

SYMPOSIUM EP01

TUTORIAL: Introduction to Pyroelectric, Piezoelectric, and Ferroelectric Materials
November 25 - November 25, 2018

* Invited Paper

TUTORIAL Introduction to Pyroelectric, Piezoelectric and Ferroelectric Materials

Sunday Morning, November 25, 2018
Hynes, Level 2, Room 201

Polar materials continue to be an important class of functionality for modern applications that provides direct and indirect convolution of structure and chemistry from the atomistic to the macroscopic level. This tutorial will introduce researchers to the basic physics of polar response, its connection to fundamental structure and symmetry, synthesis of polar materials and characterization methods. Topics will also cover the connection between polar properties and desirable functionality in application such as sensing and optoelectronic properties. This tutorial will then culminate with hands-on exercises to explore the functionality, synthesizable ability, and characterizability of polar materials in the Materials Project.

8:30 AM

Fundamentals of Pyroelectric, Piezoelectric, and Ferroelectric Materials Susan Trolier-McKinstry; The Pennsylvania State University

10:00 AM BREAK

10:30 AM

Harnessing the Materials Project to Discover New Polar Materials Shyam Swaraknath; Lawrence Berkeley National Laboratory

SYMPOSIUM EP01

New Materials and Applications of Piezoelectric, Pyroelectric and Ferroelectric Materials
November 26 - November 29, 2018

Symposium Organizers

Shyam Dwaraknath, Lawrence Berkeley National Laboratory
David Ginley, National Renewable Energy Laboratory
Laura Schelhas, SLAC National Accelerator Laboratory
Abdelilah Slaoui, Laboratoire des Sciences de l'ingénieur, de l'Informatique et de l'Imagerie, iCUBE-CNRS

* Invited Paper

SESSION EP01.01: Computational Design of New Materials
Session Chairs: Shyam Dwaraknath and David Ginley
Monday Morning, November 26, 2018
Hynes, Level 1, Room 103

8:30 AM EP01.01.01

Optimization of Si/ZnO/PEDOT:PSS Tri-Layer Heterojunction Photodetector by Piezo-Phototronic Effect Using Both Positive and Negative Piezoelectric Charges Fangpei Li, Wenbo Peng, Zijian Pan and Yongning He; Xi'an Jiaotong University, Xi'an, China.

Piezo-phototronic effect has been extensively introduced to improve the performances of optoelectronic devices by utilizing external-strain-induced positive or negative piezoelectric charges (piezo-charges) to modulate the generation, separation, transportation, and recombination of charge carriers. However, in most cases till today, only the piezo-charges with one polarity (*i.e.*, positive or negative) are effectively utilized. In this work, we fabricated an

n-Si/n-ZnO/p-PEDOT:PSS tri-layer heterojunction photodetector (HPD) and systematically investigated the piezo-phototronic effect on its performances simultaneously utilizing both positive and negative piezo-charges for the first time.

In experiment, the photo-responses of the HPD to 405 nm and 648 nm laser illuminations under different externally applied compressive strains indicate the existence of an optimized compressive strain to achieve the maximized enhancements. For example, the photoresponsivities to 405 nm and 648 nm laser illuminations are gigantically improved, and reach 0.218 A/W (under -10.73% compressive strain) and 0.012 A/W (under -6.52% compressive strain), respectively. Compared to photoresponsivities under strain free condition, the enhancements achieve over 3000% and 1800%, respectively. Other figure of merits as a function of compressive strain, such as photocurrent and specific detectivity, also exhibit a similar optimizing tendency.

The optimizing phenomena are due to the positive and negative piezo-charges at n-Si/n-ZnO and n-ZnO/p-PEDOT:PSS interface, respectively, that introduce different adjustments to the local energy band diagrams which have either enhancing or weakening effects on the behaviors of photo-generated carriers. Under a relatively small compressive strain, the enhancing influences play a dominant role so the photo-responses are improved. As strain rises, some weakening influences outgrow others, therefore the photo-responses are degraded. This competition mechanism is a combined result of both positive and negative piezo-charges, and eventually produces an optimized modulation to the photo-responses of the HPD. Theoretical validation is implemented by finite element analysis simulations and simulation results show that the strain-induced variations in energy band diagrams in the vicinity of the n-Si/n-ZnO and n-ZnO/p-PEDOT:PSS interfaces are both in good accordance with the proposed working mechanisms.

This work not only presents the utilization of both positive and negative piezo-charges to optimize the performances of the HPD by the piezo-phototronic effect, but also provides a deep understanding of how the piezo-charges of two opposite polarities work together in one optoelectronic device, hopefully proposing the idea of introducing the piezo-phototronic effect into three-/multi-layer devices in future applications.

8:45 AM EP01.01.02

Defective Metal Oxides—New Generation of Electrostrictor Materials [Simone Santucci](#), Simone Sanna, Nini Pryds and Vincenzo Esposito; Energy Conversion and Storage, Technical University of Denmark, Roskilde, Denmark.

Lead Zirconate Titanate ($\text{Pb}(\text{Zr,Ti})\text{O}_3$) (PZT) is the dominating electromechanically active functional material with a wide range of applications in electronics and micro-actuation, e.g. in MEMS. However, currently it is difficult to grow highly crystalline PZT directly on silicon due to the interfacial chemical reactions between the lead (Pb) and silicon at elevated temperatures required for the PZT crystallization. A possible solution to avoid interdiffusion is to grow PZT on insulating diffusion barrier layers such as ZrO_2 or TiO_2 that protect the silicon wafer substrate. This solution, however, brings complex processing steps and can result in an overall decreasing of the device electromechanical performances.

The recent discovery of “non-classical” electrostriction in some defective metal oxides such as (Y, Nb)-Stabilized $\delta\text{-Bi}_2\text{O}_3$ ($\text{Bi}_7\text{Nb}_{2-x}\text{Y}_x\text{O}_{15.5-x}$) [1] and gadolinium-doped ceria ($\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2.8}$) (CGO) [2] drew a great interest as a promising candidate for the new generation of electromechanical micro devices. Particularly, CGO is not only an environmental friendly material but it is also highly compatible with silicon technology since cerium does not diffuse into silicon. Moreover, CGO shows better performances as compared to the best performing commercial lead based ceramics, e.g. the electrostrictive coefficient of CGO is in a range between 20-110 m^4/C^2 [1,2,3] vs 0,02 m^4/C^2 of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) [4].

In this work, we demonstrate the great potential and some limitations of CGO by growing thin films directly on TiN/Si substrates, where a TiN deposition of 80 nm serves as bottom electrode for the CGO electrostrictor. The direct deposition yields impressive electrostrictive performances (50 m^4/C^2) and long term stability for CGO films of ca. 1 μm in thickness.

References:

1. N. Yavo et al., *Adv. Funct. Mater.* 2016, **26**, 1138–1142.
2. R. Korobko et al., *Adv. Mater.* 2012, **24**, 5857–5861.
3. R. Korobko et al., *Sensors and Actuators A* 2013, **201**, 73–78.
4. J. Kuwata et al 1980, *Jpn. J. Appl. Phys.* **19** 2099.

9:00 AM EP01.01.03

First-Principles Studies of the Effects of Oxygen Vacancies on the HfO_2 -Based Ferroelectric Tunnel Junction [Jinho Byun](#), Taewon Min and Jaekwang Lee; Physics, Pusan National University, Busan, Korea (the Republic of).

Owing to the recent advances in the oxide growth technology, ferroelectricity has been stabilized even in a few nm-thick films, which makes it possible to realize the oxides-based ferroelectric tunneling junction (FTJ) combining the quantum-mechanical tunneling phenomena and switchable spontaneous polarization into novel device functionality. Among various ferroelectric oxides, HfO_2 is the most promising material for FTJ devices since it has the great advantage of complementary metal-oxide-semiconductor (CMOS) process compatibility. Despite this considerable attention, the influence of oxygen vacancies on the tunneling current has not been clearly understood yet. Here, using first-principles density functional theory calculations, we explored the role of interfacial oxygen vacancy on the tunneling current in the TiN/ HfO_2 /metal devices at the atomic scale. We find that the tunneling current in defective HfO_2 is enhanced by over three orders of magnitude compared to plain HfO_2 thin film. Our results show that the modulation of electronic properties via interfacial oxygen vacancy has a significant impact on HfO_2 -based FTJ device performance.

This research was supported by the MOTIE (Ministry of Trade, Industry & Energy (#10080643) and KSRC (Korea Semiconductor Research Consortium) support program for the development of the future semiconductor device.

This work was also supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (2018R1A2B6004394)

9:15 AM EP01.01.04

Dynamical Mean Field Theory Investigation of Piezoresistive Thin-Film Rare Earth Compounds Contacted to Metal Electrodes [Ivan Rungger](#)¹, Evgeny Plekhanov², Debalina Banerjee², Andrea Droghetti³, Dennis News⁴, Cedric Weber² and Glenn J. Martyna⁴; ¹National Physical Laboratory, Teddington, United Kingdom; ²Kings College London, London, United Kingdom; ³University of the Basque Country, San Sebastian, Spain; ⁴IBM Thomas J Watson Research Center, Yorktown Heights, New York, United States.

The emerging piezoelectric transistor technology is based on heterostructures combining piezoelectric materials and piezoresistive thin films acting as ON/OFF switches and memories. Rare earth piezoresistive compounds such as SmS , SmSe and SmTe exhibit a reversible metal-insulator phase transition driven by either light, voltage or pressure, which can be applied by the piezoelectric. For device applications the contact with the metal electrodes critically affects switching behaviour in nanoscale piezoresistive materials, which has not been studied so far. Here we present first principles calculations to model these phase transitions both in the bulk and in nanoscale thin films used in transistor applications, and predict how switching can be induced by mechanical and electrical means in nanoscale devices. Importantly, density functional theory with semi-local exchange correlation functionals cannot correctly treat the strongly correlated electrons in the f-orbitals of Sm. We overcome this limitation by using our recent implementation of the dynamical mean field theory, and show good agreement with experimental data for the electrical and mechanical switching properties.

9:30 AM EP01.01.05

Three-Dimensional Interconnected Piezoelectric Ceramic Foam Based Composites as Flexible, High-Performance Piezo/Pyroelectric Materials for Concurrent Mechanical and Thermal Energy Harvesting [Sulin Zhang](#)¹, Qing Wang¹, Guangzu Zhang² and Peng Zhao¹; ¹The Pennsylvania State University, University Park, Pennsylvania, United States; ²Huazhong University of Science and Technology, Wuhan, China.

Flexible Piezoelectric (PZT)-polymer composites with superior piezoelectric effect have received much attention for a wide range of applications, particularly in energy harvesting. However, classical PZT-polymer composites with low-dimensional ceramic fillers suffer from low piezoelectricity, owing to the poor load-transfer efficiency from the polymer matrix to the active ceramic fillers. The fundamental mechanics is that the load-transfer efficiency for these composites scales with the ratio of the stiffness of the polymer matrix to that of the ceramic fillers, a value typically on the order of 10^{-5} . Here we introduce a cost-effectively producible ceramic-polymer composite consisting of three-dimensional (3-D) interconnected piezoelectric microfoams in polydimethylsiloxane (PDMS) matrix. The resulting composite breaks the conventional scaling law of the load-transfer efficiency, and enables continuous strain and heat transfer, giving rise to exceptionally improved piezo and pyroelectric effects as compared to those based on low-dimensional ceramic fillers. The 3-D composite is also mechanically flexible, robust, and durable, able to sustain thousands of thermomechanical cycles without noticeable degradation, while yielding stable piezo/pyroelectric signals. We further demonstrate that combining the piezo and pyroelectric effects of the 3-D composites enable concurrent mechanical and thermal energy harvesting. These attributes, along with the scalable production, make the 3-D composite attractive to a wide range of applications in soft robotics, wearable electronics, and artificial muscles and skins, etc.

9:45 AM EP01.01.06

Potential Ferroelectric Binary Oxides Beyond Hafnia [Rohit Batra](#)^{1,2}, Huan Tran¹, Brienne Johnson³, George Rossetti¹, Jacob L. Jones³ and Rampi Ramprasad²; ¹University of Connecticut, Storrs, Connecticut, United States; ²Georgia Institute of Technology, Atlanta, Georgia, United States; ³North Carolina State University, Raleigh, North Carolina, United States.

In the past couple of years, there have been extensive empirical and theoretical efforts to elucidate the surprising phenomenon of ferroelectricity recently discovered in hafnia (HfO₂) thin films (<30 nm) [1-5]. While the origin of this unexpected ferroelectric (FE) behavior is associated with the formation of the metastable orthorhombic *Pca2₁* phase owing to unusual thermodynamic or processing conditions [2,4], the most critical lesson to be learned from the example of hafnia is that even binary oxides can be FE if low-lying metastable (or stable) polar phases are present. Thus, in this contribution, we extend the findings from the case of hafnia to discover new FE binary oxides, as opposed to the traditionally explored class of perovskite-structured oxides, using computations. We employed a combination of structural search methods, first principles computations and group-theoretical considerations to find at least six simple oxides as potential ferroelectric candidates. Among them, a previously unexplored candidate, CaO₂, was successfully synthesized in the polar *Pna2₁* phase, in accordance with our theoretical predictions. Furthermore, the high occurrence (~40 %) of low-energy polar phases among the oxides considered in this work strongly advocates the possibility of discovery or engineering ferroelectricity in many more simple oxides beyond hafnia.

References:

- [1] M. H. Park et al., *Advanced Materials* 27, 1811 (2015)
- [2] T. D. Huan et al., *Physical Review B* 90, 064111 (2014)
- [3] R. Batra et al., *Applied Physics Letters* 108, 172902 (2016)
- [4] R. Batra et al., *Journal of Physical Chemistry C*, 121, 4139 (2017)
- [5] R. Batra et al., *Chemistry of Materials*, 29, 9102 (2017)

10:00 AM BREAK

10:30 AM *EP01.01.07

Accelerated Materials Design of Novel Polar Materials [Kristin A. Persson](#)^{2, 1}; ¹Lawrence Berkeley National Laboratory, Berkeley, California, United States; ²Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States.

Novel polar multifunctional materials are needed for next generation sensors, energy converters, and high-performance computing. Leveraging the growing body of computational resources, from the prediction of novel materials with target properties to their characterization and synthesis, it is possible to accelerate the pace of discovery. In this talk we will utilize the data and analysis resources of the *Materials Project* (www.materialsproject.org) which is harnessing the power of supercomputing coupled with a sophisticated software infrastructure that carries out, organizes and disseminates 100-1000s of calculations per week – enabling effective screening, prediction and tandem exploration together with experimental teams. We will survey the available methods and data, exemplified through a recent realization of a novel metastable piezoelectric material, from prediction to successful synthesis and testing. Finally, we will comment on future directions in this exciting field, in particular the need for predictive synthesis.

11:00 AM EP01.01.08

Kinetic Monte Carlo Simulations of Organic Ferroelectrics [Tim Cornelissen](#), Indre Urbanaviciute and Martijn Kemerink; Linköping University, Linköping, Sweden.

Organic ferroelectric materials are emerging as a class of materials that may find application in a broad range of fields; for instance, they might solve the ‘missing memory’ problem in printed electronics. However, a full understanding of their switching kinetics on all length and time scales is still lacking. A variety of computational models have been employed to tackle this problem and to study different aspects of organic ferroelectrics. However, these are usually restricted to idealized morphologies or short time scales.

In contrast, we have developed an electrostatic model that, when used in kinetic Monte Carlo simulations, can reproduce the ferroelectric properties and kinetics on experimental time scales and for realistic 3D morphologies. We apply this model on the prototype small molecular ferroelectric trialkylbenzene-1,3,5-tricarboxamide (BTA).

We simulate hysteresis loops and depolarization curves and find a good agreement with experiments. Like the experiments, the dependence on frequency and temperature of our model results can be interpreted in the framework of thermally activated nucleation limited switching. Specifically, we find two different modes of switching, each associated with their own kinetics and energetics. One mode corresponds to a full rotation of the dipoles, while the other mode only flips the component along the polarization axis. The existence of these two modes is confirmed by molecular dynamics simulations. Both simulation methods find that the second mode has a lower coercive field and thus is the one occurring in polarization switching experiments.

We also investigate the effect of structural disorder on the ferroelectric properties. When the disorder in the system is increased, the retention time

decreases dramatically, while the coercive field remains mostly unchanged. For device applications a high retention time and moderate coercive field is required. Aside from providing a detailed insight into polarization switching processes on experimental length and time scales, our model thus is also able to provide guidance in improving the performance of ferroelectric devices.

11:15 AM *EP01.01.09

Lone Pair Engineering for Multi-Functional Polar Semiconductors [Aron Walsh](#); Imperial College London, London, United Kingdom.

Beyond the group oxidation state (N), post-transition metals can adopt a lower ($N-2$) oxidation state, which is associated with a metal s^2 lone electron pair. Solid-state lone pairs, as found in the compounds formed of ions such as In(I), Sn(II), Sb(III), and Te(IV), are linked to the formation of asymmetric local coordination environments and non-centrosymmetric crystal structures [1]. Lone pairs underpin the physical properties of many piezoelectric, pyroelectric and ferroelectric materials.

I will discuss progress in the understanding of structure and reactivity of lone pair containing compounds, including the driving force for structural distortions and how they can be controlled to enable novel functionality. Applications areas to be discussed will include thermoelectric devices that incorporate high levels of phonon anharmonicity (e.g. SnSe [2]), photovoltaic cells based on photoferroic semiconductors (e.g. Pb and Sn halide perovskites [3]), as well as new classes of ternary V-VI-VII semiconductors based on Bi and Sb chalcogenides [4,5] that encompass photocatalysts, Rashba semiconductors, and topological insulators.

1. Stereochemistry of post-transition metal oxides: revision of the classical lone pair model. Chem. Soc. Rev. 40, 4455 (2011)
2. Anharmonicity in the high-temperature Cmcm phase of SnSe: soft modes and three-phonon interactions. Phys. Rev. Lett. 117, 075502 (2016)
3. Spontaneous octahedral tilting in the cubic inorganic caesium halide perovskites $CsSnX_3$ and $CsPbX_3$ ($X = F, Cl, Br, I$). J. Phys. Chem. Lett. 8, 4720 (2017)
4. Quasi-particle electronic band structure and alignment of the V-VI-VII semiconductors SbSI, SbSbBr, and SbSeI for solar cells. Appl. Phys. Lett. 108, 112103 (2016)
5. Bismuth oxyhalides: synthesis, structure and photoelectrochemical activity. Chem. Sci. 7, 4832 (2016)

SESSION EP01.02: Experimental Realization of Predicted Materials Including Synthesizability
Session Chairs: Bor-Rong Chen and Susan Trolier-McKinstry
Monday Afternoon, November 26, 2018
Hynes, Level 1, Room 103

1:30 PM EP01.02.01

Enhancement of Ferroelectricity in Perovskite Oxides by Sulfurization [Muhammad Sheeraz](#), Ill Won Kim, Chang Won Ahn and Tae Heon Kim; Department of Physics and Energy Harvest Storage Research Center, University of Ulsan, Ulsan, Korea (the Republic of).

Sulfurization, an anion substitution to oxide materials is considered a progressive route for designing new multi-functional materials artificially and realization of unusual physical properties which do not exist in nature. Sulfur among the other anions has got major attraction due to its isoelectronic nature and large ionic radius compared to oxygen. However, the sulfurization to polycrystalline perovskite other than bulk single crystal perovskite oxides is rarely reported due to the synthetic limitation. Despite this an alternative feasible synthetic route is developed to better understand the structural and physical properties sulfur is doped quantitatively at atomic level. Sulfur doped ferroelectric perovskite $[Pb(Zr,Ti)O_3]$ is grown epitaxially by employing the thiourea (CH_4N_2S) solution at various mole ratio using sol gel method. Microscopic analyses of electronic and crystal structures reveal that oxygen ions are substituted by sulfur atoms with tetragonal distortion. In response to this structural phase transition, macroscopic ferroelectric polarization is enhanced, although a band gap is reduced. More details of theoretical calculations and experimental results will be presented in conjunction with a discussion about the potential usage of our synthetic technique in aspect of novel material design.

1:45 PM EP01.02.02

Anisotropy Control for Enhanced Performance Magnetolectric Nanocomposites Matthew Bauer, Austin Kubart and [Jennifer Andrew](#); Univ of Florida, Gainesville, Florida, United States.

Nanostructured composite materials have the potential to overcome challenges in many areas of materials research, which cannot be addressed by more conventional single-phase materials. The unique properties of these composite materials often arise due to unique phenomena that occur at the interface between the phases being coupled. An additional control is the anisotropy of the individual phases and the resultant composite, which can be used to control the magnitude and direction of composite properties. For example, ferroelectric and ferromagnetic materials can be combined to form composites with enhanced multiferroic or exchange coupling properties. Here, I will present on these composite materials prepared using the electrospinning technique, generating materials with controllable anisotropy and resultant properties. Specifically, Janus type nanofibers, where two phases are coupled longitudinally, are used to create an anisotropic building block that allow access to both surface and bulk properties of each phase. This novel architecture is linked to an anisotropic interface between the coupled phases, and a model is developed relating fiber composition to interfacial area and resulting functional properties. Applications of these composites as zero-power magnetic field sensors will also be presented.

2:00 PM EP01.02.03

Ferroelectric HfO₂ Growth from HfCl₄-ZrO₄ Solid Solution for Stress/Strain Induced Grain Formation and Defect Control at Oxide-Semiconductor Interface [Mahmut Sami Kavrik](#)¹, Evgueni Chagarov¹, Michael Katz², Norman Stanford², Albert Davydov², Min-Hung Lee³ and Andrew Kummel¹; ¹University of California, San Diego, La Jolla, California, United States; ²National Institute of Standards and Technology, Gaithersburg, Maryland, United States; ³National Taiwan University, Taipei, Taiwan.

Recent findings in ferroelectric HfO₂ and discovery of negative capacitance may provide unexpected improvements in CMOS due to scalability of

HfO₂ and ease of integration. Ferroelectricity can be induced into thin film HfO₂ via doping (Al, Y, Gd, Si), but the composition window for each dopant is narrow, sometime only +/-2%. Conversely, Zr doped HfO₂ has a broad stoichiometry window (+/- ~15%) in which ferroelectricity can be stabilized. The mechanism for stability of the phases of HfO₂, ZrO₂, and HZO (Hf_{1-x}Zr_xO₂) were investigated with DFT-MD to determine the origin of larger process window of ferroelectric phase for the binary HfZrO oxides. It was shown that for all three oxides although the bulk states of the monoclinic phase ("m") are more stable than either the orthorhombic ferroelectric ("f") phase or tetragonal ("t") phases and even the surface free energy does not favor f-phase formation. Instead, the higher surface area per unit cell induced by the stress/strain due to post annealing of the amorphous oxide with a crystalline capping layer such as TiN can favor the orthorhombic f-phase since it has a larger area per unit cell than the monoclinic phase; the only requirement is that epitaxial crystallization occurs over at least 5 unit cells of the capping layer. Consistent with this hypothesis, high resolution TEM images of TiN/HZO/Si gate stacks shows regions of epitaxial alignment between HZO and TiN. To improve the consistency of HZO ferroelectric gates, a new method of deposition was developed. The conventional method of Zr doping into HfO₂ employs consecutive ALD cycles of ZrO₂ and HfO₂ in a nanolaminate structure from separate precursors. This process may limit intermixing of the Hf and Zr when the oxide is scaled to 1.5 nm as required for commercial CMOS devices. Furthermore, this process can limit the defect control at the oxide semiconductor interface due to necessity of the precise control of the oxidant between dosing of each precursors to maintain precise stoichiometry. Control of oxidant for growth of HZO on SiGe is particularly challenging since oxidant dosing must be differentially controlled at the interface to avoid GeOx formation; for example O₃ intermittent dosing during growth of HZO on SiGe has been shown to lower the interface defect density. In this work, an alternative method was investigated in which HfCl₄ and ZrCl₄ solid mixture was employed; this relies upon the vapor phase composition being a function of the solid-state composition. Ferroelectric Hf-ZrO₂ was grown in Ni/HZO/TiN/Si structure from single solid mixture precursor and >25uC/cm² polarization was observed in 6 nm HfZrO₂ grown from single solid mixture. In second step, ferroelectric Hf-ZrO₂ on Si_{0.3}Ge_{0.7} was grown from single solid mixture precursor and MOSCAPs were fabricated. Electrical analysis revealed low defect interface formation with D_{it} of <3x10¹² and low leakage current density of <1x10⁻¹⁰ (A/cm²) similar to the control HfO₂ devices on SiGe.

2:15 PM EP01.02.04

ZnO-Activated Low Temperature Reactive Sintering of High Coercive Field Lead Zinc Niobate Based Piezoelectrics [Michael Brova](#)^{1,2}, [Beecher H. Watson](#)^{1,2}, [Elizabeth Kupp](#)^{1,2}, [Mark Fanton](#)³, [Richard Meyer](#)³ and [Gary L. Messing](#)^{1,2}; ¹Material Science and Engineering, The Pennsylvania State University, State College, Pennsylvania, United States; ²Materials Research Institute, The Pennsylvania State University, State College, Pennsylvania, United States; ³Applied Research Laboratory, The Pennsylvania State University, State College, Pennsylvania, United States.

A major limitation of many high performance relaxor-based ferroelectric materials is their Curie temperatures. The recently developed Pb(In_{1/2}Nb_{1/2})O₃-Pb(Zn_{1/3}Nb_{2/3})O₃-PbTiO₃ perovskite solid solution has a high rhombohedral to tetragonal phase transition temperature (T_m) and Curie temperature (T_c), while also possessing a large piezoelectric charge coefficient (d₃₃), mechanical quality factor (Q_m), and coercive field (E_c). In order to lower the sintering temperature and minimize number of heat treatments necessary to fabricate PIN-PZN-PT ceramics, we investigated reactive sintering of ZnO-doped PIN-PZN-PT. Reactive sintering reduced the required processing temperature from 1150°C to 800°C when compared to traditional sintering. ZnO-doping stabilized the perovskite phase, reduced the sintering temperature, and significantly increased the reaction and densification. This effect is attributed to a modification in the defect chemistry of PIN-PZN-PT perovskite and an intermediate pyrochlore phase. Electromechanical properties of reactively sintered ZnO-doped PIN-PZN-PT ceramics are compared with those synthesized by conventional sintering.

2:30 PM BREAK

3:00 PM EP01.02.05

Low Temperature Reactive Sintering and Reactive Templated Grain Growth of CuO-Doped Lead-Based Piezoelectric Ceramics [Beecher H. Watson](#)¹, [Michael J. Brova](#)¹, [Scott Mixture](#)², [Mark Fanton](#)¹, [Richard Meyer](#)¹ and [Gary L. Messing](#)¹; ¹The Pennsylvania State University, State College, Pennsylvania, United States; ²Alfred University, Alfred, New York, United States.

Ternary lead-based Pb(In_{1/2}Nb_{1/2})O₃-Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PIN-PMN-PT) ferroelectric ceramics are leading candidates for next-generation textured piezoelectrics. Fabrication of those bulk textured ceramics requires high sintering temperatures of ~1200°C-1250°C to initiate epitaxial growth and long hold times to achieve full texture development. Holding at high sintering temperatures presents a significant challenge because of the volatility of certain constituents (e.g. PbO) and the limitation of developing multilayered actuators, requiring the use of platinum electrodes. In this work, we explore new doping strategies (such as CuO) to reduce the sintering temperature and through reactive sintering to initiate epitaxy at lower temperatures. The effects of CuO doping on the kinetics of perovskite phase formation and reactive sintering were studied using *in situ* x-ray diffraction as well as diffraction analysis on samples heated under isothermal conditions. Reactive sintering conditions of CuO-doped PIN-PMN-PT ceramics were explored by isothermally treating ceramic green bodies at temperatures below 900°C, with a relative density of 95-97% achieved at remarkably low temperatures of 790°C for 6.7 h. Using a reactive sintering approach, we adapted a reactive templated grain growth (RTGG) system using BaTiO₃ microcrystal platelets to seed the phase transformation of the PIN-PMN-PT perovskite at much lower temperatures than previously demonstrated in the TGG process (~1200-1250°C).

3:15 PM EP01.02.06

Influence of Anneal Parameters on Strained TiN Layers in Ferroelectric HfO₂ Capacitors [Teresa Buttner](#)¹, [Patrick Polakowski](#)¹, [Konrad Seidel](#)¹, [Joachim Metzger](#)² and [Robert Binder](#)²; ¹Center Nanoelectronic Technology, Fraunhofer Institute for Photonic Microsystems, Dresden, Germany; ²Globalfoundries, Dresden, Germany.

The ferroelectric (FE) behavior of HfO₂ strongly depends on the crystalline structure and is observed when the high symmetrical non-centrosymmetric orthorhombic phase is dominant. Therefore, it is necessary that controlled crystallization positively influences the crystal phases of HfO₂ and reducing the stability of unfavored structures like tetragonal or monoclinic crystal phases.¹ Numerous studies investigated various process parameters and proved that various dopants, film thickness or annealing conditions have an impact on FE properties and ferroelectric phase stability.²⁻⁴ Early work on HfO₂ ceramics identified mechanical stress as further parameter to induce orthorhombic phase in hafnium oxide.⁵ In further studies on undoped HfO₂³ and silicon doped⁶ thin films indicated that the crystalline phase is mechanically influenced by capping layers.

In this work we investigate differently strained TiN electrodes and their influence on ferroelectric films in metal-ferroelectric-metal (MFM) stacks to identify ideal stress conditions for enhanced ferroelectricity in HfO₂ thin films. First electrical results confirmed FE behavior for all MFM samples with differently strained TiN Top Electrodes (TE) ranging from -4 GPa to 0 GPa, but showed marginal difference in ferroelectric performance. These results are in contradiction to fundamental research of ceramic hafnium oxide. Thus, this leads to the assumption that the different applied stress levels were equalized during subsequent processing. To examine the influence of TiN film properties in respect to process parameters applied in the MFM flow, the strained TiN layers were investigated individually on blanket wafers by using the same TiN film conditions. The samples were annealed with different temperatures and gas ambient conditions (Ar, N₂ and NH₃) and with/without a-Si and poly-Si encapsulation. Finally, we did a full material analysis, characterized the wafers regarding change in stress, composition, sheet resistivity, structure and thickness for pre and post anneal treatment. The results confirmed the first assumption, that due to a subsequent thermal treatment the films stress has been equalized. The tensile stress was relaxed or changed into compressive stress after annealing, which resulted in equal stress data for all used TiN conditions.

Possible solutions to overcome these findings and to maintain stress levels after thermal processing will be discussed. Further MFM experiments were

conducted by lowering anneal temperatures, removing of TiN TE and subsequent TE deposition or deposition of stressed TiN on annealed relaxed TiN films.

References:

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3:30 PM DISCUSSION TIME

3:45 PM *EP01.02.08

Applying Chemistry to Make Today's Best Tunable Millimeter Wave Dielectric Even Better Darrell G. Schlom¹, Natalie M. Dawley¹, Eric Marks², Aaron M. Hagerstrom², Megan E. Holtz^{1,3}, Gerhard H. Olsen³, J. Zhang¹, Christian J. Long², James C. Booth², Craig J. Fennie³, David Muller^{3,4} and Nathan D. Orloff²; ¹Department of Materials Science and Engineering, Cornell University, Ithaca, New York, United States; ²Communications Technology Laboratory, National Institute of Standards and Technology, Boulder, Colorado, United States; ³School of Applied and Engineering Physics, Cornell University, Ithaca, New York, United States; ⁴Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York, United States.

Tunable dielectrics are key constituents of emerging high-frequency devices in telecommunications—including tunable filters, phase shifters, and baluns—and for miniaturizing frequency-agile microwave and millimeter-wave components. Today's tunable dielectric with the highest figure of merit at room temperature is strained films of (SrTiO₃)₆SrO. The low loss at frequencies up to 125 GHz comes from the defect mitigating nature of the (SrTiO₃)₆SrO Ruddlesden-Popper structure; the tunability arises from imposing strain to induce a ferroelectric instability. Unfortunately the necessity for strain limits the film thickness to around 50 nm, which reduces the device tuning that can be achieved. In this talk we describe a chemical alternative to strain to induce a ferroelectric instability—the introduction of barium into this Ruddlesden-Popper titanate. No barium-containing Ruddlesden-Popper titanates are known, but this atomically engineered superlattice material can be made thicker and we demonstrate a 300% improvement in the figure of merit of this new, metastable (SrTiO₃)_{n-m}(BaTiO₃)_mSrO tunable dielectric over its predecessor, (SrTiO₃)₆SrO.

4:15 PM EP01.02.09

Lift-off of Ultrathin Single-Crystalline Layers for Flexible Ferroelectric Tunneling Memristors Zhengdong Luo¹, Dae-Sung Park² and Marin Alexe¹; ¹University of Warwick, Coventry, United Kingdom; ²Martin-Luther-University Halle-Wittenberg, Halle, Germany.

Recently, there has been an upsurge in pursuing the flexible devices for next generation of smart electronics. Among a large number of reported devices, integration of single-crystal functional oxides films onto the flexible substrates is rare because of the challenging fabrication process. Functional oxides, showing a rich variety of complex emergent properties including memristive effects, photovoltaics, multiferroic effects and so on, have become promising high-tech functional materials beyond their traditional role as dielectrics. Therefore, integration of functional oxides thin films and flexible substrates would add a wide range of exciting applications to the flexible electronics library. Here, we demonstrate a successful fabrication of single-crystal form ferroelectric oxides films on PET flexible substrates. We will discuss the lift-off of the ferroelectric films from the growth substrate by etching a water-soluble sacrifice layer Sr₃Al₂O₆ layer, the transfer of those 2D single-crystal membranes onto the PET substrates and the functional electronic properties of the resulting ferroelectric thin film/PET flexible memristors. Moreover, we will show the transfer of other oxides films using the same lift-off method and discuss some potential interesting applications like flexible bulk photovoltaic devices and so on.

SESSION EP01.03: Poster Session I: Growth and Characterization of Piezoelectric, Pyroelectric and Ferroelectric Materials

Session Chairs: David Ginley and Abdelilah Slaoui

Monday Afternoon, November 26, 2018

8:00 PM - 10:00 PM

Hynes, Level 1, Hall B

EP01.03.01

Flexible Robust and High-Density FeRAM from Organic Ferroelectric Nano-Lamellae by Self-Assembly Mengfan Guo¹, Jianyong Jiang¹, Jianfeng Qian¹, Chen Liu¹, Jing Ma¹, Ce-Wen Nan¹ and Yang Shen^{1,2}; ¹School of Materials Science and Engineering, State Key Lab of New Ceramics and Fine Processing, Tsinghua University, Beijing, China; ²Center for Flexible Electronics Technology, Tsinghua University, Beijing, China.

Ferroelectric memory device is endowed with high data storage density by nanostructure designing, while the robustness of ferroelectrics is also impaired. Especially for flexible memories based on organic ferroelectrics, low Curie point limits their thermal endurance and stability. Herein, we fabricate a ferroelectric random access memory (FeRAM) based on ferroelectric lamellae by self-assembly of poly(vinylidene fluoride-co-trifluoroethylene). The FeRAM exhibits high data storage density and promoted thermal stability. Written data shows enhanced thermal endurance and little volatilization after thermal cycles. These results provide a novel strategy for improving robustness of organic flexible FeRAMs.

EP01.03.02

Effects of Post-Draw Processing on the Structure and Functional Properties of Electrospun PVDF-HFP Nanofibers Adriano A. Conte¹, Khosro Shirvani², Wei Xue², Xiao Hu³ and Vince Beachley¹; ¹Biomedical Engineering, Rowan University, Glassboro, New Jersey, United States; ²Mechanical Engineering, Rowan University, Glassboro, New Jersey, United States; ³Physics, Rowan University, Glassboro, New Jersey, United States.

The current surge in wearable electronics has initiated a need for alternative energy sources. Energy harvesters that employ piezoelectric materials are capable of harnessing the mechanical energy from muscular contractions to power portable devices. The present study examined the properties of polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP) nanofibers fabricated from conventional electrospinning, and an automated track collector system that contains a post-drawing component. The polymer solution was originally processed by means of the traditional technique, flat-plate electrospinning, which produced a fiber arrangement with random orientations. When carrying out mechano-electrical testing and analysis these fibers

yielded negligible voltage. The solution was subsequently processed employing a post-drawing electrospinning procedure, exclusive to our research laboratory, that permitted fiber alignment and individual nanofiber post-drawing immediately upon collection, prior to total solvent evaporation. Fibers that endured post-drawing displayed an increase in crystal alignment in the direction of the fiber axis (verified by polarized FTIR), and resulted in higher voltages than undrawn fibers and fibers from the traditional electrospinning method. It was examined that fibers produced by means of the post-drawing technique, with varying draw ratios ($DR = \text{Final length}/\text{Initial length}$) including DR-2 and DR-3, exhibited improved piezoelectric characteristics. Mechanical properties of the nanofibers were also enhanced as a result of post-drawing. This investigation suggests that the post-drawing practice results in PVDF-HFP nanofibers that are more suitable for piezoelectric applications than conventionally electrospun nanofibers.

EP01.03.03

Epitaxial AlN Thin Film for High Performance Surface Acoustic Wave Devices Junning Gao, Jianbai Jiang and Guoqiang Li; School of Materials Science and Engineering, South China University of Technology, Guangzhou, China.

Aluminum nitride is a wide bandgap piezoelectric semiconductor that has superior hardness and thermal conductivity. It also has the electromechanical coupling factor and dielectric constant that fit perfectly for the band width needed in bulk acoustic wave (BAW) filters which serve at tremendous quantity in smart phones. Over the years, polycrystalline thin films of AlN have been used almost exclusively as the piezoelectric substrate in commercial BAW filter products. It is also a potentially outstanding candidate for commercial surface acoustic wave (SAW) devices. However, a major disadvantage for polycrystalline AlN used in SAW devices is the existence of grain boundaries which increase insertion loss and pass band ripple. The main stream SAW filters choose LiNb(Ni)O₃ single crystalline wafer as the piezo-substrate at present. To realize the full potential of AlN in SAW devices, it is necessary to refrain the negative influences of the grain boundaries, which make high quality single crystalline or epitaxial AlN highly desirable. This presentation will talk about the results of a study on the SAW devices fabricated on epitaxial AlN thin films. The films were grown on (0001) sapphire substrates by molecular beam epitaxy and the devices were fabricated by lift-off processes which use photolithography and sputtering to produce patterned electrodes. The epitaxial AlN thin films have good material quality showing by the relatively small full width of half maximum value of XRD (0002) rocking curve of around 100 arcsec and the small roughness of 1.8 nm. The SAW devices with center frequencies of 355 MHz and 714 MHz both exhibit much suppressed pass band ripples and improved out of band rejections comparing to those on polycrystalline thin films. It is therefore verified that the epitaxial form of AlN is better suited for high quality SAW devices.

EP01.03.04

Atomic-Scale Growth of GdFeO₃ Perovskite Thin Films by a Novel Bimetallic Precursor Christoph Bohr¹, Pengmei Yu², Mateusz Scigaj², David Graf¹, Corinna Hegemann¹, Thomas Fischer¹, Mariona Coll² and Sanjay Mathur¹; ¹Institute of Inorganic Chemistry, University of Cologne, Cologne, Germany; ²Institut de Ciencia de Materials de Barcelona, ICMAB-CSIC, Campus UAB, Barcelona, Spain.

Multiferroic thin films of GdFeO₃ are of significant importance due to their G-type antiferromagnetic behaviour and thus potential candidates for magnetic storage devices. Fabrication of single-phase GdFeO₃ films is challenging due to demixing into homometallic oxides and formation of thermodynamically preferred Gd₃Fe₅O₁₂. Herein we report the first selective synthesis of epitaxial GdFeO₃ perovskite films through atomic layer deposition of a bimetallic precursor [GdFe(O^tBu)₂(C₅H₅N)₂] on SrTiO₃. Based on the preformed Gd-Fe bonds in the molecule, phase pure GdFeO₃ films were accessible by atomic layer deposition experiments. The suppression of phase separation was validated by X-ray diffraction and X-ray photoelectron spectroscopy. Furthermore, magnetic properties of the material were determined by temperature dependent magnetization measurements and demonstrated comparable results as reported for thin films. Based on these results, the presented bimetallic precursor is suitable for the fabrication of high performance magnetic data storage devices.

EP01.03.05

Morphology Control of Pb(Zr,Ti)O₃ Nanocrystals by Surfactant-Assisted Hydrothermal Method Yoko Takada¹, Ken-ichi Mimura¹ and Kazumi Kato²; ¹Inorganic Functional Materials Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Nagoya, Japan; ²National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan.

Lead zirconate titanate Pb(Zr,Ti)O₃ (PZT) is a ferroelectric material with excellent dielectric and piezoelectric properties. PZT films have been prepared using various fabrication techniques such as sol-gel process, metal organic decomposition, and pulsed laser deposition. Recently, hydrothermal method has attracted increased attention because it could produce homogeneous and uniform nano-sized particles with high crystallinity without high temperature crystallization process. In this study, PZT particles were synthesized by a surfactant-assisted hydrothermal method and the effect of the surfactant on the morphologies of the PZT particles was investigated.

PZT particles were synthesized from lead acetate trihydrate and water-soluble zirconium and titanium complex aqueous solution by hydrothermal method. A high-alkaline medium and surfactant were added into the PZT precursor solution to dissolve the precursor source in the aqueous solution and to control the crystal growth, respectively. After hydrothermal reaction with stirring, PZT particles were separated from liquid phase and followed by rinsing and drying several times.

When the surfactant was not added into the reaction solution, large-sized PZT particles with rough surfaces were synthesized. On the other hands, nano-sized PZT particles with facet were synthesized by adding the surfactant and it was confirmed that the added surfactant had the effect of inhibiting the growth of the certain faces of particles. The simple spot pattern in the electron diffraction pattern revealed that this nano-sized PZT particle synthesized by the surfactant-assisted hydrothermal method at 230°C had high crystallinity and it was a single crystal. Unlike conventional fabrication techniques with high temperature crystallization process above 600°C, PZT nanocrystals with high crystallinity were obtained by the surfactant-assisted hydrothermal synthesis.

EP01.03.06

Fabrication of Ferroelectric CeO₂-HfO₂ Solid Solution Thin Films and Their Characterization Takahisa Shiraishi¹, Sujin Choi¹, Takao Shimizu², Takanori Kiguchi¹, Hiroshi Funakubo² and Toyohiko Konno¹; ¹Tohoku University, Sendai, Japan; ²Tokyo Institute of Technology, Yokohama, Japan.

HfO₂-based materials are fluorite-type oxide and were well known as multifunctional materials. In recent years, ferroelectricity has discovered just in HfO₂-based thin films with a metastable orthorhombic phase (*O*-phase), and these materials have attracted much attention as novel ferroelectrics.

Especially, ZrO₂-HfO₂ solid solution thin films with *O*-phase showed the excellent ferroelectric properties and a wide process window.

CeO₂-HfO₂ solid solutions had been applied to various devices as high-k dielectrics. Therefore, from the viewpoint of multi-functionality, it is important to fabricate CeO₂-HfO₂ solid solution thin films with *O*-phase. In this study, we report on the successful growth of (001)-oriented epitaxial ferroelectric HfO₂-CeO₂ solid solution thin films.

20 nm-thick CeO₂-HfO₂ films were deposited on (100)YSZ substrates by ion-beam sputtering method. The deposition temperature and atmosphere were maintained at room temperature and Ar, respectively. After that, the deposited films were annealed at 900 °C for 10 min in N₂ atmosphere. Film composition was controlled by change the concentration of CeO₂ in sputtering target. The crystal structure of deposited films was investigated by XRD measurement and S/TEM observation, and the electrical properties were investigated using impedance analyzer and ferroelectric tester.

From XRD measurements, it was found that the obtained films were solid-solution because the diffraction peak derived from films shifted to low 2θ angle with increasing CeO₂ concentration. In addition, all films were epitaxially grown on (100)YSZ substrates. STEM observation revealed that CeO₂-HfO₂ films had multidomain structures composed of *O*-phase and a stable monoclinic phase. In fact, *P-E* hysteresis loops caused by ferroelectricity were clearly observed at optimum CeO₂ concentration, and the maximum remanent polarization was about 10 $\mu\text{C}/\text{cm}^2$.

This research was supported by Japan Society for the Promotion of Science (JSPS) KAKENHI Grant No. 17J03160, 16K18231, 16K14378, 18H01701. And a part of this work was also supported by Nippon Sheet Glass Foundation for Materials Science and Engineering.

EP01.03.07

Engineering Domain and Superdomain Architectures in PbTiO₃ Thin Films Eric Langenberg¹, David Bugallo Ferrón², Megan E. Holtz^{1,3}, Hanjong Paik¹, Elias Ferreira-Vila², Eva H. Smith¹, Hari P. Nair¹, David Muller³, Gustau Catalan⁴, Neus Domingo⁴, Francisco Rivadulla² and Darrell G. Schlom^{1,5}; ¹Department of Materials Science and Engineering, Cornell University, Ithaca, New York, United States; ²CiQUS-University of Santiago de Compostela, Santiago de Compostela, Spain; ³School of Applied and Engineering Physics, Cornell University, Ithaca, New York, United States; ⁴Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC, Barcelona Institute of Science and Technology, Bellaterra, Barcelona, Spain; ⁵Kavli Institute at Cornell for Nanoscale Science, Ithaca, New York, United States.

The engineering of nanoscale ferroelastic structures has attracted significant attention in the last few years. These nanostructures are reconfigurable and non-volatile, making them attractive for applications that harness the changes in electronic properties that arise at the ferroelectric-ferroelastic domain walls or novel (nano-)electromechanical devices based on ferroelastic switching. Here, we study the interplay between epitaxial strain, film thickness, and electric field in the creation, modification, and design of distinct ferroelectric-ferroelastic domain and superdomain architectures in the archetype ferroelectric PbTiO₃.

PbTiO₃ thin films, with thicknesses between 20 and 75 nm, were grown on SrTiO₃, DyScO₃, TbScO₃, and GdScO₃, SmScO₃ and PrScO₃ substrates by reactive molecular-beam epitaxy, spanning strains from -1.36% compressive to +1.54% tensile. X-ray diffraction, scanning transmission electron microscopy and piezoresponse force microscopy (PFM) were used to probe the evolution of the ferroelectric domains in PbTiO₃ as functions of both epitaxial strain and film thickness. In addition, the conducting PFM tip was used to apply a dc bias voltage to assess the reconfigurability of the ferroelastic structures and study their stability over time.

Our results show that for large compressive strain pure *c*-domains PbTiO₃ thin films are obtained. On reducing the compressive strain, a gradual increase in the population of *a*-domains embedded in a matrix of *c*-domains takes place, giving rise to *a/c* domain architectures; the density of domain walls increases on reducing compressive strain. For tensile strains a competing scenario of *a/c* and *a₁/a₂* superdomains (ferroelastic structures formed by individual domains) is found; the ratio between both populations can be tuned by varying strain and thickness, enabling the superdomain architecture to be engineered at will. Furthermore, superdomains behave as independent entities; their size dramatically increases with thickness (reducing the superdomain wall density), in a similar fashion as individual ferroic domains behave in ferromagnetic, ferroelectric, and ferroelastic materials.

Applying an out-of-plane dc biased voltage to the domain and superdomain patterns reveals that the ferroelastic structures in PbTiO₃ are electrically very malleable, especially when *a/c* and *a₁/a₂* superdomains coexist. For example, a vertical electric field fully converts the as-grown superdomain architecture into *a/c* superdomains. Moreover, depending on the ferroelectric switching of the individual *c*-domains, ordered *a/c* superdomains can be achieved. The stability, however, of the electrically written *a/c* superdomain structures strongly depends on strain: under low tensile strain they are stable for days, whereas at moderate tensile strains they rapidly convert into *a₁/a₂* superdomains—the same equilibrium state as the as-grown films.

EP01.03.08

Fabrication and Properties of Multiferroic Composites by PLD for Voltage-Driven Magneto-Optic Spatial Light Modulator Yuichi Nakamura¹, Naohide Kamada¹, Taichi Goto^{1,2}, Hironaga Uchida¹ and Mitsuteru Inoue¹; ¹Toyohashi University of Technology, Toyohashi, Japan; ²JST PRESTO, Kawaguchi, Japan.

Spatial light modulators (SLMs) are devices to control the amplitude, phase and polarization of light and are an important component of such as optical communication and optical computing systems. Magneto-optic SLM (MOSLM) using Faraday rotation can modulate light through the direction of magnetization with ultra-high speed and robustness. A voltage-driven MOSLM, which is composed of piezoelectric and magnetic materials, can be driven with relatively low power consumption. The structure in which columnar magnetic materials are embedded in the piezoelectric material is expected to increase the modulation of light easily by increasing the thickness. In order to apply this structure to MOSLM, simultaneous growth of the piezoelectric material such as PbZr_{0.52}Ti_{0.48}O₃ (PZT) and BaTiO₃ (BTO) and a magnetic rare earth iron garnet (Bi:RIG) is needed. In this study, we investigated the growth conditions for obtaining the aligned BTO film on nonmagnetic single crystalline Gd₃Ga₅O₁₂ (GGG) substrate and Bi:RIG/BTO composites.

At first, we checked several materials which can grow epitaxially on GGG substrate by pulsed laser deposition (PLD) method since it would be required to form columnar structure by simultaneous growth technique. As a result, we found that the (111) aligned CoFe₂O₄ (CFO) film could be grown on GGG (111) substrate. Furthermore, the BTO film preferentially oriented in the (111) plane could also be grown on CFO buffered GGG (111) substrate. Pole figure analysis of this sample revealed that the (111) oriented BTO film has two in-plane orientations in the plane. This means that this aligned film of BTO on CFO/GGG is not single crystalline feature but polycrystal with two specific crystal alignments. However this would not be a crucial issue to grow columnar structure by simultaneous growth; the relation between BTO and Bi:RIG crystal at the interface may be kept since the columnar size is usually several 10 to 100 nm order and would be smaller or comparable to the that of BTO grain. The detail about the composite films of BTO and Bi:RIG using this CFO buffered GGG substrate will be discussed. This work was supported in part by the Grants-in-Aid for Scientific Research (S) 26220902, (B) 16H04329 and Strategic international research network promotion program No. R2802

EP01.03.09

Structural, Magnetic and Electrical Characterization of Nanoscale Ba(Ti_{1-x}Fe_x)O₃—Stoichiometric Control Over a Multiferroic Oxide Using a Near-Room Temperature Non-Aqueous Synthesis Method Julien Lombardi¹, Stephen O'Brien¹ and Zheng Gai²; ¹City College of New York, New York, New York, United States; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Low temperature chemical solution processing of nanocrystalline perovskite oxides can be attractive due to the ability to (i) enable precise control over stoichiometry and structure in the product and (ii) offer thin film integration options in device electronics for which high temperatures are not suitable. Ba(Ti,Fe)O₃ is a useful system for the exploration of multiferroic properties as a function of structure, based upon a model of intersubstitution of the B site cation. A series of iron-substituted barium titanate nanocrystals were synthesized using a hybrid sol-gel synthesis method, known as gel-collection, at 60°C. The as-prepared nanocrystals are fully crystalline, uniform in size (~8 nm) and dispersible in polar organic solvents. The synthesis method could effectively control Fe substitution over a full range of $x = 0, 0.1, 0.2, 0.3, 0.5, 0.75$ and 1.0 , enabling a systematic study of the relative effect of Fe addition to the parent BaTiO₃ compound. In the case of $x = 0.0-0.3$, a model of Fe doping suffices with predictable trends in magnetic and dielectric behavior. In the case of $x = 0.5$ and up, Fe impacts the structure. Powder X-ray diffraction (XRD) initially indicated single phase nanocrystalline samples for $x < 0.3$. PDF analysis... size and morphology of the nanocrystals was analyzed by the transmission electron microscope (TEM) showing uniform shape and size (~8 nm) nanocrystals. Magnetic characterization (both magnetic hysteresis loops and zero field and field cooling measurements) was carried out on a magnetic

properties measurement system (MPMS) and showed increased magnetization with increasing Fe ion concentration. Frequency dependent dielectric measurements were performed at room temperature on spin coated 0-3 nanocomposites of BFT and polyvinyl-pyrrolidone and show stable dielectric constants at 1 MHz of 27.0, 26.0, 24.6, 24.5, 23.6, and 22.2 for BFT samples with $x = 0, 0.1, 0.2, 0.3, 0.5,$ and 0.75 concentrations respectively. The decrease in dielectric constant with increasing Fe concentration is due to the contribution of the electrons in the d orbital leading to a more leaky material.

EP01.03.10

Engineering Growth of Magnetostrictive Thin Films by Pulsed Laser Deposition for Magnetoelastic Coupled Future Voltage Controlled Spintronic Devices [Rajesh Kumar Rajagopal](#)¹, J. Arout Chelvane² and Venimadhav Adyam¹; ¹IIT Kharagpur, West Bengal, India; ²Defence Metallurgical Research Laboratory, Hyderabad, India.

Multiferroic devices, consisting of coupled ferromagnetic and ferroelectric phases, are of great importance in the drive towards creating faster, smaller and more energy efficient voltage control magnetic random access memory (MRAM) devices for information storage and communication technologies. Such devices require a strong magnetoelastic coupling between the ferromagnetic and the ferroelectric interface, this is obtained by using large magnetostriction materials as a ferromagnetic layer. Magnetostrictive Fe based amorphous alloys of $\text{Fe}_{70.2}\text{Co}_{7.8}\text{Si}_{12}\text{B}_{10}$ (FeCoSiB) and $\text{Fe}_{81}\text{Ga}_{19}$ (GdFe) amorphous alloys are of great interest for their ultrahigh saturation magnetization, low coercivity, and high magnetic permeability.

Wide varieties of the growth techniques are available for the fabrication of thin films, among the methods, pulsed laser deposition (PLD) is a thin film growth technique which has the advantage of stoichiometric transfer of the elements on to the substrate. By understanding the growth of amorphous thin film by PLD has the advantage of the in-situ growth of high quality epitaxial ferroelectric materials are grown at high temperature, and magnetostrictive materials can be grown on top of the ferroelectric thin film.

In this present study, we have prepared the highly magnetostrictive FeCoSiB and GdFe thin films deposited on the Si substrate using PLD. The prepared films show the soft ferromagnetic property with coercivity of 25 Oe as given in the Fig. 1(a). Pulsed laser deposition induced uniaxial anisotropy in the GdFe thin shown in Fig. 1(b). The thickness dependent composition variation of the thin film was analysed using Auger electron spectroscopy. We also present the growth of this alloy on oxide substrates, magnetotransport characteristics and magnetic domain structure by Magnetic force microscopy (MFM).

EP01.03.11

Growth of Orientation-Controlled (K,Na)NbO₃ Thick Films at 240°C by Hydrothermal Method and Their Piezoelectric Applications [Hiroshi Funakubo](#)¹, Akinori Tateyama¹, Yoshiharu Ito¹, Yoshiko Nakamura¹, Takao Shimizu¹, Yuichiro Orino¹, Minoru Kurosawa¹, Hiroshi Uchida², Takahisa Shiraishi³, Takanori Kiguchi³, Toyohiko Konno³ and Nobuhiro Kumada⁴; ¹Tokyo Institute of Technology, Yokohama, Japan; ²Sophia University, Tokyo, Japan; ³Tohoku University, Sendai, Japan; ⁴Yamanashi University, Koufu, Japan.

(K, Na)NbO₃ has a relatively high piezoelectric property among lead-free piezoelectric materials with high environmental adaptability. Their films have been prepared by various methods. Hydrothermal method can prepare (K, Na)NbO₃ films at low temperature [1-3] and possible to control film composition that has been pointed out to be difficult for various preparation methods due to high deposition temperature and vapor pressure of K and Na elements. In this study, orientation-controlled (K,Na)NbO₃ films with 1-100 μm in thickness were prepared by hydrothermal method and their crystal structure, electrical properties, and piezoelectric properties were investigated.

{100}-oriented (K_{0.8}Na_{0.2})NbO₃ thick films up to 17 mm in thickness in one batch was achieved at 240°C on SrRuO₃-coated SrTiO₃ substrates and totally 100 mm-thick films were obtained by repeating this process. Well saturated hysteresis loops were obtained after the post annealing at 600 °C and the obtained remanent polarization and coercive field of 2 μm-thick films were 6 μC/cm² and 30 kV/cm, respectively. The effective piezoelectric coefficient measured using cantilever, e_{31f} , was -9.2 C/m². This value is one of the largest value for (K,Na)NbO₃ films deposited on single crystal substrates. This hydrothermal process also possible to direct prepare piezoelectric (K,Na)NbO₃ films at 120°C on organic substrates.

This research was partially supported by Japan Science and Technology Agency (JST), Adaptable and Seamless Technology transfer Program through Target-driven R&D (A-STEP).

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EP01.03.12

Ferrimagnetism and Ferroelectricity in Ga_{0.5}Cr_{0.5}FeO₃ Epitaxial Thin Films [Tsukasa Katayama](#)¹, Shintaro Yasui² and Mitsuru Itoh²; ¹The University of Tokyo, Tokyo, Japan; ²Tokyo Institute of Technology, Tokyo, Japan.

Multiferroic materials which exhibit both ferroelectric and ferromagnetic properties have attracted considerable attentions. GaFeO₃-type iron oxide is one of promising multiferroic materials due to the large spontaneous magnetization and polarization near room temperature. However, magnetic substitution is difficult due to instability of the substituted GaFeO₃. In this study, we successfully fabricated Ga_{0.5}Cr_{0.5}FeO₃ epitaxial thin films through epitaxial stabilization. These films simultaneously exhibit in-plane ferrimagnetism and out-of-plane ferroelectricity. X-ray absorption spectroscopy and X-ray magnetic circular dichroism measurements of the Ga_{0.5}Cr_{0.5}FeO₃ film reveal that the valence states of the Fe and Cr ions are trivalent, and some Fe ions are located at the T_d Ga1 sites in the Ga_{0.5}Cr_{0.5}FeO₃ film. The Ga_{0.5}Cr_{0.5}FeO₃ film shows a unique temperature dependence of the magnetization behavior with a higher Curie temperature (240 K) as compared to the GaFeO₃ film. The effects of Cr substitution on the magnetic properties are strongly affected by the sites of the Fe³⁺ ($3d^5$) and Cr³⁺ ($3d^3$) ions. Furthermore, the films show ferroelectricity at room temperature. Interestingly, the change in the ferroelectric parameters via Cr substitution is very little, which disagrees with the previously proposed polarization switching mechanism. Our findings would be key to understand genuine polarization switching mechanism of the multiferroic GaFeO₃ system.

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EP01.03.13

Mechanical Induced Aligned P(VDF-TrFE) Fibers via Electrospinning for Wearable Motion Sensing [Shaoyang Ma](#) and Lei Wei; Nanyang Technological University, Singapore, Singapore.

Polymer piezoelectric materials are widely used in wearable smart devices as they are flexible lightweight, stretchable, environment-friendly and chemically stable, and poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) is a representative piezoelectric polymer. To construct piezoelectric polymer fibers, electrospinning is a versatile technique. Compared to randomly distributed electrospun fibers, aligned P(VDF-TrFE) fibers possess better electrical properties and larger response to mechanical stimuli. Here, we demonstrate a simple dynamical mechanical induced process which enables the formation of large-scale highly aligned electrospun P(VDF-TrFE) fibers obtained under low rotation speed. And the resultant fibers exhibit enhanced mechanical and piezoelectric properties and can be further used as wearable motion sensors.

We collect the initial P(VDF-TrFE) fiber using low speed rotating drum. The as-spun P(VDF-TrFE) fibers still contain residual solvent, thus they are easy

to deform under applied external force. The electrospun P(VDF-TrFE) thin film is then peeled off the aluminum foil and mounted in the clamps of a linear travel stage driven by a controller for the following mechanical stretching process. As a result, the initial orientations can be globally unified, which leads to the realignment of a large amount of electrospun P(VDF-TrFE) into highly oriented fiber bundles.

The strain and stress curves are measured to investigate the mechanical properties. With the increasing of aligned fiber proportion, the electrospun P(VDF-TrFE) fibers can withstand larger external stress under the same strain, which means the shape change of better aligned electrospun P(VDF-TrFE) fibers is smaller than its random distributed counterpart under the same applied tension. This advantageous mechanical property makes highly aligned P(VDF-TrFE) fibers more suitable for wearable motion sensors. But electrospun P(VDF-TrFE) fibers with alignment proportion exceeding 90% show poorer mechanical endurance.

Then, the electrical property is characterized. The electrical response first increases with the increase of aligned fiber proportion, which is agreed with the simulation study using COMSOL, but dropped when the fibers are highly paralleled (aligned fiber proportion > 80%). The highest output of 84.92 mV is achieved by P(VDF-TrFE) fibers with ~80% aligned proportion, about 266% of their randomly distributed counterpart (31.92 mV).

The ~80% aligned P(VDF-TrFE) fibers are further twisted into bundles and yarns and made into wearable sensors to monitor the bending angle of the elbow. The output signal for bending 45°, 90°, and 135° are 10.6 mV, 20.3 mV, and 42.5 mV, respectively. Furthermore, multiple P(VDF-TrFE) fiber bundles can be used in a combined way to monitor the direction of arm swing.

EP01.03.14

Scandium Nitride Thin-Film Wetting Layers for Aluminum Scandium Nitride Films Deposited on Sapphire by Reactive Magnetron Sputtering Zachary J. Biegler^{1,2}, Hadley A. Smith^{1,3}, Rachel L. Adams^{1,4}, Kurt Eyink^{1,4}, Brandon M. Howe¹, John S. Cetnar⁵, Madelyn J. Hill¹, Andrew M. Sarangan² and Amber N. Reed¹; ¹Materials and Manufacturing Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio, United States; ²Electro-Optics and Photonics, University of Dayton, Dayton, Ohio, United States; ³Physics, University of Dayton, Dayton, Ohio, United States; ⁴Mechanical Engineering, University of Dayton, Dayton, Ohio, United States; ⁵Sensors Directorate, Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio, United States.

Throughout recent years, transition metal nitrides (TMNs) have garnered increased interest due to applications in optoelectronics and plasmonics due to high chemical and thermal stability, a wide range of material properties, the ability to influence film characteristics by varying deposition parameters, and the ability to alloy TMNs together to tune desired properties. One such material is aluminum nitride, a piezoelectric material with a high temperature stability and thermal conductivity but a somewhat lackluster piezoelectric coefficient. Nonetheless, by alloying AlN with scandium, one may increase the piezoelectric coefficient of AlN by a factor of 3.25. [1]. This increase is limited by the phase transition of Al_{1-x}Sc_xN from hexagonal to cubic at scandium concentrations greater than x = 0.43 [1]. Growth of single crystal, epitaxial Al_{1-x}Sc_xN thin films has proven challenging due to the tendency of AlN to not effectively wet to the Al₂O₃ substrate surface. One possible solution is to deposit a thin wetting layer between the AlN and the substrate. ScN was chosen as a possible wetting layer between the Al₂O₃ substrate and the Al_{1-x}Sc_xN film due to previous success of single crystal, epitaxial growth of ScN (111) on Al₂O₃ (0001), the inclusion of Sc in the Al_{1-x}Sc_xN film, the possible use of ScN as a bottom contact to the piezoelectric Al_{1-x}Sc_xN film, and the similarity between lattice constants of ScN (111) and AlScN (0001). However, multiple domains of ScN can form due to the cubic nature of ScN films growing on the hexagonal Al₂O₃ substrate, possibly interfering with the desired growth of Al_{1-x}Sc_xN. As such, a thickness suite of ScN thin films ranging from less than an nanometer to up to 10nm were grown through controllably unbalanced magnetron sputtering. These films were examined through x-ray diffraction (XRD), atomic force microscopy (AFM), and spectroscopic ellipsometry in order to determine what thickness of ScN would produce the least amount of these domain variances. Preliminary XRD coupled scans show highly oriented ScN on Al₂O₃ with glancing angle scans showing no additional phases present in the ScN film. AFM surface analysis showed root mean square (RMS) roughness between 0.430nm and 0.911nm for films between 0.5nm and 10nm, corresponding to one to two monolayers of roughness. Additionally, thin films of Al_{1-x}Sc_xN films were deposited both on bare substrate and with the additional ScN wetting layer, at similar thicknesses to the ScN thin films. These were also characterized using XRD, AFM, and spectroscopic ellipsometry to determine the effect of the ScN thickness and domains on the Al_{1-x}Sc_xN film crystallinity and piezoelectric properties.

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EP01.03.15

Magnetron Sputter Deposition of Pyroelectric PZT Thin Films—From Simulation to Experiment Peter K. Petrov¹, Andrey Berenov¹, Ryan Bower¹, Sarah Fearn¹, Roger Whatmore¹, Lars Allers², Philippa Stephens², Brian Moffat³, John Phair³, Valery Volpyas⁴ and Andrey Kozyrev⁴; ¹Imperial College London, London, United Kingdom; ²Korvus Technology Ltd, Newington, United Kingdom; ³Pyreos Ltd, Edinburgh, United Kingdom; ⁴St Petersburg Electrotechnical University “LETI”, St Petersburg, Russian Federation.

Thin films of lead zirconate titanate (PbZr_xTi_{1-x}O₃ - PZT) are of considerable interest for a range of applications, including piezoelectric MEMS (with x=0.52) and pyroelectric thermal IR sensing (with x=0.30 [1]). Thin films of PZT (x=0.15 to 0.42) have in the past been grown onto platinumized Si substrates by sputtering from multiple metal targets [2], but there are considerable technological benefits to deposition from a single ceramic target [3].

This paper will discuss the process of magnetron sputter deposition of PZT thin films from a single ceramic target. We used Monte-Carlo simulation method based on the algorithm, presented in [4], to describe the sputter atoms transport process and their delivery on the substrate. The modeling was carried out taking into account the geometry and dimensions of the deposition system, and the sputter target erosion zone. A complementary SIMS analysis of the PZT sputter target was carried out to identify the type of sputtered particles (e.g. single atoms, binary compound, clusters), which were further used in the simulation process.

Finally, we will present the structural and electrical properties of the sputtered PZT films (e.g. crystal structure, stoichiometry, dielectric permittivity, loss, pyroelectric coefficient etc.) and discuss their dependence on the existence of particular species in the gas phase during the sputtering process.

Acknowledgements

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EP01.03.16

Initiated Chemical Vapor Deposition (iCVD) of Multilayered P(VDF-TrFE) Thin Films—Controlling the Chemical Composition Along the

Thickness Omid M. Moradi¹, Ali Tufani¹, Gozde Ozaydin Ince^{1,2,3} and Ibrahim B. Misirlioglu^{4,5,2}; ¹Materials Science and Nanoengineering, Sabanci University, Istanbul, Turkey; ²Nanotechnology Research and Application Center (SUNUM), Sabanci University, Istanbul, Turkey; ³Center of Excellence for Functional Surfaces and Interfaces (EFSUN), Sabanci University, Istanbul, Turkey; ⁴Faculty of Engineering and Natural Sciences, Sabanci University, Istanbul, Turkey; ⁵Integrated Manufacturing Technologies Research and Application Center, Sabanci University, Istanbul, Turkey.

Fabrication of ferroelectric polymers at lower temperatures, thickness control and film conformality in polymeric multilayer structures are required for full integration of the ferroelectric polymers to the modern integrated devices. Also, designing of multilayer ferroelectric films requires precise control over the deposition parameters.

We use Initiated Chemical Vapor Deposition (iCVD) method to deposit 10-30 nm ferroelectric layers and fabricate multilayer poly [(vinylidene fluoride-co-trifluoroethylene) P(VDF-TrFE)] thin films. We control the thickness of the layers and control the chemical composition in each layer along the thickness. Also, the change in dielectric constant and dielectric loss at moderately low and high frequencies for each multilayer configuration will be discussed. Hence, we report the frequency dependence of dielectric constant, loss tangent, imaginary electric modulus of multilayered thin films.

EP01.03.17

Multiferroic Polarons in Doped Perovskite Oxides Takahiro Shimada, Tao Xu, Takayuki Kitamura and Hiroyuki Hirakata; Kyoto Univ, Kyoto, Japan.

Control over the electron behaviors is essential for the quest of the unusual coexistence of seemingly conflicting physical properties in condensed matter science. Although the coexistence of ferroelectricity, conductivity and magnetism in a single-phase material has attracted considerable attention due to the fundamental interest and tremendous technological promise, the mutually exclusive mechanisms among them hinder the discovery of multifunctional conducting multiferroics. Here, we propose a novel material design approach for electron engineering, by which we realize an unusual coexistence of these conflicting properties. We demonstrate from first-principles that the appropriate mechanical strain turns the excess electrons in doped BaTiO₃ from free carrier configuration to localized polaronic state through the modulation of electron-phonon coupling. The resulting localized spin-polarized electron survives the host ferroelectricity and consequently manifests itself as multiferroic polaron. The multiferroic properties coexist with the electronic conductivity arising from high hopping mobility of polaron, and thus enable the doped epitaxial BaTiO₃ to act as multiferroic conducting material. This mechanical control over electron configuration opens up a new possibility for unusual coexisting properties and new technologies.

EP01.03.18

Theoretical Prediction of Piezoelectric and Thermodynamic Stability of New LiNbO₃-type Al(Sc,In,Tl)O₃ Kaoru Nakamura; CRIEPI, Yokosuka, Japan.

LiNbO₃ structure, belongs to the space group of R3c, is frequently referred as “strained perovskite structure”. Recently, many compounds have found to be possible to form LiNbO₃-type structure under the high-pressure condition, and some of them were quenchable phase. By systematic first-principles prediction of piezoelectricity and phase stability of possible combination of A-site and B-site ions, we have found new Al-based LiNbO₃-type piezoelectric materials. Dynamical stability analysis on AlScO₃, AlInO₃ and AlTlO₃ showed no unstable phonon mode. Formation energies of each compound were predicted to show negative value at high pressure. Predicted piezoelectric constants e_{33} and d_{33} of each compound were larger than those of LiNbO₃. Especially, e_{33} and d_{33} values of AlTlO₃ were anomalously large to be 10.7 C/m² and 56.6 pC/N. By utilizing the formalism of density functional perturbation theory, piezoelectric constants of each compound were decomposed into elastic and dielectric contribution from each atom. As a result, large piezoelectricity of Al(Sc,In,Tl)O₃ was found to be originated in the large strain-displacement coupling.

EP01.03.19

Effects of Structure Parameters on Piezoelectricity in Wurtzite Materials—First-Principles and Statistical-Learning Calculations Hiroyoshi Momida and Tamio Oguchi; Osaka Univ, Osaka, Japan.

Piezoelectric wurtzite materials such as ZnO and GaN have recently received a lot of attention as piezotronics and piezo-phototronics device materials. The wurtzite-type piezoelectric materials, especially AlN, have another advantage of applicability in high-temperature environments such as sensors in automobile engines, because their noncentrosymmetric crystal structures are thermodynamically stable even at high temperatures. However, the piezoelectric constants of wurtzite-type materials are generally much smaller than those of the perovskite-based materials such as Pb(Zr_xTi_{1-x})O₃ by a few orders. It remains a challenge to explore better piezoelectric wurtzite materials, and there have been many reports aiming to enhance piezoelectricity by element doping into parent materials. Among the wurtzite materials, the highest piezoelectricity has been experimentally discovered for Sc_xAl_{1-x}N (about 25 pC/N for $x \sim 0.5$). Novel low-cost materials, which are superior to Sc_xAl_{1-x}N, have not been synthesized yet as there are no clear and general materials-design criteria practically usable for enhancing the piezoelectricity of wurtzite materials.

In this study, we calculate longitudinal piezoelectric constants (e_{33}) of more than a dozen binary wurtzite materials, which are listed in a structure database, by using the first-principles methods, and we investigate possible correlations between the piezoelectric constants and several material parameters using the statistical-learning methods [1]. As a result, it is theoretically shown that wurtzite materials with high e_{33} generally have small lattice constant ratios (c/a) almost independent of constituent elements, and approximately expressed as $e_{33} \propto c/a - (c/a)_0$ with ideal lattice constant ratio $(c/a)_0$. We find that this relation also holds for highly-piezoelectric ternary materials such as the calculated e_{33} values of Sc_xAl_{1-x}N [2]. Therefore, this material-design criterion can be applicable to the case in doped ternary materials. We have conducted a computational search for high-piezoelectric wurtzite materials by identifying materials with smaller c/a values. It is theoretically proposed that the piezoelectricity of ZnO can be significantly enhanced by partial substitutions of Zn with Ca. Though the calculated value of e_{33} of Ca_xZn_{1-x}O is still smaller than that of Sc_xAl_{1-x}N, we expect that Ca_xZn_{1-x}O is at a definite advantage in materials cost and natural abundance of constituent elements.

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EP01.03.20

Physical Reality of the Preisach Model for Organic Ferroelectrics Tim Cornelissen¹, Indre Urbanaviciute¹, Xiao Meng², Rint Sijbesma² and Martijn Kemerink¹; ¹Linköping University, Linköping, Sweden; ²Eindhoven University of Technology, Eindhoven, Netherlands.

Since the seminal work by Ferenc Preisach in 1935, the so-called Preisach model, in which a real, non-ideal ferroic material is described as the sum of a distribution of ideal ‘hysteresons’, has been a cornerstone in the fields of ferromagnetism and ferroelectricity. However, the physical reality of the model in ferroelectrics has been hard to establish, limiting its further applicability and utility. Here, we show how an experimental Preisach distribution-based analysis can quantify the energetic disorder and elucidate the concomitant dispersive polarization switching kinetics common for different classes of ferroelectrics.

We experimentally determine the Preisach (hysteron) distribution for two differently structured ferroelectric systems, the liquid crystalline

benzenetricarboxamide (BTA) and the polycrystalline copolymer P(VDF-TrFE). For BTA a broad circular distribution is found, in contrast to the narrow elliptical distribution for P(VDF-TrFE). We explain how this broadening can be directly related to the materials' morphology: in BTA the ferroelectric domains consist of strongly interacting columns, while P(VDF-TrFE) consists of non-interacting crystallites. Our explanation is supported by simulations using a simple electrostatic model. The offered insight in the shape of the Preisach distribution is especially relevant for ferroelectric multi-bit data storage applications.

The model also provides an explanation for the dispersive switching kinetics observed in most ferroelectrics, and the underlying distribution in switching times. By measuring the switching kinetics of discrete parts of the Preisach plane, we can directly extract this distribution. The combination of the Preisach model, the thermally-activated nucleation-limited switching formalism and the adapted Kolmogorov-Avrami-Ishibashi theory provides a full and consistent description of the measured macroscopic switching kinetics in terms of device morphology and energetic disorder.

Our results reveal that the in principle mathematical construct of the Preisach model has a strong physical basis and is a powerful tool to explain polarization switching processes of different types of ferroelectrics.

EP01.03.21

First-Principles Calculations of Lattice Dynamics and Thermodynamic Properties of the New Pre-Perovskite PbTiO₃ Phase Mengjun Zhou^{1,2}, Yi Wang², Yanzhou Ji², Long-Qing Chen^{2,1} and Ce-Wen Nan¹; ¹School of Materials Science and Engineering, State Key Lab of New Ceramics and Fine Processing, Tsinghua University, Beijing, China; ²Department of Materials Science and Engineering, The Pennsylvania State University, State College, Pennsylvania, United States.

Recently, the emergence of pre-perovskite PbTiO₃ nanowires have attracted increasing research interests. In this work, systematic first-principles calculations were performed to investigate the lattice dynamics and thermodynamic properties of the new pre-perovskite PbTiO₃ phase. The stability of pre-perovskite PbTiO₃ at finite-temperature was analyzed in terms of the lattice contribution, and its thermodynamic properties were obtained and compared with those of cubic and tetragonal PbTiO₃. The pressure-temperature phase diagram for these three types of PbTiO₃ was established, indicating that pre-perovskite PbTiO₃ can be stable under negative pressure. These theoretical insights are useful for understanding the origin of phase transitions among pre-perovskite, traditional cubic and tetragonal PbTiO₃ phases, hence providing meaningful guidance for future experimental study and potential applications of pre-perovskite PbTiO₃.

EP01.03.22

A Rhombohedral Ferroelectric Phase in Epitaxially-Strained Hf_{0.5}Zr_{0.5}O₂ Thin Films Yingfen Wei¹, Pavan Nukala^{1,4}, Mart Salverda¹, Sylvia Matzen², Hongjian Zhao³, Jamo Momand¹, Arnold S. Everhardt¹, Graeme R. Blake¹, Philippe Lecoeur², Bart J. Kooi¹, Jorge Íñiguez², Brahim Dkhil⁴ and Beatriz Noheda¹; ¹University of Groningen, Groningen, Netherlands; ²Center for Nanoscience and Nanotechnology, Université Paris-Saclay, Paris, France; ³Materials Research and Technology Department, Luxembourg Institute of Science and Technology, Esch-sur-Alzette, Luxembourg; ⁴Laboratoire Structures, Propriétés et Modélisation des Solides, Université Paris-Saclay, Paris, France.

After decades of searching for robust nanoscale ferroelectricity that could enable integration into the next generation memory and logic devices, hafnia-based thin films have appeared as the ultimate candidate because their ferroelectric (FE) polarization becomes more robust as the size is reduced. This exposes a new kind of ferroelectricity, whose mechanism still needs to be understood. Towards this end, thin films with increased crystal quality are needed. We report the epitaxial growth of Hf_{0.5}Zr_{0.5}O₂ (HZO) thin films on (001)-oriented La_{0.7}Sr_{0.3}MnO₃/SrTiO₃ substrates. The films, which are under epitaxial compressive strain and are (111)-oriented, display large FE polarization values up to 34 μC/cm² and do not need wake-up cycling. Structural characterization reveals a rhombohedral phase, different from the commonly reported polar orthorhombic phase. This unexpected finding allows us to propose a compelling model for the formation of the FE phase. In addition, these results point towards nanoparticles of simple oxides as a vastly unexplored class of nanoscale ferroelectrics.

EP01.03.23

Mesoscopic Varistor Modelling Kyle Taylor and Erion Gjonaj; Institut für Theorie Elektromagnetischer Felder, Technische Universität Darmstadt, Darmstadt, Germany.

This newly developed modelling framework for the simulation of electric current flow in ZnO varistors is based on an equivalent circuit representation of the varistor microstructure where the grain boundaries are represented by nonlinear resistors in the circuit. The present approach extends on similar models introduced earlier by including the effect of mechanical stress on the grain boundary conductivity. This effect is based on the coupling between the semiconducting and the piezoelectric properties of ZnO. The stress-induced piezoelectric polarization modifies the interface charge at the grain boundaries. This changes the effective potential barrier and therefore leads to a stress induced modification of the current voltage characteristics of the grain boundary. The model used for the calculation of single grain boundary conductivities is based on the theory of Blatter et al. and Verghese et al.. It includes a self-consistent solution for the interface charge and for the potential barrier of the boundary, taking into account the local stress in the grain. Using the above model, the grain boundary potential barriers are parametrized with respect to voltage and piezoelectric charge density. Such tabulated data can be easily incorporated in the modeling of larger varistor structures. 2D and 3D varistor models are constructed using appropriate Voronoi tessellations as well as measurement data obtained by EBSD scans. The mechanical stress distribution within the material is calculated by FEM. The electrical resistance of each grain boundary is then determined according to the local voltage and piezoelectric polarization charge. Finally, the electric current flow patterns within the microstructure and the corresponding current-voltage characteristic of the bulk material are obtained by solving the nonlinear circuit equations for each applied voltage and mechanical stress condition of the sample. The simulated characteristics reveal a significant sensitivity of the bulk electrical conductivity to mechanical stress. Furthermore, the simulations demonstrate the current concentration effect in the voltage breakdown region. Further topics of interest, which have been addressed by the modeling, include the influence of microstructural inhomogeneities, the investigation of the properties of purposely tailored microstructures (such as sandwiched polycrystalline layers) and the influence of sintering temperature on residual stresses and varistor characteristics.

EP01.03.24

Improvement in Magnetic Properties by Coating Surfactants on M-Type Strontium Hexaferrite Tej P. Poudel¹, Deepa Guragain¹, Jeotikanta Mohapatra², Sunghyu Yoon³, J. Ping Liu² and Sanjay R Mishra¹; ¹Department of Physics and Material Science, University of Memphis, Memphis, Tennessee, United States; ²Department of Physics, The University of Texas at Arlington, Arlington, Texas, United States; ³Gunsan National University, Gunsan, Korea (the Republic of).

M-type SrFe₁₂O₁₉ were synthesized via auto consumption method and coating Polyvinylpyrrolidone (PVP) Polyethylene Glycol (PEG) and Cetyltrimethyl Ammonium Bromide (CTAB) on crystals of hexaferrite. The effects of PVP, PEG and CTAB on the formation, structure, morphology, magnetic and dielectric properties of the SrFe₁₂O₁₉ nanoparticles were studied. X-ray diffraction results show perfect match of phase of SrFe₁₂O₁₉. Morphological

changes including grain and lattice parameter were seen increased with coating. With the coating of PVP, PEG and CTAB, powder particles growth can be seen in hexagonal plates. Increase in saturation magnetization, M_s , remanence magnetization, M_r , and coercivity, H_c , with different surfactant was observed. A slight increase in Curie temperature (765 K) is observed for samples coating with CTAB as compared to that of sample prepared in absence of coating. These results can be taken as coating surfactant like PVP, PEG and CTAB act as a crystallization agents, controlling the nucleation and growth of $\text{SrFe}_{12}\text{O}_{19}$ crystal. The study shows good impact on the scope of improving magnetic properties of ferrites without substitution of metal ions.

EP01.03.25

A Tunable Piezoelectric MEMS Sensor for the Detection of Weak Magnetic Signals Florian Niekie¹, Simon Fichtner^{1,2}, Christine Kirchhof², Dirk Meyners², Eckhard Quandt², Bernhard Wagner^{1,2} and Fabian Lofink¹; ¹Fraunhofer Institute for Silicontechnology (ISIT), Itzehoe, Germany; ²Christian-Albrechts-Universität zu Kiel, Kiel, Germany.

Piezoelectric MEMS devices are well established in the field of filters, e.g. RF filters for communication applications. The modal behavior and thus the filter characteristics are strongly affected by the in-plane and out-of-plane geometry and are therefore controlled by the design. A post-fabrication adjustment is difficult and commonly made with irreversible processes far away from application conditions, for example modifying the residual stress in the resonating structure by annealing processes.

Here we present the study of a piezoelectric resonator, whose modal characteristics can be tuned using additional piezoelectric elements. This concept allows a flexible and reversible adjustment of the modal behavior in the application under operation conditions. The design is made of three parallelly-oriented mechanically-coupled fixed-fixed unimorph cantilevers. This allows using the outer cantilevers as actuators to vary the stress on the central unimorph structure. The resulting piezoelectric resonator exhibits a modal behavior which can be tuned by a DC voltage on the two additional piezoelectric elements. Devices have been fabricated using silicon technology on 8-inch wafers. A sputter deposited 1 μm thick AlN layer is used as active material. The suspended cantilevers have been realized from a poly-Si layer using backside release.

While the principle is generally applicable to achieve tunable piezoelectric MEMS filters, this study focuses on the use as magnetoelectric sensors for weak magnetic signals, e.g. for biomagnetic applications [1]. To achieve the sensitivity to a magnetic field, a magnetostrictive FeCoSiB layer is added on the unimorph structure. The piezoelectric and magnetostrictive layers build a magnetoelectric composite capable of converting a magnetic signal into an electrical signal via the mechanical coupling. The resonance of the cantilever structure is employed to enhance the mechanical response for certain frequencies and thus the electrical signal. The fabricated devices are used to study the fundamental relationship between sensitivity and stress in the resonator structure.

Several benefits of the presented tunable magnetoelectric sensor are anticipated. The frequency can be adjusted precisely to the magnetic signal in the measurement to get the highest benefit from the resonance effect. In addition, different measurements with varying signal frequencies can be addressed without having to change the sensor. Superimposed magnetic signals at different frequencies can be measured with a single sensor in a serial manner, due to the filter effect of the narrow-bandwidth resonance amplification.

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EP01.03.26

A First-Principles Study of the $\text{LaAlO}_3/\text{SrTiO}_3$ (111) Interface Taewon Min, Jinho Byun and Jaekwang Lee; Pusan National University, Busan, Korea (the Republic of).

The emergent discovery of two-dimensional electron gas (2DEG) at the $\text{LaAlO}_3/\text{SrTiO}_3$ (LAO/STO) heterostructure with n-type interface has attracted considerable attention over the past decade. Despite several mechanisms such as polar catastrophe, oxygen vacancy and cation intermixing have been suggested, the origin of 2DEG remains still unclear. Recently, unlike LAO/STO (001) interface, a wide 2DEG distribution have been reported at the LAO/STO (111) interface. According to the polar catastrophe, although the p-type 2DEG is expected at the LAO/STO (111) interface consisting of $[\text{Ti}]^{4+}/[\text{LaO}_3]^{3-}$ layers, the n-type 2DEG has been experimentally observed. Here, using a first-principles density functional theory calculations, we explore the origin of wide n-type 2DEG at LAO/STO (111) interface at the atomic scale. Compared with LAO/STO (001) interface, we find that the oxygen adsorption on the $[\text{Al}]^{3+}$ -terminated LAO (111) surface and following surface reconstruction play a key role in forming n-type 2DEG and the existence of critical thickness.

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EP01.03.27

Design and Fabrication of ZnO Nano-Architectures with High Piezoelectric Coefficient and Elastic Limit Seokjung Yun^{1,4}, Hoon Kim¹, Dahye Shin², Seongwoo Cho¹, Changdeuck Bae³, Dongchan Jang² and Seungbum Hong¹; ¹Department of Materials Science and Engineering, Korean Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); ²Department of Nuclear and Quantum Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); ³Department of Energy Science, Sungkyunkwan University, Suwon, Korea (the Republic of); ⁴Memory Business, Samsung Electronics Co., Ltd., Hwaseong, Korea (the Republic of).

Piezoelectric ceramics are used for sensors and actuators as they have high piezoelectric coefficient. However, due to the brittle nature of ceramics coming from the fact that the size of flaw or crack determines the ultimate strength and elastic strain limit, it is still a challenge to use them for flexible or stretchable devices. In this study, we introduce ZnO truss nanostructure which shows high piezoelectric coefficient confirmed by local piezoresponse map and high elastic limit measured by nano-indenter.

The photoresist SU8 was used for the template of ZnO truss structure via 3D photolithography. We used low temperature atomic layer deposition to coat the SU8 truss template with conformal ZnO thin film. The piezoelectric characteristics of the ZnO/SU8 composite truss were analyzed by Dual AC Resonance Tracking Piezoresponse Force Microscopy (DART-PFM) where the effective piezoresponse was 37.8 pm/V. This is almost three times larger than the piezoelectric coefficient reported for bulk ZnO (8 – 10 pm/V). The stress vs strain curve was measured by nano-indenter, and showed linear behavior up to ~4%, which is more than 10–20 times the strain limit of bulk ZnO. We expect that our novel ZnO truss nanostructure can serve as basic materials component for future haptic enhanced applications.

8:15 AM EP01.04.01

Switchable and Rectifying Conductivity in Molecular Ferroelectrics Indre Urbanaviciute, Tim Cornelissen and Martijn Kemerink; Linköping University, Linköping, Sweden.

The broken inversion symmetry in ferroelectric semiconductors causes the bulk photovoltaic effect. The same symmetry considerations predict a non-equivalence between electrical currents flowing parallel and anti-parallel to the polarization direction. While ferroelectrically-switchable current rectification in metal-ferroelectric-metal diodes has been observed due to interfacial phenomena like injection or tunneling barrier modulation, a coupling between bulk conductivity and polarization has not been observed. Here, we present a class of molecular ferroelectrics that show a polarization-dependent bulk conductivity.¹

We have synthesized disc-like semiconducting organic molecules that are functionalized with strong dipolar side groups.² These materials self-assemble into supramolecular polymers, which provides long-range polar order that supports collective ferroelectric behavior of the side groups, as well as charge transport through the stacked semiconducting cores.

We find that the ferroelectric polarization couples to the charge transport and leads to a bulk conductivity that is both switchable and rectifying. When sweeping the applied electric field, the conductivity is switched from a high to low state at the ferroelectric coercive field. Detailed analysis of the current-voltage curves shows that the current is a combination of Ohmic and space-charge-limited currents. This demonstrates that it truly is the bulk conductivity that is modulated by the ferroelectric polarization.

A simple quasi-1D hopping model is developed to investigate the effect of the asymmetric potential caused by the polarization. This model reproduces the experimental on/off ratio using reasonable parameters.

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8:30 AM EP01.04.02

Photo-Induced Phenomena of Strongly Correlated YMnO₃ Ferroelectric Epitaxial Films Norifumi Fujimura¹, Takeshi Yoshimura¹, Takayuki Hasegawa² and Masaaki Nakayama³; ¹Osaka Prefecture University, Osaka, Japan; ²University of Hyogo, Ako, Japan; ³Osaka City University, Osaka, Japan.

We have studied the photo-induced phenomena using strongly correlated YMnO₃ ferroelectric thin films. Unipolar material YMnO₃ are suitable for studying the effect of the ferroelectric polarization on the photo-induced current. The clear relationship between the direction of the polarization and the photo-induced current was recognized using (0001) YMnO₃ epitaxial films. The current switching corresponding to the polarization switching is also observed under the illumination of white light. To study the origin of the photo-induced current originated from the photo-induced carrier generation, the light energy dependence of the photo-induced current was investigated. The small peak at 1.75 eV and broad peak at around 2.5 eV are observed at room temperature. The peak at 1.75 eV corresponds to the optical absorption at 1.7 eV that generated by the electron transition between Mn 3d (x^2-y^2)(e_{2g} state)/O 2p hybridized band and upper Mn 3d ($3z^2-r^2$)(a_{1g} state) orbital [1]. The broad peak of photo-induced current corresponds to the broad photoluminescence excitation spectrum at around 2.5 eV, which is never observed in absorption measurement but reported as the hidden optical channel. After the introduction of the origin of photo-induced current of YMnO₃ is discussed including associated with the carrier generation and the emission process, ultrafast dynamics of coherent optical phonon correlated with the antiferromagnetic transition in a hexagonal YMnO₃ epitaxial film is discussed. The observations of the coherent optical phonon using a reflection-type pump-probe technique at various temperatures, excitation powers and energies were carried out. We detected an oscillatory structure with a frequency of ~5.1 THz, which is assigned to the coherent optical phonon with A1 symmetry, in a time-domain signal. It was found that the coherent optical phonon can be observed at temperatures from 10 K to room temperature, while the oscillation amplitude markedly decreases with an increase in temperature around ~70 K corresponding to the Néel temperature. The temperature dependence of the oscillation amplitude indicates that the coherent optical phonon is sensitive to the spin-lattice coupling connected with the antiferromagnetic transition [2].

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8:45 AM *EP01.04.03

Materials Design for the Bulk Photovoltaic Effect—Theoretical Limits and Novel Materials Liang Z. Tan and Andrew M. Rappe; University of Pennsylvania, Philadelphia, Pennsylvania, United States.

The bulk photovoltaic effect (BPVE) is the generation of photocurrents in the bulk of a single-phase material. It holds advantages over traditional photovoltaics based on p-n junctions, such as above-band gap photovoltages, and current generation in the bulk without the need for interface engineering. Despite numerous theoretical and experimental research efforts into the BPVE, there has been no systematic investigation into its maximum magnitude attainable in solid-state materials. In this talk, we present an upper bound on the dominant microscopic mechanism of BPVE: the shift current response. We show that this bound depends on the band gap, band width, and geometrical properties of the material in question. As a proof of principle, we perform first-principles calculations of the response tensors of a wide variety of materials, finding that the materials in our database do not yet saturate the upper bound. This suggests that new large BPVE materials will likely be discovered by future materials research guided by the factors mentioned in this work. These results imply that small band gap materials can potentially host large BPVE. As examples, we propose materials which are tuned across a band-gap-closing phase transition from a normal semiconductor into a topological insulating phase. This class includes some inorganic layered semiconductors, such as BiTeI, and inorganic halide perovskites, such as CsPbI₃. We show that this results in a dramatic enhancement of photocurrent as well as an abrupt reversal in its direction. Using first-principles calculations, we show that that this effect is robust across different materials systems as long as such a

transition into a topologically insulating phase is present.

9:15 AM EP01.04.04

Band Gap Modulation and Interface Engineering in Solution Deposited BiFe_{1-x}Co_xO₃ Thin Films [Mariona Coll](#), Pamela Machado, Mateusz Scigaj, Jaume Gazquez, Antonio Sanchez-Diaz, Ignasi Fina and Mariano Campoy-Quiles; ICMAB-CSIC, Bellaterra, Spain.

In this work we study the chemical substitution of the transition metal in BiFeO₃ by Co-ions to explore the potential to judiciously engineer the optical band gap and examine its impact on the ferroelectric properties and the photoresponse. Nonetheless, the stabilization of BiFe_{1-x}Co_xO₃ (BFCO) phases shows a rather narrow growth window requiring high pressure synthetic conditions. Here by using low-cost chemical solution deposition we have been able to stabilize by epitaxial growth the perovskite BFCO phase modulating the band gap from 2.7 to 2.4 eV while preserving robust ferroelectricity ($P_r = 60 \mu\text{C}/\text{cm}^2$). Photoresponse measurements performed at 520 nm and 1.5 W/cm² on 100 nm BFCO films show a clear enhancement of the current density compared to pristine BFO films. Also, we observe that the magnitude of the current can be modulated by applying a voltage of a particular polarity and this effect is stronger in cobalt substituted films. Towards an all-oxide device, the use of selective layers and transparent conducting oxides are also assessed to further improve the incident photon to charge carrier efficiency of these devices. With this comprehensive study we demonstrate the complexity but also the richness of this system for future light harvesting applications.

9:30 AM *EP01.04.05

Bulk Photovoltaic Effect as Quantum Mechanical Shift Current in Polar Semiconductors [Masashi Kawasaki](#)^{1,2}; ¹Department of Applied Physics and Quantum Phase Electronics Center (QPEC), The University of Tokyo, Tokyo, Japan; ²RIKEN Center for Emergent Matter Science (CEMS), Wako, Japan.

We discuss a novel manifestation of quantum mechanical current flow in solids upon photoexcitation. From old days, bulk photovoltaic effect has been known to exist in non-centrosymmetric crystals such as poled ferroelectrics [1]. Naive explanation was that the drift current flows due to electric field uncompensated by insufficient formation of electric double layer on the surfaces of polar crystals. Now, it is proposed and confirmed that a quantum mechanical effect, described by the Berry's connection of Floquet bands, drives photocurrent called "shift current" as a second order optical process [2, 3]. We present experimental observations of photovoltaic effect in such polar materials systems as LaFeO₃/SrTiO₃ interfaces [4], a ferroelectric organic TTF-CA [5], and a polar semiconductor SbSI [6]. Ultrafast THz spectroscopy [7] and device physics [8] studies have elucidated interesting features of the shift current.

- [1] W. T. H. Koch et al., *Ferroelectrics* 13, 305 (1976).
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- [3] T. Morimoto, N. Nagaosa *Science Advances* 2, e1501524 (2016).
- [4] M. Nakamura et al. *Phys. Rev. Lett.* 116, 156801 (2016).
- [5] M. Nakamura et al. *Nature Commun.* 8, 281 (2017).
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- [7] M. Sotome, N. Ogawa, et al. *arXiv*:1801.10297
- [8] M. Nakamura et al. submitted.

10:00 AM BREAK

10:30 AM *EP01.04.06

Ferroelectric Inorganic Perovskite Oxides for Photovoltaic Applications Alessandro Quattropani¹, Daniel Stoeffler², Jean-Luc Reshpringer², Guy Schmerber², Silviu Colis², Gilles Versini², Mircea Rastei², Bohdan Kundys², Aziz Dini², Abdelilah Slaoui¹ and [Thomas Fix](#)¹; ¹Cube CNRS-Univ Strasbourg, Strasbourg, France; ²IPCMS - Université de Strasbourg and CNRS, Strasbourg, France.

Ferroelectric (FE) materials are under intense scrutiny for photovoltaic applications (PV), following the demonstration of above 8% conversion efficiency in FE-based solar cells [1]. In these cells, there is no need for a p-n junction because the electric polarization from ferroelectricity is responsible for the current flow. The key issue for the development of oxide absorbers for PV is their bandgap that is generally above 3 eV.

In this work, we produced Bi₂FeCrO₆ (BFCO) oxide materials by pulsed laser deposition (PLD). The structural, optical and electrical properties are presented. High quality epitaxial growth and phase-pure films are demonstrated by X-ray diffraction. We have studied the evolution of parameters such as the bandgap versus the growth conditions, proving that it can be adjusted from 1.9 to 2.6 eV [2]. The ferroelectric properties are investigated by piezoresponse force microscopy (PFM). We observe that light influences the state of polarization of BFCO. Finally, devices based on BFCO are fabricated and their photovoltaic properties are analysed.

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- [2] A. Quattropani, D. Stoeffler, T. Fix, G. Schmerber, M. Lenertz, G. Versini, J. L. Reshpringer, A. Slaoui, A. Dini and S. Colis, *Journal of Physical Chemistry C* 122, 1070 (2018)

11:00 AM EP01.04.07

Temperature Dependence and Quantification of Giant Negative Electrostriction in Copper Indium Thiophosphate Sabine M. Neumayer¹, Eugene Eliseev³, Michael A. Susner¹, Alexander Tselev⁴, Brian J. Rodriguez², John Brehm⁵, Sokrates Pantelides⁵, Stephen Jesse¹, Sergei V. Kalinin¹, Michael McGuire¹, Anna Morozovska³, Petro Maksymovych¹ and Nina Balke¹; ¹Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ²University College Dublin, Dublin, Ireland; ³National Academy of Sciences of Ukraine, Kyiv, Ukraine; ⁴University of Aveiro, Aveiro, Portugal; ⁵Vanderbilt University, Nashville, Tennessee, United States.

Layered van der Waals crystals like ferroelectric CuInP₂S₆ (CIPS) provide a range of intriguing functional properties. They open a straightforward path to ultrathin ferroic structures through exfoliation and avoiding dangling bonds. They enable electric-field tunable interfaces with 2d materials like graphene and transition-metal dichalcogenides (TMDs). And they exhibiting an intermediate optical band gap while maintaining ferroelectric or antiferroelectric properties. Recently, we measured giant negative electrostriction of CIPS that leads to very large out-of-plane piezoelectric coefficients despite a small polarization of only a few $\mu\text{C}/\text{cm}^2$. Here we demonstrate the effect of large negative electrostriction below and above the Curie temperature using scanning-probe-force microscopy and quantify piezoelectric and electrostrictive tensor elements using density-functional theory and Landau-Ginzburg-Devonshire calculations [1]. The piezoelectric tensor element d_{33} is temperature dependent and can exhibit values up to -100 pm/V in the ferroelectric state, which is larger than values reported for polyvinylidene fluoride. At 100°C, which is above the Curie temperature, the relative permittivity of CIPS is dependent on the applied electric field, allowing to tune the electrostrictive response, which opens up further opportunities for applications. Finally, we established atomistic origin of electrostriction in this material rooted in the multiwell potential of the Cu ions and pointing to new approaches to enhance piezoelectric

performance of these materials.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. The research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy.

[1] Neumayer et al, "Giant negative electrostriction and dielectric tunability in a van der Waals layered ferroelectric", arXiv:1803.08142 (2018)

11:15 AM EP01.04.08

Large Negative Magnetolectric Effect in Fe Substituted Ferroelectric $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ Ceramics—A Combined Experimental and Theoretical Study Mukesh Kumari^{1, 2}, Sushma Shantapuri¹ and Ratnamala Chatterjee¹; ¹IIT Delhi, New Delhi, India; ²Physics, National University of Singapore, Singapore, Singapore.

In recent years, great attention has been paid to synthesize materials with simultaneous polarization and a net magnetization due to their constructive practical applications in spintronics and non-volatile memory.¹ However, such materials are difficult to obtain as the conditions for observation of spontaneous polarization and a net magnetization are mutually exclusive.² Craig J. Fennie proposed a theoretical scheme/criteria to design structures of perovskite oxides (ATiO_3 , A = Mn, Fe and Ni), such that a polar distortion at Ti-site (B-site of perovskite unit cell) can induce weak ferromagnetism and the direction of magnetization can be switched by application of electric field (known as magnetoelectric (ME) coupling)³. Following this scheme, in one of our earlier works⁴, we have demonstrated experimentally that a partial substitution of Ti^{4+} (B-site) with Fe^{3+} in a pure ferroelectric system $\text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ (BZT) gives rise to a reasonably large ME coupling. In these samples, it was observed that the electrical polarization favors the magnetization switching such coupling is termed as positive magnetoelectric (P-ME) coupling. However, one of the major drawbacks in the BZFT series is that the solid solubility limit of Fe in the main matrix of BZT. Thus, In order to have a broader range to test the hypothesis given by Craig J. Fennie, we looked for another strong ferroelectric oxide.

In the present work, we choose $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ (BNT) as our ferroelectric matrix which is an excellent ferroelectric oxide with large remnant polarization $\sim 38 \mu\text{C}/\text{cm}^2$ (in comparison of BZT $\sim 21 \mu\text{C}/\text{cm}^2$)⁵ and high Curie temperature (T_c) ~ 330 °C. We substituted Ti with Fe ions systematically as $\text{Bi}_{0.5}\text{Na}_{0.5}\text{Fe}_x\text{Ti}_{1-3x/4}\text{O}_3$ with $x = 0, 0.005, 0.01, 0.02, 0.05, 0.1$ and 0.2 , using solid state reaction route. Interestingly, in this BNT based series, the solid solubility of Fe substitution in this BNT matrix could be increased upto 20%; giving us a broader range to test the hypothesis given by Craig J. Fennie. Moreover, the most interesting feature observed here is the negative ME (N-ME) coupling shown by these samples. It is observed that there is a decrease of $\sim 19\%$ (at 40 kOe) in magnetization in poled sample ($x = 0.05$) in comparison to the unpoled one. To understand this N-ME effect, we have developed a Landau-Devonshire thermodynamic model and estimated theoretical value of ME coupling $\text{co.} \sim 430 \text{ kV}/\text{cm Oe}$. Our Temperature dependent dielectric studies reveal that there is a small down shift in ferroelectric Curie temperature with increasing x . Ferroelectricity is still maintained in all the substituted samples.

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11:30 AM EP01.04.09

Epitaxial Piezoelectric Langasite Thin Films for High-Temperature Application Hendrik Wulfmeier, Li Zhao, René Feder and Holger Fritze; Institute of Energy Research and Physical Technologies, Clausthal University of Technology, Goslar, Germany.

Epitaxial growth of thin piezoelectric oxide films is of great importance for the minimization of devices applied in sensors and actuators at high-temperatures (HT) and in oxidizing atmospheres. The latter prevents e.g. the application of aluminum nitride. Langasite ($\text{La}_3\text{Ga}_5\text{SiO}_{14}$, LGS) is of special interest as it is an oxide crystal that is piezoelectrically excitable up to its melting point at 1473 °C. To achieve crystalline LGS films, a growth process must be developed. A key challenge is the evaporation of Ga suboxides occurring during film preparation under high-vacuum conditions and at elevated substrate temperatures.

In this work, the homo- and hetero-epitaxial deposition of LGS thin films on LGS single crystals, Si and SiO_2 substrates by pulsed laser deposition (PLD) is presented. For preparation of targets the oxides La_2O_3 , Ga_2O_3 and SiO_2 are mixed. PLD is performed at a substrate temperature of several hundred °C. To counterbalance the Ga deficit during deposition two strategies are discussed. First, an enhanced Ga content in the PLD target is applied by using off-stoichiometric targets. The second approach focuses on an increased oxygen partial pressure (up to 10^{-2} mbar) during deposition (typical base pressure 10^{-6} mbar). Combining these adaptations allows for the growth of stoichiometric LGS thin films.

Films deposited on LGS substrates do not show any additional X-ray diffraction reflexes nor broadening of the peaks of the single crystalline substrates. Therefore, the homoepitaxial approach can be considered as successfully performed. The deposition on Si and SiO_2 under the same conditions leads to the formation of polycrystalline films. However, post-annealing at 800 °C increases the crystallinity. The stoichiometry and homogeneity of the cations La, Ga, Si is characterized by secondary neutral mass spectrometry. The composition remains constant with film thickness, representing stable process parameters. However, as expected, strong dependence is seen on the deposition parameters.

An application based on these efforts is the preparation of monolithic electrodes for resonators. Typically, LGS resonators are equipped with metallic electrodes which suffer under degradation (oxidation, evaporation etc.) at extremely high temperatures. Oxide electrodes with matched thermal expansion promise to show better long-term stability. For this purpose the conductivity of the LGS films is increased by partial replacement of La_2O_3 with SrO_2 as Sr doping increases the concentration of oxygen vacancies. For 33 % Sr at the original La site a conductivity enhancement of 2 orders of magnitude is observed. The resonance frequency and the inverse Q-factor of resonators with such monolithic electrodes is discussed as a function of temperature (30-1000 °C) and electrode thickness. They are compared with traditional resonators with Pt electrodes.

11:45 AM EP01.04.10

Hydrothermal Synthesis of Yb Doped Bismuth Ferrite Crystallites and Their Structural, Magnetic and Ferroelectric Characteristics Cagri Ozdilek and Ahmet Macit Ozenbas; Metallurgical and Materials Engineering, Orta Dogu Teknik University, Ankara, Turkey.

Multiferroic materials have attracted a great deal of attention because of their ferroelectric, ferromagnetic and ferroelastic properties in a single material. They enable to control electrical polarization under the application of magnetic field, or magnetization under the application of electric field. Due to its promising feature, they have gained a remarkable usage area in non-volatile information storage, spintronics, multiple state memories and sensors. Among multiferroics, BiFeO_3 (BFO) is one of the possible candidate for room temperature multiferroic materials. There are several methods to synthesize BFO varying from conventional solid state reaction to sol-gel technique.

In this study, one of the multiferroic material, BiFeO₃ (BFO) was investigated. It was hereby with this work proposed a hydrothermal method to synthesize BFO powders. Well-crystallized BFO and Yb-doped BFO (Bi_{1-x}Yb_xFeO₃; x = 0, 0.01, 0.03, 0.05, 0.1) particles have been synthesized successfully for the first time with NaOH as a mineralizer. XRD patterns confirmed that almost all of peaks were indexed to BFO (ICDD 00-020-0169) with small amount of secondary phases. Rietveld analysis via GSAS program showed rhombohedral structure for all cases and indexed as R3c space group. SEM images of all samples were displayed spherical morphology with a diameter of various size at 30 μm. Undoped BFO displayed Neel temperature at around 370°C and Curie temperature nearly 850°C attained by simultaneously taken DSC/DTA/TGA analysis. %64.3 weight percent loss was mainly ascribed to decomposition of nitrate and evaporation of water. Those were also proven by in-situ XRD in which crystallization of BFO completed itself at almost 600°C and transformation of crystal structure from rhombohedral to monoclinic was attained between 800°C - 850°C corresponding to its Curie temperature. In comparison with un-doped BFO, Yb-doped BFOs exhibit small reduction from its T_C as a result of substitution of Yb³⁺ for Bi³⁺ ions. XPS results demonstrated Fe-O & Bi-O & Yb-O bonds along with presence of Bi³⁺, Yb³⁺ and Fe³⁺ rather than Fe²⁺. This proved that Yb has been successfully doped in BFO without forming any secondary phases. The change in the polarization and remnant polarization values were measured for the crystallites and hysteresis curves were observed. The maximum polarization values were achieved above 0.5 μC/cm² at around 50 kV/cm. Lastly, VSM technique revealed remanent magnetization (M_r) nearly 0.02 (emu/g) at 2T. In conclusion, all these results proposed the outstanding extrinsic ferroelectric and magnetic behavior of Yb-doped BiFeO₃ in a single phase.

SESSION EP01.05: New Applications of Piezoelectric, Pyroelectric and Ferroelectric Materials

Session Chairs: Bor-Rong Chen and Shyam Dwaraknath

Tuesday Afternoon, November 27, 2018

Hynes, Level 1, Room 103

1:30 PM EP01.05.01

Preparation of κ -Al₂O₃-Type Ferroelectric Single Crystal and Single Domain Epitaxial Thin Film and Their Properties [Shintaro Yasui](#)¹, Koki Tachiyama¹, Tsukasa Katayama^{1,2}, Takuro Dazai¹, Yosuke Hamasaki³, Huan He⁴, Hui Wang⁴, Jianding Yu⁴ and Mitsuru Itoh¹; ¹Tokyo Institute of Technology, Yokohama, Japan; ²The University of Tokyo, Tokyo, Japan; ³National Defense Academy, Yokosuka, Japan; ⁴Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China.

κ -Al₂O₃, same as ϵ -Fe₂O₃, GaFeO₃ structures, structured materials whose space group is *Pna*2₁, are one of very attractive multiferroics because of coexistence of ferroelectric and ferrimagnetic properties at room temperature. Ferroelectric property of this material has been investigated using single crystal and epitaxial thin films.[1] However, measurement of ferroelectricity is prevented by very large leakage current in GaFeO₃ single crystal. Moreover, this structured single crystal, except to GaFeO₃, is difficult to prepare due to metastable phase. On the other hand, the measurement of ferroelectric property was achieved by formation of high quality epitaxial thin film[2,3]. However their measured polarization values were one order smaller than calculated one[4]. We resulted that this issue was originated to three-fold structural variant which is formed on (111)SrTiO₃ single crystal. Therefore, we have tried to prepare GaFeO₃ single crystal and then prepare single crystal κ -Al₂O₃ structured thin films on GaFeO₃ single crystal substrate. GaFeO₃ single crystal was prepared by floating zone method using 10 atom oxygen pressure. Then we cut and polished this single crystal for preparation of thin films using substrate. Sc_{0.5}Fe_{1.5}O₃ epitaxial thin films were fabricated on (001)GaFeO₃ single crystal by pulsed laser deposition method. Growth temperature and oxygen pressure for deposition condition were 800°C and 300 mTorr, respectively. Laue image of prepared GaFeO₃ single crystal measured along *001* zone axis is in good agreement with simulated one. From X-ray diffraction(XRD) *2θ-θ* patterns of Sc_{0.5}Fe_{1.5}O₃/(001)GaFeO₃ thin films and (001)GaFeO₃ single crystal substrate, κ -Al₂O₃-type structured Sc_{0.5}Fe_{1.5}O₃ thin film was grown along *001* direction. XRD phi scan at {013}Sc_{0.5}Fe_{1.5}O₃ and {013}GaFeO₃ shows two-fold peaks at same phi degree. This result indicates that prepared Sc_{0.5}Fe_{1.5}O₃ thin films is single domain epitaxial thin films without structural variant. We will report ferroelectric, dielectric, leakage, magnetic properties of GaFeO₃ single crystal and Sc_{0.5}Fe_{1.5}O₃ single domain epitaxial thin film. [1]T. Arima *et al.*, *Phy. Rev. B* **70**, 064426 (2004). [2] M. Gich *et al.*, *Adv. Mater.* **26**, 4645 (2014). [3] T. Katayama *et al.*, *Adv. Funct. Mater.* **28**, 1704789 (2018). [4]D. Stoeffler, *J. Phys.: Condens. Matter* **24**, 185502 (2012).

1:45 PM EP01.05.02

Tunable Dielectrics from First Principles—Effect of Chemistry and Epitaxial Strain [Gerhard H. Olsen](#), Natalie M. Dawley, Darrell G. Schlom and Craig J. Fennie; Cornell University, Ithaca, New York, United States.

Progress in miniaturization of electronic devices, such as antennas and tunable filters, relies on continued development of thin film dielectric materials. Ruddlesden-Popper (RP) oxides based on strontium titanate (STO) have emerged as promising candidate materials, as they are highly tunable by electric fields and can be operated at +10 GHz frequencies with low dielectric losses. Such films can be grown on a range of substrates by molecular-beam epitaxy (MBE), but a remaining challenge is the trade-off between dielectric performance, improved by large epitaxial strains, and the maximum thickness that can be achieved before relaxation and high dislocation density of the film occurs. Here, we use first-principles calculations to investigate the effects of modifying the STO-based dielectrics with barium titanate (BTO). While BTO-based RPs cannot be synthesized with conventional methods, metastable RP phases with high Ba content can be grown using MBE. Our calculations show that even a small chemical modification both reduces the effective strain, allowing thicker coherent films to be grown, and at the same time enhances ferroelectricity to compensate for the reduced strain.

2:00 PM EP01.05.03

Negative Longitudinal Piezoelectric Effect of CuInP₂S₆ from First Principles [John Brehm](#)⁵, Marius Chyasnachichus², Nina Balke², Sabine M. Neumayer¹, Michael A. Susner³, Michael McGuire¹, Panchapakesan Ganesh¹, Petro Maksymovych¹ and Sokrates Pantelides⁴; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ³Air Force Research Laboratory, Dayton, Ohio, United States; ⁴Vanderbilt University, Nashville, Tennessee, United States.

Two-dimensional materials are of scientific and technological interest as they run the gamut of electronic classifications from metal, to semiconductor, to insulator while being able to be easily joined to other materials with controlled number of layers. Metal thiophosphates offer a rich class of 2D materials, comprising metal ions occupying octahedrally coordinated sites in the with [P₂S₆]⁴⁻ triangular lattice, leading to a variety of magnetic, structurally correlated and polar ground states. Copper indium thiophosphate (CuInP₂S₆) is one such member of this family and has been noted for its ferrielectric characteristic. In this talk, we present the results of density functional theory calculations that explore the effect of strain on both the structure and polarization of CuInP₂S₆. We show CuInP₂S₆ exhibits a negative longitudinal piezoelectric coefficient, and a strain-induced phase transition between two phases, differentiated by the relative displacement of Cu within the individual layers. The existence of two phases may also explain the experimentally observed inhomogeneity of piezoresponse observed experimentally. More generally, these calculations reveal the crucial role played by the van-der-Waals

gap in defining their functional properties.

2:15 PM EP01.05.04

Unified Models of Combinatorial Ferroelectric Films for RF Materials Discovery [Eric Marks](#)^{1,2}, Aaron M. Hagerstrom¹, Jasper Drisko¹, Christian J. Long¹, James C. Booth¹, Ichiro Takeuchi² and Nathan D. Orloff¹; ¹Communications Technology Laboratory, National Institute of Standards and Technology, Boulder, Colorado, United States; ²Department of Materials Science and Engineering, University of Maryland, College Park, Maryland, United States.

Voltage-tunable radio frequency (RF) electronics are critical for fifth-generation (5G) millimeter-wave telecommunications; applications include frequency-agile filters and tunable phase shifters. For the former, these materials allow handsets to communicate on many frequencies. For the latter, they enable phased-array antennas for beam-steering, which mitigates atmospheric attenuation and interference. State-of-the-art tunable materials are too lossy for these applications because the 5G network requires the use of high carrier frequencies to meet capacity demands. This problem requires new, highly-tunable, low-loss compounds that can support 5G.

Combinatorial methods provide an opportunity to rapidly screen many candidate materials, and develop better models of materials behavior as a function of composition, frequency, and applied DC voltage. These models inform the search for materials with optimal properties. The primary advantage of combinatorial experiments is that full materials systems are synthesized simultaneously, maintaining constant experimental conditions over the full sample space.

In this presentation, we will explain a novel approach to extract the frequency-dependent complex permittivity and voltage-tuning behavior of combinatorial thin-film composition spreads from DC – 110 GHz. We tested our approach on the well-studied Ba-doped SrTiO₃ (BSTO) system, emphasizing 5G frequency bands, and developed a unified model of the frequency dependence, voltage tunability and composition. Such models assist in the design of 5G RF electronics, and are related to thermodynamic quantities. This relationship points to a potential path connecting optimal RF performance to materials through first-principles theory.

2:30 PM *EP01.05.05

Coupling Between Ferroelectricity and Chemistry on Mesoscopic and Atomic Scales [Sergei V. Kalinin](#); Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Ferroelectricity on the nanoscale has remained a subject of much fascination in condensed matter physics for the last several decades. It is well-recognized that stability of the ferroelectric state necessitates effective polarization screening, and hence screening mechanism and screening charge dynamics become strongly coupled to ferroelectric phase stability and domain behavior. Similarly, atomic scale defects can strongly affect polarization stability and affect wall pinning and nucleation and give rise to relaxor states. In this presentation, I will illustrate several recent results on ferroelectric and ferroic – chemical coupling on mesoscopic and atomic scales. In the nanoscale systems, the ferroelectric state is fundamentally inseparable from electrochemical state of the surface, leading to emergence of coupled electrochemical-ferroelectric states. These considerations further stimulate the development of the novel SPM modalities addressing time-dependent dynamics and chemical changes during SPM imaging, and studying the mechanisms for these transformations from atomically-resolved data. I will further delineate the applications of *in-situ* SPM – time of flight secondary ion mass spectrometry (ToF SIMS) to map the changes in surface chemistry during tribological and local electrochemical experiments, including ferroelectric polarization switching and pressure-induced resistance changes in oxides. On the atomic scales, significant inroads in local ferroelectric behaviors can be obtained from atomically-resolved studies of ferroelectric materials that allow direct visualization of materials structures and order parameter fields. These approaches further necessitate analysis and data mining of large volumes of information, and first examples of deep learning analysis on STEM data to infer local materials behavior and kinetics of point-defect reactions will be illustrated.

This research was sponsored by the Division of Materials Sciences and Engineering, BES, DOE, and was conducted at the Center for Nanophase Materials Sciences, sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division.

3:00 PM BREAK

3:30 PM *EP01.05.06

The Discovery and Realization of Multifunctional Lead-Free Piezoelectrics [Lauren Garten](#)^{1,2}, Shyam Dwaraknath⁴, Julian Walker⁵, John Mangum³, Paul Ndione¹, Yoonsang Park⁵, Dan Beaton¹, Venkataraman Gopalan⁵, Brian P. Gorman³, Laura Schelhas⁶, Michael F. Toney⁶, Susan E. Trolrier-McKinstry⁵, Kristin A. Persson⁴ and David Ginley¹; ¹National Renewable Energy Laboratory, Golden, Colorado, United States; ²Sandia National Laboratories, Albuquerque, New Mexico, United States; ³Colorado School of Mines, Golden, Colorado, United States; ⁴Lawrence Berkeley National Laboratory, Berkeley, California, United States; ⁵The Pennsylvania State University, University Park, Pennsylvania, United States; ⁶SLAC National Accelerator Laboratory, Menlo Park, California, United States.

Theory tools have advanced to the point that we can now rapidly predict new multifunctional piezoelectric materials. Here, first-principles density functional perturbation theory tools within the Materials Project are used to identify promising new lead-free piezoelectric materials. One of these phases is P4mm SrHfO₃, which is predicted to be energetically accessible (within 50 meV of the convex hull), have a high piezoelectric response (for a lead-free compound), and be ferroelectric at room temperature. Combining computationally optimized substrate selection and synthesis conditions allowed us epitaxially stabilize the novel P4mm phase of SrHfO₃. The films were found to be structurally consistent with the theory predictions. A large signal effective converse piezoelectric response of 5.2 pm V⁻¹ for a 35 nm film is observed. These films also exhibit ferroelectricity, with a moderate coercive field and polarization, and a high breakdown strength. Thus, we show that the coupled theory-experimental approach developed here provides a route to discover and realize other new lead-free piezoelectric polymorphs. Building upon this approach, multiple properties were targeted simultaneously, identifying other candidate narrow bandgap piezoelectrics for bulk photovoltaic effect solar cells and piezotronic (piezoelectric-electronic) applications.

4:00 PM *EP01.05.07

Regenerative Electroceramics for High Temperature Energy Converters [Anke Weidenkaff](#), Wenjie Xie and Xingxing Xiao; University of Stuttgart, Stuttgart, Germany.

Electroceramics are needed for diverse energy converters (1,2). The prerequisite for a durable active material is the constant regeneration of the structure under thermochemical and heating cooling cycles. Perovskite-type ceramics as well as their nanocomposites are prospective candidates for multifunctional high temperature energy converters. Their good performance relies on their flexible crystal structure being able to accommodate defects during thermal

redox processes. The design of our materials is based on theoretical predictions and a deep knowledge on composition-structure-property relationship. The perovskite structure allows diverse substitution reactions to tune the band structure, charge carrier density and mobility as well as thermal and ionic transport. The electronic mobility can become high while the thermal conductivity can be low. Strongly correlated electronic systems are employed as additional design elements for a targeted materials design (3).

The resulting high temperature oxide materials as well as low temperature intermetallic (half-Heusler) and chalcogenite phases are characterized and tested in in-situ high temperature applications to improve the efficiency and energy density of energy conversion devices.

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4:30 PM EP01.05.08

Piezo-Phototronic Effect on Performance Enhancement of Anisotype and Isotype Heterojunction Photodiode Zijian Pan, Wenbo Peng, Fangpei Li and Yongning He; School of Microelectronics, School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an, China.

The piezo-phototronic effect has been confirmed as a promising methodology to optimize the performances of optoelectronic devices. However, not only positive effects but also negative effects may be produced in some types of photodiodes (PDs) by the piezo-phototronic effect, resulting in the restriction of the PDs' photoresponse performance enhancement. In order to obtain as large photoresponse performance enhancement as possible, it is essential to investigate how the piezo-phototronic effect influences the photoresponse performance of PDs with different device configurations and structures. Here, we have thoroughly investigated the piezo-phototronic effect on the photoresponse performance enhancement of anisotype (p-Si/n-ZnO) and isotype (n-Si/n-ZnO) heterojunction PDs. The experimental results show that distinct photoresponse performance enhancement of the p-Si/n-ZnO and the n-Si/n-ZnO heterojunction PDs are both achieved by the piezo-phototronic effect. The photoresponsivity enhancement can reach maximized values of 151.06% and 54.95% for the p-Si/n-ZnO and the n-Si/n-ZnO heterojunction PDs, respectively, under -1.0% externally applied compressive strain condition and 6.00×10^{-3} W 405 nm laser illumination, additionally indicating that the magnitude of the photoresponse performance improvement of the p-Si/n-ZnO heterojunction PD is much larger than that of the n-Si/n-ZnO heterojunction PD. The fundamental working mechanisms of how the piezo-phototronic effect influences the photoresponse performances of the p-Si/n-ZnO and the n-Si/n-ZnO heterojunction PDs are systematically investigated by carefully analyzing their different energy band diagrams under a series of externally applied compressive strain conditions, to explore the in-depth physics beneath the experimental phenomenon. Our proposed mechanisms together with the finite element analysis theoretical simulation results reveal that, two positive effects are introduced to and contribute to the photoresponse performance improvement of the p-Si/n-ZnO heterojunction PD, whereas one positive effect and two negative effect are introduced to the photoresponse performance improvement of the n-Si/n-ZnO heterojunction PD. These three effects compete with each other and finally lead to a weakened photoresponse performance improvement compared with the case of the p-Si/n-ZnO heterojunction PD. This work not only presents in-depth understandings about the piezo-phototronic effect on the photoresponse performances of PDs with different device configurations and structures, but also provides methodology guidance to achieve optimized photoresponse performances of optoelectronic devices by the piezo-phototronic effect.

4:45 PM EP01.05.09

A Novel CMOS Compatible III-V Semiconductor Based Ferroelectric with Intriguing Properties Simon Fichtner^{1,2}, Fabian Lofink² and Bernhard Wagner^{1,2}; ¹CAU Kiel, Institute for Material Science, Kiel, Germany; ²Fraunhofer Institute for Silicon Technology, Itzehoe, Germany.

We regret that, due to ongoing patent applications, we are as of now still unable to discuss aspects that would reveal the composition of the new ferroelectric compound (such as its crystal structure) and the intended applications or related literature. We are however certain that we will be able to share all relevant information in the end of August the latest. For the same reasons, this work is still pending journal publication.

The drive towards miniaturization of piezoelectric sensors and actuators as well as the introduction of ferroelectric functionality into integrated circuit (IC) technology have led to substantial scientific and commercial interest in ferroelectric thin-films. Many of the more important ferroelectrics are perovskite oxides, with typical disadvantages such as low paraelectric transition temperatures, non-linear displacement or compatibility issues with complementary metal-oxide-semiconductor (CMOS) technology. Here, we report experimental results of a first material of what can be expected to be a new group of CMOS compatible ferroelectrics with remarkable properties: Solid-solutions based on a technologically significant subgroup of the III-V compound semiconductors.

Virtually leakage current free polarization hysteresis loops with large remnant values of up to $110 \mu\text{C}/\text{cm}^2$ are obtained on polycrystalline thin-films grown by sputter-deposition. Untypical for a polycrystalline ferroelectric, sharp switching events give rise to an almost perfectly square hysteresis. Systematic tuning of the coercive fields from 1.8 MV/cm to 5 MV/cm was achieved by varying the composition of the solid solution and, independently, via permanent process induced lateral straining of the films. Both mechanisms, as the occurrence of ferroelectricity itself, can be related to a continuous distortion of the initial III-V crystal structure with increased alloying or strain. The inverse piezoelectric effect reveals highly linear strain regimes over a wide range from -0.3% to 0.4% - a direct result of the narrow polarization switching events. Moreover, polarization inversion appears to be complete, as direct and inverse piezoelectric coefficient measurements result in largely identical absolute coefficient values for both polarization states. Measurements of the direct piezoelectric effect after annealing at up to 600°C revealed only a slight decline of the piezoelectric performance without subsequent repolarization, therefore setting a high lower limit of 600°C for the paraelectric transition temperature of the material.

We are confident that these findings could make a valuable contribution towards a more extensive implementation of ferroelectric functionality in thin-film technology.

SESSION EP01.06: Characterization of Semiconducting Piezoelectric, Pyroelectric and Ferroelectric Materials

Session Chairs: Shyam Dwaraknath and Anke Weidenkaff

Wednesday Morning, November 28, 2018

Hynes, Level 1, Room 103

8:00 AM EP01.06.01

Flexible and Controllable Piezo-Phototronic Pressure Mapping Sensor Matrix by Organic/Inorganic Hybrid LED Array Rongrong Bao and Caofeng Pan; Chinese Academy of Sciences, Beijing, China.

Functional tactile sensing device is mandatory for next-generation robotics and human-machine interfaces since the emulation of touching requires large-scale pressure sensor arrays with high-spatial resolution, high-sensitivity, and fast-response [1]. Some tactile sensors fabricated with organic transistors or micro-structured rubber layer pressure sensor arrays have been reported [2]. While with a resolution at the order of millimeter, these devices have not yet met the requirements of artificial skins whose spatial resolution is near 50 μm . Our group have demonstrated pressure sensor array based on piezotronic and piezo-phototronic effects [3]. An ultra-high resolution of 2.7 μm was derived from piezo-phototronic pressure sensor array using ZnO nanowire (NW)/p-GaN LEDs array [4]. These devices provide stable, fast response, as well as parallel-reading detections of spatial pressure distributions. However, the lacking of flexibility with a rigid sapphire substrate prevents the NW-LEDs array device from applications as smart skin; and the pressure measuring range of the device is in a relatively high pressure region. Therefore, a flexible pressure mapping system with moderate spatial-resolution become necessary and may find numerous potential applications in human-machine interfaces.

Recently, we designed and fabricated a flexible LED array composed of PEDOT:PSS and patterned ZnO NWs with a spatial resolution of 7 μm for mapping of spatial pressure distributions by using the piezo-phototronic effect. These devices possess a wide range of pressure measurements from 40 MPa to 100 MPa depending on the growth conditions of ZnONWs. Furthermore, a LED array composed of PEDOT:PSS and CdS nanorods had been demonstrated for mapping spatial pressure distributions. The emission intensity of which depends on the local strain owing to the piezo-phototronic effect. Therefore, pressure distribution is obtained by parallel-reading the illumination intensities of LED arrays based on electroluminescence working mechanism. The spatial resolution is achieved as high as 1.5 μm . Flexible LED device array has been prepared by CdS nanorod array on Au/Cr/Kapton substrate.

The flexibility and stability of these LED arrays mapping system was studied. The outstanding flexibility, high resolution and controllability of these pressure mapping sensors provide promising technologies for future applications in biological sciences, human-machine interfacing, smart sensor and processor systems, and even defense technology.

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8:15 AM EP01.06.02

Ferroic and Multiferroic Behavior in Fe Doped BaTiO₃ Single Crystals Peter Finkel¹, Margo L. Staruch¹ and Markys G. Cain²; ¹NRL, Washington, District of Columbia, United States; ²Electrosiences Ltd, Surrey, United Kingdom.

Single crystals of BaTiO₃ (BTO) that have been doped at the titanium site with Fe³⁺ or Mn³⁺ have previously been shown to demonstrate large and recoverable electrostrain of up to 0.8 % that is thought to be due to the alignment of defects (i.e. O²⁻ vacancies) with the crystallographic symmetry in the ferroelectric state when the samples are aged. [1,2] This results in a restoring force where the ferroelectric domains favour alignment with the defect dipoles, giving rise to a large reversible strain due to repeated non-180° domain rotation. There is also the possibility that the incorporation of a magnetic ion could give rise to a magnetic signature and even possibly multiferroic coupling in these doped samples, the possibility of which has not been previously investigated. In this presentation, results from magnetic measurements and polarization measurements with bias magnetic fields will be discussed for a 0.5% Fe doped BTO crystal. Impact of repeated cycling at different electric fields and the recoverability of this large strain will also be presented.

8:30 AM EP01.06.03

Flexible Transparent Nonvolatile Transistor Based on Aluminum-Doped Zinc Oxide/ Lead Lanthanum Zirconate Titanate Heteroepitaxial Structure Meng-Fu Tsai¹, Jie Jiang² and Ying-Hao Chu^{1,3,4}; ¹Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu, Taiwan; ²Key Laboratory of Low Dimensional Materials and Application Technology of Ministry of Education, Xiangtan, China; ³Department of Electrophysics, National Chiao Tung University, Hsinchu, Taiwan; ⁴Material and Chemical Research Laboratories, Industrial Technology Research Institute, Hsinchu, Taiwan.

With the rise of Internet of Things, flexible and transparent electronic devices are expected to fulfill rising technical requirements which silicon-based electronics cannot achieve. As known to everyone, the advancement of transistors is most close to the development of technology. However, the performance of present flexible and transparent transistors have been restricted due to the poor crystallinity. In order to make a high quality nonvolatile transistor with full transparency and lower energy consuming, here, we demonstrated a transparent ferroelectric field effect transistor (TFE-FET) on muscovite substrate. With a high quality aluminum-doped zinc oxide as active channel layer and high transparency lead lanthanum zirconate titanate as ferroelectric layer, this heteroepitaxy performs excellent electrical properties. Moreover, this flexible TFE-FET not only shows high transparency and high thermal stability, but also exhibits promising stability against to mechanical strain during a series of bending tests. Our study demonstrates an unusual concept to achieve flexible transparent nonvolatile transistor for development of next-generation smart devices.

8:45 AM EP01.06.04

Organic Ferroelectric Tunnel Junctions for Synaptic Computation Sayani Majumdar; Aalto University, Espoo, Finland.

The performance of current information processors are predominantly based on complementary metal-oxide-semiconductor (CMOS) transistors. However, CMOS scaling have started to face significant challenges and besides the physical limits, the conventional computing paradigm based on binary logic and Von Neumann architecture is becoming increasingly inefficient with onset of big data revolution and growing complexity of computation. Neuromorphic computing is the state-of-the-art research trend in the field of memory and logic devices where the goal is to build a versatile computer that is efficient in terms of energy and space, homogeneously scalable to large networks of neurons and synapses, and flexible enough to run complex behavioral models of the neocortex as well as networks inspired by neural architectures. Memristors, with their gradually modified conductivity level can mimic the biological synapses. Low energy consumption, ultrafast operation and small dimensions are the most essential requirements for a memristor to perform tasks similar to a synapse and become as efficient as human brain. A ferroelectric tunnel junction (FTJ), where gradual modulation of conductance can be achieved by controlled rotation of ferroelectric domains can act very efficiently as a synapse. Also the non-volatility of the stored information in the ferroelectric memories make them even more attractive as potential candidates for future neuromorphic computing building blocks. Here, we report on the performance of FTJs with a spin-coated organic ferroelectric P(VDF-TrFE) tunnel barrier. We have measured up to 10⁷% tunneling electroresistance (TER) effect in these FTJs on a semiconducting Nb-doped STO bottom electrode at room temperature that persists until the ferroelectric Curie point of P(VDF-TrFE). ¹Also these junctions show very clear and reproducible memristive behavior based on variable amplitude and duration of the applied voltage pulses, fast switching, long data retention of the high, low and different intermediate states, short and long-term potentiation (STP & LTP) and depression and spike-time-dependent-plasticity (STDP) which is extremely promising for neuromorphic applications. ²Our recent experiments suggest based on the morphology of the ferroelectric film and the top electrode material, the available number of computational states in these devices can be significantly modified that can bring advantages for the synaptic computational devices. ³

References

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- [3] S. Majumdar *et al.* . (Manuscript under preparation).

9:00 AM EP01.06.05

Piezoelectric β -PVDF:Yb Composite with Photochromic Properties Pedro Perdigon Lagunes, Eduardo Malagon, Jimena de la Mora, Yessica P. Reyes-Castro, Octavio Estevez and Raul Herrera-Becerra; Universidad Nacional Autonoma de Mexico, Mexico City, Mexico.

Nowadays piezoelectric systems have been studied and used in interesting daily applications, such as smartphone cameras, accelerometers and microphones [1]. Another interesting area for piezoelectric materials is energy harvesting, as transducers capable of convert vibrations, electromagnetic waves or even wind/water flow into electric potential difference [2]; this might lead to improve our actual collection of renewable power sources, and will let us explore other energy solutions. Even though these materials are promising with their applications, there are some limitations such as energy dissipation through Joule heating [3]. In addition, the most common piezoelectric materials are based in ceramic materials, hence, they are susceptible to wear fatigue. An interesting option is to use instead piezoelectric polymers, these materials are flexible, fatigue resistant and biochemical resistant due to their chemical composition. One of the most renowned materials of this type is PVDF (Poly vinylidene fluoride), a semi-crystalline fluoropolymer stable to harsh thermal, chemical and UV environments [4]. Its β phase (β -PVDF) has demonstrated the best piezoelectric response from all the other phases. Therefore, β -PVDF is an excellent option to be used as a piezoelectric material for renewable energies and sensors. In addition, this material, owing to its chemical endurance might be used also as a wearable biosensor/actuator that tracks in real time changes on blood pressure. Nevertheless, the real challenge is to obtain a predominant β -PVDF phase; this is because PVDF, as a semi-crystalline polymer, still has an entropic tendency to rearrange its molecules in lower energy state. We solved this problem by doping the polymer with ytterbium ions (Yb^{3+}) in different concentrations below 10% in weight. As the electronic density of Yb^{3+} interacts with the polymer chains, a fixed order is promoted into the PVDF structure with a tendency of a b structure. In addition, an unexpected optical result was found; when β -PVDF:Yb is exposed to sunlight, it presents a photochromic response that correlates to the interaction absorption frequencies of the Yb^{3+} . Thus, we consider that a piezoelectric polymer with photochromic characteristics, it is an interesting system to be further explored for technological applications in relevant fields.

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9:15 AM EP01.06.06

Electro-Chemo-Mechanical Actuator Operating at Room Temperature Eran Mishuk, Evgeniy Makagon, Sidney Cohen, Ellen Wachtel and Igor Lubomirsky; Weizmann Inst of Science, Rehovot, Israel.

Chemical expansion of a solid refers to dimensional change due to change in stoichiometry. Dimensional change due to charged defects redistribution in an electric field has been termed the electro-chemo-mechanical (ECM) effect. Such instability is clearly deleterious for batteries or fuel cells, but, as recently suggested, has potential for use in actuation[1]. A typical ECM actuator scheme includes: electrode1\WB1\solid-electrolyte(SE)\WB2\electrode2, where WB denotes working-body solids with large chemical expansion coefficient. The main advantage of ECM is that it can deliver simultaneously large strain and large stress, which is difficult to achieve with other actuation mechanisms. We have constructed a room temperature ECM nanocrystalline membrane actuator (2mm diameter; $\approx 2\mu\text{m}$ thick) with Gd-doped ceria as SE. We tested two alternatives for WB's: (1) metal/(metal oxide) or (2) ceria/metal nanocrystalline composite. Electrical and electromechanical measurements demonstrated that actuator response with metal/metal oxide WB is limited by the rate of oxygen diffusion from the solid electrolyte to the metal surface. Actuators with ceria/metal composite WB provide faster response time ($\approx 20\text{sec}$) and larger vertical displacement ($>3.5\mu\text{m}$). Our findings suggest that ECM may become a viable actuation mechanism.

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9:30 AM BREAK

10:00 AM EP01.06.07

A Pathway Toward 100mV Switching of Ferroelectricity Yen-Lin Huang¹, Bhagwati Prasad¹, Shang-Lin Hsu¹, Everton Bonturim¹, Yunlong Tang¹, Arnoud S. Everhardt¹, Chia-Ching Lin², Tanay Gosavi², S Manipatruni², D Nikonov², I Young² and Ramamoorthy Ramesh^{1,3}; ¹University of California, Berkeley, Berkeley, California, United States; ²Exploratory Integrated Circuits, Components Research, Intel Corporation, Hillsboro, Oregon, United States; ³Department of Physics, University of California, Berkeley, Berkeley, California, United States.

The demand for ultra low-powered high-speed devices has pushed scientists and engineers to consider new approaches that involve many aspects, such as materials engineering, device architectures, power management, etc., for the next generation electronics. Ferroelectrics offer a promising route toward a nonvolatile and low power consumption per bit operation (~ 10 aJ/bit) if one can switch the ferroelectric polarization by 100 mV. Here we demonstrate a reliable pathway to achieve 100 mV switching by the heterostructure: $\text{SrRuO}_3/\text{La-doped BiFeO}_3/\text{SrRuO}_3$. BiFeO_3 exhibits a robust ferroelectricity at room temperature and possesses a large polarization $\sim 80 \mu\text{C}/\text{cm}^2$, which can be a burden during switching. Substituting Bi with La enables BiFeO_3 to be switched at a lower voltage due to the suppressing of rhombohedral distortion and resulting in a reduced polarization down to $\sim 40 \mu\text{C}/\text{cm}^2$ and a lower Curie temperature as well. Moreover, in order to further reduce the coercive voltage, the thickness of the ferroelectric layer also needs to be scaled. However, thinner ferroelectric films generally face multiple issues such as leakage, and depolarization effect, which will lead to an unmeasurable or degraded ferroelectricity. A detailed chemical analysis revealed a limited interdiffusion, which limits the leakage current as well, at the interface between the metal and ferroelectric layer by cross-sectional TEM/EDX. We also explore several oxide metal electrode materials, such as SrRuO_3 , LaNiO_3 , and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$, to minimize the depolarization effect and the contact potential difference. By carefully controlling the interfaces, film growth, and La doping concentration, the coercive voltage of ~ 100 mV can be achieved in a 20 nm $\text{La}_x\text{Bi}_{1-x}\text{FeO}_3$ film. Our results not only provide a profound understanding of low-voltage ferroelectric switching as well as pave the way to the low-power information storage/processing technology.

10:15 AM *EP01.06.08

Acoustically Driven Ferromagnetic Resonance Driven Excitation of Vacancy Centers Sayceef Salahuddin; University of California, Berkeley,

Berkeley, California, United States.

Sound waves flowing in a piezoelectric crystal could be exploited to excite a ferromagnetic resonance. Here we shall discuss our recent work that aims to exploit such ferromagnetic resonance as a way to couple to nearby defect centers. Specifically, we have studied the nitrogen vacancy centers in diamond. We find that it is indeed possible to couple to these NV centers efficiently, even at zero external magnetic field. These findings may allow drive defect centers purely electrically.

10:45 AM DISCUSSION TIME

11:00 AM EP01.06.10

Electrically Tuned Photoelectrochemical Properties of Ferroelectric PVDF/Cu/PVDF-NaNbO₃ Photoanode [Simrjit Singh](#)^{1,2} and Neeraj Khare²; ¹Panjab University, Chandigarh, India, Ludhiana, India; ²Physics, Indian Institute of Technology Delhi, New Delhi, India.

In recent years, photo-electrochemical (PEC) water splitting with an aim to generate hydrogen (H₂) as a clean and renewable fuel has been the subject of intense research interests [1]. Ferroelectric semiconductors have been demonstrated to exhibit enhanced PEC properties as these can be polarized with the application of an external electric field resulting in a built-in potential which helps in separating out the photogenerated charge carriers. In addition to this, by changing the polarization direction, the energy band alignment at the electrode/electrolyte interface can be modulated in a way that it can help in easy transfer of the charge carriers from electrode to electrolyte [2-4].

In this paper, we investigated the PEC properties of ferroelectric PVDF/Cu/PVDF-NaNbO₃ PEC cell and demonstrated that PEC properties can be tuned with ferroelectric polarization and piezophototronic effect. Photocurrent density is enhanced from ~0.71 mA/cm² to 1.97 mA/cm² by changing the polarization direction. Furthermore, due to flexibility and piezoelectric properties of PVDF/Cu/PVDF-NaNbO₃ PEC cell, a further ~26% enhancement in the photocurrent is obtained using the piezophototronic effect. A model depicting the modulation of band alignment between PVDF and NaNbO₃ with electric field is proposed to explain the observed tuning of the PEC properties. Electrochemical Impedance spectroscopy measurements supports the validity of the proposed model.

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11:15 AM *EP01.06.11

PETMEM: Piezoelectronic Transduction Memory Device—A European Research Project Update [Markys G. Cain](#); Electrosciences Ltd, Farnham, United Kingdom.

Computer clock speeds have not significantly increased since 2003, creating a challenge to invent a successor to CMOS technology able to resume the improvement in clock speed and power performance. The key requirements for a viable alternative are scalability to nanoscale dimensions - following Moore's Law - and simultaneous reduction of line voltage in order to limit switching power. Achieving these two aims for both transistors and memory allows clock speed to again increase with dimensional scaling, a result that would have great impact across the IT industry. PETMEM is a European partnership amongst Universities, Research Institutions, SMEs and a large company that will focus on the development of new materials and characterization tools to enable the fabrication of an entirely new low-voltage, memory element. This element makes use of internal transduction in which a voltage state external to the device is converted to an internal acoustic signal that drives an insulator-metal transition. Modelling based on the properties of known materials at device dimensions on the 15 nm scale predicts that this mechanism enables device operation at voltages an order of magnitude lower than CMOS technology (power is reduced two orders) while achieving 10GHz operating speed. In this presentation the first two years results will be summarised with a focus on new piezoelectric and new piezoresistive materials development, and some performance properties of our first demonstrator device will be discussed.

11:45 AM EP01.06.12

Efficient Piezocatalytic Activity Driven by the Piezoelectric Effect of BaTiO₃ Nanowires [Jiang Wu](#), Ni Qin and Dinghua Bao; Sun Yat-Sen University, Guangzhou, China.

Recently, a novel catalysis technology, which named piezocatalysis, has received significant attention due to independence of light irradiation. Here, we report the new advances in the piezocatalysis of BaTiO₃ and further investigate the relationship between piezoelectric potential and piezocatalysis. In this work, we successfully synthesized BaTiO₃ nanowires and nanoparticles by a two-step hydrothermal method. It was found that the BaTiO₃ nanowires exhibit effectively enhanced piezocatalytic activity under ultrasonic vibration compared with the BaTiO₃ nanoparticle. To explore the origin of the excellent piezocatalysis performance of BaTiO₃ nanowires, the distribution of piezoelectric potential in these nanomaterials was simulated by the finite element method (FEM) with the aid of COMSOL multiphysics software package. On the basis of the piezoelectric potential analysis by FEM stimulation, the enhanced piezocatalytic activity of the BaTiO₃ nanowires can be attributed to the larger piezoelectric potential along the polar axis. A relatively larger piezoelectric potential of the catalyst surface can induce a greater shift of conduction band and valance band, resulting in easier and faster immigration of the electrons and holes, during reacting with dissolved oxygen and hydroxyl to form superoxide radicals and hydroxyl radicals. Furthermore, we demonstrate that the intrinsic charge carriers (not piezoelectric charges) in piezoelectric crystallites play the role of charge transfer in the catalysis process through regulating the concentration of charge carriers in catalyst. This study provides further understanding of piezocatalysis of piezoelectric nanomaterials as well as insights on the relationship between piezoelectric potential and piezocatalysis.

SESSION EP01.07: Bulk Photovoltaic Materials
Session Chairs: Lauren Garten and Abdelilah Slaoui
Wednesday Afternoon, November 28, 2018
Hynes, Level 1, Room 103

1:30 PM EP01.07.01

Electric Field Manipulation of Ferroelectric Vortices—In Situ TEM [Christopher T. Nelson](#)^{2,3,1}, [Zijian Hong](#)⁴, [Cheng Zhang](#)^{5,2}, [Ajay Yadav](#)³, [Sujit Das](#)³, [Anoop R. Damodaran](#)³, [Shang-Lin Hsu](#)^{3,1}, [James D. Clarkson](#)³, [Miaofang Chi](#)², [Philip D. Rack](#)^{5,2}, [Long-Qing Chen](#)⁴, [Lane W. Martin](#)³ and

Ramamoorthy Ramesh^{3, 1}; ¹Lawrence Berkeley National Laboratory, Oak Ridge, Tennessee, United States; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ³University of California Berkeley, Berkeley, California, United States; ⁴Pennsylvania State University, State College, Pennsylvania, United States; ⁵The University of Tennessee, Knoxville, Tennessee, United States.

Arrays of ferroelectric vortices formed in ferroelectric / paraelectric thin film multilayers with a predominant Néel-type rotational character [1] and emergent chirality [2] are an enticing foray into topological complexity that is typically the purview of magnetic systems. The nanometer length scale and direct electrical field manipulation makes ferroelectric polarization texture an attractive counterpart to spin systems wherever parity exists. Moreover, electric field control of vortex array blocks has been demonstrated by scanning surface probe [3] in geometries where the vortex structure is degenerate with classic a_1/a_2 domains [4]. In this work using in situ TEM we present the electric field response of these ferroelectric vortices length scales concomitant with the vortex structure (nm). In geometries where the vortex structure is highly stable, applied electric fields induce vortex asymmetry within the PTO layer manifesting as shifts of the rotation centers. In this manner the vortex structure adapts to applied fields via short range small domain wall translations without need of nucleation events. In geometries degenerate with a_1/a_2 domains, deterministic switching between vortex and a_1/a_2 structures can be achieved as in bulk [3].

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[3] A Damodaran, et al., Nat. Mater. **16** (2017), p. 1003.

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[5] Authors acknowledge support by the U.S Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract number DE-AC05-00OR22725

1:45 PM EP01.07.02

Electronic Conductivity of Charged Ferroelectric Nanodomains Stuart R. Burns², Ye Cao³, Alexander Tselev⁴, Rama K. Vasudevan¹, Joshua Agar⁵, Lane W. Martin⁵, Mark Huijben⁶, Sergei V. Kalinin¹, Nagarajan Valanoor², Anna Morozovska⁷ and Petro Maksymovych¹; ¹Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ²University of New South Wales, Sydney, New South Wales, Australia; ³The University of Texas at Dallas, Dallas, Texas, United States; ⁴University of Aveiro, Aveiro, Portugal; ⁵University of California, Berkeley, Berkeley, California, United States; ⁶ University of Twente, Enschede, Netherlands; ⁷National Academy of Sciences, Kyiv, Ukraine.

Ferroelectric nanodomains are inevitably created upon polarization reversal. They provide a natural setting to explore conductive properties of ferroelectrics, because the repolarization nuclei are decorated by weakly charged domain walls, and because they can be created and subsequently tuned on demand by appropriately chosen electric field. As such, nanodomains are a model system to probe presently open questions surrounding domain wall conductance, such as pathways to increase conductance (through carrier density and possibly mobility), understanding the stability of conductive walls and the origin of the screening charge.

We have measured conductance of two different kinds of ferroelectric nanodomains, aiming to maximize polarization charge in the ferroelectric volume. In the first case, a radially symmetric electric field is applied to a ferroelectric with substantial component of in-plane polarization – in our case the 100-oriented film of BiFeO₃. Such nanodomains are intentionally unstable but arguably achieve the largest possible polar discontinuity. Indeed, we observe near-record high local conductivity for ferroelectric as well as metastability in applied electric field, producing an electronic function of a volatile resistive switch. However, the net conductance is not metallic in this case. Phase-field modeling reveals localization of polarization charge to near-electrode region, effectively screening applied electric field. We anticipate that conductance will be dramatically enhanced in the ultrathin limit, where the volume of polar discontinuity becomes comparable to the overall film thickness. On the other hand, we have investigated the signatures of inclined domain walls in lead zirconate titanate at the instance of ferroelectric switching by microwave probe, which is sensitive to the bulk volume of the film. We have again observed the largest microwave conductance among accessible polarization configurations, as well as profound metastability of nanodomains in a relatively broad range of applied fields. An inspection of the dielectric properties of domain walls at and above their depinning field was carried out to separate the contributions of domain wall motion from nanodomain hysteresis. This analysis provided further evidence for electronic (rather than displacive) origin of microwave conductance for ferroelectric structures created by localized electric fields. Finally, we will comment on the stability of the charged configurations based on detailed analytical modeling of charged domain walls in various screening scenarios. Charged domain walls appear to be generally unstable for polarization exceeding ~ 10 microC/cm², even with efficient supply of the screening carriers. Support provided by the U.S. Department of Energy, Basic Energy Sciences, Materials Science and Technology Division. Microscopy experiments performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

2:00 PM *EP01.07.03

Electrochemical Phenomena of Polarization Switching in Ferroelectrics Anton V. Ievlev, Sergei V. Kalinin and Olga Ovchinnikova; Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Polarization switching in ferroelectric materials underpins a broad gamut of applications ranging from random access memory, tunneling barriers, data storage, and ferroelectric ceramics. Classically, the polarization switches due to a co-existence of energetically equivalent crystallographic states, that can be altered with an external electric field. To stabilize polarization, charge discontinuity at surfaces and interfaces requires compensation, or screening, to avoid long-range electrostatic fields that destabilize the ferroelectric phase. Most studies consider polarization screening to be chemically inert; leaving the composition of the ferroelectric intact. However, analysis of extant ferroelectric phenomena suggests higher complexity. It is well known that multiple polarization switching cycles can accumulate damage at interfaces, dubbed “ferroelectric fatigue.” Typically, tens or hundreds of thousands switching events are required, and the exact mechanisms remain controversial. Furthermore, polarization-dependent photovoltaic effects in perovskites suggest that even under optimal screening conditions a considerable electric field remains in the material. Thus, switching is associated with high fields, which can chemically alter material composition.

Here we utilize multimodal approach combining time of flight secondary ion mass spectrometry (ToF-SIMS) with atomic force microscopy (AFM) to explore the structure property interplay of ferroelectrics during polarization switching in lead zirconate titanate (PZT, PbZr_{0.2}Ti_{0.8}O₃) thin films. Using this multimodal imaging platform, we demonstrated that chemical phenomena plays significant role in ferroelectric switching process. Specifically, we found that local ferroelectric switching by the AFM tip, significantly alters the chemical composition in the 3-nm-thick surface layer of the sample, forming reversible concentration wave, of Pb⁺ ions. Furthermore, investigations of the polarization cycling in the PZT sample with copper electrodes, showed penetration of the copper cations into the structure of PZT. This explains ferroelectric fatigue phenomenon, leading to decrease in spontaneous polarization with sample cycling.

Altogether, explored chemical phenomena associated with ferroelectric switching will enhance fundamental understanding of ferroelectric phenomena and aid in the practical application of ferroelectrics in devices.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility, and using instrumentation within ORNL's Materials Characterization Core provided by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of

Energy.

2:30 PM BREAK

3:30 PM *EP01.07.04

Reliability of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ Thin Films for Actuators Susan E. Trolier-McKinstry, Wanlin Zhu, Kathleen Coleman, Betul Akkopru-Akgun, Michael Lanagan and Clive Randall; The Pennsylvania State University, University Park, Pennsylvania, United States.

Lead zirconate titanate ($\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$, or PZT) films are of interest for piezoelectric microelectromechanical systems as actuators, e.g. in inkjet printers, adjustable optics, micromirrors, and ultrasound transducer arrays. In many cases, these actuators are driven at higher electric fields than would be characteristic of bulk ceramic actuators. Thus, understanding the factors that control the electrical and mechanical reliability of these films under aggressive conditions for electric fields and strains is critical. To address this, acceptor (1-4% Mn) and donor (1-4%) doped PZT films were grown. Thermally stimulated depolarization current (TSDC) measurements in Mn doped PZT films showed one depolarization peak with an activation energy of 0.6-0.8 eV, associated with ionic space charge presumably due to ionic migration of oxygen vacancies. The magnitude of the depolarization current peak increases with increasing degradation times, suggesting the dissociation of defect dipoles during electrical degradation. A similar depolarization current peak attributed to existence of mobile oxygen vacancies was also observed for undoped and Nb doped PZT films; the magnitude of this peak increases on lowering Nb or PbO contents. An additional TSDC peak, associated with trapped charges was found in both Nb doped PZT films and undoped PZT films annealed under low PbO partial pressure. The trap depth is estimated to be 1.1 ± 0.03 eV, which is attributed to trapped electronic charge carriers at reduced Ti on the B site. Electron energy loss spectroscopy studies of degraded Nb doped samples confirmed localized Ti reduction near the cathode. A model describing the failure mechanisms will be presented.

4:00 PM EP01.07.05

Measurements of Polarization Switching Dynamics in the Tens of Picoseconds Aaron M. Hagerstrom¹, Eric Marks¹, Xiaohang Zhang², Christian J. Long¹, James C. Booth¹, Ichiro Takeuchi² and Nathan D. Orloff¹; ¹National Institute of Standards and Technology, Boulder, Colorado, United States; ²University of Maryland, College Park, Maryland, United States.

Technological applications of ferroelectric materials often depend on their tuning under an applied electric field. In recent years, polarization switching processes have attracted interest for their role in transient negative capacitance, which could be used to increase transistor energy efficiency. Switching processes also govern how quickly a microwave-frequency device based on ferroelectric materials can be reconfigured. Despite the technological motivations to study switching speed, high-frequency measurements remain difficult. In particular, separating the behavior of the measurement circuit from the behavior of the material under test is increasingly difficult with increasing frequency. Interpretation of measurements often requires complicated models of both the material and the measurement circuit. In this talk, we describe a new method for quantifying switching dynamics through nonlinear mixing products up to 40 GHz. From our measurement technique, we are able to empirically describe the dynamical switching behavior of the material under small signals in the tens of GHz without making any physical assumptions about the material itself. We apply this method to $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ as a proof of concept, and show that our frequency-dependent results agree with a physical model derived from Landau-Ginzberg-Devonshire (LGD) theory.

4:15 PM EP01.07.06

Thermally Stable Sr_2RuO_4 Electrode for Ferroelectric BaTiO_3 and Photocatalytic Rh: SrTiO_3 Films Ryota Takahashi^{1,2} and Mikk Lippmaa¹; ¹Univ of Tokyo, Chiba, Japan; ²JST PRESTO, Tokyo, Japan.

Sr_2RuO_4 is the $n=1$ member of the $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ Ruddlesden-Popper family and a well-known metallic oxide that becomes superconducting below 1K. Since it is thermodynamically the most stable phase in this ruthenate family, it can be grown at very high temperatures compared to several other metallic oxides such as Fe_3O_4 , SrRuO_3 , or $(\text{La,Sr})\text{MnO}_3$. Moreover, the oxygen pressure window is wider than for many other oxides, notably SrRuO_3 , that are commonly used as metallic electrodes in oxide device structures. We present the results of a study on the thermal stability of Sr_2RuO_4 thin film electrodes and demonstrate the usefulness of this electrode layer material for high-temperature growth of ferroelectric BaTiO_3 films¹ and photocatalytic Rh: SrTiO_3 films².

The Sr_2RuO_4 electrode films were prepared on BHF-treated $\text{SrTiO}_3(001)$ substrates by pulsed laser deposition. Atomic force microscopy revealed atomically smooth surfaces for 20-nm-thick Sr_2RuO_4 films. To investigate the thermal stability, ferroelectric BaTiO_3 thin films were deposited at 700-1000°C on the Sr_2RuO_4 electrode layer. Pyroelectric hysteresis loop measurements were used to verify that the BaTiO_3 films grown on Sr_2RuO_4 electrodes were ferroelectric, implying that the Sr_2RuO_4 electrode layers were thermally stable even during high-temperature deposition at 1000°C in 100 mTorr of oxygen. The wide oxygen pressure window of Sr_2RuO_4 electrode was investigated by the deposition of Rh: SrTiO_3 thin films for photoelectrochemical water splitting electrodes. At growth temperature of around 800°C in 10^{-6} Torr of oxygen, the Sr_2RuO_4 electrode formed an atomically sharp interface with the film even at high growth temperatures and low oxygen pressures, yielding atomically flat Rh: SrTiO_3 photocathode films.

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SESSION EP01.08: Poster Session II: Applications of Piezoelectric, Pyroelectric and Ferroelectric Materials

Session Chairs: Shyam Dwaraknath and Abdelilah Slaoui

Wednesday Afternoon, November 28, 2018

8:00 PM - 10:00 PM

Hynes, Level 1, Hall B

EP01.08.01

Improve Energy Harvesting from Ocean Wave Energy by Using 3D Printed Devices with Aim of Frequency Modulation in Piezoelectric Based Wave Energy Harvesters and Scavengers Sina Baghbani Kordmahale; Electrical Engineering, Texas A&M University, College Station, Texas, United States.

There are various methods to harvest sustainable energy from various resources (1, 2). We have used piezoelectric Macro Composite Fibers (MFCs) combined with soft material and 3D printed solid parts to harvest energy from the sea and ocean waves. Durable, low cost, low maintenance, and efficient

wave energy harvesters alongside the availability of powerful waves can provide a sustainable green energy source for various applications. The commercialized wave energy harvesters have problems like: expensive complicated elements, heavy structures, too much mechanical and moving parts which will increase the unit price, high deployment, and maintenance expenses. In the proposed design, the flexible MFCs are sandwiched between two 3D printed slabs with saw-tooth surfaces and are encapsulated in a soft elastomer block. Ecoflex 030 is chosen as the soft elastomer (3, 4). The soft material casting method has been used to form the encapsulation and shape the Ecoflex based slabs (5). The different 3D printed blocks, with various saw-tooth periods and amplitudes, were used in this experiment to prove the hypothesis of efficiency of proposed design. In total, four different combination of period and amplitude of saw-tooth used in this experiment and it is approved that the higher amplitude and shorter period of saw-tooth on the surface, will cause on higher energy harvesting. The fabricated samples, placed and tested in a wave flume tank horizontally and the open circuit voltage and power measurement have done on the samples. The designed structure can harvest remarkably more energy in comparison with formerly designed wave energy harvesters which were just based on the soft materials, MFCs and anchoring in some cases. So this improved design could increase the efficiency of piezoelectric based wave energy harvesters and also can be a mesoscale model for piezoelectric based smaller scavengers. While the same design can be used for silicon-based mems structures, still the same 3D printing, like the one in this article, can be more economical for small scavengers too.

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EP01.08.02

Stretchable, Transparent and Self-Healing Triboelectric Nanogenerators with Ionic Current Collector Kaushik Parida and Pooi See Lee; Nanyang Technological University, Singapore, Singapore.

Triboelectric nanogenerators have emerged as a promising power source for portable and stretchable electronic devices. However most of the nanogenerators use metallic electrodes, thus the devices could not achieve high stretchability and transparency, simultaneously. This work demonstrates the use of an ionic conductor as the current collector in a triboelectric nanogenerator, resulting in a highly transparent, stretchable and self-healing device. The device has a transparency of 92% transmittance, it can sustain a tensile strain up to 700%, and autonomously self-healable. The energy harvesting performance of ionic triboelectric nanogenerator is 12 times higher than that of the metallic based triboelectric nanogenerator. The resulting device demonstrates an extremely stretchable, highly transparent self-heal power source to be used as a power supplies for sensors, wearable electronics and soft robotics.

Reference

K. Parida, V. Kumar, W. Jiangxin, V. Bhavanasi, R. Bendi, P. S. Lee, *Adv. Mater.* 2017, **29**, 1702181

EP01.08.03

Electromechanical Properties of Flexible Piezoelectric Nanogenerator (PENG) Using Different Patterns of Vertically-Aligned BaTiO₃ Nanotubes Camelle Kaye A. Aleman, James Albert B. Narvaez and Candy C. Mercado; University of the Philippines Diliman, Quezon City, Philippines.

With the advancement catered by the use of lead-free piezoelectric nanogenerators (PENGs) for flexible electronics in energy harvesting, the challenge is to design an efficient system which is high power-producing. For this study, structural engineering approach was implemented to improve the electromechanical response of PENGs. Effects of varying patterns of the one-dimensional, vertically-arrayed BaTiO₃ nanotubes used in PENG devices, theoretically baselined with concepts on pile patterning and geometries in building foundations, on their output power were observed. Different patterns of vertically-arrayed, tetragonal phase BaTiO₃ nanotubes were synthesized via in situ conversion of selectively-anodized TiO₂ nanotubes on Ti substrates using hydrothermal process. Selective anodization which established the patterning of the BaTiO₃ was achieved through photolithography using a negative photoresist dry mask. The patterns of two sets vary in the diameter (1 mm and 1.5 mm), and the arrangement (linear and staggered arrays) of the circles printed on the mask. The methodology produced highly crystalline BaTiO₃ nanotubes based on the obtained X-ray diffractogram and EDX analysis. SEM images showed that the synthesized nanotubes had an average length of 66 μm and inner diameter of 67 nm. In addition to this, the study established that selective anodization using photoresist dry film mask can be utilized in creating patterned BaTiO₃ without significant loss in accuracy of pattern. Using this material, PENG devices were fabricated. The PENGs comprised a sandwich structure of Ti- BaTiO₃ nanotube-graphite-Ti and were further made flexible by encapsulating the structure with polydimethylsiloxane. The cantilever-type PENG devices were subjected to repeated bending stresses using a rotating motor to determine the effect of different BaTiO₃ patterns on the output voltages of the devices under constant cyclical stress. It was observed that pile characteristics such as pile diameter, pile arrangement, and pile spacing which was brought about by the varied diameter and arrangement parameters, affect the output voltage and voltage behavior of the PENG devices. Decrease in both BaTiO₃ nanotube array spacing and pattern diameter, increases the lateral displacement of the piezoelectric material and decreases the pile stiffness, respectively; all conditions consequently leading to an increase in the output voltage of the device. It was observed that the voltage behavior is dependent on the pile-matrix-pile interaction which is affected largely by adjacent pile spacing. Furthermore, the piezoelectric test showed that the highest peak to peak output voltage generated by the unpoled devices reached up to 1.9 V using the pattern with linear arrays of smaller circle diameter. The research, overall, is majorly a proof of concept study wherein the aim was to see the effect of patterning the piezoelectric material on the output voltage values of the fabricated PENG devices.

EP01.08.04

Nobel Lead Free Relaxor Multiferroic for High Energy Storage Application Mohan K. Bhattarai, Sita Dugu, Alvaro Instan and Ram Katiyar; Physics, University of Puerto Rico, Rio Piedras, San Juan, Puerto Rico, United States.

We synthesized modified Barium zirconate titanate electro ceramics by a conventional solid-state reaction method with stoichiometric formula Ba_{1-x}La_{2x/3}Zr_{0.30}Ti_(0.70-3y/4)Fe_yO₃ (BLZTF), where y = 0.01 & 0.0 ≤ x ≤ 0.06 & investigated its structural, microstructural, dielectric, electrical, ferroelectric and magnetic properties. X-ray diffractometry was used to probe the phase purity and to derive the crystallographic parameters. A uniform distribution of grains on the surface of the sample was observed from scanning electron micrographs (SEM) recorded on pellets. The stoichiometry of the chemical compositions was examined using energy dispersive x-ray (EDS) analysis method. We carried out dielectric measurements on Ag/PLZTS/Ag metal-ferroelectric-metal capacitors using impedance analyzer as a function of temperature (100-600 K) and frequency (10²-10⁶ Hz). We observed enhanced dielectric constant in doped BZT. The room temperature magnetic measurements (M-H) were obtained using a vibrating sample magnetometer.

Additionally, we observed thin PE hysteresis loop, suggesting that synthesized materials is relaxor multiferroics and promising materials for high energy storage applications.

EP01.08.05

Foam-Type Piezoelectric Composite for Internal Cochlear Implant Jeongjae Ryu, Jinwon Oh, Kwangsoo No, Seungbum Hong and Steve Park; KAIST, Daejeon, Korea (the Republic of).

A cochlear implant is a device for people with hearing loss caused by inner ear damages. Despite its great use to improve hearing, the microphone and other electronics of the cochlear implant, typically located outside the ear, are not aesthetically attractive. Therefore, many studies to insert a cochlear implant into the body have been conducted. In this study, we present a new approach for fabricating piezoelectric sensors that are attached on the cochlea. We made a foam-type piezoelectric composite not to interfere with the movement of auditory ossicles. Generally, to avoid the aggregation of piezoelectric particles in a polymer layer, MWCNT has been used, but it is being suspected for its toxicity. On the other hand, we coated biocompatible polydopamine on piezoelectric particles and then dispersed them in the PDMS layer. We calculated porosity of the composites and measured their stress-strain curves. We characterized the output performance as a function of the frequency of sound. We anticipate that the foam-type piezoelectric composite is promising as a sensor capable of detecting the sound pressure for cochlear implant.

EP01.08.06

Field and Frequency Dependence of Magnetodielectric Coupling in Ni/PZT/Ni Multiferroics Fernando Aponte¹, Roberto Masso¹, Gopalan Srinivasan² and R Palai¹; ¹University of Puerto Rico, San Juan, Puerto Rico, United States; ²Physics, Oakland University, Oakland, Michigan, United States.

Spin capacitors have the potential to store both the electronic charge and magnetic spin that can produce conventional electric current and spin polarized current. The time evolution of spin polarized electrons injected into the piezoelectric material can be used for accurate sensing of magnetoelectric fields. To further study the application of multiferroic spin capacitors for future use in memory applications, Ferromagnetic/Ferroelectric/Ferromagnetic tri-layer artificial multiferroelectric structures in spin capacitor configuration were fabricated by sputtering ferromagnetic Nickel (Ni) electrodes on lead zirconate titanate (PZT). Magnetocapacitance, magnetoimpedance, and phase angle measurements were carried out by a wide range of frequencies (100 Hz – 5 MHz) and magnetic fields (0T – 2T) at room temperature. We also compared the magnetodielectric measurements of the Ni/PZT/Ni spin capacitor with Ni/PZT/Ag and Ag/PZT/Ag tri-layers structures and their behavior. Two PZT layer thickness were studied, including 200 μm and 1 mm PZT. Ni/PZT/Ni spin capacitor shows a significantly different behavior compared to conventional PZT capacitor with Ag electrode and mixed electrode capacitor with one ferromagnetic and one conventional electrode. The spin capacitor (Ni/PZT/Ni) with the 1 mm PZT layer show mayor resonance peaks at ~ 166 kHz and at ~ 890 kHz, where the first peak is not present in the other capacitor structures. Second level peaks are found at 231 kHz, 444 kHz, 2.03 MHz and at 3.2 MHz. This las peak in the spectrum is shared with the three structures. The second level peaks have and $\sim 32\%$ intensity compared to the mayor peaks at ~ 166 kHz and at ~ 890 kHz. There is a notable reduction on the intensity of the peaks when the ferromagnetic electrode is present, with the mayor difference between the conventional capacitor having a 83% higher intensity ($\epsilon=55586$) compared with the Ni/PZT/Ag capacitor ($\epsilon=10015$) and a 57% reduction between Ni/PZTAg and Ni/PZTNi. For the 200 μm sample, the three structures of capacitor share a very similar behavior, with a certain shift for the Ni/PZT/Ag capacitor, where Ni/PZT/Ni and the conventional capacitor share the resonance peak at ~ 260 kHz and Ni/PZT/Ag has a shift of 50 kHz towards higher frequencies (308 kHz). And similar to the 1 mm layer PZT samples, there is a reduction in dielectric peak permittivity, with the conventional capacitor being the highest and lowering with the presence of the ferromagnetic electrode with a difference of 28% between the conventional capacitor and Ni/PZT/Ag, and a 33% difference in reduction between Ni/PZT/Ag and Ni/PZT/Ni. The Lorentz model was used to study the peaks behavior by fitting the equation into dielectric measurements per range of frequencies and obtaining information from selected peaks.

EP01.08.07

Ultrafast Zero-Bias Photocurrent in GeSe Single Crystals—A Promising New Ferroelectric Photovoltaic Material Kateryna Kushnir¹, Ying Qin², Guangjiang Li¹, Sefaattin Tongay² and Lyubov V. Titova¹; ¹Worcester Polytechnic Institute, Worcester, Massachusetts, United States; ²School of Engineering of Matter, Transport and Energy, Arizona State University, Tempe, Arizona, United States.

Solar cells based on bulk photovoltaic effect (BPVE) may provide an efficient alternative to traditional p-n junction-based ones [1,2]. The prevailing mechanism behind BPVE is a shift current, a zero-bias photocurrent that can occur in a non-centrosymmetric material as excitation of an electron from the valence to the conduction band, resulting in a coherent spatial shift of the electron charge density. Ferroelectric semiconductors have been predicted to exhibit significant shift currents, spurring the search for ferroelectric semiconductor candidates for BPVE with bandgaps in the visible range [1-3]. Theory predicts that monolayer group-IV monochalcogenides are multiferroic and capable of generating significant shift currents [3,4]. Previously, we have demonstrated ultrafast shift current following above bandgap excitation of GeS nanosheets [5].

Here, we present the evidence of a shift current response in a single crystalline GeSe with μm thickness. While the stacking sequence of the layers in this van der Waals material results in inversion symmetry in the bulk, this symmetry is broken at the surface, and a spontaneous surface polarization can exist in the same armchair direction as in a monolayer GeSe [3,4,6]. We have detected the ultrafast shift currents in GeSe single crystalline flakes using terahertz (THz) emission spectroscopy [5]. Detecting free space propagating electromagnetic pulses emitted by the sample excited at normal incidence by the ~ 100 fs, 800 nm or 400 nm pulses allows contact-free, all-optical monitoring of the transient photocurrents that result in this emission. We find that photoexcited GeSe crystals emit nearly single-cycle THz pulses in response to either 800 nm (1.55 eV) or 400 nm (3.10 eV) excitation. Excitation fluence, orientation and polarization dependence of the THz emission confirms that shift currents flowing along one crystallographic direction, presumably determined by the spontaneous polarization of the surface layer, are responsible for the observed emission. Stronger THz emission in response to 400 nm excitation, compared to the equivalent fluence of 800 nm excitation, stems from stronger absorption of 400 nm light by GeSe, which leads to the higher excitation of a surface layer. Highly efficient shift current photoexcitation in GeSe and the optical absorption that covers the entire visible range suggests applications of these layered materials in third generation BPVE photovoltaics.

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EP01.08.08

Enhanced Photodetection of Au-g-C₃N₄/CdS/ZnO Based Flexible Heterojunction Device Utilizing Piezo-Phototronic Effect Sourabh Pal¹, Sayan Bayan² and Samit K. Ray²; ¹Advanced Technology Development Centre, Indian Institute of Technology Kharagpur, Kharagpur, India; ²Department of Physics, Indian Institute of Technology Kharagpur, Kharagpur, India.

Two dimensional (2D) materials and their derivatives have attracted the scientific community owing to their promising application in photonic and optoelectronic devices. In recent times, 2D graphitic-carbon nitride (g-C₃N₄) has been found to be a potential material for various photophysical properties. This n-type semiconductor is characterized by interesting electronic structure originating from the lone pair of nitrogen and electron delocalization in which the band gap can be easily tuned¹. Nanosheets of g-C₃N₄ both in the pristine form and in heterojunction with other semiconductors are found to be promising for optoelectronic device applications². The fabrication of heterostructured devices through the integration of g-C₃N₄ with various promising materials may offer the basis of futuristic flexible optoelectronic devices. Amongst different semiconductor nanostructures, zinc oxide (ZnO) is a well studied material owing to its distinguished performance in the field of optoelectronics. Apart from the well known ultraviolet (UV) light emission properties, piezoelectric properties of ZnO are also fascinating due to its tremendous scope in the application of high performance photodetectors³. Coupling the piezoelectric polarization with the semiconducting properties under mechanical stimuli can definitely lead to the modified output of the host material through modification in the local interface and charge carrier transport³. Herein, we report on efficient and enhanced photoconductivity in ZnO based hybrid heterojunction with CdS and Au nanoparticle loaded g-C₃N₄ nanosheets under bending state. In the present investigation, the scheme of g-C₃N₄/CdS/ZnO based heterojunction has been adopted due to elevate charge carrier separation under visible light, which can be further enhanced (~ 18 times at 530 nm) by plasmonic effects with the exploitation of Au loaded g-C₃N₄ nanosheets. Strain induced piezopotential development in ZnO has also been witnessed in the hybrid heterojunction and it has been found this piezo-potential can efficiently trigger the photoconductivity response (~ 10² times as compared to normal state) through the modification in band alignment at the interface of the hybrid heterojunction.

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EP01.08.09

Large Local-Compressive Stress-Induced Improvements in Piezoelectric Characteristics of Lead Zirconate Titanate Thin Films on a Ni Nanodots-Array Chan Su Han, Ahra Cho, [Da Bin Kim](#) and Yong Soo Cho; Yonsei University, Seoul, Korea (the Republic of).

This manuscript introduces a nonconventional way to improve piezoelectric properties of PZT thin films substantially by forming Ni nanodots-array on a Si substrate with the assistance of uniform magnetic field upon deposition. The existence of Ni nanodots induces extra compressive stress at the initial stage of film growth due to an enormous difference of ~94% in thermal expansion coefficient between the Ni and PZT film. The level of thermal mismatch is typically not allowable at the regular film interface. Specifically, heavily 12 mol% Nb-doping was selected for the sputtering process since the heavy doping has been recently reported to uniquely produce the *in situ* domain formation during deposition when combined exclusively with the Ir/TiW bottom electrode. Interestingly, the relatively high content of 12 mol% Nb is all dissolved into the perovskite structure without segregation. The final film/electrode structure corresponds to Pt/Nb-doped PZT/Ir/TiW/Ni nanodots/SiO₂/Si. The role of an AlNiCo magnet used here provides uniform external magnetic field strength to facilitate consolidation of the Ni nanodots at high temperature. This nanodot approach induces local large compressive stress only around the region of Ni nanodots so that the film structure can be sustained. As a result of this unique local stress approach, a substantial enhancement of effective piezoelectric coefficient by ~33% is obtained from the changed crystal orientation and easier domain formation. The shift of polarization-electric field curve indicates the presence of internal field in the domain structure. This *in situ* process does not require the subsequent annealing and poling procedure, which have been commonly demanded for piezoelectric materials. So the adoption of Ni nanodots with the *in situ* processing creates very unique improvements.

EP01.08.10

ZnO-BaTiO₃-Epoxy Multifunctional Electro-Active Thin Films—Enhancement in Electron Transport Regimes by Comparison of ZnO Nanowires and Nanoparticle Composites [Walker Tuff](#)¹, Saquib Ahmed² and Sankha Banerjee¹; ¹California State University, Fresno, Fresno, California, United States; ²Mechanical Engineering, Buffalo State College, Buffalo, New York, United States.

Piezoelectric and electro-active composites are investigated as new generation self-powered energy harvesting devices for a wide range of applications from the industrial to the medical field while maintaining high reliability, durability and sensitivity over wide range of frequencies. The electrical, dielectric and piezoelectric properties can be enhanced by embedding electro-active and conductive inclusions in the matrix material. The present work involves the fabrication of three-phase, multifunctional lead-free, BaTiO₃-Epoxy-ZnO (nanowire) and BaTiO₃-Epoxy-ZnO (nano-particle) composite and flexible thin films. The volume fraction of the BaTiO₃ phase was held constant at 40%, while the volume fraction of the ZnO nanowire phase was varied from 1% to 10%. The work compares the role of ZnO nanowire and ZnO nano-particle inclusions distributed in an epoxy matrix to fabricate three-phase composites. The influences of several factors on the effective electromechanical properties of the composites are also analyzed. The dipoles of the electro-active phases were aligned using a plasma-microdischarge (Corona) poling technique. The piezoelectric strain coefficients, dielectric constant, dielectric loss tangent, capacitance, impedance, resistance, and conductance of the samples were measured and compared as a function of poling regime. The impedance and dielectric spectra of the composites were recorded over a frequency range of 20 Hz to 10 MHz. The fractured surface morphology and distribution of the phases were observed with the aid of Electron Dispersion Spectroscopy (EDS) and a Scanning Electron Microscope (SEM). The crystal structure of different phases in the composite were also characterized used Raman Spectroscopy.

EP01.08.11

Thickness Scaling of Ferroelectricity and Electrical Conductivity in Multiferroic BiFeO₃ [James Steffes](#)¹, Ramamoorthy Ramesh² and Bryan D. Huey¹; ¹University of Connecticut, Storrs Mansfield, Connecticut, United States; ²University of California, Berkeley, Berkeley, California, United States.

Computed tomography atomic force microscopy (CT-AFM) is presented as a novel experimental modality for nanometer-scale measurements of the size-dependence of functional properties in the room temperature multiferroic BiFeO₃. Intrinsic and extrinsic properties of ferroelectric thin films are known to have strong dependencies on electrical and mechanical boundary conditions, resulting in finite size effects in electronic and magnetic properties at length scales below several hundred nanometers. By combining recently-developed CT-AFM techniques with piezoresponse force microscopy (PFM) and conductive AFM (CAFM), nanometer-scale three-dimensional imaging of ferroelectric domains and conductive defects at polarization discontinuities has been achieved in thin film BiFeO₃. CT-AFM additionally provides a platform for quantifying the thickness dependence of the local spontaneous polarization, ferroelectric coercive field, and electrical conductivity in BiFeO₃ across two decades of thickness. The thickness-resolved ferroelectric properties of BiFeO₃ acquired with CT-AFM strongly correlate with both Landau-Ginzburg-Devonshire phenomenological theory and the semi-empirical Kay-Dunn scaling law for ferroelectric coercive fields, providing an unambiguous determination of a stable and switchable polar state in BiFeO₃ at thicknesses below 5 nm. Complementary tomographic PFM and CAFM data reveals the geometric dependence of polar discontinuities on the heterogeneous electrical conductivity of BiFeO₃ as a function of film thickness, which shows strong agreement with the model of Schottky emission for

bulk BiFeO₃ as well as several electrically-conducting defect types in BiFeO₃. Along with complementary transmission electron microscopy (TEM) analysis, this work provides new insights into the relationship between thickness and ferroelectric properties in heteroepitaxial multiferroics.

EP01.08.12

Understanding Ferroelectric Properties of BaTiO₃ Using ReaxFF Reactive Force Fields Dooman Akbarian¹, Dundar Yilmaz¹ and Adri van Duin^{1,2,3}; ¹Mechanical Engineering, The Pennsylvania State University, State College, Pennsylvania, United States; ²Chemical Engineering, The Pennsylvania State University, State College, Pennsylvania, United States; ³Materials Science and Engineering, The Pennsylvania State University, State College, Pennsylvania, United States.

Ferroelectric perovskites such as barium titanate (BaTiO₃) have had numerous applications in nonvolatile memories, transducers, micro sensors and capacitors because of their unique properties such as spontaneous polarization, piezoelectric and pyroelectric effects, as well as large dielectric constants. In order to design and optimize these devices, it is essential to obtain detailed, atomistic-scale insight of the BaTiO₃ ferroelectric perovskite. Currently, there are three approaches to model the ferroelectric behavior of BaTiO₃: Phenomenological, First-principles and Force field-based methods. Phenomenological models are not able to provide atomistic level description of the ferroelectric perovskites. First-principles methods such as the density functional theory (DFT) are considered as the most accurate models, however, because of heavy computational costs these methods can be only viable for relatively small systems and short time scales. Moreover, since the DFT models are mainly limited to zero kelvin, most of ferroelectric properties of the perovskite materials such as hysteresis loop, sequential phase transitions and domain wall motions cannot be investigated using the first-principles methods. Force field based methods can provide the computational speed required to perform molecular dynamics (MD) simulations with system sizes and time scales sufficiently large to describe the full chemistry of the ferroelectric perovskites. ReaxFF reactive force fields first developed for hydrocarbons and later applied to different systems such as ceramics, metals and their oxides and provided precise results for those systems. We developed the first reactive force field for BaTiO₃ systems which captures both chemical and electro-mechanical properties of the material. We performed realistic size molecular dynamics simulations to investigate the phase transition sequence, ferroelectric and thermal hysteresis loops for the BaTiO₃ crystal structure. Furthermore, we investigated the effects of oxygen vacancies and different surface terminations on the material polarization.

EP01.08.13

Spiral Domain Walls in Ferroelectric PbTiO₃ Thin Films Christopher T. Nelson^{2,3,1}, Zijian Hong⁴, Ajay Yadav³, Sujit Das³, Anoop R. Damodaran³, Shang-Lin Hsu^{3,1}, Long-Qing Chen⁴, Lane W. Martin³ and Ramamoorthy Ramesh^{3,1}; ¹Lawrence Berkeley National Laboratory, Oak Ridge, Tennessee, United States; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ³University of California Berkeley, Berkeley, California, United States; ⁴Pennsylvania State University, State College, Pennsylvania, United States.

Defects in the ferroelectric topology such as domain walls are dynamically controllable low-dimensional entities that can manifest local non-bulk properties such as a 2D electron gas[1,2]. Domain walls try to adopt electrical neutrality, i.e. the Polarization has a constant flux ($\nabla \cdot \mathbf{P} = 0$), and those that violate this either compensate the bound charge or low energy configurations including geometries that ensure pay a price of high electrostatic energy. As a result, charged domain walls can exhibit significant property differences to the bulk[2], but are typically metastable or present in low remnant polarization systems with a sufficient screening charge density such as improper ferroelectrics. In ferromagnetic systems, where screening charges are unavailable, complex topologies such as vortex and multi-vortex domain walls can arise instead and be utilized in race-track style memory architectures. Generally, equivalent topological complexity is lacking for ferroelectrics which have both screening charges and favor Ising character domain walls rather than the rotating Bloch or Néel-type domain walls which conserve the polarization magnitude. However, significant Néel-type character has been achieved at morphotropic phase boundary compositions[3] and through geometric confinement[4]. In this work we utilize the latter, thin dielectrically bound PbTiO₃ films, to realize the formation of spiral domain walls to stabilize electrostatically charged configurations akin to vortex domain walls observed in ferromagnetic strips. Moreover, as a field-controllable feature, these domain walls illustrate a mechanism to manipulate ferroelectric vortices.

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EP01.08.14

Studies on Magnetic and Electrical Properties of Gallium Ferrite Multiferroic Thin Film Sita Dugu¹, Dhiren K. Pradhan², Shalini Kumari³, Mohan K. Bhattarai¹, Alvaro Instan¹ and Ram S. Katiyar¹; ¹Department of Physics, University of Puerto Rico, San Juan, Puerto Rico, United States; ²Geophysical Laboratory, Washington, District of Columbia, United States; ³Department of Physics, West Virginia University, Morgantown, West Virginia, United States.

Magnetoelectric materials might hold the future for the ultimate memory, spintronics, and other multifunctional devices as they exhibit simultaneous ferroelectric and ferromagnetic behaviors and permit control and switching of the magnetic order parameters via an electric field, and polarization with a magnetic field. Orthorhombic gallium Ferrite is a prominent multiferroic due to its piezoelectricity and ferrimagnetism coupled with magnetoelectric effects. Herein we studied the dielectric, ferroelectric and magnetic behavior of ~ 200nm highly oriented orthorhombic GaFeO₃ thin film deposited on a SrRuO₃ buffered SrTiO₃ substrate by optimized Pulsed Laser Deposition method. SrRuO₃ was deposited at an optimized temperature of 680°C under an oxygen pressure of 200 mTorr, with a laser energy density ~ 1.5 J/cm² and a frequency of 10 Hz. Subsequently, GaFeO₃ was grown on the top of SrRuO₃ at 725°C with oxygen pressure 300mT and energy density ~ 2 J/cm² at a frequency of 5 Hz. The film was then cooled at the rate of 2°C/min under the pressure of 200mT. The θ -2 θ large angle x-ray scans (10° to 90°) showed highly oriented film grown at (00l) direction without any secondary peaks. Surface morphology was analyzed with AFM studies which showed the film is smooth, free of microcracks, pores or holes with average surface roughness around 2-3 nm. Temperature-dependent magnetization behavior was studied at both field-cooled and zero-field-cooled conditions in between 5- 395 K using several magnetic fields (such as 100 Oe, 500 Oe, and 1000 Oe) identify the Neel transition temperature T_N around 225 K. Ferroelectricity of GaFeO₃ was demonstrated by polarization hysteresis and PFM measurement. The film exhibits the net switching polarization of ~12 $\mu\text{C}/\text{cm}^2$ with a maximum field of 700kV/cm. The single phase RT GFO shows multiferroic behavior with a magnetoelectric coupling which might be a potential candidate for spintronic and microelectronic applications.

EP01.08.15

Influence of Metal Element Addition on Crystal Structure of AlN Piezoelectric Thin Film Masato Uehara, Sri Ayu Anggraini, Hiroshi Yamada and Morio Akiyama; National Institute of Advanced Industrial Science and Technology, Saga, Japan.

It is vital to adopt piezoelectric materials for microelectromechanical systems (MEMS), where aluminum nitride (AlN) has been regarded as an attractive

candidate for featuring a sensor, an energy harvester and a bulk acoustic wave resonator. Akiyama et al. have dramatically improved by Sc-Addition but the Sc-AlN is expensive for industrial uses. We succeeded in improvement of the piezoelectric coefficient by simultaneous addition of Mg-Nb. The improvement is comparable to Sc-AlN. According to other paper, Mg-Hf, Mg-Zr, and Mg-Ti are also effective. The lattice constant ratio c/a of wurtzite decreases by addition of the effective elements.

In this paper, we have investigated the influence of various element addition on AlN crystal structure. With single addition of Mg and Ca, considerable decrease of crystallinity was confirmed. This would be caused by a problem of charge compensation. In case of Nb and Ti, the crystallinity decrease was smaller but the other phase formation was observed. In case of Sc, above phenomena were not observed until addition ratio of 0.5. The change in the a -axis is similar for each element additions and increases monotonically. On the other hand, the change of c -axis was different. By Sc addition, the c -axis increased to the addition ratio of 0.3 and decreased with addition of more. For the other elements, the c -axis increased until the addition ratio at which crystallinity decrease or other phase formation was observed. Particular, by Nb and Ti addition, the c -axis increase was large. These ion radii are not particularly large, but rather the Ti ionic radius is the smallest. The large increase of c -axis can not be explained by ion radius. The electronegativity of Nb and Ti is large compared with Mg, Ca, and Sc, and the fraction of covalent bonding would be larger than them. The fraction of covalent and ionic bonding would be related with the change of crystalline structure such as c/a ratio. We think that by addition of Sc and Mg the fraction of ionic bonding would increase and the crystalline would soften, leading to piezoelectric increase of AlN.

EP01.08.16

Stroboscopic Materials Testing by Synchrotron X-Rays on the Sub-Nanosecond to Picoseconds Time Scale Klaus-Dieter Liss^{1, 2, 3}; ¹Guangdong Technion - Israel Institute of Technology, Shantou, China; ²Technion – Israel Institute of Technology, Haifa, Israel; ³MMMB, University of Wollongong, Wollongong, New South Wales, Australia.

X-ray diffraction is a very common method to analyze strain fields and crystallographic phases in a wide range of materials, including functional materials such as multiferroics. The presentation resumes my work on stroboscopically time resolved synchrotron X-rays probing materials under periodic external stimulus. Ultrasonic strain fields can be evaluated as a function of oscillation period, in both low and high frequency cases, where additional diffraction phenomena take place. Switching of electric fields in ferroelectric material reveal phase transformation response. An overview on the technique, examples and future potential, particularly to ferro and piezoelectrics will be given.

EP01.08.17

Ferroelectric Lead Free $\text{Na}_{0.52}\text{K}_{0.44}\text{Li}_{0.04}\text{Nb}_{0.84}\text{Ta}_{0.10}\text{Sb}_{0.06}\text{O}_3$ Material—Giant Electromechanical Response with Intrinsic Polarization and Resistive Leakage Analyses Abid Hussain and Binay Kumar; Department of Physics and Astrophysics, University of Delhi, New Delhi, India.

Environment friendly lead free $\text{Na}_{0.52}\text{K}_{0.44}\text{Li}_{0.04}\text{Nb}_{0.84}\text{Ta}_{0.10}\text{Sb}_{0.06}\text{O}_3$ (NKLNTS) ceramic was synthesized by solid state reaction method in search of a potential candidate to replace lead based ceramics such as PbZrO_3 - PbTiO_3 (PZT), $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - PbTiO_3 (PMN-PT) etc., for various applications. The ceramic was calcined at temperature 850 °C and sintered at 1090 °C. The powder XRD pattern revealed the formation of pure perovskite phase having tetragonal symmetry with space group $P4mm$ of the synthesized ceramic. The surface morphology of the ceramic was studied using Field Emission Scanning Electron Microscopy (FESEM) technique. The well defined grains with homogeneous microstructure were observed. The average grain size was found to be ~ 0.6 μm . A very large value of piezoelectric charge coefficient (d_{33} ~ 754 pm/V) was obtained for the synthesized ceramic which indicated its potential for use in transducers and actuators. In dielectric measurements, a high value of ferroelectric to paraelectric phase transition temperature (T_m ~ 305 °C), a high value of maximum dielectric permittivity ~ 2110 (at 1 kHz) and a very small value of dielectric loss (<0.6) were obtained which suggested the utility of NKLNTS ceramic in high temperature ferroelectric devices. Also, the degree of diffuseness (γ) was found to be 1.61 which confirmed a relaxor ferroelectric behavior in NKLNTS ceramic. P-E hysteresis loop was traced and the value of spontaneous polarization was found to be ~ 11 $\mu\text{C}/\text{cm}^2$ at room temperature. The pyroelectric coefficient was obtained to be very high (p ~ 1870 $\mu\text{Cm}^{-2} \text{ } ^\circ\text{C}^{-1}$) for the present case indicating its applicability in pyroelectric detector applications including fire and burglar alarms, infrared imaging, etc. NKLNTS ceramic showed fatigue free behavior over 10^7 switching cycles. Remanent hysteresis task was performed to determine the true-remanent (or intrinsic) polarization of NKLNTS ceramic by eliminating non-switchable components which showed that a major portion (83.10 %) of the remanent polarization (P_r) is switchable in the sample which makes NKLNTS ceramic a suitable material for memory switching devices applications. Time-Dependent Compensated (TDC) hysteresis task was carried out which revealed resistive leakage free nature of the ceramic. The performance of NKLNTS ceramic was found to be superior to many lead based piezoceramics and hence can effectively replace them for use in piezoelectric, pyroelectric and long duration ferroelectric applications.

EP01.08.18

Thermal-Induced Ferroelastic Domains in Barium Titanate Qianwei Huang¹, Zibin Chen¹, Feifei Wang², Simon Ringer^{1, 3}, Haosu Luo⁴ and Xiaozhou Liao¹; ¹School of Aerospace, Mechanical and Mechatronic Engineering, The University of Sydney, Sydney, New South Wales, Australia; ²Key Laboratory of Optoelectronic Material and Device, Department of Physics, Shanghai Normal University, Shanghai, China; ³Australian Centre for Microscopy and Microanalysis, The University of Sydney, Sydney, New South Wales, Australia; ⁴Key Laboratory of Inorganic Functional Materials and Devices, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai, China.

Ferroelectric materials have extensive applications in electric devices due to their unique properties. The ferroelectric/ferroelastic domain structures in ferroelectric materials can be manipulated via external stimuli including heat, electric bias and mechanical stress. Previous researches on how heat (or temperature) affects ferroelectric domain structures were normally carried out at temperatures close to phase transition points. Here we show that temperature variation far away from a phase transition point could have a significant effect on the ferroelectric/ferroelastic domain structure in ferroelectric materials. Our results indicate that thermal-induced degradation or thermal stability of ferroelectrics is not negligible.

In our work, barium titanate (BaTiO_3) single crystals were slowly heated to several temperatures in the range of ~ 40 – 60°C (the Curie point is ~120°C) in the transmission electron microscope (TEM) and were kept at each temperature for detailed structural characterization. As the temperatures were far below the Curie point and higher than the ambient temperature, the BaTiO_3 remains as a stable tetragonal phase. It is surprising to see that nano-sized lamellar domains appeared along the [110] direction within the initial domains at a small temperature range of ~ 50°C. The new domain structure disappeared above or below the temperature range and the phenomenon was repeatable. The orientation of the newly formed domain walls indicated that the new domains were 90° ferroelastic domains. The mechanism for the formation of the new domain structure will be discussed based on detailed TEM investigation results.

EP01.08.19

Visualization of Domain Structure and Switching Property of $\text{Hf}_{0.5}\text{Zr}_{0.5}\text{O}_2$ for the Ferroelectric Field Effect Transistors Hoon Kim¹, Seokjung Yun¹, Seongwoo Cho¹, Myungsoo Seo², Min-Ho Kang³, Yang-Kyu Choi² and Seungbum Hong¹; ¹Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); ²Department of Electrical Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); ³Department of Nano-process, National Nanofab Center (NNFC), Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Zr-doped HfO₂ (HZO), a conventional gate dielectric material, has attracted much attention for displaying negative capacitance in Field Effect Transistors (FETs) and its potential application for next generation nonvolatile memory devices. Furthermore, compared to conventional ferroelectric materials, HZO is more suited to FET fabrication because of its higher scalability, thermal stability, and compatibility with Si processes. Despite the material's potential, there is few research on its ferroelectric properties due to its limited window of allowable thickness at the nanoscale. Herein, we analyzed the ferroelectric properties and domain structures of HZO to understand the negative capacitance reported in HZO and mechanism behind ferroelectricity and related domain structure as well as its switching behavior at the nanoscale. First, in order to understand the switching characteristics of HZO thin films, we measured and analyzed the polarization versus electric field (PE) loops. Second, we investigated the domain structures of HZO using angle-resolved PFM, which entails using vertical and lateral PFM as well as the rotation angle of the sample to derive the sample's complex polarization state. We envision that our results will elucidate the origin of negative capacitance in terms of the domain structure of HZO film and contribute to the development of ultralow power logic transistors and future nonvolatile memory devices.

EP01.08.20

Effects of Post Metal and Forming Gas Annealing on Characteristics of Ferroelectric FinFETs with HfZrO_x Gate Dielectric Myungsoo Seo^{1,2}, Min-Ho Kang³, Wu-Kang Kim¹, Jae Hur¹, Seokjung Yun^{4,5}, Hoon Kim⁴, Seungbum Hong⁴ and Yang-Kyu Choi¹; ¹School of Electrical Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); ²Foundry Business, Samsung Electronics, Yongin, Korea (the Republic of); ³National Nanofab Center, Daejeon, Korea (the Republic of); ⁴Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of); ⁵Memory Business, Samsung Electronics, Hwasung, Korea (the Republic of).

Since excellent ferroelectric (FE) characteristics were demonstrated with a CMOS-process compatible thin hafnium-based material, FE field-effect-transistors (FETs) have attracted considerable attention as a promising candidate for next-generation nonvolatile memory, analog synaptic devices for neuromorphic systems, and steep slope devices called negative capacitance (NC) FETs, with low power consumption. Among various HfO₂ thin film dopant materials suitable for FE operation, such as Si, Zr, Y, and Al, Zr is well-known as showing stable characteristics thanks to having almost identical chemical properties with Hf. HfZrO_x (HZO) films consist of tetragonal, orthorhombic, and monoclinic phases. The orthorhombic phase is known to be responsible for the ferroelectricity of the thin film. Annealing after FE deposition, for example post metal annealing (PMA) or forming gas annealing (FGA), leads to crystallization which is a key factor in the final ferroelectric characteristics of the HZO thin film. Even though the effects of PMA and FGA on metal-ferroelectric-metal (MFM) capacitors have been investigated by several research groups, there has been no report on metal-ferroelectric-insulator-silicon (MFIS) structured FE FETs yet. In this work, the effects of PMA and FGA on characteristics of a highly-scaled FE FinFET with a 10 nm thick HZO film were carefully investigated. The effects of PMA at temperatures from 400 °C to 900 °C for 30 s were examined. An FGA split experiment was conducted with various temperatures and hydrogen (H₂) gas content ratios. First, changes of orthorhombic phase peak were investigated by spectral measurements with the grazing incidence X-ray diffraction (GI-XRD), and changes in domain behavior were also investigated using piezoresponse force microscopy (PFM). MFM capacitors with a TiN top and a TiN bottom electrode exhibited different butterfly-like features in capacitance-voltage (*C-V*) characteristics and polarization-electric field (*P-E*) hysteresis loops by split conditions. Finally, the electrical characteristics of the highly-scaled FE FinFETs were compared to those of the MFM capacitors for the first time under various conditions. The FE FinFETs were fabricated with a fin width of 50 nm, a fin height of 100 nm, and a gate length of 120 nm on bulk silicon wafers with gate last processes. The optimized PMA and FGA conditions determined in this experiment are expected to provide insights into the use of FE FETs as next-generation memory, synaptic devices for neuromorphic systems, and steep slope-based logic applications.

EP01.08.21

Magnetodielectric Coupling in BiFeO_{1-x}-GdMnO_x Multiferroics Roberto Masso¹, Satya N. Tripathy², Ricardo Martinez Valdes¹, Dillip K. Pradhan², Fernando Aponte¹ and R Palai¹; ¹Univ of Puerto Rico, San Juan, Puerto Rico, United States; ²Physics, National Institute of Technology, Odisha, India.

Magnetolectric (ME) multiferroic materials are promising materials for this novel multifunctional applications. BiFeO₃ (BFO), ferroelectric T_c ~ 830 °C and antiferromagnetic TN ~ 370 °C, is one the rarest single-phase room temperature multiferroic materials with many interesting physical phenomena. However, high leakage current of BFO and weak magnetolectric (ME) coupling are detrimental for applications. A strong ME coupling is an important requirement for practical applications. To enhance the ME coupling in BFO, we doped with GdMnO₃ (GMO), an oxide ferromagnetic. In this present work, we report synthesis and characterized BFO_{1-x}-GMO_x (BFO-GM) solid solutions (0.0 ≤ x ≤ 0.2) by auto-combustion method. The materials have been systematically characterized and examined to study the possibility of the compositional driven structural phase transition and its correlation with the ME coupling. The structural, microstructural, Raman spectroscopy, dielectric, ferroelectric, magnetic, and magnetodielectric properties were studied as a function of field (magnetic and electric), frequency, and temperature. For quantitative understanding, various modified theoretical models (Maxwell-Wagner, universal power law, Debye, etc.) were used to model the data. We found that BFO with 10% GMO doping shows strong ME effect. Details of this study will be discussed in the presentation.

EP01.08.22

Easy Control of Ferroelectric Vortices Array by Sweeping Field Ye Ji, Lele Ma, Linjie Liu, Weijin Chen and Yue Zheng; State Key Laboratory of Optoelectronic Materials and Technologies, Sun Yat-Sen University, Guangzhou, China.

Plenty of novel ferroelectric domain structures are pursued for over a decade due to both theoretical interest (topology phase transition, emergent phenomena, etc.) and practical use. Specifically, ferroelectric vortex with at least two-fold chirality and small size, is a competitive candidate for high capacity memory storage. Accordingly, manipulation of vortex chirality is of fundamental significance. Several proposed approaches have made notable progress by introducing local field with distinctive origins such as external inhomogeneous electric field and mechanical dislocation to break the circular symmetry of vortex (or discrete rotational symmetry for flux-closure structure). However, these approaches are either hard to perform or need *a priori* knowledge of imperfection which severely restrict the universality. In this paper, we generalize the symmetry broken idea to the sweeping direction in a time-dependent sweeping process, facilitating a simple yet robust vortex switching method conducted by phase field modeling. We firstly consider that a biased tip sweeps over a vortex where the electric field is no need to be stronger than that totally destroys the vortex. The sweeping process will produce a dominant dipole region (DDR) which serves as a new nucleus. Based on this mechanism, we propose a BaTiO₃/SrTiO₃ (BTO/STO) composite nanowire system for 1D memory architecture where each BTO block can form vortex thus carry information with STO block being the isolation zone. The vortex orientation can be tuned as well for multi-bit storage. The sweeping method is successfully employed into this system under varies conditions. Note that the coupling between adjacent BTO blocks is tuned by thickness of STO blocks. While strong coupling may cause crosstalk, it also provides a new controlling factor within the framework of sweeping method. To address this, we perform simulations of sweeping temperature field. Since the DDR exhibits no preferential orientation under temperature field, the neighboring part of adjacent BTO block behind the sweeping field will induce a DDR with same orientation to reduce gradient energy, therefore determines the final chirality. We hope the sweeping method will promote the understanding of vortex switching and be beneficial to device development.

EP01.08.23

Strain, Temperature and Electric-Field Effects on the Phase Transition and Piezoelectric Responses of $Ka_{0.5}Na_{0.5}NbO_3$ Thin Films Mengjun Zhou^{1,2}, Jianjun Wang², Long-Qing Chen²,¹ and Ce-Wen Nan¹; ¹School of Materials Science and Engineering, State Key Lab of New Ceramics and Fine Processing, Tsinghua University, Beijing, China; ²Department of Material Science and Engineering, The Pennsylvania State University, State College, Pennsylvania, United States.

$KNbO_3$ -based solid solution system is environment-friendly with good electromechanical performance. This work established the misfit strain-strain and temperature-strain phase diagrams for $K_{0.5}Na_{0.5}NbO_3$ thin films and calculated the polarization switching, phase transition, and piezoelectric responses of $K_{0.5}Na_{0.5}NbO_3$ thin films under various strains, temperatures and electric fields. The results show that the piezoelectric coefficient d_{33} can be enhanced near the phase boundaries. For the ferroelectric phase with nonzero out-of-plane polarization component, an optimal electric field is identified for maximizing d_{33} , which is desired in applications such as thin-film piezoelectric MEMS, transducers for ultrasound medical imaging and energy harvesting. The present results are expected to provide guidance for future experimental study of $K_xNa_{1-x}NbO_3$ thin films and the optimization of ferroelectric thin film-based devices.

EP01.08.24

IR-Active Modes Detected by Tip-Enhanced Raman Spectroscopy in $SrTiO_3$ Nanostructures—Field Gradient or Strain Gradient Contribution? Azza Hadj Youssef¹, Chahinez Dab¹, Jiawei Zhang¹, Gitanjali Kolhatkar¹, Alexandre Merlen² and Andreas Ruediger¹; ¹Institut National de la Recherche Scientifique, Varennes, Quebec, Canada; ²IM2NP, UMR 7334 CNRS, Universities of Aix Marseille and Toulon, Toulon, France.

Strain engineering and its effect on electromechanical coupling is an emerging powerful concept adopted by nanodevices. At the nanoscale, strain gradient dramatically increases leading to the emergence of new functionalities in thin films. Thus, its impacts on the crystal dynamics and physical properties are expected to be significant.

$SrTiO_3$ is an incipient ferroelectric perovskite, which has been extensively studied for its applications in electronics and electro-optic devices. When subjected to a biaxial strain, $SrTiO_3$ thin films show polar properties due to structural distortion. The structural distortion has a giant impact on the Raman modes, which correspond to the zone-center optical phonons symmetry, forbidden in bulk system. Raman spectroscopy of forbidden vibrational modes has been identified as a qualitative diagnostic tool for studying the strain effects and for providing vibrational spectroscopic information on the dynamic behavior of thin films. Tip-enhanced Raman spectroscopy (TERS), where the Raman and apertureless near-field scanning optical microscopy are combined with the contribution of a metallic tip, provides a comprehensive approach to those modes with improved sensitivity and spatial resolution.

In this work, we experimentally investigate strain-induced polarisation by monitoring vibrational Raman and IR-active modes in $SrTiO_3$ thin films (15 nm or less) deposited on platinized MgO (100) substrates by radio-frequency magnetron sputtering. In these films, the strain gradient is generated by the lattice-mismatch between the film and the substrate. We employ conventional Raman spectroscopy to investigate the effect of the interfacial strain gradient on the optical phonon modes of $SrTiO_3$ thin films. We detect first-order polar transverse optic TO_1 , TO_2 and TO_4 modes that indicate a lowering of the crystal symmetry for the $SrTiO_3$ and thus the appearance of spontaneous polarization generated in localized strained regions.

Second, to present an evidence of the existence of the nano-polar regions with respect to conventional Raman spectroscopy, (TERS) measurements were recorded on a $SrTiO_3$ thin film. The gold tip introduces an electric field gradient contribution to the signal amplification of the polar phonons and it images the surface of $SrTiO_3$ nanostructures based on the optical phonon mode response. Finally, we discuss the field gradient contribution to the significant signal enhancement as well as to the appearance of symmetry-forbidden IR-active modes and first-order Raman modes associated to the nano-polar regions induced by local structural distortions.

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Nanoscale Linear Dielectric Constant Imaging Using $\partial C/\partial z$ -Mode Scanning Nonlinear Dielectric Microscopy Yoshiomi Hiranaga and Yasuo Cho; Tohoku University, Sendai, Japan.

The continued miniaturization of electronic devices containing dielectric materials has increased the impact of nanoscale linear dielectric constant distributions on device characteristics [1]. As a result, more precise control of process damage is required to ensure the fabrication of reliable highly integrated devices, and the nanoscale analysis of dielectric constant has become important. Dielectric constant assessments over nanoscale regions require the measurement of capacitance with sufficiently high sensitivity. Various techniques for the measurement of local capacitance based on scanning probe microscopy (SPM) have been proposed to date, including scanning capacitance microscopy (SCM) [2], scanning microwave microscopy (SMM) [3], microwave impedance microscopy (MIM) [4] and scanning nonlinear dielectric microscopy (SNDM) [5]. SNDM is an especially useful technique as it is highly sensitive to variations in capacitance on the order of 10^{-22} F/Hz [6]. As a result, SNDM can detect capacitance variations even when employing extremely sharp probe tips, and so is a very effective means of obtaining improved spatial resolution. Conventional SNDM is typically used to determine nonlinear dielectric constant and to visualize dielectric (or electrical) anisotropy in ferroelectrics and semiconductors. In contrast, there have been only a few reports concerning linear dielectric constant imaging using SNDM [7-9]. Herein, we propose a novel method for linear dielectric constant imaging, termed $\partial C/\partial z$ -mode SNDM ($\partial C/\partial z$ -SNDM), that substantially reduces the effects of stray capacitance and enables quantitative imaging with high spatial resolution.

$\partial C/\partial z$ -SNDM technique employs probe-height modulation to suppress disturbances originating from stray capacitance and to improve measurement stability. This method allows local dielectric constant distributions to be examined with extremely low noise levels (approximately 0.01 aF) by virtue of the highly sensitive probe. A cross-section of a multilayer oxide film was visualized using $\partial C/\partial z$ -SNDM as a demonstration, and numerical simulations of the response signals were conducted. Moreover, the beneficial aspects of higher-harmonic response imaging are discussed herein, taking into account assessments of spatial resolution and quantitation.

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Investigation of Piezoelectric Responses of BaTiO₃ Nanorod Bundle Arrays [Moon-hyeok Choi](#), Seon Min Jang, Sang-Mok Chang and Su Chul Yang; Department of Chemical Engineering, Dong-A University, Busan, Korea (the Republic of).

Low-dimensional piezoelectric nanostructures with nanoparticles, nanorods, thin films have been studied for potential applications of energy harvesters, self-powered sensors, and piezoelectric transistors. For a decade, one-dimensional (1D) nanostructures have been widely approached for miniaturization in piezoelectric field, however, there are still critical limitations of insufficient piezoelectricity and unstable standing on a conductive substrate. In this study, lead-free BaTiO₃ nanorod bundle arrays (NBA) with highly piezoelectric properties were synthesized on conductive fluorine-doped tin oxide substrate via a two-step process consisting of TiO₂ epitaxial growth and BaTiO₃ conversion. First, in order to develop framework of NBA, effects of pH and Ti precursor on TiO₂ nanostructures were investigated with adjusting area density, aspect ratio and free standing. It is illustrated that area density was enlarged as an increase in Ti precursor concentration and increase in pH, respectively. Optimum TiO₂ NBA was found to exhibit single-rod diameter of 10 nm, bundle diameter of 100 nm, no-aggregation, and high area density over 60 %. Next, M-shaped TiO₂ nanorod bundles were developed via chemical etching process to conduct complete perovskite BaTiO₃ conversion. During chemical etching, top surface was found to be more etched compared to side wall because of the higher surface energy of (001) with Z-axis than (110) with X and Y axis. As a result of XRD analysis, it is noted that the M-shaped nanostructure can offer large diffusion sites of Ba²⁺ ions determining perovskite phase. The effective BaTiO₃ conversion using M-shaped nanostructures was confirmed with volume expansion and ion mapping by SEM and STEM analysis, respectively. Finally, the final structure of perovskite BaTiO₃ NBA was found to exhibit a feasible piezoelectric response of 3.56 nm with a clear phase change of 180° from the single BaTiO₃ bundle, by point piezoelectric forced microscopy analysis. In conclusion, BaTiO₃ NBA with high piezoelectric properties could be a promising nanostructure for various nanoscale electronic devices.

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Two-Dimensional Analysis of Nanoscale Contact Electrostatics in Hysteretic Materials—To Switch or Not to Switch, Part Trois Sabine M. Neumayer, Sergei V. Kalinin, Nina Balke and [Petro Maksymovych](#); Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

A major task for piezoresponse force microscopy (PFM) is to detect and quantify piezoelectric displacements near the present sensitivity limit of ~ 1 pm/V. Measuring the relatively weak piezoresponse is needed to probe new candidate ultrathin ferroelectrics, such as HfO₂ thin films and quasi-2D layered ferroelectrics, while high sensitivity measurements are likewise beneficial to understand the performance of sensors, actuators, energy harvesters. The challenge of the measurement is primarily rooted in the contribution of electrostatic interaction, thermal expansion and other forces to the net measured signal, which may obscure or even disguise the detection of piezoelectric response.

Recently, we applied contact mode Kelvin probe force microscopy (cKPFM) to differentiate electrostatic and piezoelectric contributions in PFM measurements [1,2]. In this talk, we will present a new approach to visualize and analyze cKPFM measurements aimed at improving and eventually automating the relevant data analysis. The approach, which we refer to as the field-response function, treats applied fields during the measurement and the write cycle on equal footing, thereby mapping the measured probe displacement onto a 2D grid of applied potentials. Though relatively simple, the change of the representation brings in significant benefits: (1) the relevant information of the cKPFM measurement is captured as a single image, presenting regions of stable, unstable or metastable states; (2) ferroelectric switching and electret-type behaviors are clearly differentiated; (3) the response function can in general be acquired with arbitrary sequence of applied fields, not necessarily sequential voltage cycling; (4) from the few representative cases, such as pre-breakdown window of lead zirconate titanate, it is becoming progressively clear that a simple picture of additive piezoresponse and electrostatics is not generally valid in PFM, even for well established ferroelectrics; (5) fitting the whole field-response function enables feature detection toward and subsequent supervised and unsupervised classification of characteristic responses, which we will demonstrate using Gaussian process regression combined with multivariate clustering analysis. These developments enhance the ability of PFM to probe “difficult” ferroelectrics and advance cKPFM toward to analysis of defect chemistry and more generally hysteretic materials, such as electrets, electroresistive, phase change materials and mixed electron-ion conductors. This research was sponsored by the Division of Materials Sciences and Engineering, BES, US DOE. Experiments were conducted at the Center for Nanophase Materials Sciences, a DOE Office of Science User Facility.

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Carrier Concentration-Dependent Piezotronic and Piezo-Phototronic Effects in ZnO Thin-Film Transistor Zijian Pan, [Wenbo Peng](#), Fangpei Li and Yongning He; Xi'an Jiaotong University, Xi'an, China.

The piezotronic and piezo-phototronic effects have been confirmed as promising methodologies to optimize the performances of electronic/optoelectronic devices. However, these strain-induced modulations (i.e., piezotronic and piezo-phototronic effects) are strongly dependent on the carrier concentration of the piezoelectric semiconductor. In this work, the carrier concentration dependence of both the piezotronic and piezo-phototronic effects are carefully and systematically investigated in ZnO thin-film transistors (TFTs) by varying manufacturing process and introducing 365 nm UV illumination to modulate the carrier concentration of ZnO film. The experimental results show that significant performance improvement can be obtained in the ZnO TFTs by the piezotronic and piezo-phototronic effects but strongly depend on the carrier concentration in the ZnO films: (1) For the moderate carrier concentration ZnO NW TFT, distinct performance improvement is achieved in the ZnO NW TFT by the piezotronic effect with a maximum enhancement of 48.89% in saturation field-effect mobility μ_{sat} observed. (2) Whereas, the photoresponse performance of the ZnO NW TFT to 365 nm UV illumination shows no modulation by the piezo-phototronic effect due to the screening effect that is dramatically strengthened/enhanced by the significant increase of the photogenerated carrier concentration. (3) For the ultra-low carrier concentration ZnO seed TFT, there is almost no change in performances of the ZnO seed TFT when introducing the piezotronic effect, which is because the ultra-low carrier concentration ZnO seed film exhibits “piezoelectric characteristic” much more than “semiconductor characteristic” and therefore its semiconductor characteristic is difficult to be modulated by the external compressive strain. (4) By introducing 365 nm UV illumination to the ZnO seed TFT, the photogenerated carrier concentration in ZnO seed film becomes moderate and therefore significant photoresponse improvement of the ZnO seed TFT is obtained by the piezo-phototronic effect with a maximum enhancement of 56.37% in photoresponsivity R observed. In all, significant performances improvement can be obtained in the ZnO TFT by the piezotronic/piezo-phototronic effect only when the carrier concentration in the ZnO is moderate, while there is no obvious modulation in performances of the ZnO TFT when the carrier concentration is ultra-low or ultra-high. This study presents in-depth understanding about the carrier concentration dependence of the piezotronic and piezo-phototronic effects in ZnO TFT and also provides feasible, compatible and adjustable methodologies to enhance/optimize the performances of electronic/optoelectronic devices.

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Water Actuation Through Nanomembranes Using Surface Acoustic Waves (SAW) Zamart Ramazanov³, Kurbangali B.

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Nanofiltration technology for water desalination and other fluids purification from salts, germs, bacteria and viruses are based on the so called Nanopumping (NP) effect, when a fluid flow through nanomembranes and nanochannels is actuated using Surface Acoustic Waves (SAW) is presented. The paper considers processes of water nanofiltration through a carbon nanomembrane using ultrasonic waves, which generated surface acoustic waves (SAW) devices under different RF powers and frequencies. We considered droplet of water volume in the 2–20 μl range, and use SAW devices with different frequencies from 34 to 116 MHz. The effect of frequency on microfluidic performance, such as moving, atomization, and passage of nanodroplets has been studied using a video camera in a range of SAW power. This identified that SAW with higher resonant frequencies have increased power values for moving, atomization, and passage of droplets through nanopores. The device consisted of a Lithium niobate (LiNbO_3) piezoelectric substrate and a carbon nanomembrane placed on the substrate. Such nanopumping devices will be of practical interest for the development of future energy sources, e.g., for fuel cells, hydrogen energy, pharmaceutical processes and nanoengine for medical robots, as well as for use in a wide variety of chemical, food and agricultural applications. It is demonstrated that the process of nanofiltration of water includes the processes of droplet moving, atomization and passage through nanopores and will be useful for future water desalination processes. The dependences of the travel time of droplet moving and atomization of water on the power, frequency and volume of the droplet were established. It is shown that with increasing of power and frequency of SAW, the filtration process proceeds rapidly and has a power-law character.

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Pyroelectric Properties of BiFeO_3 Thin Films [Lei Zhang](#)¹, Oliver Paull², Daniel Sando², Gabe Velarde¹, Shishir Pandya¹, Nagarajan Valanoor² and Lane W. Martin^{1,3}; ¹Department of Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States; ²School of Materials Science and Engineering, University of New South Wales, Sydney, New South Wales, Australia; ³Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States.

Pyroelectric materials that exhibit changes of spontaneous polarization with temperature variation are of great interest for application such as thermal sensing and waste-heat energy harvesting. Owing to large electrical fields that can be applied at modest voltages and the possibility of direct integration on semiconductors, pyroelectric thin films, in particular, have received considerable attention recently. Scientific investigation of pyroelectric thin films has, however, traditionally been challenging due to possible convolution of pyroelectric responses with thermally-stimulated currents that prevent an accurate determination of the intrinsic pyroelectric properties. Recently developed electrothermal test platforms which are microfabricated for the thin-film geometry, however, now allows for the direct measurement of pyrocurrent and an accurate extraction of pyroelectric coefficient utilizing phase-sensitive local heating and thermometry [1].

In this work, we leverage such an experimental approach to understand the pyroelectric response of one of the most widely-studied ferroelectric materials recently – BiFeO_3 . In particular, we explore the evolution of pyroelectric response as a function of strain – probing the effects in rhombohedral- and tetragonal-like, as well as mixed-phase versions of BiFeO_3 heterostructures – with an emphasis on understanding how temperature-driven competition of different structural ground states impacts pyroelectric response. Here we study BiFeO_3 films grown on a range of substrates including DyScO_3 (wherein small compressive strains produce strained versions of the parent rhombohedral structure) and LaAlO_3 (where large compressive strains produce both single-phase tetragonal-like and mixed-phase structures which exhibit intimate mixtures of the two structural polymorphs depending on the film thickness) [2]. Of great interest is the fact that the relative fraction of the rhombohedral- and tetragonal-like phases is strongly temperature- and electrical-field-dependent. As such, the interconversion of the two phases with temperature change implies the potential for large changes in the out-of-plane spontaneous polarization and, in turn, pyroelectric response. Here we will present results of strain- and thickness-dependent evolution of the BiFeO_3 structure and subsequent study of pyroelectric, dielectric and ferroelectric effects made possible by the use of our novel microfabricated electrothermal device structures. This approach will provide a complete picture of the electrothermal response of this interesting system.

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Room Temperature Ferroelectricity in Multiferroic $\text{Al}_x\text{Fe}_{2-x}\text{O}_3$ Epitaxial Thin Films [Badari Narayana A. Rao](#)¹, Tsukasa Katayama², Shintaro Yasui¹ and Mitsuru Itoh¹; ¹Tokyo Institute of Technology, Yokohama, Japan; ²Department of Chemistry, The University of Tokyo, Tokyo, Japan.

Single-phase multiferroic materials have attracted considerable attention among scientists, due to the strong drive in the industry towards device miniaturization, faster processing speed and addition of new functionalities. Currently, most of the discovered materials are multiferroic only at low temperatures, thereby hindering their induction into practical devices. $\kappa\text{-Al}_2\text{O}_3$ type $\text{Al}_x\text{Fe}_{2-x}\text{O}_3$ ($x\text{-AFO}$) oxides belong to a relatively new class of metastable multiferroic compounds (space group: $Pna2_1$), which can be stabilized as thin films [1]. We have found that some compositions of $x\text{-AFO}$ can exhibit both ferrimagnetism and ferroelectricity at room temperature. The $x\text{-AFO}$ system is attractive compared to other systems such as GaFeO_3 [2] since both Al and Fe are environment friendly, and abundantly available in the earth's crust. Similar to GaFeO_3 , the ferrimagnetic easy axis for $x\text{-AFO}$ is observed along the a -axis and ferroelectricity along the c -axis [1]. Though epitaxial films of $x\text{-AFO}$ have been grown earlier, only indirect evidences of room temperature ferroelectricity in $x\text{-AFO}$ are available in literature till date [1,3]. Large leakage currents in these $x\text{-AFO}$ films made it difficult to carry out ferroelectric and magnetoelectric measurements at room temperature. We have used pulsed laser deposition technique to successfully fabricate epitaxial thin films of $x\text{-AFO}$ on Nb-doped SrTiO_3 (111) substrates. We were able to significantly reduce the leakage current for our films by careful tuning of deposition parameters, to attain films with very smooth surface and small grain size. Direct ferroelectric measurements could be carried out on the films at room temperature, showing good hysteresis loops for $x\text{-AFO}$ ($x = 0.5 - 1.0$). While the ferroelectric characterization showed that the coercive electric field increases with increasing x , magnetic measurements showed that the coercive magnetic field decreases with increasing x . Furthermore, magnetocapacitance was observed at room temperature, thereby demonstrating their potential as a promising multiferroic material.

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Yttrium Iron Garnet Waveguide for Forward Volume Spin Wave Interference [Taichi Goto](#)^{1,2}, Takuya Yoshimoto¹, Caroline A. Ross³, Koji Sekiguchi⁴, Alexander Granovsky⁵, Yuichi Nakamura¹, Hironaga Uchida¹ and Mitsuteru Inoue¹; ¹Toyohashi University of Technology, Toyohashi, Japan; ²JST PRESTO, Kawaguchi, Japan; ³Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ⁴Yokohama National

University, Yokohama, Japan; ⁵Lomonosov Moscow State University, Moscow, Russian Federation.

Yttrium iron garnets (YIG, $Y_3Fe_5O_{12}$) are well-known as an excellent material for spin wave (SW) waveguide because of its low magnetic damping constant. However, demonstrated functionalities of spin waves were limited because of the difficulty of fabrication and patterning of thin YIG films. In addition, the integration of SW-excitation antennas onto YIG waveguide is also important for device development. In this study, ~50 nm thick single crystalline YIG was grown on a 10 mm x 10 mm x 0.5 mm rare-earth substituted gadolinium gallium garnet (SGGG) substrate by pulsed laser deposition (PLD). The substrate was (111) oriented. The temperature of the substrate during growth was ~850°C under an oxygen pressure of 2.6 Pa. The base pressure was 2.0×10^{-4} Pa. The grown YIG was characterized by 2θ - ω x-ray diffraction. The x-ray was monochromated using two Ge(220) single crystals. The obtained diffraction pattern showed clear fringes, showing flat surface and the deposited thickness was ~50 nm. The reciprocal space map showed fully strained film state. The unit cell length was 1.2476 nm. The magnetic properties were measured by vibrating-sample magnetometer, showing an in-plane coercivity of 0.37 Oe, an out-of-plane saturation magnetic field of 1.73 kOe, and a saturation magnetization of 1.80 kG (= 143 emu/cc). The estimated magnetic anisotropy energy K_u was -9.88×10^5 GOe. The strained lattice angle was 90.4° . This YIG was patterned into 400 nm x 100 nm using phosphoric acid at 140°C, with the etching process being controlled using an oil bath. Its taper angle was 15° with respect to the in-plane direction. Onto this YIG waveguide, three coplanar waveguides were fabricated with ~50 nm distances and SW interference was demonstrated. A magnetic field of 2.80 kOe was applied perpendicular to the film. The phase of the SW was changed, and the synthesized SW based on interference was confirmed. These showed the YIG was successfully patterned as SW waveguide and the uniformity of the quality of single crystalline YIG was sufficiently high for showing SW interference. This was an important milestone of development of a SW integrated circuits.

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In Situ Study of Inter-Ferroelectric Phase Transitions In Domain Engineered Ferroic Crystals [Markys G. Cain](#)¹, Peter Finkel², Margo L. Staruch², Paul Thompson³ and Didier Wermelle³; ¹Electrosiences Ltd, Farnham, United Kingdom; ²U.S. Naval Research Laboratory, Washington, District of Columbia, United States; ³XMAS CRG, ESRF, Grenoble, France.

It is well established that domain engineered ferroelectric single crystals deliver an order of magnitude improvement in piezoelectric properties compared to conventional PZT. The unusual electromechanical properties of these domain engineered single crystals of $PbZn_{1/3}Nb_{2/3}O_3$ - $PbTiO_3$ (PZN-PT) and $PbMg_{1/3}Nb_{2/3}O_3$ - $PbTiO_3$ (PMN-PT) have been demonstrated for the compositions poised at the ferroelectric rhombohedral (FR) side of the morphotropic phase boundary (MPB), with domain engineering regarded as one of the most significant breakthroughs in relaxor ferroelectrics for enhanced actuation performance. To exploit the extremely large actuation capabilities of these new single crystal piezoelectric materials, the stability of their crystallographic variants is critical as well as the ability of the material to respond quickly to changes in electrical or stress fields. The latter is determined through an understanding of the dynamical nature of the materials' domain switching response. In this work, we explored this stability using in situ electric field synchrotron X-ray diffraction at the XMaS beamline (BM28), at the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The electric field induced and mechanical stress induced ferroelectric-ferroelectric phase transitions were studied as a function of frequency, field and static stress in the relaxor ferroelectric system $Pb(In_{1/2}Nb_{1/2}O_3)$ - $Pb(Mg_{1/3}Nb_{2/3}O_3)$ - $PbTiO_3$ (PIN-PMN-PT) (lead indium niobate – lead magnesium niobate – lead titanate) for compositions close to the morphotropic boundary. The novel in situ PE loop and strain measurement system was used on the XMaS facility, with strain measured using a strain gauge affixed to the side of the sample. The X-Ray data was collected in a synchronous manner to the application of electric field.

Preliminary results show that X-ray diffraction is in good agreement with macroscopic observations and phenomenological models confirming our proposed transformational pathway. Our data is taken using full 2D X-Ray images (Pilatus 2M camera) allowing us to very rapidly explore the nature of competing crystallographic transformations arising across quite a large reciprocal space. Finally, we performed glancing angle measurements that permit imaging of the crystallography just beneath the surface of the crystal face allowing calculation of strain transfer through heteroepitaxial interfaces in composite multiferroics. The phenomena presented in this work are envisioned to be universal in domain engineered ferroics enabling mechanical stress to be used for strain- and polarization-control of electromechanical energy conversion. The results will shed more light on the nature of this reversible transformation between two ferroelectric phases, including the mechanism responsible for incredible lack of fatigue after millions of cycles, and advance towards the development of a wide range of ferroic and multiferroic devices.

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Structural Correlation of Ferroelectric Behavior in Mixed Hafnia-Zirconia High-k Dielectrics for FeRAM and NCFET Applications [Vineetha Mukundan](#)¹, Karsten Beckmann¹, Steven Consiglio², Kandabara Tapily², Robert Clark², Gert Leusink², Nathaniel Cady¹ and Alain Diebold¹; ¹Colleges of Nanoscale Sciences and Engineering, SUNY Polytechnic Institute, Albany, New York, United States; ²TEL Technology Center, America, LLC, Albany, New York, United States.

The recent discovery of ferroelectric behavior in doped hafnia-based dielectrics, attributed to a non-centrosymmetric orthorhombic phase, has led to attractive applications such as negative differential capacitance field-effect-transistors (NCFET) and ferroelectric random access memory devices (FeRAM) [1]. Alloying with similar oxides like ZrO_2 , doping with specific elements such as Si, novel processing methods, encapsulation and annealing schemes are also some of the techniques that are being explored to target structural modifications and stabilization of the non-centrosymmetric phase. In this study, we utilized synchrotron-based x-ray diffraction in the grazing in plane geometry (GIIXRD) to determine the crystalline phases in hafnia-zirconia (HZO) compositional alloys deposited by atomic layer deposition (ALD). Here we compare and contrast the structural phases and ferroelectric properties of mechanically confined HZO films in metal-insulator-metal (MIM) and metal-insulator-semiconductor (MIS) structures. Both MIM and MIS structures reveals a host of reflections due to non-monoclinic phases in the d-spacing region between 1.75Å to 3.25Å [2-4]. The non-monoclinic phases are believed to consist of distorted tetragonal and orthorhombic phases and a suppression of the monoclinic phase in MIM structures compared to the MIS structures was observed. We also report the structural changes with different Hf:Zr ratios (1:4, 4:1 and 1:1) and overall thickness of the HZO film (10nm, 7nm, 5nm, and 3nm). The correlation of the electrical properties with the structural analysis obtained by GIIXRD highlights the route to obtaining non-centrosymmetric orthorhombic phases which enable ferroelectricity [5,6]. Additionally, this work highlights the importance of understanding the effects of the underlying substrate (metal vs. Si) for different target applications.

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Second Harmonic Generation in Ferroelectric HfO₂ Based Metasurfaces Fei Huang^{1,2,6}, Jun Qin^{1,2}, Xinyue Li^{3,4}, Longjiang Deng^{1,2}, Huigao Duan⁵, Jialiang Xu^{3,4} and Lei Bi^{1,2}; ¹National Engineering Research Center of Electromagnetic Radiation Control Materials, Chengdu, China; ²University of Electronic Science and Technology of China, Chengdu, China; ³Tianjin University, Tianjin, China; ⁴Collaborative Innovation Center of Chemical Science and Engineering, Tianjin, China; ⁵State Key Laboratory of Advanced Design and Manufacturing for Vehicle Body, Hunan University, Changsha, China; ⁶Department of Electronic Engineering, Stanford University, Stanford, California, United States.

Hybrid nonlinear photonic structures, in which nonlinear optical materials such as ferroelectrics are incorporated in the near field of a nanophotonic structure, provide a new way to significantly boost the nonlinear photonic effects at the nanoscale. However, several challenges prevent on-chip integration of such hybrid nonlinear metasurface with standard CMOS fabrication technologies, such as material compatibility, scaling and operation wavelength range. Recently, ferroelectric HfO₂ thin films have attracted great research interest. As a widely applied high-K oxide material for gate dielectrics, this material is compatible with CMOS technologies. Room temperature ferroelectric properties in such materials can maintain down to a film thickness of 3-5 nm, with similar remnant polarization compared to thicker films. These unique properties ignite great research interest on this material for microelectronic applications. However, to the best of our knowledge, there has been no report on using such materials for second harmonic generation applications.

Here, we demonstrate an on-chip hybrid nonlinear metasurface for second harmonic generation using nanometer thick ferroelectric yttrium doped HfO₂ thin films. XRD, hysteresis loop and PFM are measured to verify its ferroelectricity. Optical constant characterizations of ferroelectric HfO₂ indicate an wide optical band gap of 4.8 eV for Y:HfO₂ thin films. Gold metasurfaces with different grating width ranging from 50 nm to 125 nm are fabricated by EBL. By incorporating a 24 nm thick ferroelectric Y:HfO₂ thin film in a plasmonic metasurface nanocavity, we observed one order of magnitude enhancement of SHG compared to bare ferroelectric HfO₂ thin films. Moreover, a 3 fold enhancement of SHG is observed in the hybrid metasurface compared to a control device using non-ferroelectric HfO₂ showing almost identical linear optical properties, demonstrating a major contribution of SHG from ferroelectric Y:HfO₂. We also demonstrated good scalability of such devices down to a Y:HfO₂ thickness of 13 nm with another 2 fold enhancement of SHG. Using numerical simulations, we demonstrate a SHG coefficient $\chi^{(2)}$ of 5 pm/V of the polycrystalline Y:HfO₂ thin films, which is comparable to 5%MgO:LiNbO₃ (9.4 pm/V) epitaxial thin films and UV transparent materials such as BaB₂O₄ (4.4 pm/V). These findings demonstrate the promising potential of ferroelectric HfO₂ for on-chip nonlinear photonic devices, which also provide a general way of high efficiency SHG using on-chip hybrid nonlinear metasurfaces.

EP01.08.36

Towards Infinite Polarization Retention in Thin-Film Small-Molecular Organic Ferroelectrics Indre Urbanaviciute¹, Subham Bhattacharjee², Michal Biler³, Tim Cornelissen¹, Mathieu Linares³, Rint Sijbesma² and Martijn Kemerink¹; ¹IFM, Linköping University, Linköping, Sweden; ²Macromolecular and Organic Chemistry, Eindhoven University of Technology, Eindhoven, Netherlands; ³Theoretical Chemistry and Biology, KTH Royal Institute of Technology, Stockholm, Sweden.

With increasing demand for cheap, efficient, lightweight and flexible electronics, a matching memory technology is required. Ferroelectricity-based memory devices assure non-volatility and low energy consumption, while organic materials, potentially used for this purpose, guarantee easy processability, low cost and advantageous physical properties including flexibility. It has been speculated that a recently discovered class of organic ferroelectric materials – columnar discotic liquid crystals – could offer an intriguing possibility to extend bit density limits of the conventional memory devices substantially, if these discrete ferroelectric molecular columns were addressed individually. However, despite being very well established in the field of electro-optics, ferroelectric liquid crystals lacked interest from a memory device perspective due to modest remnant polarization and/or poor polarization retention.

Here, we demonstrate how simple structural modification of a prototypical supramolecular ferroelectric liquid-crystal benzene-1,3,5-trisamide (BTA) leads to significant improvements in the main ferroelectric properties and results in materials with extrapolated data retention time of more than 10 years in thin-film solution-processed capacitor devices.

The BTA is a C₃ symmetry molecule consisting of a π -stacking benzene core, to which three free-to-rotate dipolar amide groups (O=C-NH), having a dipole moment of 3 Debye each, and flexible solubilizing alkyl (-CH₂)_n chains are attached. We show that all the core properties of the ferroelectric – remnant polarization, coercive field, polarization retention time and operation temperature range – increases continuously in BTAs with shortening of the alkyl chain length (from C₁₈H₃₇ to C₆H₁₃)¹. The optimal hexyl-tailed BTA material demonstrates performance close to that of P(VDF-TrFE): remnant polarization of ~60 mC/m², fast polarization switching, low fatigue and polarization retention of several months at room temperature. Furthermore, if linear tails are changed to branched (achiral ethylhexyl and heptylhexyl), effectively infinite data retention is achieved. The origin of these improvements is discussed in context of electrostatic and steric interactions, as well as inherent morphological layer properties, the latter being the dominant.

Easy-processability, room temperature operation, remnant polarization as high as of the P(VDF-TrFE), and polarization retention exceeding commercial requirements distinguish the BTA material from other small-molecular organic ferroelectrics and makes it a perspective choice for applications that require cheap, flexible and lightweight ferroelectrics. The study results, furthermore, bring more understanding into the field and propose guidelines for further advancement in molecular engineering.

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EP01.08.37

Synthesis, Microscopy and Spectroscopic Characterizations of Rare Earth- Doped BaTiO₃ Nanocubes for Optical and Ferroelectric Applications Benard Kavay^{2,1}; ¹Science of Advanced Materials, Central Michigan University, Mount Pleasant, Michigan, United States; ²Chemistry and Biochemistry, Central Michigan University, Mount Pleasant, Michigan, United States.

Rare-earth doped BaTiO₃ nanocubes have been synthesized using a highly versatile, energy-efficient solvothermal route at temperatures as low as 150 °C. Transmission electron microscopy images of the as-synthesized Ba_{1-x}Ln_xTiO₃ (0.01 ≤ x ≤ 0.09; Ln = La³⁺, Ce³⁺, Nd³⁺) showed highly monodisperse and self-assembled nanocubes with a mean particle size of 20 ± 2 nm for all nominal dopant compositions. High resolution transmission electron microscopy was used to explore in detail the atomic planes, polarization direction, distribution of individual dipoles and the ferroelectric domains within a single nanocube. Also, piezoelectric force microscopy and lithography techniques were employed to further understand the ferroelectric behavior of the Ln-doped BaTiO₃ nanocubes. It was determined that all Ln-doped BaTiO₃ nanocrystals present a ferroelectric behavior at room temperature with maximum values of the permittivity around the Curie temperature. Dielectric spectroscopy measurements were performed by using vacuum sintered pellets of the as-synthesized nanocubes and measured at both the megahertz and terahertz electric field frequencies. We observed significantly higher dielectric constant values up to 6000 for lower dopant concentrations. An FTIR technique was employed to study the surface characteristics of the nanocubes and the nature of binding of the capping ligand molecules to the surface of the nanocrystals. It was determined that the oleic acid ligand used as a capping agent binds to the Ba ions in the Ln-doped BaTiO₃ crystal structure via a bidentate coordination mechanism. The insulating properties of the Ln-doped BaTiO₃ was further

determined using diffuse reflectance spectroscopy and the Kubelka-Munk theory of reflectance. The band gaps of the as-synthesized nanocubes were determined for all different Ln dopants and various concentrations.

EP01.08.38

Electrostatic Force Driven Oxide Heteroepitaxy for Interface Control Mengjiao Wu, Ren Zhaohui and Han Gaorong; Materials Science and Engineering, Zhejiang University, Hangzhou City, China.

Oxide heterostructure interfaces create a platform to induce intriguing electric and magnetic functionalities for possible future devices. A general approach to control growth and interface structure of oxide heterostructures will offer a great opportunity for understanding and manipulating the functionalities. Here we report that an electrostatic force, originating from a polar ferroelectric surface, can be used to drive oxide heteroepitaxy, giving rise to an atomically sharp and coherent interface by using a low-temperature solution method. These heterostructures adopt a fascinating selective growth, show a saturation thickness and the reconstructed interface with concentrated charges accumulation. The ferroelectric polarization screening, developing from a solid-liquid interface to the heterostructure interface, is decisive for the specific growth. At the interface a charge transfer and accumulation take place for electrical compensation. The facile approach present here can be extremely useful for controlling oxide heteroepitaxy and producing intriguing interface functionality via an electrostatic engineering.

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EP01.08.40

Imaging and Engineering the Dynamic Motion of Multiferroic Domain Walls by an Electron Beam Michele Conroy¹, Alan Harvey¹, Charlotte Cochard², Kalani Moore¹, Roger Whatmore³, Alexei Gruverman⁴, Marty Gregg² and Ursel Bangert¹; ¹Bernal Institute, University of Limerick, Limerick, Ireland; ²Centre for Nanostructured Media, Queen's University Belfast, Belfast, United Kingdom; ³Imperial College London, London, United Kingdom; ⁴University of Nebraska Lincoln, Lincoln, Nebraska, United States.

Recently there has been a dramatic increase of research activity in multiferroic materials.1-4 More specifically in charged domain walls (DWs) within these materials.5,6 These previously overlooked features are now seen as new form of two-dimensional (2D) material in their own right. With all the potential unique characteristics that make 2D materials such as graphene, DWs have become a new field of research. The main aspect that sets DWs apart from other 2Ds is the ability to create, destroy and move them by an external field or physical force. They're dynamic nature immediately suggests a potential role for them as interconnects in completely new forms of agile or adaptive nanoscale circuitry. In this study we use the electric field applied by the scanning electron microscope (SEM) probe to study the motion of charged DWs in the improper ferroelectric material Cu₃B₇O₁₃Cl.⁷ By changing the applied voltage, current and magnification we conducted a detailed quantification of the DW dynamics due to applied electric field. Focused ion beam (FIB) lamellas were prepared of these selected regions within the bulk crystal and the DWs in cross-section were analyzed by transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM). Weak beam dark field TEM and selected area diffraction analysis revealed there was distinct domains within the cross sections after the SEM probe DWs studies. This was not seen in lamellas formed from regions with low dose imaging per FIB lamella formation. Suggesting that above a certain dose, and thus electric field new DWs are formed. Additionally the geometry of the DWs seen in cross section are significantly different depending on their freedom of movement seen in the SEM probe study. 1 Evans, D. M. et al. The nature of magnetoelectric coupling in Pb (Zr, Ti) O₃-Pb (Fe, Ta) O₃. *Advanced Materials* 27, 6068-6073 (2015). 2 Eerenstein, W., Mathur, N. D. & Scott, J. F. Multiferroic and magnetoelectric materials. *Nature* 442, 759, doi:10.1038/nature05023 (2006). 3 Ramesh, R. & Spaldin, N. A. in *Nanoscience And Technology: A Collection of Reviews from Nature Journals 20-28* (World Scientific, 2010). 4 Spaldin, N. A. Multiferroics: from the cosmically large to the subatomically small. *Nature Reviews. Materials* 2, 17017 (2017). 5 Ma, J. et al. Controllable conductive readout in self-assembled, topologically confined ferroelectric domain walls. *Nature Nanotechnology*, doi:10.1038/s41565-018-0204-1 (2018). 6 Scott, J. F. et al. Superdomain dynamics in ferroelectric-ferroelastic films: Switching, jamming, and relaxation. *Applied Physics Reviews* 4, 041104 (2017). 7 McQuaid, R. G., Campbell, M. P., Whatmore, R. W., Kumar, A. & Gregg, J. M. Injection and controlled motion of conducting domain walls in improper ferroelectric Cu-Cl boracite. *Nature communications* 8, 15105 (2017).

SESSION EP01.09: Physics of Semiconducting Piezoelectric, Pyroelectric and Ferroelectric Materials
Session Chairs: Lauren Garten and Wilfrid Prellier
Thursday Morning, November 29, 2018
Hynes, Level 1, Room 103

8:00 AM *EP01.09.01

Quantifying Voltage-Modulated Electromechanical Sensitivity and Hysteresis Measurements on the Nanoscale Liam Collins², Aleksander Labuda¹, Olga Ovchinnikova² and Roger Proksch¹; ¹Asylum Research, Santa Barbara, California, United States; ²Center for Nanophase Materials Sciences, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Since the very early days of atomic force microscopy (AFM), voltage modulation (VM) of AFM has been used to try to quantify a host of electronic, electrochemical and electromechanical functionalities across nanometer length scales. The critical importance of such information has resulted in the development of a plethora of VM-AFM techniques for exploration of either long or short-range forces. Of relevance for ferroelectrics, piezoresponse force microscopy (PFM) imaging and spectroscopies have effectively opened the door to the exploration of nanoscale ferroelectric properties. The rise of PFM,

however, can also be associated with the emerging trend of claims of ferroelectricity in materials which were subsequently thought to be not ferroelectric,[1] even unlikely materials such as soda-lime glass. Furthermore, quantification of piezoelectric properties with PFM is notoriously difficult, and is known to be influenced by parasitic effects including factors such as long range electrostatic forces, tip-sample contact stiffness variations, cantilever frequency dependent dynamics. In this talk, we will explore the parasitic effects during normal PFM operation, including some recent results that:

Demonstrate that some hysteretic interactions surprisingly originate from common long-ranged dynamics. This hysteresis seems to be linked to sample surface water, suggesting that ionic dynamics in the surface water layer must be accounted for in nanoscale electromechanical measurements. Demonstrate experimental approaches for using interferometric AFM[2] for quantifying both the inverse piezo sensitivity, d_{eff} and hysteresis loops.

Since surface water is ubiquitous in ambient conditions for even mildly hydrophilic surfaces, these observations may explain the plethora unexpected hysteretic behavior discussed above. Finally, another significant result of the interferometric approach is that it allows putting quantitative limits on the electromechanical sensitivity. For example, we have demonstrated that [endif]--> for soda-lime glass mentioned above, much smaller than that implied by conventional VM-AFM measurements.

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8:30 AM EP01.09.02

Spin Mixing and Loss of Spin Polarization During Tunneling in Ferromagnet/Ferroelectric Junctions—Is a Strong Ferroelectric Polarization Desirable? Ibrahim B. Misirligolu^{3,1,2}, Canhan B. Sen³, Wael B. Aldulaimi³ and Omid B. Moradi³; ¹Sabancı University Nanotechnology Application Center, Sabancı University, Istanbul, Turkey; ²Integrated Manufacturing Technologies Research and Application Center, Sabancı University, Istanbul, Turkey; ³Faculty of Engineering and Natural Sciences, Sabancı University, Istanbul, Turkey.

Electric field control of magnetization allows further miniaturization of integrated circuits relying on functional layers for binary bit processing and data storage as it eliminates the need for bulky sophisticated systems to induce magnetic fields. Tailoring magnetoelectric coupling inherent to the bulk of multiferroic thin films and piezoelectric strain control of spin orientation in magnetic layers have been two approaches standing out. One other phenomena, namely spin-dependent screening has been studied especially from the perspective of spin selective tunnel junctions. In this work, we analyze the spin-dependent screening of ferroelectric polarization in a film interfacing electrodes with a magnetic structure using the continuity equations in continuum media. The effect of ferroelectric polarization on the ferromagnetism of the electrodes near the interfaces are discussed in the light of our results. The competition between the electrostatic screening and the mean-field exchange between spins in the ferromagnetic (FM) electrodes gives rise to a reduction in the net magnetic moment near the interface extending to a distance comparable to the Thomas-Fermi screening length. This apparent loss of magnetic order at the interface is due to spin mixing that is held partly responsible for reduction in the tunnel magnetoresistance (TMR) effect. In fact, even in an ideal system with no other effects to cause spin flips, our results imply that interface states can lead to great losses in spin polarization during tunneling. It is shown that the local density of states (LDOS) for spin subbands can vary significantly near the interfaces due to the competition between the magnetic and electrostatic energies, which is in good agreement with recent first principles results. We compute the tunneling currents for up and down spins using the Wentzel-Kramers-Brillouin approximation as a function of "ferroelectric strength", generating maps of bias when one loses spin polarization in the tunnelling currents. We find that the spin polarization tends to disappear for increasing values of ferroelectric polarization in direct connection with the increase in subband LDOS for minority spins at the interface relative to that of bulk DOS. We argue that the reduction in TMR due to spin mixing at the interfaces will be much more prominent in comparison to defect scattering and magnon-driven losses in spin polarization.

8:45 AM EP01.09.03

Correlation Between the Structural, Ferroelectric, Piezoelectric and Dielectric Properties of Lead-Free BCT-BZT Piezoelectrics Bhavna C. Keswani, Yesh D. Kolekar and S I. Patil; Department of Physics, Savitribai Phule Pune University (formerly known as University of Pune), Pune, India.

We report the structural, ferroelectric, piezoelectric and dielectric properties correlation in lead-free $x\text{Ba}_{0.92}\text{Ca}_{0.08}\text{TiO}_3-(1-x)\text{BaTi}_{0.96}\text{Zr}_{0.04}\text{O}_3$; $x = 0.55, 0.45$ (abbreviated as 55BCT8 and 45BCT8, respectively) piezoelectric ceramics. These piezoelectrics were synthesized by conventional solid state reaction method and further analyzed using different characterization techniques such as x-ray diffraction (XRD), Raman spectroscopy, scanning electron microscope (SEM), polarization-electric field (P-E) loop, strain-electric field (S-E), etc. XRD analysis along with the Rietveld refinement shows that the 55BCT8 and 45BCT8 piezoelectrics possess both the tetragonal (T: space group $P4mm$) and orthorhombic (O: space group $Amm2$) crystal structure which is further confirmed from Raman spectroscopy analysis. Also, the structural phase transitions with temperature were studied in details from the temperature dependent Raman spectroscopy analysis. The scanning electron micrographs shows dense microstructure for both the piezoelectrics with larger grain size 7-10 μm for 45BCT8. Also, the elemental mapping analysis indicates the homogeneous distribution of the constituent elements. The presence of P-E and S-E hysteresis loop confirms the ferroelectric and piezoelectric nature of these piezoelectrics. Further, the polarization current density-electric field curves show the presence of two sharp peaks in opposite directions which suggests the two stable states with opposite polarity. The higher values for maximum polarization ($P_{\text{max}} = 22.47 \mu\text{C}/\text{cm}^2$), remnant polarization ($P_r = 11.61 \mu\text{C}/\text{cm}^2$), coercive electric field ($E_c = 4.77 \text{ kV}/\text{cm}$) and % Strain ($S_{\text{max}} \sim 0.21$) were observed for 55BCT8 while higher values of piezoelectric coefficients ($d_{33} \sim 220 \text{ pC}/\text{N}$ and $d_{33}^* \sim 295 \text{ pm}/\text{V}$) and electrostrictive coefficient ($Q_{33} \sim 0.0509 \text{ m}^4/\text{C}^2$; higher than the conventional lead based piezoelectrics ($0.026 \text{ m}^4/\text{C}^2$) i.e. $\text{PbMgNbO}_3\text{-PbTiO}_3$) were observed for 45BCT8. Temperature dependent dielectric measurements at different frequencies show the phase coexistence (T + O) near room temperature (consistent with XRD and Raman spectra analyses); exhibiting O to T phase transition at 280 K and 298 K for both the 55BCT8 and 45BCT8, respectively. Moreover, the Curie temperature (T_c) $\sim 410 \text{ K}$ observed to be same for both the studied piezoelectrics. The observed trends in the ferroelectric, piezoelectric and dielectric properties can be explained in detail on the basis of structural phase contribution (55BCT8: 28% T + 72% O & 45BCT8: 41% T + 59% O) as analyzed from Rietveld fitted XRD pattern and Raman spectrum of 55BCT8 and 45BCT8. The observed properties shows that the environment friendly lead-free piezoelectrics in the present work are suitable for ferroelectric memory device, piezoelectric sensor, capacitor, etc. applications and can replace the toxic lead based piezoelectric ceramics (e.g. $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$, $\text{PbMgNbO}_3\text{-PbTiO}_3$, etc).

9:00 AM EP01.09.04

Stability, Transport and Electromechanical Properties of $\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$ Piezoelectric Crystals at Elevated Temperatures Yuriy Suhak¹, Ward L. Johnson², Andrei Sotnikov³, Hagen Schmidt³ and Holger Fritze¹; ¹Clausthal University of Technology, Goslar, Germany; ²National Institute of Standards and Technology, Boulder, Colorado, United States; ³Leibniz Institute for Solid State and Materials Research Dresden, Dresden, Germany.

Application of piezoelectric materials at elevated temperatures faces many restrictions including thermally induced changes of the dielectric, piezoelectric and electromechanical properties, increased loss with temperature, and chemical instability (decomposition, oxidation). In this respect, piezoelectric

crystals of the langasite (LGS, $\text{La}_3\text{Ga}_5\text{SiO}_{14}$) family are recognized as excellent candidates for high temperature applications as their piezoelectric activity is present up to temperatures above 1300 °C. CTGS ($\text{Ca}_3\text{TaGa}_3\text{Si}_2\text{O}_{14}$) is a relatively new crystal of the langasite family which has a fully ordered structure with lower conductivity and loss than LGS.

This work focuses on detailed and thorough investigations of CTGS temperature behavior. In particular, the full set of dielectric, piezoelectric, and elastic constants are determined in the temperature range from 4.2 K to 900 °C. Further, the electromechanical loss is determined as a function of temperature and described in the framework of a model that includes several physical mechanisms. Moreover, investigations of atomic transport mechanisms in CTGS are carried out at temperatures up to 1300 °C and correlated with electromechanical properties. Finally, the evaluation of CTGS long-term stability at high temperatures is performed by examination of its electric conductivity and resonant properties.

CTGS crystals used in this study are grown by the Czochralski technique by IKZ (Berlin, Germany), Fomos-Materials (Moscow, Russia) and SICCAS (Shanghai, China). The material constants are determined using two independent methods, namely resonant and ultrasonic pulse-echo. Additionally, piezoelectric coefficients are derived using laser Doppler vibrometry. The investigations of electromechanical loss are performed by means of impedance spectroscopy and a tone-burst excitation technique. The sample preparation process, measuring techniques and crystal cuts and geometries used for the investigations are described in [1, 2].

The analysis of ionic transport mechanisms is performed in the temperature range of 1000-1300 °C by application of stable tracer isotope ^{18}O and subsequent secondary ion mass spectrometry and provides oxygen self-diffusion coefficients of CTGS. These coefficients are found to be at least 3 orders of magnitude lower than those of LGS, confirming better high-temperature stability of CTGS.

Long-term measurements of CTGS conductivity and resonance frequency are performed in air during one year of uninterrupted thermal treatment at 1000 °C. The resonance frequency is found to change by about 0.4% during 8000 hours of heat treatment.

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9:15 AM EP01.09.05

Physical Nature of Negative Capacitance Emerged in Ferroelectric-Gate FETs [Kenshi Takada](#)², Takeshi Yoshimura¹ and Norifumi Fujimura¹; ¹Osaka Prefecture University, Sakai, Japan; ²Osaka Prefecture University, Sakai, Japan.

Recently, the power consumption of integrated circuits has increased because the scaling of the operating voltage is limited. To solve this issue, it is necessary to overcome the limit of subthreshold swing of 60 mV/decade at 300 K. Negative capacitance FET (NCFET), in which gate dielectric is replaced with a ferroelectric material, is attracting much attention because of the capability of overcoming the limitation by using the NC effect of ferroelectric. A number of papers have demonstrated sub-60 mV/decade switching in ferroelectric-gate FETs.¹⁾ However, the physical nature of emerging the NC have not been clarified. To investigate the physical nature, we simulated the time-developed electrical behaviors, such as the voltage across the ferroelectric layer (V_F), surface potential of semiconductor (ψ_s) and electric displacement of ferroelectric layer (D_F), for the applied voltage (V_G) in metal-ferroelectric-semiconductor capacitor (MFS) by using Landau-Khalatnikov equation which includes the dynamics of ferroelectric polarization switching. In this simulation, the ferroelectric properties similar to ferroelectric HfO_2 films were used, because the HfO_2 film is expected to be the most suitable for the ferroelectric-gate insulator in the NCFETs due to its compatibility with the complementary metal-oxide-semiconductor (CMOS) process and scaling ability.

As the results, when V_G is swept from negative to positive, the entire V_G and the depolarization voltage from a semiconductor (p-type) due to the remanent polarization are simultaneously applied to the ferroelectric layer before polarization switching. Whereas, after polarization switching, V_G divides into the ferroelectric layer and surface potential of semiconductor because of the formation of depletion layer at the semiconductor surface. Therefore, V_F decreases with increasing D_F ($\partial D_F / \partial V_F$) indicating that NC emerges. For this reason, transient NC in MFS capacitor is realized under the effect of the depolarization field from semiconductor due to the remanent polarization before polarization switching and the non-linear response of a semiconductor and a ferroelectric materials against external electric field after polarization switching.^{2,3)} The subthreshold slope of I_D - V_G characteristics is below 10mV/decade due to the effect of the transient NC. The simulations were also performed by using the ferroelectric properties with different remanent polarization ($P_r=10, 15, 20 \mu\text{C}/\text{cm}^2$). As the results, NC is recognized regardless of the remanent polarization, as far as the carrier modulation at the semiconductor surface against the potential change is much faster than the ferroelectric switching speed.⁴⁾

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9:30 AM EP01.09.06

Negative Piezoelectric Effect in the Organic Supramolecular Ferroelectric BTA [Indre Urbanaviciute](#)¹, Xiao Meng³, Yingfen Wei², Tim Cornelissen¹, Rint Sijbesma³ and Martijn Kemerink¹; ¹IFM, Linköping University, Linköping, Sweden; ²Faculty of Science and Engineering, University of Groningen, Groningen, Netherlands; ³Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, Netherlands.

Due to their softness and flexibility, organic ferroelectrics may become relevant for a wide variety of applications like conformal and/or flexible sensors and actuators for which inorganic ferroelectrics are unsuited. Yet, with the notable exception of the ferroelectric copolymer P(VDF-TrFE), the piezoelectric properties of organic ferroelectrics are only sparsely known and far from completely understood. The vast majority of piezoelectric materials demonstrate a positive piezoelectric effect. Even though it has been recently discussed that the negative piezoelectric coefficient could be theoretically found in certain ferroelectrics¹, in practice PVDF and its copolymers have remained the only ferroelectric materials showing this anomalous effect of longitudinal contraction with increasing applied field.²

Here, we investigate the piezoelectric activity in an archetypical class of organic ferroelectrics – small-molecular liquid-crystalline BTA (benzene-1,3,5-tricarboxamide)³. Interestingly, both the large- and small-signal piezoelectric responses, measured interferometrically on BTA solution-processed thin-film capacitors, reveal a pronounced negative piezoelectric effect with d_{33} reaching values as high as $-20 \text{ pm}/\text{V}$. The measured ‘inverted’ piezoelectric butterfly hysteresis loops are of close-to-ideal form with a well-expressed negative slope.

The dipolar disc-like BTA molecules self-assemble in columns that further pack tightly in a hexagonal lattice. In real device conditions this ordering is interrupted by zones with higher disorder. Therefore, the negative d_{33} in such structure can be explained by the so-called dimensional effect, which considers the ferroelectric layer as a set of rigid dipoles that are distributed in an easily deformable matrix. The dimensional effect is also considered to underly the negative electrostrictive and piezoelectric coefficients in P(VDF-TrFE). We show that in BTA the magnitude of d_{33} increases with increasing disorder and remnant polarization. Comparison of the piezoelectric response under large- and small-signal conditions further reveals that irreversible

extrinsic polarization switching processes dominate the large-signal strain.

Studies on the ferroelectric liquid-crystal BTA enrich our general understanding about the negative piezoelectric effect in soft ferroelectrics and reveal the application potential of the material for cost-efficient flexible piezoelectric devices.

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9:45 AM BREAK

10:15 AM *EP01.09.07

Strain and Size Effects on the Structure and Properties of Relaxor Ferroelectric Thin Films Jieun Kim¹, Hiroyuki Takenaka⁵, Yubo Qi², Anoop R. Damodaran¹, Abel Fernandez¹, Ran Gao¹, Shishir Pandya¹, Margaret McCarter³, Andrew M. Rappe² and Lane W. Martin^{1,4}; ¹Materials Science and Engineering, University of California, Berkeley, Berkeley, California, United States; ²Department of Chemistry, University of Pennsylvania, Philadelphia, Pennsylvania, United States; ³Department of Physics, University of California, Berkeley, Berkeley, California, United States; ⁴Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States; ⁵Department of Physics, University of Nebraska–Lincoln, Lincoln, Nebraska, United States.

The large field-induced strains produced by single crystals of solid solutions between relaxors and ferroelectrics make them technologically important materials. Understanding and ultimately controlling these large effects requires intimate knowledge of how the local polar order and resulting small-sized domains separated by low-angle domain walls form and evolve under applied stimuli. Traditionally, the evolution of polar structures in relaxors with various thermodynamic forces including temperature, composition, electric field, and hydrostatic pressure has been studied in bulk single crystals. The instability under large, non-hydrostatic pressure (such as uni- or bi-axial strain) in bulk materials, however, has limited our understanding of how these polar entities evolve under driving forces that enhance long-range order. In addition, there is a lack of understanding of how relaxors behave in low dimensions (*i.e.*, size effects). In this work, we use a combination of thin-film epitaxy, X-ray diffuse scattering, dielectric and ferroelectric characterization, and molecular-dynamics simulations to investigate the evolution of and correlations between polar structures and properties in the prototypical relaxor ferroelectric 0.68PbMg_{1/3}Nb_{2/3}O₃-0.32PbTiO₃. First, we investigated the effect of epitaxial strain to understand the relationship between structure and properties of relaxors under a driving force towards enhanced long-range order. Increasing the bi-axial, in-plane compressive strain (from -0.5 to -1.5%) drives an increase in the dielectric maximum temperature (from 150 to 210°C), intermediate temperature (from 230 to 320°C), and the Burns temperature (from 290 to 350°C). Diffuse-scattering experiments reveal marked strain-induced changes in the diffuse-scattering pattern, namely from a classical butterfly- to a disc-shaped pattern; which is attributed to polarization rotation and an increase of the correlation length of polar domains (from 8 to 25 nm). Molecular-dynamics simulations provide direct visualization of the domain structures and analysis of local dynamics reveals that such changes are due to the anomalous correlation behavior of unit cells with complex chemistries. Using the same thin-film platform, we further explored size effects in relaxor thin films. Here we demonstrate that reducing the size, contrary to popular belief, first enhances relaxor behavior until a threshold thickness below which the critical temperatures that characterize various relaxor phases (*i.e.*, dynamic, static, and frozen) collapse together, indicating destabilization of the relaxor state. Using temperature-dependent diffuse scattering and ferroelectric measurements, we demonstrate that the relaxor loses their defining characteristics below this threshold thickness. The mechanism for destabilization of relaxor behavior below the critical thickness is discussed in terms of faster dynamics of polarization fluctuations in ultrathin relaxor films.

10:45 AM EP01.09.08

Surface Pyroelectricity in SrTiO₃ Elena Meirzadeh¹, Evgeniy Makagon¹, Dennis V. Christensen², David Ehre¹, Meir Lahav¹, Nini Pryds² and Igor Lubomirsky¹; ¹Weizmann Inst of Science, Rehovot, Israel; ²Department of Energy Conversion and Storage, Technical University of Denmark, Roskilde, Denmark.

Single crystals of perovskite-structured SrTiO₃ are used in a variety of applications ranging from catalysis to substrates for epitaxial thin film growth. Although SrTiO₃ is paraelectric (space group Pm-3m), it is incipient ferroelectric. Surface structure of SrTiO₃ changes under various conditions and has been thoroughly studied over the years both computationally and experimentally. It has been suggested that the crystal undergoes surface relaxation leading to the formation of a near-surface polar layer[1]. Improvements in current measurement equipment during the last decade have increased the sensitivity of pyroelectric measurement[2], allowing us to measure surface pyroelectricity from single crystals of SrTiO₃. Our results provide a direct experimental proof for the presence of a near-surface polar layer in this material. We have found that annealing the crystals in the presence of TiO₂ powder eliminates the surface pyroelectricity while chemical treatment with dilute nitric acid restores it. One can expect that the existence of the surface pyroelectric layer might affect the structure and macroscopic properties of the functional materials for which SrTiO₃ is used as a substrate.

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[2] a) E. Meirzadeh, I. Weissbuch, D. Ehre, M. Lahav, I. Lubomirsky, *Acc. Chem. Res.* 2018, 51; b) D. Ehre, E. Mirzadeh, O. Stafsudd, I. Lubomirsky, *Ferroelectrics* 2014, 472.

11:00 AM EP01.09.09

Optimizing a Floating-Base Bipolar Heterojunction Phototransistor by Piezo-Phototronic Effect Fangpei Li, Zijian Pan, Wenbo Peng and Yongning He; Xi'an Jiaotong University, Xi'an, China.

Recently, extensive research works have demonstrated significant modulation on photoresponse performances by the piezo-phototronic effect in various optoelectronic devices. However, although piezo-charges of both positive and negative polarities always appear in pairs and in same amount simultaneously and equally, most research works till today only utilize piezo-charges of one polarity, either positive or negative, excluding the potential combined advantages of utilizing both positive and negative piezo-charges at the same time. In this work, a p-Si/n-ZnO/p-PEDOT:PSS bipolar heterojunction phototransistor is fabricated, and its strain-induced enhancements in photoresponses are reported: the photoresponsivity is improved from 62.80 to 90.30 mA/W (with an improvement of almost 50%) and the specific detectivity is improved from 0.31×10^9 to 0.42×10^9 Jones (with an enhancement of about 35%). Experimental results also show interesting optimizing behaviors, of which the fundamental physics are thoroughly explained by carefully analyzing the strain-induced modulations in local energy band diagrams at p-Si/n-ZnO and n-ZnO/p-PEDOT:PSS interfaces, respectively. For the first time, the piezo-phototronic effect has been validated in a ZnO-based bipolar heterojunction phototransistor, where the device structure of two back-to-back p-n heterojunctions possesses great possibility to achieve low noise, large photoresponsivity and high speed qualities. More importantly, by

successfully utilizing both positive and negative piezoelectric charges in one device, this work advances the practical applications of the piezo-phototronic effect in tri-/multi-layer device structures where excellent performances can be expected.

11:15 AM EP01.09.10

Tunable Electroresistance and Electro-Optic Effects of Transparent Molecular Ferroelectrics Shenqiang Ren; University at Buffalo, The State University of New York, Buffalo, New York, United States.

Recent progress in molecular ferroelectrics (MOFEs) has been overshadowed by the lack of high-quality thin films for device integration. We report a water-based air-processable technique to prepare large-area MOFE thin films, controlled by supersaturation growth at the liquid-air interface under a temperature gradient and external water partial pressure. We used this technique to fabricate ImClO_4 thin films and found a large, tunable room temperature electroresistance: a 20-fold resistance variation upon polarization switching. The as-grown films are transparent and consist of a bamboo-like structure of (2,-1,0) and (1,0,-2) structural variants of $R3m$ symmetry with a reversible polarization of $6.7 \mu\text{C}/\text{cm}^2$. The resulting ferroelectric domain structure leads to a reversible electromechanical response of $d_{33} = 38.8 \text{ pm}/\text{V}$. Polarization switching results in a change of the refractive index, n , of single domains, $\Delta n/n = 0.3$. The remarkable combination of these characteristics renders MOFEs a prime candidate material for new nanoelectronic devices. The information that we present in this work will open a new area of MOFE thin-film technologies.

11:30 AM EP01.09.11

Blowing Polar Skyrmion Bubbles in Oxide Superlattices Zijian Hong^{1,2} and Long-Qing Chen¹; ¹The Pennsylvania State University, State College, Pennsylvania, United States; ²Department of Mechanical Engineering, Carnegie Mellon University, Pittsburgh, Pennsylvania, United States.

Particle-like topological structures such as skyrmions and vortices have garnered ever-increasing interests due to their rich physical insights and potential broad applications in spintronics. Here we discover the reversible switching between polar skyrmion bubbles and ordered vortex arrays in ferroelectric superlattices under an electric field, reminiscent of the Plateau-Raleigh instability in fluid mechanics. An electric field phase diagram is constructed, showing a wide stability window for the observed polar skyrmions. A “volcano”-like pontryagin density distribution is formed, indicating the formation of a smooth circular skyrmion. The topological charge Q at different applied field is calculated, verifying the field-driven topological transition between $Q = 0$ and $Q = \pm 1$ states. This study is a demonstration for the computational design of field-induced topological phase transitions, giving promise for the design of next-generation nanoelectronic devices.

11:45 AM EP01.09.12

Inducing Magnetism in the Electron Gas at $\text{LaAlO}_3/\text{GdTiO}_3/\text{SrTiO}_3$ Interfaces Nikita Lebedev¹, Martin Stehno², Abhimanyu Rana⁴, Alexander Brinkman³ and Jan Aarts¹; ¹Kamerlingh Onnes Laboratory, Leiden University, Leiden, Netherlands; ²Physikalisches Institut (EP 3), Universität Würzburg, Würzburg, Germany; ³MESA+ Institute for Nanotechnology, University of Twente, Enschede, Netherlands; ⁴School of Engineering and Technology, BML Munjal University (Hero Group), Gurgaon, India.

At the interface between band insulators LaAlO_3 (LAO) and SrTiO_3 (STO) a two-dimensional electron gas (2DEG) can be formed. There are also indications that the Ti^{3+} ions can give rise to (spurious) magnetism. However, fabricating a homogeneous spin-polarized electron gas is still a challenge. One strategy is to bring rare earth ions close to the interface. After inserting a 2-unit-cell layer of the band insulator EuTiO_3 (ETO) an anomalous Hall effect (AHE) was reported [1], as a signature for magnetism. In our work we inserted 2 unit cells of the Mott insulator GdTiO_3 (GTO) between LAO and STO. Note that the Eu-ion in ETO is divalent (like Sr), while the Gd-ion in GTO is trivalent (like La). Samples were prepared by Pulsed Laser Deposition. The temperature dependence of the sheet resistance shows that a 2DEG has formed. Gating the system at low temperatures with a negative voltage leads to a metal-insulator transition, with a Kondo like resistance minimum. For positive voltages, the system becomes increasingly metallic and shows an AHE as well as hysteretic behavior of Hall coefficient. It appears that magnetism is induced, but only at finite gate voltages.

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SESSION EP01.10: Non-Conventional Applications of Polar Materials
Session Chairs: Jennifer Andrew and Thomas Fix
Thursday Afternoon, November 29, 2018
Hynes, Level 1, Room 103

1:30 PM *EP01.10.01

Magnetolectric Sensors—PicoTesla Magnetometers and Ultracompact Acoustically Actuated Antennas Nian Sun, Hwaider Lin and Neville Sun; ECE Department, Northeastern University, Boston, Massachusetts, United States.

Recent research have demonstrated strong magnetolectric (ME) coupling realized through strain mediated interactions in layered magnetic and ferroelectric multiferroic heterostructures. Most ME effects have been demonstrated in a static or quasi-static process used in applications such as reconfigurable RF components and spintronics. However, utilizing the strong ME coupling effect dynamically at very high frequency (VHF) and ultra-high frequency (UHF) will allow for receiving and transmitting electromagnetic waves with devices on the micro-scale. Here we present the most recent progress on novel RF nanomechanical ME resonators with pico-Tesla sensitivity and a new antenna miniaturization mechanism to create acoustically actuated nanomechanical ME antennas. Modern compact antennas that rely on electromagnetic (EM) wave resonance typically have a size greater than $\lambda_0/10$, making it difficult to reach VHF and UHF. The large electromagnetic wavelength λ_0 puts a constraint on miniaturizing antennas for wireless communication systems where ultra-compact antennas can help save space. This novel concept utilizes the acoustic wave resonance due to the ME effect instead of relying on the electromagnetic wave resonance can reduce the antenna size 1-2 orders of magnitude without any performance degradation.

2:00 PM *EP01.10.02

Functional Oxide Thin Films for Diverse Applications Wilfrid Prellier; CRISMAT Laboratory, Caen, France.

Transition metal oxides often having a perovskite structure form a wide and technologically important class of compounds. In these systems, ferroelectric, ferromagnetic, ferroelastic, or even orbital and charge orderings can develop and eventually coexist. These orderings can be tuned by external electric, magnetic, or stress field, and the cross-couplings between them enable important multifunctional properties, such as piezoelectricity, magneto-electricity,

or magneto-elasticity.

Here, I will illustrate the utilization of emerging materials prepared as thin films. By growing PrVO_3 thin films epitaxially on an SrTiO_3 substrate, I will show that the role of oxygen vacancies can be rationalized to introduce a chemical strain similar to the so-called mechanical strain ($\pm 2\%$), which in turns produce a nontrivial evolution of Néel temperature in a range of 30 K. The possible ferroelectricity will also be discussed.

Financial support from ANR, Labex, and Region Normandie (INCOX project) are acknowledged.

2:30 PM EP01.10.03

Structure-Function Relations in Mixed Phase BiFeO_3 via Phase Population Control—The Roles of Electric Field and Nanoscale Stress Aaron Naden^{1,2}, David Edwards^{3,1}, Sabine M. Neumayer^{4,3}, Joseph Guy¹, Brian J. Rodriguez³, Nazanin Bassiri-Gharb⁵ and Amit Kumar¹; ¹Queen's University Belfast, Belfast, United Kingdom; ²School of Chemistry, University of St Andrews, St Andrews, United Kingdom; ³School of Physics and Conway Institute, University College Dublin, Dublin, Ireland; ⁴Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ⁵G.W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Mixed phase BiFeO_3 (BFO) films have recently attracted significant attention due to their advantageous functional properties which are often strongly related to the films' microstructures. The crystallographically mixed phase microstructure is obtained through epitaxial growth on substrates with a large lattice mismatch with the BFO film. In such systems, monoclinic phases with alternating tetragonal- and rhombohedral-like structures (which we refer to as T- and R-phase for brevity) form spontaneously in order to accommodate the epitaxial strain. Despite the favourable properties of these films, significant challenges remain in understanding the precise nature of the interplay of structural transitions and ferroelectric switching and how this meshing of phenomena influences the behaviour of mixed phase BFO.

Here we demonstrate deterministic nanoscale control of the R/T-phase population between $\sim 100\%$ and $\sim 30\%$ T-phase using electric field and nanoscale stress applied through an atomic force microscope (AFM) tip. To develop a truly holistic understanding of the impact of the phase population, we explore the effects of electric field and nanoscale stress on the electromechanical properties of the material using a variation of band excitation piezoresponse force microscopy. Simultaneous application of these external fields via the AFM tip results in enhancements in the electromechanical response which manifest in the form of peaks, or noses, in the piezoresponse loops at a single given polarity of applied electric field: when the AFM tip is biased positively relative to the bottom electrode, corresponding nominally to a downward polarisation. By collecting nanoscale electromechanical hysteresis loops and simultaneously monitoring the elastic behaviour during switching, we develop a comprehensive picture of the complex interplay of ferroelastic structural transitions and ferroelectric switching and its impact on the overall functional response. Such an understanding is a crucial step towards realising practical electronic devices, such as pressure sensors, incorporating this promising material.

2:45 PM BREAK

3:15 PM EP01.10.04

High-Field Nonlinear Dielectric and Piezoelectric Properties of Fe_2O_3 Doped PMnS-PZN-PZT Ceramics Huazhang Zhang, Jie Shen, Quan Wei, Kunkun Han, Jing Zhou and Wen Chen; State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, School of Materials Science and Engineering, Wuhan University of Technology, Wuhan, China.

High-power devices, such as ultrasonic motors, underwater acoustic transducers and piezoelectric transformers, require piezoelectric ceramics with low dielectric loss $\tan \delta$, high mechanical quality factor Q_m (low mechanical loss), and simultaneously large piezoelectric constant d_{33} and electromechanical coupling factor k_p [1-2]. In our previous work, Fe_2O_3 doped $\text{Pb}(\text{Mn}_{1/3}\text{Sb}_{2/3})\text{O}_3\text{-Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-Pb}(\text{Zr, Ti})\text{O}_3$ (PMnS-PZN-PZT) ceramics was found to possess a relatively high piezoelectric property and an extremely low dielectric loss [3], showing that the ceramics are promising for high-power applications. Nevertheless, the electric field-dependence of piezoelectric property and the origin of the low losses of Fe_2O_3 doped PMnS-PZN-PZT ceramics are still remained to be clarified.

In this study, electric field dependence of dielectric and piezoelectric properties in subswitching field range, and effect of temperature on high-field nonlinearity of dielectric property for Fe_2O_3 doped PMnS-PZN-PZT high-power piezoelectric ceramics are investigated. To characterize the domain wall motion, the electric field dependent dielectric and piezoelectric properties are discussed in terms of Rayleigh analysis [4-5]. Results show that with the increase of electric-field level, both the dielectric and piezoelectric properties deviate their low-field values and exhibit increase trends, due to the enhanced domain wall motion at high field. Rayleigh analysis reveals the contribution from lossless reversible domain wall motion to the high-field nonlinear dielectric and piezoelectric properties in Fe_2O_3 doped PMnS-PZN-PZT ceramics. This behavior is associated with the orderly distribution of defect pinning centers, and is thought to be responsible for the low losses of the ceramics. At elevated temperatures, the mobility of the oxygen vacancies increases, so that the distributions of the defect pinning centers are gradually randomized, which consequently lead to the enhancement of high-field nonlinearity.

References:

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3:30 PM EP01.10.05

Ferroelectric Materials—A New Antimicrobial Class Sandeep K. Shukla, Rahul Vaish and Satvasheel Powar; Indian Institute of Technology Mandi, Mandi, India.

Bacterial contamination is one of the major concerns around the world especially in developing countries where safe drinking water and bacterial diseases are still a primary risk. Current antibacterial substances suffer from their own limitations such as sustainability, resistance, and cost. Herein, we propose a novel method for bacterial disinfection using ferroelectric materials. Ferroelectric materials like $\text{Ba}_{0.85}\text{Ca}_{0.15}\text{Ti}_{0.9}\text{Zr}_{0.1}\text{O}_3$ (BCTZO), BaTiO_3 possess remnant polarization on the surface as a result of aligned dipoles, attained through electric field poling. The effect of poling on the photocatalytic performance of ferroelectric materials have been investigated. The improved photocatalytic performance of poled samples attributed to the charge separation capability of poled samples. The antibacterial property of ferroelectric materials found to be surface selective as the positive side of ferroelectric materials electrostatically attracts negatively charged bacterial cells. The effect of photocatalysis on bacterial degradation studied further under UV irradiation. The antibacterial performance of poled ferroelectric material was tremendously improved in combination with UV irradiation. The complete bacterial eradication attained in less than 60 min of exposure when tested in combination. DCFDA assay study confirmed that the reactive oxygen species produced during electrolysis of water is one of the crucial factors for this remarkable photo-driven antibacterial performance. Poled ferroelectric materials exhibited excellent piezocatalytic property for resazurin ink (Rz) and bacterial degradation. Interestingly, a synergistic effect observed against Rz ink and bacteria employing Ferro-photocatalysis and piezocatalysis. With these promising results, we believe, Ferrocatalysis will open new ways for disinfection of

drinking water, food products, and environmental pollutants.

3:45 PM EP01.10.06

Polymer-Based Efficient and Robust Piezoelectric Energy Harvesters Deepa Singh^{1,2}, Aditya Choudhary¹ and Ashish Garg¹; ¹Department of Materials Science and Engineering, Indian Institute of Technology Kanpur, Kanpur, India; ²Department of Physics and Astronomy, Western University, London, Ontario, Canada.

Ferroelectric materials are the most sought out electronic materials because of their multifunctional applications in energy harvesting, sensing, memory and biomedical applications. Organic devices based on ferroelectricity are a promising approach towards the development of a low cost, low temperature, solution processed technology. Here, we demonstrate flexible devices with MgO-Poly(vinylidene fluoride-trifluoroethylene)(PVDF-TrFE) nanocomposites. P(VDF-TrFE) is known for its high remnant polarization, low switching time and highly insulating properties. Incorporation of a small amount of MgO leads to improved dielectric, ferroelectric and piezoelectric performance without affecting its other electrical properties such as leakage current and breakdown strength: two long-lasting problems with nanocomposites. MgO, a hygroscopic material, is considered to have inherent –OH bonds at its surface. These –OH bonds form hydrogen bonds with PVDF-TrFE as estimated by FTIR measurements. This interaction further improves electric fatigue and leakage current by reducing the gauche defects such as chain folding and kinks.

PVDF-TrFE polymer can sustain larger strains compared to conventional inorganic materials due to their flexibility. This makes them more appropriate for harvesting energy from mechanical fluctuations. Flexible nanocomposite devices exhibit 50% improvement in piezoelectric properties. The piezoelectric coefficient (d_{33}) value of ~ -65 pm/V was obtained for 2wt % MgO/P(VDF-TrFE) nanocomposites in contrast to pure P(VDF-TrFE) devices with d_{33} value of about -40 pm/V. In addition, output voltage response increases two times with MgO nanoparticles as compared to pure PVDF-TrFE based devices. Bending test confirmed that d_{33} values remain unaffected even after 10000 bending cycles. This corroborates the beneficial role of MgO in sensing and memory applications.