanum manganite (LMO) and lanthanum deficient strontium doped manganite (LSM), were deposited on single crystal YSZ substrates at 725°C. TEM micrographs showed a columnar manganite microstructure above a reaction layer at the interface. EDX examination revealed La and Zr excess at the reaction layer suggestive of  $\text{La}_2\text{Zr}_2\text{O}_7$  (LZO) formation. Electrical response produced a series of 3 arcs over the temperature range measured. At lower temperatures (300-450°C) an arc whose resistance had an activation energy of 1.62 eV for LMO and 1.3 eV for LSM and a weak  $\text{Po}_2$  dependence was observed. This was attributed as the activation overpotential for oxygen reduction at the cathode. The second arc, at medium temperatures (500-650°C), had lower activation energy of 0.97 eV. Conductivity calculations based on the resistance of the arc were comparable to reported values for LZO and suggests that it was due to the resistance of the reaction layer at the interface. At high temperatures (700-800°C) a third arc with a 45-degree high frequency intercept that was highly  $\text{Po}_2$  dependent was found, suggesting oxygen diffusion to the cathode surface through the contact electrode. The results showed that the undersirable LZO material forms even at low temperatures (800°C). The oxygen reduction reaction proceeds via oxygen dissociation and adsorption at the cathode interface as compared to the triple phase boundary (TPB) for porous electrodes. The activation energy for this step is lower than previously reported for LSM and the dense electrode morphology could be considered favorably against the porous electrode TPB route often considered the ideal.

**1:45 PM R8.2**

**THE USE OF XANES AND ELNES FOR THE CHARACTERIZATION OF STABILISED ZIRCONIA.** David W. McComb, Sergei Ostanin, Dimitris Vlachos, Alan J. Craven, Univ of Glasgow, Glasgow, UNITED KINGDOM; Mike W Finnis, A.T. Paxton, The Queens Univ, Belfast, UNITED KINGDOM; A. Alavi, Univ of Cambridge, Cambridge, UNITED KINGDOM.

Doped zirconia is a family of materials of scientific and technological importance, having applications as engineering ceramics, ionic conductors, oxygen sensors and oxygen ballast catalysts. At normal pressure, pure zirconia has one of three crystal structures: monoclinic, tetragonal or cubic. Addition of aliovalent dopants such as yttria can stabilise the tetragonal and cubic structures at room temperature, leading to increased toughness, ionic conductivity and resistance to thermal shock. However, the stabilisation mechanism is still relatively ill-understood despite many studies using a wide range of techniques, the results of which often appear contradictory. One of the problems is that different studies have applied different techniques to different materials. The situation is compounded by the fact that the microstructure is often complex and depends on the processing route. Multiple phases can occur on the nanometre scale and these microstructures have proved extremely difficult to characterise by electron diffraction. In this paper we will demonstrate that X-ray absorption near edge structure (XANES) and the closely related electron energy loss near edge structure (ELNES) on ionisation edges provide a clear way of identifying these phases and that ELNES can achieve this with nanometre spatial resolution. In order to make best use of this information it is important to relate it to the electronic structure of the material using suitable simulation techniques. We will report on the use of a full potential linear muffin tin orbital code to investigate the effects of the dopant species on the local atom positions and hence on the electronic structure. It will be demonstrated that the techniques developed have great potential for complete structural, chemical and electronic characterisation of complex materials on the near-atomic scale.

**2:00 PM R8.3**

**INTERFACIAL EFFECTS AND IONIC TRANSPORT IN YSZ EPITAXIAL THIN FILMS.** Igor Kosacki, Univ. Missouri-Rolla, Rolla, MO; and Christopher M. Rouleau, Solid State Div.; Paul F. Becher, Metals and Ceramics Div.; D.H. Lowndes, Solid State Div.; T.R. Armstrong, Metals and Ceramics Div.; Oak Ridge National

Laboratory, Oak Ridge, TN.

The enhanced ionic transport properties of nanocrystalline ceramics are attributed to the grain boundary and grain size-dependent defect equilibria, which become dominant when the grain size is  $< 100$  nm. Surface and interfacial effects can have significant effects in such nanostructured materials. In the present experiments, we examined their influence by characterizing the effect of the thickness of epitaxial zirconia 10 mol. % yttria (YSZ) films on the ionic conductivity. In this geometry, the fraction of the atoms at the surface and substrate interfaces, versus that within the bulk, varies with the film thickness. The YSZ films were prepared by pulsed laser deposition on (001) MgO single crystal substrates at typical depositions of 0.5 to 1 Å per pulse. The electrical conductivity was measured using two-probe impedance with an electrode configuration to measure current flow parallel to the film and substrate surfaces. The temperature dependent conductivity was correlated with the thickness of the YSZ films, which was varied from  $< 50$  nm to 2000 nm. For film thickness  $> 50$  nm, the conductivity-temperature curves were essentially identical and mimicked those obtained with cubic YSZ single crystals. However, the conductivity increased by one to two orders-of-magnitude when the film thickness was  $< 50$  nm. The associated activation energies below  $\sim 550^\circ\text{C}$  averaged 1.13 eV for both single crystals and films of every thickness. Above  $550^\circ\text{C}$ , the activation energy for films  $< 50$  nm was 0.6 eV as compared to 0.85 to 1 eV for single crystals and films thicker than 50 nm. These findings reveal that conductivity measurements on the thicker epitaxial films reproduce those for single crystals, and that conductivity enhancement similar to that observed for grain sizes  $< 50$  nm can be achieved in epitaxial films of comparable thickness.

**2:15 PM R8.4**

**THE 'BRICK LAYER MODEL': NEW INSIGHTS INTO MICROSTRUCTURE FROM AN OLD APPROACH IN IONIC CONDUCTIVITY.** Sossina M. Haile, California Institute of Technology, Materials Science, Pasadena, CA.

The validity of the 'brick layer model' for describing ion transport in polycrystalline ceramics has been examined, using Gd-doped barium cerate as a model system. In this simple model, charge is assumed to flow either through grains, along grain boundaries parallel to grains, or through grain boundaries in series with grains. Experimental validation was achieved by a.c. impedance analysis of materials with a range of grain sizes. Grain sizes were varied from 1.3 to 11  $\mu\text{m}$  (as measured directly by scanning electron microscopy) by sintering at temperatures between 1400 and 1700°C (in air). Impedance data were collected over the frequency range 20 Hz to 1 MHz under H<sub>2</sub>O saturated argon. Both the bulk and grain boundary arcs were visible in the Nyquist plots for measurements performed between  $\sim 100$  and 200°C. The nominal or total grain boundary resistance decreased with increasing grain size, as a result of the presence of fewer grain boundaries being present in the material, in accordance with the brick layer model. After accounting for grain size effects, the specific grain boundary resistivity was found to be independent of grain size, also in accordance with the brick layer model. After establishing the validity of this model, methodologies for estimating grain size and specific grain boundary resistivity (in the absence of microstructural investigations) are presented. Other consequences of this simple model are also discussed.

**3:00 PM \*R8.5**

**ELECTRICAL EFFECTS OF INHOMOGENEOUS AND HOMOGENEOUS SYSTEMS.** Joachim Maier, J. Fleig, J. Jamnik, Max-Planck-Institut für Festkörperforschung, Stuttgart, GERMANY.

The paper deals with charge and mass transport of inhomogeneous and heterogeneous systems exhibiting homophase or heterophase junctions. Of special interest are the phenomena occurring as a consequence of progressively increasing interfacial concentration in the sequence: single crystal, bicrystal, microcrystalline and nanocrystalline samples<sup>1,2</sup>. The brick-layer model is discussed in a generalized form<sup>3</sup> in which it includes bulk, interfacial core and space charge effects. Its validity is tested by space-resolved conductivity methods<sup>4</sup>. In addition to charge transport, mass transport in heterogeneous solids is studied, and the use of generalized equivalent circuits propagated, which describe the system response in both electrical and chemical excitations<sup>5</sup>.

References

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**3:30 PM R8.6**

**AC CONDUCTIVITY BASED MICROSTRUCTURAL CHARACTERISATION.** G. Sauti and D.S. McLachlan, School of

AC conductivity experiments, or Impedance Spectroscopy, at temperatures between 100 and 400 deg. C, on 3 and 8 mole % Yttria Stabilised Zirconia (YSZ), with different grain sizes and in some cases deliberately introduced impurities are presented. The results are analysed using Effective Media Theories and the Brick Layer Model. In this approach the known values of the dielectric constant and conductivities of the crystalline phase, including their frequency dependencies can be used as starting or fixed parameters or to put realistic limits on these parameters, in the granular phase. Separate measurements on 3,9 and 12 mole % YSZ single crystals were made to establish the realistic limits to the parameters. Estimates of the volume fraction of the grain boundary phase on SEM micrographs and theoretical considerations are also used as starting or fixed parameters or to impose limits on this parameter. In arriving at the final fitting parameters, the complex conductivities (dielectric constants) of the crystalline and grain boundary phases and volume fractions are chosen so as to be self-consistent. For instance the conductivities obtained from fitting the results are required to be proportional to  $\exp(-E/kT)$ . The results obtained using Effective Media Theories and the Brick Layer Model are not satisfactory and an explanation is given in terms of the microstructure upon which these theories are based. A model based on percolation theory is being developed.

### 3:45 PM R8.7

ELECTRICAL AND MAGNETIC STUDIES OF A SINGLE GRAIN BOUNDARY AND ADJACENT GRAINS CUT FROM A LONG  $La_{0.7}Ca_{0.3}MnO_3$  SAMPLE WITH A HUGE CMR. B. Vertruyen, R. Cloots, A. Rulmont, SUPRAS, Chemistry Institute, University of Liege, Liege, BELGIUM; M. Ausloos, SUPRAS, Physics Institute, University of Liege, Liege, BELGIUM; Ph. Vanderbenden, SUPRAS, Montefiore Electricity Institute, University of Liege, Liege, BELGIUM.

Fine electrical and magnetic studies of a single grain boundary (GB) and both adjacent grains are reported. They were cut from a greater than 1 cm long bar seed-grown to be a  $La_{0.7}Ca_{0.3}MnO_3$  sample. Each grain looks like a single crystal. The characterizations are astounding leading to huge enhanced features of the CMR and allowing some conjecture on, not to say proof of, some previously puzzling behaviors. Several I,V contacts where In soldered on the top of the sample, and various resistivity measurements performed. The magnetic susceptibility was measured for the bigrain configuration following the cycling method at fixed fields. A 99% CMR is found for the largest single grain. The electrical resistivity and magnetic susceptibility data are well analyzed above and below the transition(s). No hysteresis was found as a function of temperature. The role of the single GB is also of interest in order to understand why polycrystals and stretched (or not) films show some peculiar CMR at low and high fields

### 4:00 PM R8.8

IMPEDANCE SPECTROSCOPY STUDY OF IONIC DIFFUSION IN POLYCRYSTALLINE  $ZrO_2 \cdot Y_2O_3$  SOLID SOLUTION. F.C. Fonseca, E.N.S. Muccillo, R. Muccillo, Instituto de Pesquisas Energéticas e Nucleares, S. Paulo, BRAZIL.

The  $ZrO_2 + Y_2O_3$  solid solution formation has been followed by impedance spectroscopy and X-ray analyses. The experimental sequence, after mixing 8 mol%  $Y_2O_3$  to  $ZrO_2$ , was: attrition milling the mixture, drying, weighing, cold pressing, thermally treating at several different temperatures and times, performing the X-ray diffraction measurements at room temperature, applying metallic electrodes, and performing the impedance spectroscopy measurements in the 300°C-600°C temperature range. A good correlation was found between the decrease of the yttria main diffraction line and the increase of the stabilized zirconia main diffraction line, showing that solid solution is attained at the expenses of yttria, as expected. The impedance spectroscopy data  $Z(\omega, T, t)$  show that the bulk response follows a  $t^{1/2}$  law, an evidence of yttrium diffusion to zirconia. Moreover, a relationship is found between the bulk resistivity and the elimination of ion blockers for increasing sintering times. The results allowed for the determination of the activation energy for the diffusion of the slowest diffusing species ( $Zr^{4+}$ ) in  $ZrO_2 \cdot Y_2O_3$ . (CNEN, FAPESP, CNPq, PRONEX, CEPID).

## SESSION R9: COMPOSITES

Chair: Rosario A. Gerhardt

Thursday Morning, November 29, 2001  
Room 206 (Hynes)

### 8:30 AM \*R9.1

RECENT DEVELOPMENTS IN THE ELECTRICAL IMPEDANCE

CHARACTERIZATION OF SHORT CONDUCTIVE FIBER COMPOSITES. L.Y. Woo, M.A. Campo, and T.O. Mason, Northwestern Univ, Dept of Materials Science and Engineering, Evanston, IL; E.J. Garboczi, National Institute of Standards and Technology, Building Materials Division, Gaithersburg, MD.

The addition of fibers to an otherwise brittle matrix has profound influence not only on the mechanical properties (modulus, strength, toughness, etc.), but also on the electrical properties (DC conductivity, AC impedance, etc.) of the composite. This is especially so when the added fibers are highly conductive with respect to the matrix. The present study addresses the microstructure-electrical property relationships, with special attention to the impedance response, of composites containing conductive particles or small amounts of short conductive fibers. In addition to measurements on actual composites (as-fabricated and during deformation/fracture), simulations involving spherical inclusions and single wires in dielectric media (both laboratory and computer simulations) were carried out. The roles of fiber pull-out, fiber/matrix debonding, and fiber aspects (aspect ratio, orientation, etc.) were addressed. A "frequency-switchable coating" model was developed to explain the unique frequency-dependent properties of such composites. The results are completely general and are applicable to relevant conductive fiber/poorly conductive matrix situations, including ceramic, cement/concrete, and polymer matrices. Ramifications for composite manufacturing and performance (e.g., damage diagnostics) will also be considered.

### 9:00 AM R9.2

MICROSTRUCTURE AND DAMAGE OF THE INTERLAMINAR INTERFACE OF CARBON FIBER POLYMER-MATRIX COMPOSITES, MONITORED BY CONTACT ELECTRICAL RESISTIVITY MEASUREMENT. Shoukai Wang, Zhen Mei, Daniel P. Kowalik, D.D.L. Chung, Composite Materials Research Laboratory, University at Buffalo, The State University of New York at Buffalo, Buffalo, NY.

The microstructure and damage of the interlaminar interface (i.e., the interface between laminae) of continuous carbon fiber polymer-matrix structural composites were monitored in real time during dynamic changes in temperature, humidity and stress by measurement of the contact electrical resistivity of the interface. The stress was compressive, in the direction perpendicular to the interlaminar interface. Temperature, humidity and stress were all found to have reversible effects on the resistivity, due to the effects of these parameters on the interfacial microstructure, such as the extent of contact between fibers of adjacent laminae. In addition, these parameters were found to have irreversible effects on the resistivity, due to damage. The mechanism of damage differed between composites with thermoplastic and thermoset matrices. The reversible effects allow the use of the contact resistivity as an indicator of temperature, humidity and stress. The irreversible effect allows structural health monitoring.

### 9:15 AM \*R9.3

THE INFLUENCE OF FILLER PROPERTIES ON THE STRONG PTC-EFFECT OF RESISTIVITY IN POLYMER BASED CONDUCTING COMPOSITES. Joachim Glatz-Reichenbach, ABB Corporate Research Ltd., Baden-Dättwil, SWITZERLAND.

Polymer based composites are very attractive materials for a plurality of technical applications. For electrical purposes the resistivity of such materials can be tuned over many orders of magnitude from highly insulating ( $10^{14}\Omega\text{cm}$ ) to well conducting ( $10^{-3}\Omega\text{cm}$ ) states. One particular class of polymer based composites even show a strong non-linear reversible change in resistivity with temperature between conduction and insulation. Such a pronounced effect of positive temperature coefficient of resistivity (PTCR) can be technically used, for example, in self regulating heating devices, for temperature sensing or, as a very challenging and important task, for current (i.e. over- as well as short-circuit currents) limiting and interrupting devices. The PTCR-devices act similar like fuses but repetitively, which offers technical and economical benefits. In power applications the achieved native resistivity without fault has to be as low as possible in order to reduce electrical losses. Under fault situation, however, the resistance change is needed to be fast, steep and high enough to limit the fault current to a non-critical low value (J. Skindhj, J. Glatz-Reichenbach, R. Strümpfer, IEEE Trans. PWRD, 13, 489, 1998). Carbon black (CB) particles enriched polymers, as one example, do not offer resistivities below  $0.1\Omega\text{cm}$ , whereas metal particle filled composites can exceed values well below  $10\text{m}\Omega\text{cm}$  (R. Strümpfer, J. Glatz-Reichenbach, J. of Electroceramics 3(4), 329, 1999). Experimental results on resistivity and its change under active heating by Joule's losses during current flow will be presented and discussed for different composites, compounded with fillers like CB or Ni,  $TiB_2$ , WC etc.. The strong resistance change caused by break-off and separation of particle-particle micro-contacts is driven by the very different thermal

expansion coefficients of filler and matrix. It will be particularly demonstrated how the heat capacity of used filler-particles influences the dynamics of the micro-contact separation.

#### 10:15 AM \*R9.4

A PERCOLATION EQUATION FOR AND RESULTS FOR CONTINUUM PERCOLATION SYSTEMS. D.S. McLachlan, C. Chitame, W.D. Heiss, Junjie Wu, School of Physics and Materials Physics Institute, University of the Witwatersrand, Johannesburg, SOUTH AFRICA.

The eight standard percolation equations are based on scaling and eight ansatz for the behavior of the first and second order terms above and below the percolation threshold ( $\Phi_c$ ) and in the crossover region. In the crossover region, which is very close to  $\Phi_c$ , both the complex conductivity of the conducting ( $\Sigma_c$ ) and the insulating ( $\Sigma_i$ , sometimes approximated as the product of the angular frequency times the dielectric constant) components must both contribute to the conductivity of the media ( $\Sigma_m$ ). Recent experimental results will be presented to show that these equations, with the exception of real  $\Sigma_m$  above  $\Phi_c$  and the first order terms in the crossover region, are only valid in the limit  $\Sigma_i/\Sigma_c = 0$  and that the dielectric loss term (real  $\Sigma_m$ ) below  $\Phi_c$  is always incorrect. A single analytical equation, which reduces to the standard percolation expressions in seven (except for real  $\Sigma_m$  below  $\Phi_c$ ) of the limits for  $\Sigma_i/\Sigma_c = 0$ , is presented and is shown to quantitatively fit the first and second order terms of the experimental data, for a number of continuum percolation systems, over the entire frequency and composition range. Unfortunately, the exponents that are necessary to fit the data to the above analytical equation are usually not the universal ones observed in computer simulations and not always related to each other by the RC or any other model. The first order data can all be scaled onto single continuous curves, which can be fitted using the above equation, which is therefore, as required, a scaling equation.

#### 10:45 AM R9.5

PERCOLATION PROPERTIES OF CELLULAR COMPOSITE SYSTEMS. C. Chitame and D.S. McLachlan, School of Physics and Materials Physics Institute, University of the Witwatersrand, Johannesburg, SOUTH AFRICA.

Percolation phenomena were studied in a series of seven composites with a cellular structure i.e small conductor particles embedded on the surfaces of much larger spherical insulating particles. The results of this study will be presented. Measurements made on the composites include dc and ac electrical conductivity, dielectric constant,  $1/f$  or flicker noise and magnetoresistance. These measurements were done below and above the dc percolation threshold, except for the magnetoresistance and noise measurements, which were only made on samples on the conducting side. Results arising from these extensive measurements were fitted to the percolation power laws to give various exponents, which are given mostly in tabular form. Among the items to be highlighted are: (I) The exponents from ac conductivity, which are compared with the predictions of the intercluster polarisation (RC) model. (II) The frequency dependent dielectric constant, which gives an exponent  $s'$ , different from the dc conductivity exponent  $s$  on the insulating side. (III) Flicker noise measurements, made on two sizes of samples consistently give two sets of exponents  $k$  and  $w$ , one close to and one further from the percolation threshold. (IV) The fact that the exponent obtained from room temperature magnetoresistance differs from the previously measured value of  $\sim 0.30$ , while the magnetoconductivity exponent from the same samples appears to correlate with the dc conductivity exponent  $t$ .

#### 11:00 AM R9.6

ELECTRICAL CONDUCTIVITY OF IONIC AND ELECTRONIC MIXTURE. Gyeong Man Choi, Joon Hee Kim, and Young Min Park, Dept of Materials Science and Engineering, Pohang University of Science and Technology, Pohang, KOREA.

Mixed ionic-electronic conductors (MIECs) which have both ionic and electronic species as charge carriers have a wide range of applications, such as electrodes in fuel cells, electrocatalytic reactors, and gas separating membranes. They may have either electronic or ionic species as the majority charge carriers. In addition to the single-phase mixed conductors, they may be fabricated by mixing two different phases of materials. Although these composites have been less studied than the single phase MIECs, the combined properties are often superior to single phase MIECs, and properties not seen in an individual phase may appear in the composite phase. YSZ-based composite systems were chosen to test the effect of transition-metal-oxide (TMO) addition on the electronic conductivity of composite. To induce mixed conductivity, electronic-conducting TMOs such as NiO and  $Mn_2O_3$  were added into YSZ above the solubility limit. While the solid solubility of NiO in YSZ is limited that of  $Mn_2O_3$  is large. In this work, mixed conducting yttria (8 mol%)

stabilized zirconia (YSZ) - TMO composites were prepared in full composition range and the electrical conductivity of the composites was measured by 4-probe d.c. conductivity. Electromotive force (emf) measurements of the galvanic cell, current-voltage measurements in ion blocking condition and the oxygen-partial-pressure dependent conductivity have been used to determine the contribution of the ionic and electronic charge carriers on the conductivity. Thus the composition-dependent electrical properties were used to explain the percolation behavior of electronic charge carriers in ionic matrix. Although the total and ionic conductivity of dense YSZ-TMO composite decreased with the increasing TMO content, the partial-electronic conductivity increased. The composition-dependent conductivity of NiO and  $Mn_2O_3$ -added systems will be discussed.

#### 11:15 AM R9.7

THERMOPOWER-MICROSTRUCTURE CORRELATION IN n-ZnO/p-NiO TWO-PHASE MIXTURES. Han-Il Yoo, Dong-Sook Sinn, Seoul National University, School of Materials Science and Engineering, Seoul, KOREA.

Thermopower of p-NiO/n-ZnO two-phase mixtures with a fixed composition (volume fraction of n-ZnO, 0.12) has been examined against temperature (in the range of room temperature to  $1000^\circ\text{C}$ ) as well as against the average grain size of the majority phase p-NiO (in the range of 20 to 6  $\mu\text{m}$ ). At the room temperature, all exhibits the thermopower of the far-more conductive end-member, n-ZnO irrespective of the grain size of the majority phase, p-NiO. As temperature increases, however, there occur anomalous repetitive transitions from n- to p- to n-type, and the first, lowest transition temperature increases systematically with the increasing grain size. This thermoelectric behavior is interpreted in terms of the simple mixing rule for thermopower (i.e.,  $\theta = \sum t_i \theta_i$ ,  $t_i$  being the transference number of the  $i^{\text{th}}$  phase) upon comparison with the thermopowers of artificial, parallel and series mixtures of n-ZnO and p-NiO, and the alternations of predominant conduction paths with temperature. A possibility is indicated to tailor the thermoelectric property by controlling the microstructure of a phase mixture.

#### 11:30 AM R9.8

SINTERING BEHAVIOR OF ZrB<sub>2</sub>-ZrC COMPOSITES SINTERED BY SPARK PLASMA SINTERING PROCESS. Kyoung Hun Kim, Seung Hwan Shim, Kwang Bo Shim, Hanyang Univ, Dept of Ceramic Engineering, CPRC, Seoul, KOREA.

ZrB<sub>2</sub>-ZrC composites were fabricated by a spark plasma sintering (SPS) method and their sintering behavior and microstructure have been analysed using electron microscopy. The addition of lanthanum as a sintering aid has been found to be very effective in reducing sintering temperature, comparing with the case of no addition, and complete to densify fully at  $1800^\circ\text{C}$ . Microscopic observation confirms that the La element accelerate mass transport by the formation of the liquid phase during the initial stage of the SPS process and then recrystallized to produce La-containing secondary phase at grain boundaries and grain boundary triple junctions. And also the grain boundary characteristics of the composite have been analysed using a SEM-EBSF technique.

#### 11:45 AM R9.9

TEMPERATURE DEPENDENT PROPERTIES OF PZT FIBER FILLED POLYMERS FOR LOW LOSS AND HIGH PERMITTIVITY IN MICROWAVE APPLICATIONS. David C. Maybury, John W. Schultz, Georgia Tech Research Institute, Atlanta, GA; Rosario A. Gerhardt, Georgia Institute of Technology, School of Materials Science and Engineering, Atlanta, GA.

Some novel antenna applications require a high-permittivity, low-loss substrate material. Other desirable properties include flexibility, low density, and easy manufacture. This combination of properties can be achieved by loading a polymer matrix with high permittivity particulates. Mixtures of silicones and epoxies blended with PZT fibers were studied for this application. The high polarizability of the PZT fibers, which have an aspect ratio of approximately 25, allow for higher dielectric constants to be achieved at lower fill fractions than can be achieved with isotropic particles. The dielectric properties of the mixtures were measured with X-band waveguide and impedance analysis. The microstructures were evaluated with optical and scanning electron microscopy. With a PZT volume fraction of 0.2, a real permittivity of approximately 10 has been measured. Additionally, the PZT composite was shown to exhibit a sudden 15% change in real permittivity at  $-50^\circ\text{C}$ , signifying an unidentified phase change. The data are compared to several effective media models across the full temperature range. The data are also compared to Finite Difference Time Domain (FDTD) models of their microstructure as well.

SESSION R10: VARISTORS AND  
PIEZOELECTRIC MATERIALS

Chair: Mohammad A. Alim  
Thursday Afternoon, November 29, 2001  
Room 206 (Hynes)

**1:30 PM \*R10.1**

**ACOUSTIC OSCILLATIONS FROM CURRENT PULSES.**

Gerald D. Mahan, Dept of Physics, University of Tennessee, Knoxville, TN.

Varistors are usually ZnO ceramics which contain other metal oxides at the 1% level. They have very nonlinear current-voltage characteristics which make them suitable for fuses which clamp voltage surges. A fast current pulse causes the varistor to heat and undergo rapid expansion. The expansion triggers acoustic oscillations. We calculate the response of a cylindrically shaped material to a pulse on the microsecond time scale. The first step is to obtain the breathing modes of acoustic oscillation of the cylinder. These modes are calculated using a Rayleigh-Ritz variational method introduced by Demarest for cubes. The boundary conditions are derived, which give the amplitude of each acoustic mode in response to the sudden heating. The results are illustrated by calculations on a station arrester made of a ZnO ceramic. Time dependent stresses are calculated in response to a 4-10 microsecond pulse.

**2:00 PM \*R10.2**

**SINGLE GRAIN BOUNDARY CHARACTERIZATION OF ELECTRONIC INTERFACE STATES IN ZnO: Pr VARISTORS.**

Kazuo Mukae, Akihiko Ohi, Fuji Electric Corp. R&D Ltd, Yokosuka, JAPAN; Akinori Tanaka, Iiyama Fuji Co. Ltd, Iiyama-City, JAPAN.

Electronic interface states at grain boundaries in ZnO: Pr varistors were directly observed by single grain boundary measurement. Micro-electrodes which were fabricated by photo-process on the surface of the ZnO ceramics enabled the direct measurements of electric characteristics of single grain boundaries. Photo-capacitance spectroscopy and photo iso-thermal capacitance transient spectroscopy (photo-ICTS) were applied to these experiments. The photo irradiation was carried out not only in the range of visible light but also in the range of near infrared, i.e., 730 nm (0.7 eV) to 1770 nm (1.7 eV). Photo-capacitance in the visible area exhibited 2 peaks of capacitance increase at 700 nm (1.8 eV) and 500 nm (2.5 eV). These peaks were explained by electron excitation from trap levels in the band gap of the ZnO grains. Only a slight increase in capacitance was found in the near infrared region. However, the compensations of the source intensity spectrum and the absorption by the optical fiber revealed this increase to be a sharp peak at 1380 nm, i.e., 0.9 eV. Since this peak is originated by electron excitation from the interface states at the grain boundary, the energy for this peak indicates that the electronic states at the grain boundaries are located at 0.9eV below the top of the double Schottky barrier at the grain boundary. This result is the direct evidence which shows the value of the energy level of the interface states in ZnO varistors. The photo-ICTS peaks shifted to shorter range by the irradiation with the energies of each trap and interface level. The photo-intensity change of ICTS peaks revealed the linear relation between emission rate of the interface states and the light intensity. These relations agreed with the theory.

**2:30 PM R10.3**

**MICROSTRUCTURAL DEVELOPMENT AND PROPERTIES OF (1-x) wt% Ba<sub>0.55</sub>Sr<sub>0.45</sub>TiO<sub>3</sub>\*x wt% MgO BULK FERRO-ELECTRICS.** Costas G. Fountzoulas, Jennifer Synowczynski, and Bonnie Gersten, Weapons and Materials Research Directorate, Army Research Laboratory, APG, MD.

A study was performed to better understand the relationship between microstructure and its mechanical and electrical properties of bulk ferroelectric composite materials of (1-x) wt%Ba<sub>0.55</sub>Sr<sub>0.45</sub>TiO<sub>3</sub>\*x wt%MgO. The ferroelectric composites were fabricated by ball milling and subsequently dry pressing pellets of Ba<sub>0.55</sub>Sr<sub>0.45</sub>TiO<sub>3</sub>-MgO, 0.025 m in diameter and 0.005 m in thickness. Two powder precursors of Ba<sub>0.55</sub>Sr<sub>0.45</sub>TiO<sub>3</sub> (calcined in the solid state and hydrothermal) and MgO (calcined in the solid state and sol-gel) in two compositions (40 wt% and 60 wt%MgO) were studied at three sintering temperatures (1250, 1350 and 1450°C). The density and porosity were determined by the Archimedes technique. The microstructure was characterized by scanning electron microscopy (SEM) and optical microscopy. The crystallinity and composition was determined by x-ray diffraction (XRD). The XRD analysis of the ferroelectrics did not show any alloying combination among the various elements of the precursor materials. It also showed that all ferroelectric composites were consisted by two clearly distinguishable Ba<sub>0.55</sub>Sr<sub>0.45</sub>TiO<sub>3</sub> and MgO compounds for all compositions and all sintering temperatures. The nanohardness and Modulus of Elasticity were determined with the aid of a nanoindenter. The dielectric properties were characterized by a combination of parallel plate capacitor measurements. The relationship between the microstructure and the mechanical and

electrical properties of the ferroelectric material will be discussed in detail.

**3:15 PM \*R10.4**

**GIANT PIEZORESISTIVITY IN BARIUM TITANATE CERAMICS AT ROOM TEMPERATURE AND ITS MECHANISM.**

Makoto Kuwabara, Univ of Tokyo, Dept of Materials Engineering, Tokyo, JAPAN.

Giant piezoresistive effects (stress-sensitive resistance) of more than five orders of magnitude (in gage factor) were observed in single grain boundaries formed in thin semiconducting barium titanate ceramic bars with a diameter in the range of 10-20 μm at room temperature. Under cyclic mechanical stress (applied using a piezoactuator at a frequency in the range of 10-100MHz), we carried out current measurements and observation of ferroelectric domain morphology for many single grain boundaries with a polarizing microscope simultaneously. It has been found that a distinct change in current across a grain boundary was always accompanied by a significant change of the domain morphology in the vicinity of the grain boundary. We further observed a synchronous motion of a 90° domain wall in the samples with the cyclic mechanical stress applied, which caused no distinct change in current as far as the domain wall moves inside a grain away from both ends of the grain (i.e., grain boundaries). The obtained results indicate that the occurrence of the piezoresistivity in barium titanate ceramics is directly connected with surface charge compensation at grain boundaries by spontaneous polarization. We cannot explain the mechanism of piezoresistivity in barium titanate ceramics with Heywang's model, which has been widely accepted as one that can most adequately explain it.

**3:45 PM \*R10.5**

**INTEGRATION OF COLOSSAL MAGNETORESISTIVE La<sub>2/3</sub>Ca<sub>1/3</sub>MnO<sub>3</sub> WITH FERROELECTRIC SbsI. S. R. Surthi, S. Kotru, and R.K. Pandey**, Department of Electrical and Computer Engineering, The University of Alabama, Tuscaloosa, AL.

Integrated structures consisting of two or more materials having different physical properties have recently gained importance for understanding the mechanisms of coupled properties and for development of novel devices for many applications. The focus of this paper is to understand the coupled behavior of a colossal magnetoresistive (CMR) film of La<sub>2/3</sub>Ca<sub>1/3</sub>MnO<sub>3</sub> (LCMO) integrated with antimony sulfo-iodide ferroelectric (SbSI). We have used the pulsed laser deposition (PLD) technique for the growth of LCMO and SbSI films to produce our integrated structures. The thin films of LCMO were grown on single crystal NdGaO<sub>3</sub> substrates by selecting carefully the growth parameters. They were post annealed in flowing oxygen at 600-900°C for 0.5-12 hours. The transport properties of LCMO are very sensitive to the mixed valence of Mn, which, in turn, depends on the oxygen content for a fixed doping level of Ca. The effect of various process parameters during film growth and post-deposition annealing has been studied. The SbSI films were deposited at room temperature on platinumized Si substrates. These films were post-annealed in air at 200-250°C and characterized for ferroelectric properties at room temperature. Subsequently, SbSI/LCMO integrated structures were also fabricated by the PLD method and evaluated to determine their potential application as a non-volatile memory element. In our device we get the maximum channel modulation of approximately 10% with a low switching voltage of 2V. The integrated device exhibited good retention properties (i.e., nonvolatility for at least up to 2 hours). A small polarization loss of 5% was observed for bipolar switching for up to 10<sup>7</sup> cycles.

**4:15 PM \*R10.6**

**MODELLING THE IMPEDANCE RESPONSE OF BARIUM TITANATE CERAMICS.** Finlay D. Morrison, Marta Herraiz, Derek C. Sinclair and Anthony R. West, Department of Engineering Materials, The University of Sheffield, Sheffield, UNITED KINGDOM.

Barium titanate ceramics are extremely complex materials electrically. Depending on their fabrication, composition and microstructure, they can exhibit insulating or semi-conducting behaviour, ferro-electric or para-electric properties and either ntc or ptc conductivity characteristics. They can be compositionally, and electrically, homogeneous or heterogeneous. Approaches to the analysis and modelling of impedance data depend very much on the nature of the impedance response. An overview of the methodologies for analysing the data will be given.