SYMPOSIUM TP02

TUTORIAL: Thermal Characterization of Materials and Devices
November 25 - November 25, 2018

* Invited Paper

TUTORIAL
Thermal Characterization of Materials and Devices

Sunday Afternoon, November 25, 2018
Hynes, Level 3, Room 300

1:30 PM Thermal Characterization of Wide Bandgap Semiconductor Materials and Device Samuel Graham; Georgia Institute of Technology

The development of wide bandgap semiconductors have enabled new optoelectronic, RF, and power electronic devices and their performance and reliability are strongly coupled to their thermal behavior. In this tutorial, a number of optical and electrical methods will be reviewed which allow for the characterization of the thermal properties of wide bandgap materials including thermal conductivity and thermal interface resistance at contacts. In addition, metrology methods for mapping temperature under steady-state and high speed thermal transients relevant to RF operation will be discussed along with their limitations and areas which remain a challenge to researchers.

3:00 PM BREAK

3:30 PM
Challenges in Measuring Nano- to Micro-gram Samples: Scanning Calorimetry and Thermoviscoelasticity Gregory B. McKenna; Texas Tech University

Novel developments in making ultra-stable glasses lead to measurement challenges because extremely small amounts (nano- to micro-grams) of material are produced. We will describe work using chip calorimetry to determine the thermal properties and the cooling rate dependence of the Tg. In addition, nano-scale rheology on these materials can be carried out to determine material dynamics using a novel bubble inflation measurement method developed in our labs.

SYMPOSIUM TP02

Thermal Analysis—Materials, Measurements and Devices
November 26 - November 30, 2018

Symposium Organizers
Leslie Allen, University of Illinois at Urbana
Martin Kuball, University of Bristol
Sindee Simon, Texas Tech University
Feng Yi, National Institute of Standards and Technology

Symposium Support
National Institute of Standards and Technology
University of Illinois at Urbana-Champaign (Coordinated Science Lab and Material Science & Engineering)

* Invited Paper

SESSION TP02.01: Novel Thermal Methods and Applications
Session Chairs: Sindee Simon and Feng Yi

8:00 AM *TP02.01.01
Heat Capacity Determination—Tricks of the Trade Mary Anne White; Dalhousie University, Halifax, Nova Scotia, Canada.

Sometimes very accurate heat capacity data are required; an example would be for the calculation of a thermodynamic cycle that involves small differences between large numbers. Sometimes less accurate data would still be useful, especially if they can be acquired quickly. In this talk, some instances of each situation will be presented, along with tips to attain high-accuracy data using relaxation calorimetry, moderate accuracy with using DSC, and quantitative estimates using other means.

8:30 AM *TP02.01.02
The Boiling Temperature of Ionic Liquids—An Experimental Approach Amir Abdelaziz[1], Sergey P. Verevkin[3] and Christoph Schick[1, 2]; [1]Institute of Physics & Competence Centre °CALOR, University of Rostock, Rostock, Germany; [2]A. Butlerov Institute of Chemistry, Kazan Federal University, Kazan, Russian Federation; [3]Institute of Chemistry & Competence Centre °CALOR, University of Rostock, Rostock, Germany.

The very low vapor pressure of ionic liquids is challenging to measure. At elevated temperatures the liquids might start to decompose, at relatively low temperatures the vapor pressure becomes extremely low to be measured by conventional methods. We developed a highly sensitive method for mass loss determination at temperatures starting from 350 K up to 800 K. The technique is based on fast scanning (10 000 K s^{-1}) and an alternating current (AC) calorimeter equipped with a chip sensor, that consists of a free-standing SiN_x-membrane (thickness < 1 μm) and a measuring area with lateral dimensions of the order of 100 μm. A small droplet (diameter ca. 300 μm) of an ionic liquid is vaporized isothermally from the chip sensor in a vacuum-chamber. The surface-to-volume-ratio of such a droplet is large and the relative mass loss due to evaporation is therefore easy to be monitored by the changing heat capacity (J K^{-1}) of the remaining liquid. The vapor pressure is determined from the measured mass loss rates using the Langmuir equation. The method was successfully tested with determination of vapor pressures and the vaporization enthalpy of the archetypical ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIm][NTf$_2$]). The created in this way data set in the extremely broad temperature range 358 K to 780 K has allowed estimation of the boiling temperature of [EMIm][NTf$_2$]. The value (1120 ± 50) K should be considered as the first reliable boiling point of this ionic liquid obtained from experimental vapor pressures measured in the most possible close proximity to the normal boiling temperature.

References:
Ahrenberg, M., M. Brinckmann, J. W. P. Schmelzer, M. Beck, C. Schmidt, O. H. Keßler, U. Kragl, S. P. Verevkin and C. Schick (2014). "Determination of volatility of ionic liquids at the nanoscale by means of ultra-fast scanning calorimetry." Physical Chemistry Chemical Physics **16**(7): 2971-2980.

Neise, C., C. Rautenberg, U. Bentrup, M. Beck, M. Ahrenberg, C. Schick, O. Keßler and U. Kragl (2016). "Stability studies of ionic liquid [EMIm][NTf2] under short-term thermal exposure." RSC Advances **6**(54): 48462-48468.

Ahrenberg, M., M. Beck, C. Neise, O. Keßler, U. Kragl, S. P. Verevkin, C. Schick (2016). "Vapor Pressure of Ionic Liquids at Low Temperatures from AC-chip-calorimetry." Physical Chemistry Chemical Physics **18**(31): 21381-21390.

9:00 AM TP02.01.03
Liquid to Glass/Crystal Transitions in Ionic Liquids Studied by Fast Thermal Conductivity Measurements Carlos López-Bueno, David Bugallo Ferrón, Víctor Leborán, M.C. Giménez-López and Francisco Rivadulla; Centro de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS), Santiago de Compostela, Spain.

We have developed an experimental setup for the simultaneous measurement of the thermal conductivity and heat capacity of liquids. This system is an extension of the 3ω method [1] capable to measure a sample volume of the order of ≈500 nL, which is an important advantage for the characterization of nanofluids, in which having a large amount of sample is sometimes difficult to achieve [2]. The setup is designed for fast measurements during a thermal ramp, which along with the extremely small volume required allows the possibility of using it in a cryostat for analysing the temperature dependence of the thermal conductivity in a variety of fluids, across phase transitions, kinetic studies, etc.
Particularly, in this work we will present the study of the low temperature thermal and electrical conductivity of different ionic liquids around their liquid-to-solid transition. Using these methods we are able to identify a spinodal decomposition temperature in in 1-Ethyl-3-methylimidazolium trifluoromethanesulfonate (EMIM$^+$ TfO$^-$) around 150K. Below this temperature, the glassy phase is unstable against the formation of a crystalline phase in the whole system. This produces a 30% variation in the thermal conductivity of the system, depending on the thermal history. We discuss the possibility of using ionic liquids as configurable models to study the low temperature thermal conductivity of ionic solids.

References
[1] David G. Cahill, Review of Scientific Instruments, **1990**, 61:2, 802-808.
[2] C. López-Bueno, D. Bugallo, V. Leborán and F. Rivadulla, *Phys. Chem. Chem. Phys.*, **2018**, 20, 7277-7281.

Acknowledgements
This work was supported by the Ministry of Science of Spain (Projects No. MAT2016-80762-R), the Consellería de Cultura, Educación e Ordenación Universitaria (ED431F 2016/008, and Centro Singular de Investigación de Galicia accreditation 2016-2019, ED431G/09), the European Regional Development Fund (ERDF), the Xunta de Galicia and the European Union (European Social Fund- ESF).

9:15 AM TP02.01.04
Nanocalorimetric Investigation of the Gradient Effect on Nucleation in Thin Films Shane Q. Arlington[1], Feng Yi[2], David LaVan[2] and Timothy P. Weihs[1]; [1]Johns Hopkins University, Baltimore, Maryland, United States; [2]Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

The fabrication of many multiphase alloys, particularly in thin film systems, relies upon the nucleation of intermetallic precipitates within a solid solution. These films frequently contain sharp composition gradients which are not accounted for under Classical Nucleation Theory but are predicted to have a significant effect on the nucleation of new phases. Previous nanocalorimetric studies of Al$_3$Ni formation in nanoscale Al-Ni multilayers indicate that interdiffusion must reduce the composition gradient prior to nucleation of the Al$_3$Ni product phase, while molecular dynamics simulations show that gradients can impede nucleation in both the liquid and solid state in the Al-Ni system. Here, we investigate the gradient effect directly by controlling the as-

deposited gradient in amorphous thin films. We deposit amorphous binary metallic films with controlled composition gradients through their thickness, where the average composition of the films matches a stable intermetallic phase. We heat the films with nanocalorimeters, using a wide range of heating rates, and we assess the impact of the composition gradients on nucleation through kinetic analysis. Isoconversion analysis is performed on the nanocalorimetric dataset to evaluate the effective activation energy as a function of extent of conversion. Extensive *ex situ* characterization is performed before and after reaction to assess the structural and compositional nature of the films and the crystallites formed. Future work will include *in situ* TEM investigations of the gradient effect during isothermal crystallization of graded and non-graded films.

9:30 AM *TP02.01.05
Abrupt Size Effect Observed in Layered Materials Below Critical Size—Linking Thermal Analysis with Local Structural Analysis <u>Zichao Ye</u>[1], Lito De la Rama[1], Mikhail Efremov[2], Andre Sutrisno[3] and Leslie Allen[1]; [1]Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; [2]University of Wisconsin–Madison, Madison, Wisconsin, United States; [3]School of Chemical Sciences, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Materials often exhibit exotic properties because of "discrete regions", regions that have different chemical environment from the remaining part of the system. Material at the first level is treated as a uniform "bulk" with single sets of intrinsic and extrinsic characteristics; the next level incorporates finer details of the system by segmenting it with discrete regions, including interfaces (e.g., lamella mating boundaries), surfaces (e.g. nanoparticle spheres) and defects (e.g., gauche kinks). The effect of these discrete regions is highlighted by material miniaturization. At extremely small scale lengths (<10 nm), properties of the "whole" object (e.g., melting, lattice structure, bandgap, conductivity, optical) are dominated by the nature of "local" discrete regions. Regular thermal analysis using calorimetry has no depth perception – it only yields average thermodynamic values, whereas NMR has the unique capability to probe the local structure of each individual atom. Here we link calorimetry (NanoDSC or DSC) thermal analysis with ^{13}C NMR structural analysis to report an abrupt bulk-to-discrete transition in 2D layered silver alkanethiolate (AgSCn, n=1-16) with a critical chain length of n=7. None of the carbon group share identical chemical environment below the critical length, making AgSCn (n=2-6) uniquely different materials, even though the crystal structures of all AgSCn are preserved throughout. Extraordinary changes of thermodynamic properties, including ~500% increase of melting enthalpy and ~50ºC increase of melting point, are also observed at the bulk-to-discrete transition. This transition is universal for aliphatic layers, including n-alkanes with a critical chain length of n=11. A new 3D spatial model is constructed to divide the aliphatic chains of AgSCn into three bulk or discrete segments: (a) tail segment that forms interlayer interfaces, which are never planar structures but have 3D depth; (b) head segment that is strongly affected by the metallic core; (c) bulk mid-chain segment which shows similar properties to the hydrocarbon chains in polyethylene. The presence (multilayer) or absence (1-layer) of odd/even effect is exclusively attributed to the nature of the localized tail segment. Bulk-to-discrete transition occurs when material properties are dominated by the discrete head and tail segments over the bulk segment at/below critical length. This work is seminal to the design of novel aliphatic lamellae with tailorable properties and has applications in molecular electronics and biophysics.

10:00 AM BREAK

10:30 AM *TP02.01.06
Phase Transformations in CuZr-Based Shape Memory Thin Films Analyzed by Combinatorial Nanocalorimetry <u>Joost J. Vlassak</u> and Mark Miao; Harvard University, Cambridge, Massachusetts, United States.

We have investigated the phase transformations in sputtered CuZr-based shape memory thin films using a combinatorial nanocalorimetry technique that is capable of making differential calorimetric measurement on thin-film samples with a sensitivity as small as 12 pJ/K. We first investigate the crystallization kinetics of amorphous as-deposited equiatomic CuZr samples and demonstrate non-Arrhenius diffusion kinetics that is well described using a phenomenological model based on the fragility of super-cooled liquids. We then explore the conditions for the formation of the martensitic phase responsible for the shape memory properties of this alloy. We will show that fast, low-temperature cycling through the martensitic transformation increases the hysteresis, which we attribute to the accumulation of defects during the martensitic transformation. If, however, the austenitic phase is given sufficient time at elevated temperature to annihilate these defects, the transformation is stable under thermal cycling conditions. The addition of Ni to the CuZr alloy raises the martensite transformation temperature making it a potential high-temperature shape memory alloy. The microstructures of select CuZrNi samples have been analyzed using XRD and cross-sectional TEM. We will present the effects of composition, heat treatment, and grain size on the transformation temperature, hysteresis, and functional stability of the samples. We will also demonstrate that under certain conditions the martensitic transformation proceeds in an explosive fashion. The transformation behavior of these alloys will be discussed in light of ab initio simulations of the materials system.

11:00 AM *TP02.01.07
Physical Limits of Laser Gold Nanowarming Kanav Khosla[1], Li Zhan[1], Aditya Bhati[1], Aiden Carley-Clopton[1], Mary Hagedorn[2, 3] and <u>John Bischof</u>[1, 4]; [1]Department of Mechanical Engineering, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States; [2]Smithsonian Conservation Biology Institute, Smithsonian National Zoological Park, Washington, District of Columbia, United States; [3]Hawaii Institute of Marine Biology, University of Hawaii, Kaneohe, Hawaii, United States; [4]Department of Biomedical Engineering, University of Minnesota Twin Cities, Minneapolis, Minnesota, United States.

In this work we explore the physical limits of a new technique to rewarm vitrified droplets and zebrafish embryos impregnated with 1064 nm resonant gold nanorods that are irradiated by a Nd:YAG ms pulsed laser. Importantly, the droplets and the embryos loaded with 2 M PG are first cooled by a modified cryotop at rates estimated to be 90,000 °C/min to a visually transparent state in liquid nitrogen. Numerical modeling demonstrates possible differences in warming depending on full mixing (droplets) vs. micro-injection into the yolk of the zebrafish. Experimental measurments based on optical transparency vs. cloudy behavior are then used to judge the physical success of the procedure. From this we present a map of the successful laser power, pulse length, CPA concentrations and gold concentrations that can yield physical success for laser gold nanowarming.

11:30 AM TP02.01.08
Non-Contact Thermal Analysis with Fast and Micro-Scale Thermographical Imaging <u>Junko Morikawa</u>; Tokyo Institute of Technology, Tokyo, Japan.

Non-contact quantitative thermal imaging in micro-scale is attractive to realize the non-contact thermal analysis. It visualizes not only the typical thermal analysis on phase transitions and thermal degradation, but also the heat transfer. We propose a system of infared camera equipped with an original optics and temperature calibration algorithm, which enables to achieve the high-quality and fast-speed thermal imaging. The Infrared (IR) optical lens design has been optimized to each wavelength band of the photon type and the thermal type detectors of IR FPA. Typical applications to observe the freezing biological cells and the crystallization of organic molecular crystals are reviewed. Combined with the techniques of microscale flying spot laser and the superimpose processer, the method is applied to determine the heat transport properties. The recent instrumentation of thermospectroscopy and the high temperature imaging systems are also introduced.

11:45 AM TP02.01.09

Time-Domain Transient Fluorescence Spectroscopy for Thermal Characterization of Polymers Hao Wu[1], <u>Yanan Yue</u>[1,2], Yangheng Xiong[1] and Xin Zhang[2]; [1]School of Power and Mechanical Engineering, Wuhan University, Wuhan, China; [2]Department of Mechanical Engineering, Boston University, Boston, Massachusetts, United States.

In this work, a time-domain fluorescence spectroscopy technique is developed to characterize thermophysical properties of polymers. The method is based on fluorescence thermometry of materials under periodic pulse heating. In the characterization, a continuous laser (405 nm) is modulated with adjustable periodic heating and fluorescence excitation. The temperature rise at sample surface due to laser heating is probed from simultaneous fluorescence spectrum. Thermal diffusivity can be determined from the relationship between normalized temperature rise and the duration of laser heating. To verify this technique, thermal diffusivity of a polymer material (PVC) is characterized as 1.031×10^{-7} m^2/s, agreeing well with reference data. Meanwhile, thermal conductivity can be obtained by the hot plate method. Then, both steady and unsteady thermophysical properties are available. Quenching effect of fluorescence signal in our measurement can be ignored, as validated by longtime laser heating experiments. The uncertainty induced by uniformity of laser heating is negligible as analyzed through numerical simulations. This non-destructive fluorescence-based technique does not require exact value about laser absorption and calibration experiment for temperature coefficient of fluorescence signals. Considering that most polymers can excite sound fluorescence signal, this method can be well applied to thermal characterization of polymer-based film or bulk materials.

SESSION TP02.02: Thermal Properties of Polymers and Biomaterials
Session Chairs: John Bischof and Christoph Schick
Monday Afternoon, November 26, 2018
Sheraton, 3rd Floor, Fairfax AB

1:30 PM *TP02.02.01
Fast Scanning Calorimetry of Silk Protein <u>Peggy Cebe</u>; Physics and Astronomy, Tufts University, Medford, Massachusetts, United States.

Silk is a naturally occurring biopolymer used in textiles for over 5000 years. The properties of the *B. mori* silk protein, fibroin, are related to its secondary structures, such as helices, random coils, turns, and beta pleated sheet crystals. We have prepared fibroin by extracting it from the native cocoons and use this as a starting material for our investigations into the polymorphic structure of the protein. Using infrared spectroscopy and heat capacity measurements, we quantify the amounts of the different secondary structures. By varying processing treatments, two crystalline polymorphs, Silk I and Silk II, can be formed and their structure and properties studied using X-ray diffraction and fast scanning calorimetry (FSC). Silk degrades before melting when heated at slow rates. With FSC, we heat silk at 2000 K/s, thereby minimizing effects of thermal degradation. We show that beta pleated sheet crystals melt to form unstructured non-crystalline fibroin protein, upon the input of heat energy alone. We show that Silk I crystals melt at (565 ± 14) K, while Silk II crystals melt at (624 ± 11) K. A general method for using FSC to estimate the thermodynamic heat of fusion is presented, and demonstrated for the beta pleated sheet crystals. The FSC methods developed here for the study of silk are readily transferable to studies of other crystalline materials, such as synthetic polymers, amino acids, and proteins.

2:00 PM TP02.02.02
Thermal Transport and Flow in Polymeric Materials <u>David Venerus</u>[1,2], David Nieto Simavilla[2], Andy Kiessling[2] and Jay D. Schieber[2]; [1]NJIT, Newark, New Jersey, United States; [2]IIT, Chicago, Illinois, United States.

The strong coupling of mechanical and thermal effects in polymer processing flows has profound implications on both the processability and final properties of the material. Simple molecular arguments suggest that Fourier's law must be generalized to allow for anisotropic thermal conductivity in deforming polymeric materials. In addition, theoretical results suggest a linear relationship between the thermal conductivity tensor and the stress tensor, or a stress-thermal rule. Using a novel optical method based on Forced Rayleigh Scattering (FRS) developed in our laboratory, we obtain quantitative measurements of all components of the thermal diffusivity tensor in polymers subjected to deformation. These data have been used to carry out the first (and only) tests of the stress-thermal rule, which we have found to be valid for several polymer chemistries in both shear and elongational deformations. More recently, we have developed a novel technique based on Infrared Thermography (IRT) that complements FRS and allows for the study of a wider range of polymeric materials. The IRT technique also allows us to investigate the dependence of heat capacity on deformation. These experiments are used to develop an understanding of the molecular mechanisms of thermal transport in polymers that are essential for the development of advanced materials.

2:15 PM *TP02.02.04
Utilizing Fast-Scan Calorimetry on Polymer Crystallization and Melting with Gibbs-Thomson, Hoffman-Weeks and Thermal Gibbs-Thomson Plots <u>Akihiko Toda</u>; Hiroshima University, Higashi-Hiroshima, Japan.

Crystallization and melting behaviors of chain-folded polymer crystals are examined by fast-scan calorimetry (FSC) combined with other various methods including small angle X-ray scattering (SAXS) with Gibbs-Thomson, Hoffman-Weeks, and thermal Gibbs-Thomson plots, which offer new insights on polymer crystallization mechanism. The melting point of lamellar crystals formed isothermally at T_c was measured by FSC and calibrated in terms of the heating rate dependence on the basis of the modeling of melting kinetics for the determination of the melting point at zero heating rate T_M. By combining T_M with the crystalline lamellar thickness d_c determined by SAXS, the Gibbs-Thomson (G-T) plots of T_M and T_c against $(d_c)^{-1}$ are utilized for the determination of the equilibrium melting point of chain-extended infinite-size crystal T_M^0. The Hoffman-Weeks (H-W) plot of T_M against T_c is an alternative method of T_M^0 determination. For many polymers, both of the plots, especially the G-T plots, are curved. In order to understand the meaning of the curved G-T and H-W plots, we propose a thermal Gibbs-Thomson plot in terms of the melting point T_M and the total heat of fusion ΔH_f in the secondary stage of isothermal crystallization, during which thickening and perfecting of lamellar crystals undergo and bring the shift in both of T_M and ΔH_f with longer annealing time.

2:45 PM OPEN DISCUSSION

3:00 PM BREAK

3:30 PM TP02.02.05
Thermal Properties and Structure of Electrospun Blends of PVDF and Fluorinated Copolymers <u>Nelaka Govinna</u>, Ilin Sadeghi, Ayse Asatekin and Peggy Cebe; Tufts University, Medford, Massachusetts, United States.

We report a study of the structure and thermal properties of blends comprising poly(vinylidene fluoride), PVDF, and a random copolymer of poly(methyl methacrylate) and 1H,1H,2H,2H-perfluorodecyl methacrylate, which are candidates for applications as superoleophilic membranes for oil-water separation. Blend composition was systematically varied by controlling the PVDF-to-copolymer ratio. The role of processing method and copolymer content on structure and properties was investigated for both fibers and films. Non-woven fibrous membranes were obtained by electrospinning (ES) solutions of PVDF and copolymer, at 20% w/v in a mixed solvent, N,N-dimethylacetamide/acetone (1/1 v/v). Scanning electron microscopy showed that bead-free fibers were obtained at all compositions. Fiber diameter ranged from 0.4 μm – 1.9 μm, and thinner fibers were obtained for PVDF content above 80 wt.%. As the copolymer content in the blends increased, the degree of crystallinity and the onset of degradation for each blend decreased while the glass transition temperature (T_g) increased, as evidenced by differentail scanning calorimetry (DSC), Wide-angle X Ray Scattering (WAXS) and thermogravimetry (TG) experiments. The variation of T_g followed the Kwei model of T_g mixing in polymer blends and suggest strong intermolecular interactions between the PVDF and copolymer molecules when the copolymer is present in large quantities, and relatively weaker interaction when the copolymer fraction is smaller than 0.15. Processing conditions had a greater impact on the crystallographic phase of PVDF than the copolymer content. For crystalline ES fibers, WAXS and infrared spectroscopy indicated only polar phases were present, and beta was dominant over gamma phase at all compositions. In comparison, solution cast films also contained polar phases, with an increase of gamma phase PVDF. Melt crystallized films formed non-polar alpha phase exclusively.

3:45 PM *TP02.02.06
The Unfolding and Refolding Properties of Proteins—A Case Study on Lysozyme <u>Zhiwu Yu</u>; Department of Chemistry, Tsinghua University, Beijing, China.

Proteins, serving as the principal structural and functional units in living organisms, have highly ordered structures and conformations folded from peptide chains. When subjected to stress such as heat or chemicals, proteins may unfold. The unfolded peptide chains have the potential to refold when the stress factors are completely/partially removed. In this presentation, the unfolding/refolding behaviors of a model protein, lysozyme, are discussed in detail.

First, a method to differentiate the two-state and non-two-state unfolding of proteins is discussed. It is called an interruption-incubation protocol: protein solutions are incubated at different interrupting temperatures to allow the partial unfolding of the macro-molecules. Then the thermal behaviors of the proteins upon reheating are examined. Comparisons between lysozyme and a few other proteins including bovine serum albumin will be presented.

Second, the folding/unfolding behavior of lysozyme in the presence of micelles composed of the unstructured b-casein proteins will be presented. Depending on the b-casein/lysozyme molar ratio, a partially unfolded structure of lysozyme can occur. This partially unfolded state of lysozyme loses most of its tertiary structure and, after heating, the denatured lysozyme molecules are trapped in the charged coatings of b-casein micelles and cannot refold upon cooling. The thus obtained protein complex can be viewed as a kind of special polyelectrolyte complex micelle.

Third, the unfolding/refolding behavior of lysozyme in the presence of a negatively charged polyelectrolyte sodium poly(styrenesulfonate) or PSS will be presented. With elevated PSS concentration, a new state (state I) is first formed via a "two-state" conversion process and this state can further convert to a completely unfolded state (state II) via a "non-two-state" conversion mechanism.

Finally, the mutual influence of lysozyme and lipid liposomes consisting of neutral and negatively charged phospholipids on their thermal behaviors will be presented. Interestingly, the enrichment of the negatively charged lipids cannot be induced by the native and *ex situ* unfolded (unfolded in the absence of liposomes) lysozyme, but requires that lysozyme undergo an *in situ* unfolding process (unfolding in the presence of liposomes).

4:15 PM TP02.02.07
A Novel Approach to Evaluate Microorganism Viability and Microbial Growth Using the Highly Versatile Heat-Transfer Method (HTM) <u>Kai Betlem</u>[1], Mikhajlo Zubko[1], David Sawtell[1], Bart van Grinsven[2], Thomas Cleij[2], Peter Kelly[1] and Marloes Peeters[1]; [1]Manchester Metropolitan University, Manchester, United Kingdom; [2]Maastricht University, Maastricht, Netherlands.

The Heat Transfer Method (HTM) is a novel, versatile and low-cost thermal technique that has already shown its use in the analysis of (biological) targets ranging from small molecules, to DNA, to whole cells and bacteria. The surface can be functionalized with specific receptors (DNA, polymers) for measurements and is the central element through which the heat flux will pass. The internal temperature of the heat sink, T_1, is measured by a thermocouple and steered via a controller, which is connected to a power resistor. The front side of the chip is exposed to the liquid, where T_2 is measured at the solid−liquid interface. To extract the heat-transfer resistance R_{th} (°C/W) quantitatively, the ratio of the temperature difference $\Delta T = T_1 − T_2$ and the input power P according to $R_{th} = \Delta T/P$, is analysed. Changes at the interface will reflect in a difference in the overall thermal resistance[1].
Here, we report a novel application for the HTM with the *real-time* viability study of microbes, using yeast (*Saccharomyces cerevisiae*) as a model organism. To accompany this study, the existing flow cell was redesigned, preventing the build-up of gasses produced in the metabolic cycle yeasts, leading to an increase of the R_{th} signal corresponding with the increasing concentration of cells in the flow chamber. Therefore, it was possible to discriminate between a wild type strain (DLY640) and a temperature sensitive mutation (*cdc13-1*) based on the growth kinetics. At temperatures higher than 30 °C the mutant strain stops growing[2]. This corresponds to a decrease in temperature of the optimal growth rate of the cells compared to wild type yeast cells.
The influence of factors inhibiting the replication process of yeast cells can be followed *in real- time* using this technique. Here, the signal increase in the thermal resistance under normal growth conditions seized when changing to a growth medium depleted of nutrients, the introduction of a toxic component (Cu_2SO_4) or application of a thermal shock treatment. Upon restoring the normal conditions, only the nutrient depleted condition remained viable, in all other situations the yeast cells where permanently eliminated. These results were confirmed by classical plating experiments of yeasts that were exposed to the same conditions as during the HTM measurement.
Having the advantages of simplicity, signal processing and portability, the setup can be used on site without requiring a lab environment. The described methodology is versatile and can be adapted to study different antimicrobial properties, such as the response to antibiotics on a wide range of different microbes.
1. B. van Grinsven, K. Eersels, M. Peeters, P. Losada-Pérez, T. Vandenryt, T. Cleij and P. Wagner, ACS Applied Materials & Interfaces, 2014, 6, 13309-13318.
2. K. Betlem, S. Hoksbergen, N. Mansouri, M. Down, P. Losada-Pérez, K. Eersels, B. van Grinsven, T. Cleij, P. Kelly, D. Sawtell, M. Zubko, C. Banks and M. Peeters, Physics in Medicine, (Accepted) 2018.

4:30 PM TP02.02.08
Determination of the Thermophysical Properties of Nucleobases with Fast Scanning Calorimetry <u>Amir Abdelaziz</u>[2, 1], Dzmitry Zaitsau[3], Sergey P. Verevkin[3] and Christoph Schick[2, 1, 4]; [1]Competence Center °CALOR, Rostock University, Rostock, Germany; [2]Institute of Physics, Rostock University, Rostock, Germany; [3]Institute of Chemistry, Rostock University, Rostock, Germany; [4]Kazan Federal University, Kazan, Russian Federation.

The determination of the thermophysical properties, e.g. fusion temperature, fusion enthalpy, sublimation enthalpy and vapour pressure lay within focus of many scientific fields and industrial applications. These values are directly connected to the intermolecular forces in crystal state, provides the lattice energy, change in ordering by going from crystal to gas phase and the solubility properties of organic molecules.

In many cases investigation of thermally labile systems e.g. biomolecules at slow heating rates are accomplished with low thermal stability of them. The application of classic techniques to measure their thermophysical properties often fails, making the estimation of the corresponding thermodynamic parameters, like melting temperature, enthalpy of fusion, vapor pressure highly inaccurate or even impossible.

In the present study, fast scanning calorimetry was successfully applied for determination of the sublimation vapour pressure, enthalpies of sublimation and melting behaviour of the nucleobases cytosine, thymine, adenine, uracil and guanine, the building blocks of DNA and RNA, which are known to decompose at high temperature.

SESSION TP02.03: Poster Session I
Session Chairs: Leslie Allen, Martin Kuball, Sindee Simon and Feng Yi
Monday Afternoon, November 26, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

TP02.03.02
Noncontact Thermophysical Property Measurements of Molten Oxides by Electrostatic Levitation Furnaces Onboard International Space Station Koyama Chihiro, Haruka Tamaru, Hideki Saruwatari, Masato Ohshio, Hirohisa Oda, Yasuhiro Nakamura and Takehiko Ishikawa; Japan Aerospace Exploration Agency, Tsukuba, Japan.

Electrostatic levitation furnaces are capable to measure thermophysical properties of chemically reactive materials such as liquids of refractory metals, alloys, and oxides[1]. Since the furnaces can levitate the liquids by using Coulomb force, the liquids are not contaminated and nucleated from containers. Thus, the thermophysical properties are precisely measured under wide temperature range including undercooling range. Among the properties, we have been measuring density, viscosity, and surface tension of melt with high melting temperature (T_m). On the ground our group measured thermophysical properties of various kind of molten metals including W, Re, and Ta ($T_m \approx 3500$ K) which are difficult to measure them in an crucible[2]. However, the measurements of molten oxides were scarcely performed on the ground, because oxides are difficult to charge and then do not levitate. In order to resolve this problem and measure physical properties of oxides, our group designed and fabricated the Electrostatic Levitation Furnace onboard the ISS (ISS-ELF) [3]which enables to levitate oxides with small charge due to an effect of microgravity.

To measure molten density, one of the fundamental thermophysical properties, the capabilities of levitation and heating were checked by using Al_2O_3. As a result, each sample levitated and melted fully in dry air by four semiconductor lasers. During cooling the melt, the temperature was measured by a pyrometer. The sample images were recorded by using CCD camera and UV-light. From the image and weight after the measurement, the density was calculated. The density as a function of temperature shows good agreement with that obtained by Langstaff et al. (2013)[4] using aerodynamic levitator. It also shows about 2 % lower than our earlier results obtained by using electrostatic levitator on the ground in high vacuum condition (Paradis et al. 2004)[5]. This result proves the validity of the density measurement with the ISS-ELF. The functional check for the surface tension and viscosity measurement is being currently conducted, and detailed results will be reported later.

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TP02.03.03
Properties of Poly(Ethylene Terephthalate) Electrospun Fibers Containing Carbon Nanotubes or Graphene Andrew G. Clark and Peggy Cebe; Physics, Tufts University, Medford, Massachusetts, United States.

Electrospinning is a process used to create polymer fibers with diameters on the order of nanometers to microns. Blending polymers with nanomaterials, such as carbon nanotubes or graphene, to create nanocomposites can improve the thermal, mechanical and electrical properties of the host polymer. In this study, we investigate the effects of blending carbon-based fillers on the structural and thermal properties of electrospun fibers of poly(ethylene terephthalate). PET fiber solutions containing 1.0 wt.% multi-walled carbon nanotubes (MWCNTs) or graphene flakes were electrospun from hexafluoroisopropanol. The fibers were characterized structurally using wide angle X-ray scattering, infrared spectroscopy, and scanning electron microscopy. Thermal properties were studied using thermogravimetry and temperature modulated differential scanning calorimetry (TMDSC). Fiber diameters ranged from 670 to 900 nm. WAXS revealed that the as spun homopolymer as well as the composites containing 1.0 wt% of MWCNTs or graphene were amorphous. Prior to thermal analysis the fiber mats were dried at 85 ℃ for 20 minutes to evacuate any solvent, as well as minimize effects due to fiber shrinkage. Addition of the MWCNTs or graphene resulted in a modest decrease of the glass transition and cold crystallization temperatures. Quasi-isothermal TMDSC of the dried fiber mats reveals less mobile amorphous fraction in the blends. MWCNT-based composites had mobile amorphous fraction of 0.83 while graphene-based composites and neat PET fibers had 0.89 and 0.91, respectively. Cold crystallization during QI-TMDSC increased the solid fractions of the MWCNT composite, graphene composite and neat fibers to 0.53, 0.50 and 0.43 respectively. Future work will include investigation of the fiber composites using broadband dielectric spectroscopy.

TP02.03.04
Cyclic Phase Transformation Behavior in Shape Memory Zirconia—Single Crystals vs Polycrystals Isabel Crystal, Alan Lai and Christopher A. Schuh; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

In shape memory materials, cyclic martensitic phase transformation can accumulate damage over many cycles due to the mismatch stresses developed amongst the phases and grains. Reducing such mismatches improves the cyclic performance, as known in brittle Cu-based shape memory alloys, where structures with relatively fewer grains (i.e. oligocrystalline or single crystalline specimens) exhibit better cycling properties than conventional polycrystals. The purpose of the present work is to assess this approach in zirconia-based ceramic systems, which are attractive for their high temperature capabilities and higher transformation stresses than shape memory metals, yet are also known to be brittle and experience fracture during the martensitic

transformation. Specifically, this work compares tetragonal-to-monoclinic transformation behavior of polycrystalline and single crystalline samples of yttria-doped zirconia compositions. The evolution of transformation enthalpies and strains as well as sample mass and integrity are measured to characterize thermal cycling performance. Microscopic examination also provides insight into microstructural changes after repeated transformation.

TP02.03.05
The Shape Memory Effect in Polymer Systems Based on PMMA/PEG and Epoxy DGEBA / D230 Kátia Furlani and Ruben Rodríguez; State University of Northern Fluminense, Campos dos Goytacazes, Brazil.

Shape memory polymers (SMPs) are materials considered to be intelligent due to the ability to be programmed to fix a temporary shape and subsequently regain their original shape after the application of an appropriate stimulus. They have been studied by researchers in different fields such as chemistry, materials engineering, mechanics, biomedical sciences, and microelectronics engineering. In addition to the benefits cited, they are low cost, easy to process and can have their properties easily modified through the combination with other chemical compounds, in order to expand the field of application, taking into account the needs of the market and favoring the technological advances. In this work, we analyze and compare the thermally induced shape-memory effect (SME) of two different polymer systems, one being a thermoplastic formed by a semi-interpenetrating network of poly (methyl methacrylate) and poly (ethylene glycol) (PMMA / PEG), and the other thermosetting based of the DGEBA epoxy resin (DER 331) using the aliphatic amine Jeffamine D230 (DGEBA / D230). Each material was characterized according to its ability to deform, fix a temporary shape and recover, as well as response time and life cycle, which corresponds to the number of consecutive cycles that can be performed without failure. PMMA/PEG exhibited higher deformation rate and shape fixation, but DGEBA/D230 showed higher recovery rate and shorter response time. The differentiated behavior in the analyzed systems is directly associated to the molecular structure. The higher DGEBA / D230 cross-linking density allows for faster and more efficient response, but PMMA / PEG thermoplasticity is vulnerable to long-range molecular chain slippage.

TP02.03.06
Thermal Sensing with Luminescent Nanothermometers Operating in the Near-Infrared Pascal Gschwend, Fabian Starsich and Sotiris E. Pratsinis; ETH Zurich, Zurich, Switzerland.

Temperature measurements are fundamental in countless industrial and research applications. As the focus shifts towards small scale applications such as temperature measurements in microelectronics or nanomedicine, tranditional contact methods (thermistors, thermocouples) are not applicable.[1] Therefore, nano-scale thermometers with high spatial resolution are needed.

Luminescence thermometry is a simple and inexpensive approach to remotely measure temperatures in real time with high accuracy and good spatial resolution.[2] Here, a ratiometric approach for luminescent nanothermometry is presented on the example of $BiVO_4$ nanoparticles [3] codoped with Nd^{3+} and La^{3+}, which operate in the near-infrared window ideal for applications in biological tissue. The effect of La^{3+} codoping on the structural and luminescent properties of $BiVO_4$:Nd^{3+} is investigated and an optimal composition is found. Most importantly, through careful choice of excitation wavelength and close analysis of the emission peaks of these luminescent nanocrystals, a relative thermal sensitivity of up to 1.44 %/K was achieved, leading to temperature uncertainties down to 0.27 K. Finally, the merit of the proposed nanothermometer was demonstrated *ex vivo* within biological tissue proving the feasibility of $BiVO_4$:Nd,La for non-invasive thermometry with high spatial resolution.

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TP02.03.07
Enhanced Gel Electrophoretic Separation of DNAs with Dynamically Controlled Photothermal Temperature Gradient by Digital Micromirror Device Weike Hu and Sichao Hou; Chemical Engineering, Northeastern University, Boston, Massachusetts, United States.

Uncontrolled temperature variation in gel electrophoresis is often considered pestiferous to separation. This article describes a temperature gradient enhanced gel electrophoresis, where a controlled temperature gradient is generated inside agarose gel via photothermal effect to modulate the separation of DNA molecules. The temperature gradient generated by digital micromirror device can be discretionally patterned in both static and dynamic modes to achieve steady-state and transient thermal control. Curved separation bands have been observed in the temperature gradient for double-strand and single-strand DNAs. Compared to gel electrophoresis without gradient, the separation capability of a gel at a temperature gradient of 20 to 60 °C over 10 cm is raised up to 205% for 20 kbp DNA fragments. The enhanced separation is due to larger pore size of the gel at higher temperature, which will reduce diffusion resistance and increase migration rate. Theoretical analysis confirms that diffusion rate is proportional to temperature to the third power. Given the easiness and spatial flexibility of light modulation, the photothermally generated temperature gradient can be a powerful way to enhance separation capability of a given gel in electrophoresis.

TP02.03.08
Remote Thermal Imaging For High Throughput Materials Thermal Characterization Jingwen Liu, Sichao Hou and Ming Su; Northeastern University, Boston, Massachusetts, United States.

Thermal physical properties of materials are often characterized at low throughput. We report here the new use of infrared imaging system for high throughput, remote and non-destructive characterization of materials. The high temporal and spatial resolutions of infrared imaging allow temperatures of multiple samples to be simultaneously examined to derive the temperature dependent thermal conductivity of metal plate and along various crystal orientation, as well as to derive the temperature and enthalpy change related to phase change in organic phase change materials.

TP02.03.09
Thermal Stability and Microstructural Behavior of Sintered Iron Oxide Nanoparticles Josiane C. Souza, Edson R. Leite and Júlio César Sczancoski; Federal University of São Carlos, São Carlos, Brazil.

Iron oxide (Fe_2O_3) is one of the most abundant compounds in nature. This material has four well-known crystalline polymorphs, which exhibit different structural arrangements and physicochemical properties. These particular features have driven the use of this oxide for technological applications in water splitting, gas sensors, lithium-ion batteries, and magnetic storage devices. A fundamental concept is that controlling the thermal stability as well as final

microstructure of Fe_2O_3 at nanoscale is possible to tailor its electric and magnetic properties. Hence, the aim of our study was focused on the thermal behavior of Fe_2O_3 nanoparticles previously grown via hydrothermal reactions at 160 C for 8 h. These nanoparticles were pressed and conformed as pellets (green compact), which were sintered in a dilatometer (DIL) by using a temperature range from 30 °C to 1300 °C under argon atmosphere. This analysis revealed a size-dependent sintering mechanism, since these nanoparticles presented a lower densification temperature (≈ 750 °C) than Fe_2O_3 microparticles synthesized by other conventional routes ($\approx$1300 °C). In order to monitor the strengthening of the microstructure (neck growth between particles), densification (removal of porosity accompanied by shrinkage), and coarsening (grain growth and/or pore growth), other Fe_2O_3 pellets were sintered in the DIL at 750 °C for 12 h and 900 °C for 1 min, respectively. In this case, both presented relative densities ranging from 50% to 80%. On the other hand, scanning electron microscopy (SEM) images indicated the presence of several grain grown containing interconnected porous. For pellets sintered at 900 °C for 1 min, X-ray diffraction patterns were indexed to α-Fe_2O_3 phase, while at 750 °C for 12 h was identified a mixture of α-Fe_2O_3 and Fe_3O_4. Magnetite - cubic structure and hematite - rhombohedral structure. The existence of adsorbed water and organic compounds were detected by means of differential *thermal analysis* and thermogravimetry. These substances were able to affect the mass transport and densification process in Fe_2O_3 pellets.

TP02.03.10

Thermal Transport in Soft PAAm Hydrogels Ni Tang[1], Zhan Peng[2], Rulei Guo[2], Meng An[2], Xiandong Chen[2], Xiaobo Li[2], Nuo Yang[2] and Jianfeng Zang[1]; [1]School of Optical and Electronic Information and Wuhan National Laboratory for Optoelectronics, Huazhong University of Science & Technology, Wuhan, China; [2]School of Energy and Power Engineering, Huazhong University of Science & Technology, Wuhan, China.

As the interface between human and machine becomes blurred, hydrogel incorporated in electronics and devices have emerged to be a new class of flexible/stretchable electronic and ionic devices. The heat dissipation in the electronic devices involving hydrogels will be a serious concern if this trend continues. Thus, an in-depth understanding of the thermal conduction behaviors in hydrogels and hydrogels related devices are potentially a hot topic and have not yet been seriously explored, especially for pure hydrogels.
Here, we report the experimental measurement and simulations of thermal conductivity of polyacrylamide (PAAm) hydrogels for the first time. We show that the thermal conductivity of PAAm hydrogel can be modulated by its crosslinking density and water content. We also explore the underline mechanism that both the crosslinking density and water content attribute to thermal conductivity of hydrogels. Our study offers an excellent example for measuring and analyzing the thermal conduction behaviors of hydrogel's system. Furthermore, this work shows great significance in fundamental understanding of thermal transport in soft materials and provides design guidance for hydrogel-based devices.

TP02.03.11

Thermally Insulating Oxide Films Synthesized on Aluminum Alloy(A5052) by Chelate Flame Method Yanxin Dan[1], Takashi Kosuda[1], Atsushi Nakamura[1, 2], Keiji Komatsu[1] and Hidetoshi Saitoh[1]; [1]Nagaoka University of Technology, Nagaoka, Japan; [2]Chubu Chelest Co., Ltd, Nagaoka, Japan.

Application of thermal barrier coatings (TBCs) on hot components of gas turbines enables increase in over all engine efficiency by either lowering the metal surface temperature or maintaining the existing metal surface temperatures by decreasing cooling air flow. The technology involves choices of materials and spatial configurations, as well as survivability upon extreme temperature cycling without loss of functionality. Currently, the preferred insulating oxide material of choice for TBCs is 6–8 wt% yttria-stabilized zirconia (YSZ), which exhibits metastable tetragonal (t′) form when applied on super alloy components by plasma spraying or by electron-beam physical vapor deposition. However, t′phase becomes increasingly unstable at high temperatures, it decomposes to a mixture of tetragonal (t) and cubic(c) phases, and transforms to monoclinic (m) phase at cooling processes, accompanied with excessive volume expansion, resulting in crack formation in TBCs. To cope with these requirements, alternate TBC's materials are strongly required having higher temperature capability, better mechanical properties and lower thermal conductivity.
Thermal insulation performance of the material influences it's thermal conductivity. The thermal conductivity can be controlled by film's microstructure. The thermal conductivity of oxide films were decreased by increasing porosity. In this study, we propose a chelate flame method which is a method for obtaining an insulating oxide film from metal-ethylenediaminetetraacetic acid (EDTA) complex. We synthesized thick Er_2O_3 and Y_2O_3 films on aluminum alloy (A5052) from two types of metal-EDTA complexes (EDTA-Er-H and EDTA-Y-H) using a flame sprayer. The deposition of metal oxide in the proposed synthesis involves two mechanisms, namely, chemical reaction and physical collision. It begins with a chemical reaction in which metal–EDTA complex is decomposed and oxidized to form metal-oxide particles. Therefore, the properties of the deposited film depend on the temperature and velocity of the moving particles. It is the physical collision of the metal-oxide particles with the substrate happens, and forms a film as the accumulated layer of incident particles solidify. First, in order to optimize the fabrication conditions for TBCs, the adhesion between the A5052 and the oxide film was evaluated, and the splat morphology was investigated. Next, thick oxide films were synthesized on A5052 based on optimized synthesize conditions. Although the Y_2O_3 film synthesized on A5052 was annealed close to the melting point of the A5052 substrate, it showed strong adhesion without delaminations. As results, the obtained Er_2O_3 having porosities of 3.8 to 23.3% film with thickness of 105-125 μm, and the Y_2O_3 film having porosities of 8.1 to 21.8% with thickness of 85-163 μm were fabricated on A5052 substrate. These results indicated that thick metal oxide films with various microstructures were fabricated by chelate flame method.

TP02.03.12

Thermal and Spectral Analysis of Microencapsulated Leuco Dyes Donovan R. Bassett, Danielle Hall, Alexis Corbett, Binit Sthapit, Kannan Sivaprakasam and John E. Sinko; St. Cloud State University, Saint Cloud, Minnesota, United States.

Leuco dyes are phase-change materials that undergo characteristic thermal and spectral changes with temperature. These materials have the potential to contribute to energy savings by reducing the light absorption of structures at high temperatures. In this study, we characterized a set of microencapsulated leuco dyes with transitions at 20°C, 25°C, and 30°C. These materials were subjected to differential scanning calorimetry and thermogravimetric analysis to understand the thermodynamic behavior around the transition points. UV-Vis-NIR diffuse reflectance spectra were also collected under quasi-isothermal forced heating and cooling of coating samples. The thermal and spectroscopic results were compared as a function of temperature to establish the thermo-optical characteristics of the leuco dyes for application as energy capturing coating materials. Spectra of leuco dyes were also simulated and compared to the experimental data. The comparison of temperature-dependent optical and thermal data could provide the basis to diversify the use of leuco dyes as practical phase-change materials and in other applications.

TP02.03.13

Developing a Novel Platform for Characterizing Thermoelectric Materials for Uncooled Detectors for Land Imaging Applications Riley A. Reid[1], Emily Barrentine[2], Brendan Bramman[3], Ari D. Brown[2], Steven Cagiano[2], Nicholas P. Costen[2], Vilem Mikula[2] and Alicia T. Joseph[2]; [1]North Carolina State University, Raleigh, North Carolina, United States; [2]NASA-Goddard Space Flight Center, Greenbelt, Maryland, United States; [3]University of Waterloo, Waterloo, Ontario, Canada.

Thermal land imaging (imaging at ~8-14 μm optical wavelength) is an essential tool for understanding and managing terrestrial freshwater resources. Current thermal imaging instruments employ low temperature detectors, which require cryocoolers. Consequently, cost-saving reductions in size, weight, and power can be achieved by employing uncooled detectors. One uncooled detector concept, which NASA is pursuing, is a thermopile detector with sub-

micron thick doped-Si thermoelectric materials. In order to characterize the thermoelectric properties of the doped silicon, we designed and optimized a novel apparatus. This simple apparatus measures the Seebeck coefficient with thermally isolated stages and LABVIEW automation. We optimized thermal stability using PID tuning and optimized the thermal contact between the thin film samples and stages using electrically conductive springs. Utilizing our apparatus, we measured the Seebeck coefficient of 0.45 micron thick phosphorus-doped single crystal Si samples bonded to alumina substrates. Using these Seebeck coefficient measurements and four-wire electrical resistivity measurements, we determined the relationship between the thermoelectric figure of merit and dopant concentration. These characterization results for doped-Si will guide our thermopile detector design to provide an optimal and competitive detector alternative for future thermal imaging instruments.

TP02.03.14
Effect of Annealing Temperature and Oxygen Pressure on TiO_2 Films Grown on *c*-Cut Sapphire Substrates via Pulsed Laser Deposition <u>Alexandra Gordienko</u>[1] and Anthony B. Kaye[1, 2]; [1]Texas Tech University, Lubbock, Texas, United States; [2]United States Air Force Nuclear Weapons Center, Kirtland Air Force Base,, New Mexico, United States.

Titanium dioxide (hereafter, titania or TiO_2) is a well-studied material, but despite of its 100 year history we still don't know everything about this material. It used to be thought that only one of the tetragonal phases of titania - rutile - can be grown on sapphire substrates. That is the reason why a comprehensive study of annealing effects on both phases of titania on *c*-cut sapphire doesn't exist. In previous works, we developed two pulsed-laser deposition protocols to grow both pure rutile and pure anatase films on this substrate, these protocols are used as the basis of this study.
Titania has a number of properties that make it useful for a wide variety of applications; these include using titania as the basis for energy efficient solar cells, as photocatalytic materials to clean air and water, for self-cleaning coatings, as components of various sensor devices, and as a gate dielectric in MOSFET technologies. Further, because it is a wide bandgap semiconductor, titanium dioxide is becoming increasingly important for many next-generation modern optical and electronics applications, such as transparent electronics systems, transparent thin-film transistors, and see-through active matrix displays. The success of each of these applications depends critically upon the particular crystallographic state (anatase, rutile, or brookite) of the titania being utilized. This is why the annealing effects on the resulting phase of this material can be very important.
Titania thin films were grown via pulsed-laser deposition technique on *c*-cut sapphire substrates using two pre-determined recipes: one leading to creating pure rutile, and one creating pure anatase films.
Each of the resulting films was post-annealed in a vacuum furnace at different temperatures in 200 to 900 °C in 100 degree increments and at different oxigen pressures (5, 35 and 50 mTorr). The phase of the resulting films was later determined using x-ray diffractometry. Phase content of the films was later analyzed based on the fraction of each phase in overall peak intensity. The quality of each film was was studied using atomic force microscopy.

TP02.03.15
3D Printed Polypropylene Nanocomposites for Thermal and Electrical Conductivity Applications <u>Yuval Shmueli</u>[1], Vedant Singh[2], Daniel Chao[3], Ahmed Shata[1], Mustafa Zaidi[1] and Miriam Rafailovich[1]; [1]Stony Brook University, Stony Brook, New York, United States; [2]The Wheatley School, Westbury, New York, United States; [3]Hunter College High School, New York, New York, United States.

Polypropylene (PP) is a common polymer being used in many products in all industrial fields. However, due to its relatively high crystallinity percentages it has difficulties in being produced in the emerging plastics production technology – 3D printing. In this work we show how crystallinity in the printed structure can be advantage due to its orientation that has great potential for conductance applications and also can increase the mechanical properties. We also show how incorporation of thermal conductive nano-fillers as Graphene nano platelets (GNPs) and hexagonal Boron Nitride (hBN) at 0, 5 and 10 wt% combined with the polymer orientation can lead to optimal thermal and electrical conductivity properties of the printed products. We modified the Gcode input to the printer and studied the printing process in order to study the printing conditions for optimal interfilaments fusion and printed product properties.
We used high resolution infra-red thermal camera to measure the thermal conductivity of the printed structure. We also used high voltage resistivity meter to measure the electrical properties. In addition, we used small angle X-ray scattering (SAXS) microbeam to study the macrostructure in the printed structure as function of the radial position from the filaments "skin" and interface to the "core" of the filaments. Our results show the significant improvement to the conductivity properties when the nano-fillers are being introduced to the matrix and in particular, the graphene nano platelets.
We Acknowledge support from the National Science Foundation (Inspire Award No. 1344267) and The Morin Foundation Trust.

TP02.03.16
Evaluating the Coefficient of Thermal Expansion at Elevated Temperatures through Nanoindentation Samuel Bacon, <u>Kurt E. Johanns</u>, Phil Webb, Rich Anthony and Warren Oliver; KLA-Tencor, Milpitas, California, United States.

The characteristics of thermal expansion for materials in low volumes is vital to effective manufacturing and service life. High temperature Nanoindentation is seen as a path to effectively evaluate the properties of the thermal expansion in significantly smaller volumes then what is conventionally measured by a thermomechanical analyzer. A series of experiments were run to explore the technique using coated and uncoated samples using molybdenum, aluminum and nickel plated copper to evaluate the potential for the technique to measure material expansion on the nanometer scale. A nanoindenter is found to be able to be able to replicate measurement on bulk materials and is found to be able to provide insight into underlying mechanisms in layered materials expansion.

TP02.03.17
High IR Transparency of Ultra-Thin Drawn UHMWPE/LDPE and UHMWPE/MDPE Blended Films via Solvent Casting <u>Yassine Ait-El-Aoud</u>[1], Seong Don Hong[1], Richard Pang[1], Svetlana V. Boriskina[2], Michael Okamoto[1], Alkim Akyurtlu[3] and Richard M. Osgood[1]; [1]Natick Soldier Research, Development and Engineering Ctr., Natick, Massachusetts, United States; [2]Mechanical Engineering Department, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; [3]Electrical Engineering Department, University of Massachusetts Lowell, Lowell, Massachusetts, United States.

Polyethylene (PE) is well known polymer and has an extremely large spectrum of applications, depending on the particular molecular weight, chain length, and density. The micro and nano-structure polyethylene fibers in arrays have recently attracted great attention mainly in textile fiber industry for wearable personal thermal management. Lately, researchers have shown theoretically [1] and experimentally [2] that a particular type of polyethylene, UHMWPE[1] and Nanoporous[2] respectively, is transparent to long wave-infrared body radiation but opaque to visible light. This new passive generation of fabrics could lead to a possible wearable technologies that release heat in hot climates. UHMWPE is a type of polyethylene with extremely long molecular chains that are highly entangled and resulting in a high viscosity after melting. Therefore, UHMWPE raw materials need to be adjusted to meet the melt-spinning processing requirements. It has been shown that the processibilty and flowability of UHMWPE could be improved by 1) adding nanocomposites and/or 2) blending at certain mass ratio with low-density polyethylene (LDPE) or medium density polyethylene (MDPE). Yet, the melt-spinning of ultra-thin drawn UHMWPE/LDPE and UHMWPE/MDPE blended fibers which is our main focus aim remains a challenge whereas the blended films are feasible.
In this study, we have firstly investigated the optical properties of highly oriented ultra-thin drawn UHMWPE/LDPE and UHMWPE/MDPE

blended films in the infrared wavelength range (7mm-14mm) via solvent casting. The blended films were drawn at various draw ratio from 5 times to 100 times at 130 °C. Preliminary results showed that highly transparent films with a total transmittance surpassing 95% were obtained by a mass ratio of 8:2 w/w % at draw ratio of 60 times with high crystallinity. The solvent-cast blend films were prepared by pre-mixing polymer powders then adding the mixed powders into decalin solvent in a silicone oil bath. Gradually, the temperature of the oil was increased to 150 °C in three stages within 3 hrs and was stable within ± 0.5°C precision. Secondly, we have been working on developing a thermal model of blended fibers that predict the heat transfer. This thermal model takes into consideration all possible modes of non-radiative heat transfer (convection + conduction) and radiative interaction (total reflection +total transmission +absorption) between skin-fabric and fabric-environment. The temperature cross the fabric is assumed to be uniform and the ambient temperature is approximated large relative to the fabric surface. The air gap between the skin and the fabric is taken sufficiently small.

[1] Svetlana V. Boriskina et. al "Nanoporous fabrics could keep you cool" Science, Vol. 353, issue 6303, pp. 986-987
[2] Yi Cui et. al, "Radiative human body cooling by nanoporous polyethylene textile " Science, vol. 353 issue 6303, pp. 1019-1023, September 2016

TP02.03.18
Fabrication of Shape Memory Polymer Composites Using MWNT and Their Applications to Deployable Antennas <u>Yongsan An</u>[1,2], Yong-min Kim[1,2], Yeontae Kim[3], Jong Kyoo Park[3] and Woong-Ryeol Yu[1,2]; [1]Seoul National University, Seoul, Korea (the Republic of); [2]Research Institute of Advanced Materials, Seoul, Korea (the Republic of); [3]Agency for Defense Development, Daejeon, Korea (the Republic of).

Deployable antennas have an advantage of good transportability due to their small volume when folded. A space vehicle is launched with folded antenna, which will conduct assigned jobs after unfolded in space. Existing deployable antennas have some drawbacks such as heavy weight and small deformability. Shape memory polymer (SMP), a smart material which can recover the original shape from temporary deformation by external stimulus (e.g., temperature), can be used to overcome these disadvantages. Deployable antennas made up of SMPs have excellent properties such as lightweight, large deformability, good processability, and self-transformation capability without any power devices. However, they are not proper for aerospace application due to limited recovery force and speed caused by low stresses at rubbery states and low thermal conductivity. To enhance the mechanical and thermal properties of SMPs, the shape memory polymer composites (SMPCs) were prepared using surface-modified multi-walled carbon nanotubes (MWNTs) and an epoxy-type of SMP matrix. Raman spectroscopy was used to investigate the increased disorders in the surface of MWNTs after functionalization, which was verified by the XPS analysis. The thermal conductivity of the SMPC was measured by laser flash method. The functional groups in the surface of MWNTs formed covalent bonds with the polymer matrix so that the thermal interfacial resistance of SMPC was reduced, resulting in higher thermal conductivity. Then, the thermomechanical and the shape memory properties of SMPCs were characterized. Finally, a miniature of SMPC antenna (reflector) was fabricated and its deployment test was quantitatively characterized. Improved modulus at the rubbery state and increased thermal conductivity resulted in the high recovery force and speed.

SESSION TP02.04: Thermal Properties of Glasses I
Session Chairs: Leslie Allen and Gregory McKenna
Tuesday Morning, November 27, 2018
Sheraton, 3rd Floor, Fairfax AB

8:45 AM *TP02.04.01
Kinetics of Stabilization, Polyamorphism and Nanocrystallization in Glasses <u>John H. Perepezko</u>, Meng Gao and Wei Tang; Department of Materials Science and Engineering, University of Wisconsin-Madison, Madison, Wisconsin, United States.

Thermal analysis and calorimetry have been proven to be of great value in the examination and determination of phase equilibria and thermodynamic properties. For the most part, due to the requirement to establish well defined conditions for measurement and the limitations from equipment design, the applications have been focused on stable equilibria and phases. With the advent of chip calorimetry and Flash DSC (FDSC) which offer unprecedented high programmed heating and cooling rates some of these limitations are removed so that a more extensive examination of phase reactions with rapid kinetics and metastable equilibria is now possible. With this capability it is now possible to explore ranges of alloy metastability and to examine rapid kinetic reactions such as melting and the competition between crystallization and glass formation. These capabilities are demonstrated for the analysis of the glass-to-liquid transition and crystallization of ultrastable glasses and the investigation of vitrification in difficult glass forming metallic alloy and organic liquids. With the expanded heating rate range (up to 40,000 K/s) in FDSC the separation of overlapping glass transition and crystallization signals is possible and has been applied to develop a new method to measure the delay time for nucleation in amorphous Al alloys. Similarly, the expanded cooling rate range (up to 10,000 K/s) in FDSC has allowed for the observation of glass formation and polyamorphism in D-mannitol and the measurement of the complete Time-Temperature-Transformation (TTT) kinetics in metallic glass alloys. These areas offer many opportunities for the application of FSC that can be used to expand the accessible temperature range for the study of the kinetics and thermodynamics of phase transformation and crystallization reactions.

9:15 AM TP02.04.02
Tailoring the Microstructure of Ce-Based Metallic Glass by Fast Scanning Calorimetry <u>Bingge Zhao</u>, Mannan Wu, Qijie Zhai and Yulai Gao; Shanghai University, Shanghai, China.

Differential fast scanning calorimetry (DFSC) is capable of heating and cooling a sample at ultrafast rates, allowing freezing the high-temperature structure down to ambient temperature. Additionally, the sensitivity of DFSC is in the order of nJ/K, making it possible to detect weak thermal signal and reveal phase transitions that are invisible by conventional differential scanning calorimetry (DSC). These two features permit the quantitative analysis on the formation of metallic glass. In this study, $Ce_{68}Al_{10}Cu_{20}Co_2$ (at. %) metallic glass was in situ prepared by DFSC, during which the nucleation and crystallization are quantitively determined. With the increase of cooling rate, the nucleation is suppressed, producing the amorphous structure free of nuclei. Based on that, an isothermal annealing was followed, which tailored the microstructure ranging from relaxed local configurations to nanocrystals. By the reheating after annealing, the role of structure tailoring on glass transition, crystallization is demonstrated according to the Johnson-Mehl-Avrami (JMA) equation.

9:30 AM *TP02.04.03
In Situ **Nanocalorimetry of Thin-Film Stable Glasses** <u>Javier Rodriguez-Viejo</u>[1], Aitor Lopeandía[1], Marta Gonzalez-Silveira[1], Joan Ràfols-Ribé[1], Ana

Vila[1] and Llibertat Abad[2]; [1]Physics, Universitat Autònoma de Barcelona, Bellaterra, Spain; [2]IMB-CNM-CSIC, Bellaterra, Spain.

Highly stable glasses prepared by vapour deposition at deposition temperatures around 0.85 of their glass transition temperature exhibit higher density, kinetic and thermodynamic stability with respect to their glassy counterparts obtained directly from the liquid [1]. In these vapor-deposited glasses molecular packing is so tight that the transformation into the supercooled liquid proceeds in time scales much longer than the alpha relaxation time and occurs, for sufficiently thin films, through an heterogenous mechanism starting at the free surface [2-4]. In-situ membrane-based nanocalorimetry is an ideal tool to explore the thermodynamic properties of the glass and its transformation into the supercooled liquid during temperature upscans [5]. By using appropriate capping layers the front mechanism can be suppressed and stable glasses without free surfaces transform through a 'nucleation and growth' like process. The transformed fraction follows a sigmoidal shape and can be explained using the KJMAE model, initially derived for crystallization studies. The isothermal kinetic stability increases by a factor of 50 with respect to the uncapped stable glass. We also identify, both in thin films and bulk materials, the existence of a rejuvenation process that is compatible with a cooperative mechanism.

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10:00 AM BREAK

10:30 AM TP02.04.04
Differential Nanocalorimetry and Combinatorial Electrical Resistance Sensors for Analysis of Phase Transformation of Shape Memory Alloys <u>Juanjuan Zheng</u>[1, 2], Joost J. Vlassak[1] and Yucong Miao[1]; [1]Harvard University, Cambridge, Massachusetts, United States; [2]Huazhong University of Science & Technology, Wuhan, China.

Shape memory alloy (SMA) thin films are candidates for the development of micro-actuators. Since the characterization of phase transformations in thin-film samples requires highly sensitive measurement techniques, designing SMAs with optimized composition and heat treatments is challenging. In this study, two recently developed measurement techniques – differential nanocalorimetry and electrical resistance sensors – are used to study high-temperature SMAs. The phase transformations in CuZr thin films are investigated using a differential nanocalorimetry technique with sensitivity as small as 12 pJ/K. We use a general thermal analysis method that allows determination of the heat capacity and enthalpy of transformation of a sample when there is a significant difference in the heat capacities between sample and reference. In addition, we have developed combinatorial sensors that are capable of mapping the resistance of thin-film samples as a function of temperature and composition. The sensors have excellent temperature uniformity, and they are both inexpensive and easy to fabricate. We use the sensors to evaluate the phase transformation behavior of sputter-deposited NiTiFe SMA thin films over a range of compositions. Both the crystallization of the amorphous as-deposited samples and the martensitic transformations in the crystallized samples are readily detected using the resistance sensors. The results show a strong dependence of the phase transformation path and transformation temperatures on composition and heat treatment.

10:45 AM *TP02.04.05
Tuning the Structure of Molecular Glasses through the Kinetic Arrest of Liquid-Liquid Phase Transitions <u>Lian Yu</u>; Univ of Wisconsin-Madison, Madison, Wisconsin, United States.

The structure of a glass is usually considered just amorphous and not much different from the structure of its precursor liquid. There has been increasing evidence, however, that the structure of molecular glasses can be engineered to a great extent to achieve high density and high structural order – properties desired for many applications. These "new glasses" can be prepared by physical vapor deposition and by the kinetic arrest of first-order transitions in the liquid state. We discuss two examples in the latter category. In the case of D-mannitol (and the previously studied triphenyl phosphite), two glasses can be prepared with a large difference in enthalpy (60 J/g) and density (2 %), one by quenching the ordinary liquid and the other by annealing the ordinary liquid to induce a polyamorphic transition. In the case of itraconazole, the transition to layered liquid-crystalline structures can be bypassed partially or completely by varying the cooling rate, producing glasses with continuously tunable smectic order. For this rod-like molecule, kinetic arrest of the end-over-end rotation controls how much smectic order gets trapped in the glassy state. These two examples illustrate the potential to manipulate the structure of amorphous materials to improve their properties, and the role of FDSC in understanding liquid-liquid phase transitions. Ref.: Zhu, M.; Yu, L. *J. Chem. Phys.* **2017**, 146, 244503. Teerakapibal, R.; Huang, C.; Gujral, A.; Ediger, M. D.; Yu, L. *Phys. Rev. Lett.* **2018**, *120*, 055502.

11:15 AM *TP02.04.06
Phase Transformation in Nano-Structured Materials Measured by Fast Differential Scanning Calorimetry <u>Juergen E. Schawe</u>; Mettler Toledo GmbH, Schwerzenbach, Switzerland.

Fast differential scanning calorimetry (FDSC) is a non-adiabatically chip calorimetry technique. The commercial available Flash DSC 2+ enables typical heating and cooling rates in the order of 40,000 K/s in a temperature range between -100 °C up to 1000 °C.
This technique is used to study the formation of differently structured glasses and non-isothermal nucleating processes in bulk metallic glass alloys. Depending on the thermal history and the heating conditions monotropic polymorphic phases can be formed which can be transformed into the more stable phase on different pathways. Furthermore, we discuss a method to distinguish between heterogeneous and homogeneous nucleation processes.

11:45 AM TP02.04.07
Conjugated Polyelectrolytes are Feeling the Heat—A Ratiometric Nanothermometer for Solution, Hydrogels and Thin Polymer Films <u>Pierre Karam</u>; Chemistry , American University of Beirut, Beirut, Lebanon.

Temperature is a fundamental variable that controls and drives many chemical, biological and physical processes. Nowadays, there is a tremendous drive to explore and understand processes at the nanoscale level in many fields of science and technology. We report a self-referencing ratiometric nanothermometer based on short conjugated polyelectrolytes (CPEs). The probe is prepared by complexing a phenylene-based polymer with polyvinylpyrrolidone (PVP), an amphiphilic macromolecule that destabilizes the CPE π–π stacking. This makes it possible to shift the equilibrium between the less emissive aggregated state of the CPE (520 nm) and its more emissive single chains (450 nm) within a useful temperature range (15.0–70.0 °C). The

probe is used as a noninvasive fluorescent method for mapping thermal fluctuations in solution, hydrogel matrices and thin film polymers using an unmodified commercially available digital single-lens reflex camera (DSLR). We are currenlty exploring thermal processes in microwell structures. The reported temperature sensor has the potential to provide a wealth of information when thermal mapping is correlated with chemical or physical processes.

SESSION TP02.05: Thermal Properties of Glasses II
Session Chairs: Leslie Allen and Gregory McKenna
Tuesday Afternoon, November 27, 2018
Sheraton, 3rd Floor, Fairfax AB

1:30 PM *TP02.05.01
Nano-Scale Dynamic Measurements—Flash DSC and Nanobuble Inflation of Ultra-Stable Amorphous Fluoropolymers Gregory B. McKenna and Heedong Yoon; Texas Tech University, Lubbock, Texas, United States.

The advent of novel experimental techniques that make it possible to work with nanogram quantities of material has revolutionized the study of nanoconfined materials. Furthermore, the relevant techniques have also made it possible to investigate novel materials that are only made in extremely small quantities. It is this latter case that we address here. We have succeeded in making and characterizing ultra-stable amorphous fluorocarbon films made by vacuum pyrolysis deposition (VPD). The ultra-stable amorphous fluorocarbon is very deep in the energy landscape or deep glassy section of the "unexplored region" of glasses between the a very low fictive temperature T_f and the glass temperature T_g. By combining rapid chip scanning calorimetry (Flash DSC) with the Texas Tech nanobubble inflation method we not only determine that the deposition conditions lead to a value of T_f that is very near to the Kauzmann temperature T_K, but we are also able to measure the viscoelastic response in the temperature regime encompassing T_K to slightly above T_g and determine the temperature dependence of the dynamics in this regime. The question ultimately addressed is whether or not the relaxation time (or viscosity) diverges at a finite temperature above absolute zero and near to T_K as anticipated in theories in which an ideal glass transition is postulated. The measurements near to and above T_f give upper bounds to the equilibrium relaxation times because in the regime where $T > T_f$ the material has a lower specific volume and lower enthalpy than the equilibrium glassy state. Furthermore, because the T_f is approximately equal to T_K, which is 56 K below the T_g in this case, the range of measurements is greater than previously achieved using a 20 million year old amber material. For the amber the glass had a fictive temperature some 43.6 K below T_g. Our results confirm the amber results and are consistent with the idea that the observed Vogel-Fulcher behavior of glass-forming liquids seen above the T_g does not persist into the deep glassy state where $T > T_f$. Rather the response deviates from the super-Arrhenius behavior of the Vogel-Fulcher function and tends towards an Arrhenius-like behavior, albeit with very high apparent activation energy. These results challenge theories that demand divergence of the relaxation times or viscosities at a finite temperature as well as the idea of an ideal glass transition. The studies were only possible because of our ability to make dynamic, both calorimetric and viscoelastic, measurements on nano- to micro-gram quantities of material.

2:00 PM TP02.05.02
Profiles in Local Glass Transition Temperature Near and Across Polymer Interfaces Connie B. Roth; Emory University, Atlanta, Georgia, United States.

Local thermal analysis using fluorescence has made it possible to map out the profile in local glass transition temperature $T_g(z)$ as a function of position z across a glassy-rubbery polymer-polymer interface. Starting with the weakly immiscible system of polystyrene (PS) and poly(n-butyl methacrylate) (PnBMA) whose bulk T_g values differ by 80 K, we observed a broad and asymmetric dynamical profile in $T_g(z)$ spanning 350-400 nm from one bulk T_g value to another [*J. Chem. Phys.* 2015, 143, 111101]. We have since observed similar behavior in a number of weakly immiscible systems, consistently showing a longer-ranged $T_g(z)$ perturbation for a lower T_g polymer next to a hard interface than a higher T_g polymer next to a soft interface [*J. Chem. Phys.* 2017, 146, 203307]. More recently we have explored this difference of hard vs. soft neighboring domain by investigating the $T_g(z)$ profile in PS next to polydimethylsiloxane (PDMS) with varying crosslink density to systematically change the modulus of the neighboring domain without also changing the chemistry of the interface. We observe that the local $T_g(z)$ in PS at a distance of $z = 50$ nm away from the PS/PDMS interface can vary by 45 K when the PDMS modulus changes from ~1 to 3 MPa, supporting theoretical predictions that modulus is a controlling variable. Interestingly, the length scale $z \approx 70$-90 nm at which bulk $T_g(z)$ of PS is recovered for this more strongly immiscible system is significantly shorter than what would be expected ($z \approx 225$-250 nm) for this soft neighboring domain based on our previous results. Our studies have also discovered that this strong coupling of the dynamics across dissimilar polymer-polymer interfaces only occurs if the interface has been well formed and annealed to equilibrium suggesting that some aspect during polymer interface formation (broadening of interface, chain interpenetration, or interfacial roughening) may be significant in controlling the observed behavior. Efforts to separate these different factors have led us to investigate rough interfaces and substrates with end-tethered chains finding that low grafting densities, coinciding with the "mushroom-to-brush" crossover regime, result in large increases in local T_g, with $T_g(z)$ profiles consistent with a hard polymer interface [*ACS Macro Letters* 2018, 7, 269-274].

2:15 PM TP02.05.03
Cooperativity Length in a Glass-Forming Liquid Determined by a Combination of Calorimetric Methods and Neutron Spin Echo Spectroscopy Reiner Zorn[1], Yeong-Zen Chua[2], Christoph Schick[2], Jürn W. Schmelzer[2] and Olaf Holderer[3]; [1]JCNS-1, Forschungszentrum Jülich GmbH, Juelich, Germany; [2]Institute of Physics and Competence Centre CALOR, University of Rostock, Rostock, Germany; [3]JCNS at MLZ, Forschungszentrum Jülich GmbH, Garching, Germany.

Recent advances in AC calorimetry and in quasielastic neutron scattering (QENS) by neutron spin echo (NSE) make an experiment possible with the aim of determining the cooperativity length ξ in glass forming materials proposed more than a decade ago by E. Donth. The basic idea of this experiment is to assign a length scale to the AC-calorimetric relaxation time using the spatial resolution of QENS. By comparing the resulting ξ to the value expected from thermodynamic formulae it is possible to decide whether temperature fluctuations have to be taken into account in glass physics.
The main challenge is to find a range of relaxation times that is accessible by both methods. The use of laser modulation extends the dynamical range in AC calorimetry close to 1 MHz. On the other side, NSE spectroscopy nowadays can access relaxation times up to 1 µs. In practice, both limits cannot be attained completely for a given material. In particular, NSE is further limited by the fact that incoherent scattering is required for this type of study. Although, for these reasons, the dynamic gap could not be closed completely, we can present first results on propylene glycol. The results indicate a better agreement with a thermodynamic calculation involving temperature fluctuations.

2:30 PM TP02.05.04
T_g and Structural Recovery of Nanoconfined Polystyrene Using Nanocalorimetry Sindee L. Simon; Texas Tech University, Lubbock, Texas, United

States.

The behavior of glass-forming materials confined at the nanoscale has been of considerable interest over the past two decades with conflicting results sparking debate. Here, I will discuss recent work from my laboratory focusing on the glass transition and associated structural relaxation kinetics of nanoconfined polystyrene using the Mettler Toledo Flash differential scanning calorimeter (DSC). The advantages of the Flash DSC include sufficient sensitivity to measure enthalpy recovery for a single 20 nm-thick film, as well as extension of the measurements to aging times as short as 0.01 s and to aging temperatures as high as 15 K above nominal T_g since high fictive-temperature glass can be created by the fast cooling rates (1000 K/s). Confinement geometries studied include ultrathin films, supported rods, and stacked rods. The T_g depression of thin films is found to be a function of cooling rate, decreasing with increasing cooling rate; whereas, at the highest cooling rates, T_g is the same as the bulk within the error of the measurements. Results for rods also depend on cooling rate, but with supported rods showing elevated T_gs relative to the bulk. Structural recovery is performed as a function of aging time and temperature, and the evolution of the fictive temperature is followed. The aging behavior and relaxation time-temperature map for single ultrathin films will be compared to those for bulk material, as well as to those for nanoconfined rods and stacked samples. The results will also be discussed in the context of current controversies in the field.

2:45 PM TP02.05.05
Thermal Analysis of Liquid Coatings Using a Unique DMA Method <u>Xinzhu Gu</u>, Ed Millero, Christina Puhnaty, Qin Li and Claire Parasida; PPG Industries, Inc. , Pittsburgh, Pennsylvania, United States.

Dynamic mechanical analysis (DMA) is a highly sensitive thermal mechanical analysis technique for studying the viscoelastic behavior of polymers. It provides insight into the relationship between molecular structure and mechanical properties of polymers, therefore it is a useful tool to monitor vitrification, gelation, curing and decomposition of thermoset polymers. Coatings, in their liquid form, are not suitable for direct DMA testing. Solid supporting substrates, mainly wood and glass fiber, have been used for liquid resins to obtain solid specimens for DMA testing. Specifically, liquid resins were applied on the surface of a supporting substrate to form a sandwich structure then is subjected to DMA testing mainly in three-point bending mode. However, these substrates are not suitable for studying thin coatings due to the large stiffness differences between the substrate and coating. In this study, the liquid polymer coatings were applied to a soft absorbent substrate (i.e. Kimwipe®). The coated Kimwipe® was then used to examine cure properties and glass transition temperatures (Tg) via DMA in tension mode.

The first part of this study investigated the curing behavior of the liquid coatings using a Kimwipe® as the substrate. Before the curing reaction occurred, as temperature increased and liquid carrier evaporated from the coating composition, the modulus of elasticity gradually increased. As temperature kept increasing, rapid increase of the stiffness of polymer was observed, attributed to cross-linking reaction. This change was reflected by a change in the slope of the storage modulus as function of temperature. The inflection point occurring at a specific temperature on DMA curve suggested the onset of curing behaviors. Moreover, degrees of cure were calculated from the modulus vs. temperature curve.

In the second part of this study the dynamic mechanical properties and Tg of the solid coatings obtained from previous tests were investigated and compared with free-standing films. The Tg of coatings and free films were found to be very comparable, while the coatings showed higher storage modulus than free films, given the storage modulus of the substrate.

In summary, the Kimwipe® was proven to be a suitable substrate for the preparation of DMA testing specimens to predict the curing behavior and Tg of liquid coating for its stability during the temperature span. This technique will help understand thermal properties of liquid samples when convectional DSC technique and fabrication of free films are challenging.

3:00 PM BREAK

SESSION TP02.06: Scanning Thermal Microscopy
Session Chairs: Andrea Centrone and Martin Kuball
Tuesday Afternoon, November 27, 2018
Sheraton, 3rd Floor, Fairfax AB

3:30 PM *TP02.06.01
Nanoscale AFM Probes Enable Thermal Conductivity and Chemical Composition Imaging at the Nanoscale Georg Ramer, Vladimir Aksyuk and <u>Andrea Centrone</u>; National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

Atomic force microscopy (AFM) provides thermal, chemical, mechanical etc., properties, at the nanoscale. For example, photothermal induced resonance (PTIR)[1] combines AFM with IR (or visible) spectroscopy. In PTIR, the absorption of a laser pulse induces a rapid thermal expansion of the sample. Conventional cantilevers are too slow to track the sample thermal expansion dynamics; however, the fast sample expansion kicks the cantilever in oscillation (like a struck tuning fork), with amplitude proportional to the absorbed energy.
To capture the sample thermalization dynamic, we introduced the Scanning Thermal InfraRed Microscopy (STIRM)[2] technique. STIRM leverages nanofabricated temperature sensitive AFM probes to measure the temperature raise in the sample due to light absorption. The STIRM signal amplitude is proportional to the absorbed energy, yielding the local chemical composition; while the STIRM signal evolution can provide the sample thermal conductivity at the nanoscale (if the sample thermalization is slower than the probe).
Here we revolutionize AFM (and PTIR) signal transduction by integrating cavity-optomechanics for sensing the motion of fast, nanosized/picogram scale AFM probes with unprecedented precision and bandwidth, thereby breaking the trade-off between AFM measurement precision and ability to capture transient events.[3] Applied to PTIR/STIRM, the probe near-field ultralow detection noise and wide bandwidth improves the time resolution (10 ns, x1500), signal-to-noise ratio (50 x) and throughput (x2500). Remarkably, this synergy enables a new PTIR measurement modality: capturing the previously inaccessible fast thermal-expansion response of the sample to nanosecond laser pulses, thus allowing concurrent measurement of the chemical composition and thermal conductivity, at the nanoscale.
We validate these new capabilities using polymer films and measure the intrinsic thermal conductivity (η) of metal-organic framework (MOF) individual microcrystals, a property not measurable by conventional techniques. MOFs are a class of nanoporous materials promising for catalysis, gas storage, sensing and thermoelectric applications where accurate knowledge of η is critically important. Additionally, the improved sensitivity enables measurement of nanoscale IR spectra of monolayer this sample with high signal to noise ratio (≈ 170).
Finally, I will discuss our efforts to further increase the PTIR throughput by 200-fold, i.e. 500000x with respect to conventional measurements and to

conduct measurements in water.

We believe that cavity-optomechanics based probes are broadly-applicable and will benefit a wide range of AFM-based dynamic observations in nanoscience and biology.

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[2] Katzenmeyer, A.M. et al. Nanoscale 2015, 7, 17637-17641
[3] Chae, J. et al. Nano Lett. 2017, 17, 5587-5594

4:00 PM TP02.06.02

Influence of Temperature on Microstructure and Mechanical Properties of Polymer Composites <u>Bede Pittenger</u>, Sergey Osechinskiy, Steven V. Ulrich, Judy Mosley, Sophie Loire, Shuiqing Hu and Thomas Mueller; Bruker, Goleta, California, United States.

The relationship between the microstructure and mechanical properties of microscopic domains within polymer composites is important due to their influence on macroscopic material performance and function. Mechanical properties of polymers are time dependent, so a full understanding requires measurements over a range of frequencies and temperatures. Ideally, one would like to observe the mechanical behavior of these domains while they pass through their glass transitions in order to better understand the influence of size effects and confinement.

Atomic Force Microscopy (AFM) has the nanometer level resolution and sensitivity needed to investigate these samples, but accurate comparisons with established rheological measurements have proven to be more elusive. Resonant methods like TappingMode[1] and contact resonance[2] provide mechanical property maps at discrete frequencies that are many orders of magnitude higher than bulk measurements. Non-resonant methods like force spectroscopy[3] and PeakForce Tapping[4] provide a better match in frequency, but face challenges in calculating intrinsic mechanical properties like loss tangent and storage modulus.

Recently, new AFM modes, improved modeling, better calibration, and more optimal probe design have become available[5], expanding the possibilities for quantifying mechanical properties at the nanoscale. This presentation will demonstrate the use of this new capability in examining microscopic domains and interphase regions within a polymer composite over a wide range of frequencies and temperatures.

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4:15 PM TP02.06.03

Quantitative Thermometric Scanning Thermal Microscopy and Thermomechanical Nanoindentation from Room Temperature to >1,000C <u>Roger Proksch</u>[1] and Ami Chand[2]; [1]Asylum Research, Santa Barbara, California, United States; [2]Applied Nanostructures, Mountain View, California, United States.

The functionality and performance of polymeric materials is largely determined by a complex interplay of chemical and mechanical properties, often at the nanoscale. In order to understand these complex material systems and further improve them, it is necessary to measure and map them at that same nanoscale. Macroscopic polymer behavior is often characterized with temperature dependent mechanical analysis measurements such as dynamic mechanical analysis (DMA). Previous approaches to making similar measurements on the nanoscale, while having some success at quantifying stress and strain as a function contact area and frequency have relied on indirect measurements of the tip-sample contact temperature. Using a combination of a laser heated tip with a unique, an integrated thermocouple combined with a scriptable DMA interface, we can quantitatively evaluate temperature and frequency dependent polymer properties with sub-100nm resolution. This approach has enabled three key advances we will cover in this presentation:

1. High temperature Scanning Thermal Microscopy. The probes discussed here, coupled with photothermal heating can routinely operate at temperatures in excess of 1,000°C.
2. Localized thermal analysis combined with quantitative nanomechanical imaging. The ability to quantitatively ramp the tip temperature (estimated at rates in excess of 10^8°C /minute) allow quantitative and highly localized measurements of phase transitions, mechanical and other temperature dependent properties.
3. Fouled tip cleaning. A common problem in AFM, fouling of the tip with material from the sample, can be greatly mitigated with localized heating of the tip. We will demonstrate that repeatable quantitative modulus measurements[1] can be accomplished by cleaning the tip with a simple protocol.

The tip structure of the thermocouple integrated probe has been described elsewhere [2]. During the experiments the tip and the thermocouple materials were found to be stable in the excess of 1000° C, expanding the regime of the DMA of the polymeric material that were not possible with existing technologies.

[1] Fast, High Resolution, and Wide Modulus Range Nanomechanical Mapping with Bimodal Tapping Mode, <u>Marta Kocun</u> et al. ACS Nano, 2017, 11 (10), pp 10097–10105
[2] Micromachined Chip Scale Thermal Sensor for Thermal Imaging, Gajendra S. Shekhawat et al. ACS Nano, 2018, *12* (2), pp 1760–1767

4:30 PM TP02.06.04

Development of a Multimodal Imaging Platform Based on Photoinduced Thermal Desorption and Analysis by Atmospheric Pressure Chemical Ionization Mass Spectrometry <u>Olga Ovchinnikova</u>[2], Matthias Lorenz[2], Stephen Jesse[2], Mario Viani[1], Aleksander Labuda[1] and Roger Proksch[1]; [1]Asylum Research, Santa Barbara, California, United States; [2]Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

The key to advancing materials is to understand and control their structure and chemistry. Thorough chemical characterization can be challenging since many existing techniques analyze only a few properties of the specimen, thereby requiring multiple measurement platforms to acquire the necessary information. The multimodal combination of atomic force microscopy (AFM) and mass spectrometry (MS) transcends existing analytical capabilities for nanometer scale spatially resolved correlation of the chemical and physical properties of a sample surface. We recently introduced the utilization of a photoinduced cantilever heating technology developed by Oxford Instruments for the localized thermal desorption and analysis and presented a closed cell design for sampling on an Oxford Instruments Cypher ES microscope to interface with a Thermo Orbitrap Velos Pro mass spectrometer using inline atmospheric pressure chemical ionization (APCI). The photoinduced cantilever heating technology works with standard AFM probes that are compatible with advanced AFM modes for the nanomechanical and electromechanical characterization of samples. We previously demonstrated below 500 nm spatial

resolution for the spot-sampling by thermal desorption from thin layers and the chemical analysis of small organic molecules in full scan MS mode.

We demonstrate the application of multiple and advanced AFM measurement modes such as AMFM nanomechanical characterization on a single AFM cantilever, combined with photoinduced thermal desorption and analysis by mass spectrometry to link chemical composition with material functionality. We show the chemical analysis by mass spectrometry of gas phase species evolving from polymeric material in contact with a heated AFM probe, spatially resolved with nanometer resolution, and identify small organic molecules and characteristic fragments and pyrolysis products from the polymer. We present results from systematic studies of factors limiting the efficiency of transport and ionization of material evolving from the sample surface, with the objective to enhance the achievable spatial resolution and compound coverage of the multimodal imaging platform. Parameters studied include the timing of the photothermal cantilever heating and analysis by mass spectrometry, transport conditions for the gaseous material from the closed desorption cell to the mass spectrometer, and the operating conditions of the inline ionization stage. Computational fluid dynamics (CFD) simulations were used to study the uptake and transport of material. Experimental studies on prototype cell models prepared by additive manufacturing provide support for the modeling data.

4:45 PM TP02.06.05
Calibration Techniques for Robust Quantitative Scanning Thermal Microscopy—A Comparison of Strategies and Best Practices Adam A. Wilson[1, 2]; [1]US Army Research Laboratory, Adelphi, Maryland, United States; [2]National Research Council, Washington, District of Columbia, United States.

As we continue to improve our ability to miniaturize, manipulate and leverage materials and devices down to the nanoscale, the limit to advancement in many fields leveraging nanotechnology is accurate measurement of material properties at these scales. Scanning thermal microscopy (SThM) boasts the best available spatial resolution among thermal metrology techniques, leveraging the nanometer-scale resolution afforded by atomic force microscopy. However, SThM has suffered from a lack of consistent, reliable quantitative usage. This is largely due to tip-sample interaction, with the sample's topography leading to artifacts in the observed signal. Several recent efforts have attempted to more robustly calibrate the probe-sample thermal interaction and account for topographically-induced artifacts. Among the most commonly used thermal exchange parameter calibration strategies are the implicit (curve fitting) method, the step method, and the intersection method, which each rely on at least two materials as reference samples, while recent advancements include single-sample calibration strategies. However, to date, there has not been a comparative study between calibration methods, or efforts to demonstrate the limits of each technique.

This work compares the performance and suitability of probe-sample thermal exchange calibration strategies, discusses the most frequent failure modes, and offers guidance for best practice in quantitative usage of SThM. As an example of determination of accuracy of calibration and best practices, we demonstrate that under conditions previously published using the intersection technique (k_{low} = 1.1 $Wm^{-1}K^{-1}$ and k_{high}= 1.5 $Wm^{-1}K^{-1}$), significant deviation (>50%) in measured sample thermal conductivity is observed when measuring samples with thermal conductivity values larger than those of the reference samples, but we demonstrate that by calibrating with reference samples having a wide range of sample thermal conductivity (k_{low} = 0.5 $Wm^{-1}K^{-1}$ and k_{high} = 50 $Wm^{-1}K^{-1}$), the measured values may be expected to be accurate to within 20% for the entire range. Similar analysis will be performed on data from both previously published studies and new experimental results using the step method, the implicit method, and the novel single-sample calibration strategies to demonstrate which method(s) provide the most accurate values for local thermal conductance measurement and in what ranges and experimental conditions the quantitative accuracy may hold. This work is poised to offer a timely comparison between several emerging and widely used calibration techniques for SThM, and aims to unify efforts for improved accuracy and reliability in future quantitative studies using SThM.

SESSION TP02.07: Poster Session II
Session Chairs: Leslie Allen, Martin Kuball, Sindee Simon and Feng Yi
Tuesday Afternoon, November 27, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

TP02.07.01
Influence of Temperature on the Pop-in Load and Indentation Size Effect of Single Crystal Brittle Material Janel Chua[1, 2], Qingsong Tu[3] and Hao Wang[1]; [1]National University of Singapore, Singapore, Singapore; [2]DSO National Laboratories, Singapore, Singapore; [3]Materials Science, University of California-Berkeley, Berkeley, California, United States.

In this work, the indentation size effect (ISE) is studied for temperatures ranging from 300K to 475K using nanoindentation experiments and molecular dynamics simulations. CaF2 single crystals are indented using a high temperature nanoindenter and the pop-in load was observed to decrease with increasing temperature. Increasing the temperature of the material also led to a reduction in the material dependent plasticity length scale defined in the Nix-Gao relation as well as the hardness at infinite depths.
The experiment is supplemented with MD simulations of nanoindentation into a free surface of CaF2. A suitable CaF2 potential for high temperature was first selected via comparisons between simulated and experimental vacancy formation energy as well as melting point temperatures. Changes in dislocation structure with increasing indentation depth were then studied for various temperatures for the (111) planar direction. The study thus provides much insight into the relationship between temperature and dislocation mechanisms during nanoindentation and underscores the effect of temperature on dislocation structure and formation.

TP02.07.02
Reduction in Thermal Conductivity by Phonon Confinement Effect of In$_{0.53}$Ga$_{0.47}$As Nanofilms Jungwon Kim[1], Hoon Kim[1], Mehmet E. Kilic[1], Chhatrasal Gayner[1], Rachel Koltun[2], Hwanjoo Park[1], Aloysius Soon[1], John Bowers[2], Chris Palmstrom[2] and Woochul Kim[1]; [1]Yonsei University, Seoul, Korea (the Republic of); [2]University of California, Santa Barbara, Santa Barbara, California, United States.

Reduction in thermal conductivity of the nanostructured materials has been widely known for having the reduced phonon mean free path by its nano-size boundary scattering. At even smaller size, the phonon confinement effect from the decrease of the phonon group velocity can happen in nanostructured materials leading to further reduction in the thermal conductivity. We measured the thermal conductivity of In$_{0.53}$Ga$_{0.47}$As nanofilms with various thicknesses from 70 to 10 nm by the T-bridge method, and analyzed it by the Callaway's thermal conductivity model. It is found that the calculated thermal conductivities of below 20-nm-thick nanofilms based on the bulk In$_{0.53}$Ga$_{0.47}$As group velocity cannot accurately predict the measured thermal conductivities. The group velocities of nanofilms are evaluated by the calculation of the phonon dispersion relation, and these show that there is a significant reduction in the group velocity along the decrease in the thickness. According to these reduced group velocities, the re-calculated thermal

conductivities of below 20-nm-thick nanofilms are successfully agreed with the measured ones. The phonon confinement effect is found to be another key factor to explain the low thermal conductivities of below 20-nm-thick $In_{0.53}Ga_{0.47}As$ nanofilms.

TP02.07.03

Extraordinary Electronic Contribution to Thermal Transport in Free-Standing Graphene Nanoribbons with Low-Disorder Edges Qinyi Li[1], Wakana Okita[2], Hiroo Suzuki[2], Toshiaki Kato[2], Toshiro Kaneko[2], Yohei Komori[1], Tatsuya Ikuta[1] and Koji Takahashi[1]; [1]Kyushu University, Fukuoka, Japan; [2]Tohoku University, Sendai, Japan.

Previous research on thermal transport in graphene has focused on the lattice contribution while the electronic contribution is regarded as 0.1%~1%. Here, we report experimental evidence of extraordinary electronic contribution to heat conduction in graphene nanoribbons (GNRs) with low-disorder edges. By the electrical self-heating method, the thermal conductivity of a plasma-CVD-grown 43nm-wide suspended GNR with near-zigzag edges was measured to be below 5% of that of large pristine graphene and exhibits a temperature dependence that indicates width confinement. The electronic thermal conductivity, which is converted from the measured electrical conductivity by the Wiedemann-Franz law, reaches as high as ~20% of the total thermal conductivity at 120-360K. This finding is attributed to the different effects of edge scattering on phonons and electrons for the particular edge structure, as well as the cleanness of the as-grown sample. Even the low level of edge disorder in the near-zigzag GNR can lead to strong phonon-edge scattering, but the superior electron transport is preserved, which agrees well with previous simulations. Our work highlights the importance of electronic thermal conductivity in GNRs, and suggests the edge manipulation as a promising way to independently control electron and phonon transport in GNRs for potential thermoelectric applications.

TP02.07.04

Non-Contact Temperature Difference Measurement of Cleavage Plane Nanogap Electrodes with Large Surface Area Masaki Shimofuri, Yoshikazu Hirai, Toshiyuki Tsuchiya and Osamu Tabata; Kyoto University, Kyoto, Japan.

Vacuum nanogap electrodes are expected to significantly improve thermal power generation efficiency, which is considered difficult with conventional thermoelectric materials. In order to apply the vacuum nanogap electrodes as a thermal power generation element, the properties of nanogap, especially heat transfer at the nanogap should be investigated because enhancement of the heat transport due to the near-field heat radiation effect cannot be ignored in the vacuum gap of nanometer order. However, the measurement is difficult because it needs high temperature and spatial resolution. In addition, it is difficult to create a spatial temperature difference in a nanometer scale region. Furthermore, it is also challenging to achieve both large area and uniform narrow gap by conventional fabrication methods such as electron beam lithography, metal plating, and focused ion beam processing, where the opposing surfaces of the gap are neither parallel nor flat. Also, the emission area achieved by the aforementioned methods are only of the order of several nm2, which makes these vacuum nanogap electrodes impractical from the viewpoint of the power generation. In this research, we have proposed a method to make nanogap electrodes by exploiting the advantages of interplanar cleaving in single crystal silicon, choosing (111) as cleavage plane. In cleavage fracture, a smooth fracture surface parallel to the crystal plane is exposed, so it is expected that the opposing surface of the obtained nanogap electrodes will become parallel and smooth. We fabricated MEMS devices with silicon-on-insulator wafers with device layer thickness of 5 um, oxide sacrificial layer thickness of 2 um, handle layer thickness of 400 um, device layer surface orientation (110). Silicon beam in the device, oriented in <111> direction was cleaved by applying tensile stress using a micromanipulator. As a result, nanogap electrodes having a parallel and smooth surface area of several tens of um2 were obtained, which makes the cross-sectional area several thousand times larger than conventional nanogap electrodes. Comb drive actuators and a gold wire for joule heating were integrated in the device, and the gap distance control and heating near the nanogap electrodes were carried out. For temperature measurement, mirco-Raman spectroscopy was used. The temperature resolution in our measurement was about 1 K and the spatial resolution was 1 um or less. We were successful to produce and maintain a spatial temperature difference of up to 60 K in a 180 nm size distance. However, in order to evaluate the proximity effect of heat transfer in the vacuum nanogap, higher temperature resolution and accuracy is needed; therefore, we continue to improve the temperature measurement method and device design.

TP02.07.05

Heat Generation Property of Thick Film Ceramic Heater Consisting of $CaCu_3Ru_4O_{12}$ Akihiro Tsuruta[1], Toshio Itoh[1], Masashi Mikami[1], Yoshiaki Kinemuchi[1], Ichiro Terasaki[2, 1], Norimitsu Murayama[1] and Woosuck Shin[1]; [1]AIST, Nagoya, Japan; [2]Nagoya University, Nagoya, Japan.

We have studied a conducting oxide $CaCu_3Ru_4O_{12}$ as an alternative conducting material for Pt in various high temperature operating electrical devices such as solid oxide fuel cells and gas sensors. The resistivity of $CaCu_3Ru_4O_{12}$ is lower than 1 mΩcm even at 500°C, and the temperature dependence of resistivity is metallic. In our previous study, we have successfully formed $CaCu_3Ru_4O_{12}$ thick film on an alumina substrate by screen printing process, which is one of the practical process, via mixing with CuO as a sintering additive [1]. Then, we have fabricated a SnO_2 gas sensor using CuO-mixed $CaCu_3Ru_4O_{12}$ thick film as both electrodes and a heater on an alumina substrate (3.0 × 25 × 0.3 mm). In this study, we investigated the heat generation property of the CuO-mixed $CaCu_3Ru_4O_{12}$ thick film heater in the sensor in order to evaluate the potential of $CaCu_3Ru_4O_{12}$ [2].
The temperature of the CuO-mixed $CaCu_3Ru_4O_{12}$ thick film heater increases at least up to 600°C without any problems such as thermal runaway and hot spots, and the temperature is linearly changed with applied voltage. The heater remains intact after long-term operation at high-temperature and a large temperature change of 500°C within 10 s. We conclude that the CuO-mixed $CaCu_3Ru_4O_{12}$ thick film heater is proven to be robust and reliable, and can replace Pt heaters in gas sensor.
[1] A. Tsuruta *et al.*: *Phys. Status Solidi A* 214 (2017) 1600968.
[2] A. Tsuruta *et al.*: *Materials* 11 (2018) 981.

TP02.07.06

Influence of Heterogeneous Pnictogen-Substitution on Thermal Transport in Skutterudites Semi Bang[3], Georgy Samsonidze[1], Boris Kozinsky[2] and Daehyun Wee[3]; [1]Research and Technology Center, Robert Bosch LLC, Cambridge, Massachusetts, United States; [2]Harvard John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States; [3]Environmental Science and Engineering, Ewha Womans University, Seoul, Korea (the Republic of).

The materials class of skutterudites is considered to be one of the most promising state-of-the-art thermoelectric (TE) materials. The archetypical binary skutterudites, $CoSb_3$ exhibit excellent electrical transport properties, but the thermal conductivities of binary skutterudites are too large for TE applications. On the other hand, the pnictogen-substituted ternary skutterudites (PSTSs), which are modified by heterogeneous pnictogen-substitution with group 14 (Ge, Sn) and group 16 (S, Se, Te) elements, are experimentally observed that there is the significantly lower thermal conductivity of PSTSs than $CoSb_3$. It has been considered as the attractive features to be investigated as potential thermoelectric materials. However, the understanding of the chemical substitution effect on thermal transport in PSTSs is still insufficient.
In this study, we investigate the effect of pnictogen-substitution on thermal transport in order to gain a deeper understanding of transport phenomena in PSTSs by estimation of thermal transport properties with quasi-harmonic (QHA)-based modified Debye-Callaway model. This method is modified in order to consider various scattering mechanisms, including phonon-phonon (ph-ph; normal and Umklapp), phonon-electron (ph-el), and mass fluctuation, since

these scattering mechanisms become significant factors on the thermal transport in complex and realistic TE materials. In particular, the phonon scattering rate arising from the ph-el interaction is estimated by a newly developed method in this study. Hence, we also verify the feasibility of this developed computational methodology for thermal transport. Based on our results, we consequently provide certain guidance for the rational design of next-generation TE materials.

TP02.07.07

Optical Pump Thermoreflectance Imaging of Metal-Polymer Composite Thin Films <u>Kerry Maize</u>[1,2], Jesus A. Leon Gil[1,2] and Ali Shakouri[1,2]; [1]Birck Nanotechnology Center, West Lafayette, Indiana, United States; [2]Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana, United States.

State of the art composite materials often have complex heterogeneous or anisotropic microstructure. Measurement of microscale thermal inhomoegeneity can be helpful in understanding and optimizing performance. In their default configurations well established methods to measure thermal conductivity such as 3-ω, laser flash analysis, and time domain thermoreflectance measure average thermal response over a given sample volume and often information about microscale inhomogeneity is not included in the result. Here we introduce optically pumped thermoreflectance imaging microscopy to inspect microscale nonuniform surface temperature in thin film and bulk materials in response to laser spot heating. Experiment configuration is identical to previous examples of thermoreflectance imaging microscopy, but instead of thermally pumping the sample by an electrical signal the sample is optically pumped by a laser spot focused on the sample surface. The method is capable of rapid, noncontact thermal images of bare target materials without requiring special sample preparation such as fabricated heater lines or transducer layers. Spatial resolution is submicron (diffraction limited). Temperature resolution is 50 milliKelvin. Time resolution is 50 nanoseconds. High magnification images of laser spot heaing are presented for a PDMS polymer matrix embedded with nickel clusters. Typical Ni cluster diameter is 20 microns. Pump excitation of 10 milliwatts using an 825 nm diode laser focused to a one micron spot on the sample surface revealed nonuniform microscale temperature distribution with strong dependence on the proximity of high thermal conductance Ni clusters. Experiments are underway to demonstrate additional applications of optical pumped thermoreflectance imaging, such as separate measurement of in-plane and cross-plane thermal conductivity in anisotropic samples by varying the size of the pump laser spot size.

TP02.07.08

A Study of Undercooling Behavior of W-Ta Binary Alloys Using High Temperature ESL Equipment <u>Ilhwan Kim</u>[1], Chae Woo Ryu[1], Geun Woo Lee[2] and Eun Soo Park[1]; [1]Seoul National University, Seoul, Korea (the Republic of); [2]Korea Research Institute of Standards and Science, Daejeon, Korea (the Republic of).

The nickel or cobalt based superalloys which used for high temperature structural materials have the problem that rapidly decrease mechanical properties above 1400 °C. Because nickel and cobalt have melting temperature near 1500 °C, this physical property of superalloys limits the structural application over ultra-high temperature region. To operate as fusion reactor materials or to improve efficiency of turbine engines, development of ultra-high temperature structural new materials has to be required. As alternative materials, ceramic based heat resistant materials are suggested. But these materials have large brittleness that can be easily fractured by applied stress. On the contrary, refractory metal elements which have melting temperature over 2000 °C are ductile comparing to high temperature ceramic materials. And comparing to nickel based superalloys, refractory elements have superior mechanical properties until ultra-high temperature region. It is the reason why there are some researches for using refractory metal alloys as ultra-high temperature structural materials. However, the study of ultra-high temperature property of refractory alloys is limited by melting of crucible, high temperature oxidation and absence of equipment which is able to heat up to ultra-high temperature. Therefore containerless experiment is much required for restraining melting of container and measuring accurate thermal properties. W-Ta binary alloys, which are complete solid solution system, have high melting point above 3000 °C. The high temperature electrostatic levitation (ESL) equipment is suitable for measuring thermal properties of W-Ta binary alloy systems having such a high melting point. As a result, W-Ta alloy in levitated equipment showed deep undercooling over 600 °C. Because there is no contact between sample and crucible, homogeneous solidification behaviour with deep undercooling was observed. The microstructure was different between crucible solidified sample, and levitating solidified sample. Deep undercooling in homogeneous solidification induced fast growth of primary dendrite arms, on the other hand heterogeneous solidification induced thick and short primary dendrite arms. Finally, Microstructure was investigated to figure out solidification behaviour of each condition and to control mechanical and thermal properties of W-Ta alloys. Likewise to previous research, deep undercooling sample had long primary dendrite arms and low secondary dendrite arm spacing, which can induce higher yield strength than heterogeneous solidification sample. Ultimately, because the study of properties near melting temperature of W-Ta alloys is deficient for lack of systematic experiment, this study can be a touchstone to study of measuring property of ultra-high temperature refractory alloys.

TP02.07.09

The Role of Molecular Chain Length and Side Group Weight on Thermal Transport In Electrospun Vinyl Polymer Nanofibers <u>Xin Zhang</u>[1], Yin Zhang[2], Lin Yang[1], Qian Zhang[1], Akira Ueda[3], Matthew Fitzgerald[1], Richard Mu[4], Deyu Li[1] and Leon Bellan[1]; [1]Vanderbilt University, Nashville, Tennessee, United States; [2]Southeast University, Nanjing, China; [3]Fisk University, Nashville, Tennessee, United States; [4]Tennessee State University, Nashville, Tennessee, United States.

Polymeric materials have found extensive use in a variety of applications due to their facile synthesis and processing, low-cost and tunable and attractive properties. Since a recent studying employing molecular dynamics techniques suggested that a single-chain polyethylene (PE) could possess extremely high thermal conductivity (~350 $Wm^{-1}K^{-1}$) several research efforts have been devoted to investigating a variety of factors that may result in the enhanced thermal transport in polymer nanofibers. Recent experimental results have demonstrated that the thermal conductivity of an individual ultra-drawn polyethylene nanofiber can achieve ~104 $Wm^{-1}K^{-1}$, which is three orders of magnitude larger than that of bulk PE. However, the dependence on several critical factors, such as molecular chain length and side group composition, is still not understood.

To explore the influence of molecular chain length, we prepared PE nanofibers with four different molecular weights (M_w) using the electrospinning process. The thermal conductivity of various electrospun PE nanofibers was determined using a well-established thermal bridge device composed of suspended microheaters/thermometers. Our results indicate that nanofibers composed of higher molecular weight polymers exhibit larger thermal conductivity, which is attributed to more efficient energy transport along the polymer chain direction compared to cross chain direction. It is noteworthy that PE fibers with lower M_w (35,000 and 125,000) exhibit monotonically increasing thermal conductivity versus temperature, typical for amorphous materials. However, for higher M_w PE fibers (420,000 and 3,000,000), a peak thermal conductivity appears as temperature increases, which is a signature of phonon Umklapp scattering in crystalline materials.

To investigate the impact of side group composition, we electrospun three types of vinyl polymer nanofibers, namely polyvinylidene fluoride (PVDF), polyvinyl alcohol (PVA) and polyvinyl chloride (PVC). These polymers have the same planar-zigzag carbon backbones as PE, but with one or two hydrogen atoms replaced by different heavier side groups (OH, Cl or F) in each monomer unit. In order to examine the role of side groups, we purposely choose the molecular weight of all polymers such that their polymer chain lengths were as close as possible. The measured thermal conductivity of four different types of polymer fibers shows a clear trend indicating $\kappa_{PE} > \kappa_{PVA} > \kappa_{PVDF} > \kappa_{PVC}$, which implies that thermal conductivity decreases as the side

group becomes heavier. Additionally, it is believed that the enhanced thermal conductivity of electrospun nanofibers may correlate with their increases in Young's modulus. As such, we measured the Young's modulus of several individual electrospun PVA, PVC and PVDF nanofibers using an atomic force microscope. The measured Young's modulus of PVA was larger than that of PVC and PVDF, which agrees with the thermal conductivity trend.

TP02.07.10
Tuning Thermal and Electrical Properties of NiOx Films by UV/O3 Treatment for Resistive Memory Applications Sanchit Deshmukh[1], Raisul Islam[1], Christopher Saltonstall[2], Eilam Yalon[1], Thomas Beechem[2], Krishna Saraswat[1] and Eric Pop[1]; [1]Stanford University, Stanford, California, United States; [2]Sandia National Laboratories, Albuquerque, New Mexico, United States.

Resistive random access memory (RRAM) devices store information by switching a sub-50 nm diameter, locally conductive filament (CF) in insulating materials such as oxides like NiOx [1]. Because switching an individual CF needs both high fields and elevated temperatures, sufficient Joule heating is necessary for device operation. In this context, the thermal interfaces of the CF with surrounding oxides and metal electrodes need to be properly understood, as they govern the operation of RRAM devices. The CF thermal physics is also complicated by vacancies, whose role is not adequately understood in such oxides [2,3].

Here we probe RRAM oxide interfaces by studying vacancy-dependent thermal properties of sub-stoichiometric NiOx for the first time. We demonstrate that tuning the vacancy concentration at such interfaces can aid in tuning the electrical contact resistivity (ρC) and thermal boundary conductance (TBC) to Ni-vacancy rich NiOx films. We deposit 400 nm thick NiOx films using sputtering in an Ar:O2 ambient from a NiO target, with stoichiometry close to 1:1. We tune the Ni vacancy concentration at the top surface by treating the films with O3 under UV light for different durations. Previous work [4] shows that we can tune the electronic properties of NiOx films using this technique. Circular transfer length measurements (C-TLM) on these treated films reveal a decreasing ρC from 3.8×10^{10} to less than 1.5×10^{10} $\Omega.\mu m2$ with increasing treatment time from 0 to 30 min, while NiOx film resistivity reduces from 15 to 1 kΩ.cm.

We use similarly treated films with 60 nm thick Pt blanket top deposition post-treatment for thermal measurements. We perform time-domain thermoreflectance (TDTR) measurements to separate out the film thermal conductivity and the TBC at the top metal-film interface. With increasing UV/O3 treatment time from 0 to 30 min, we see an increase in the TBC from 175 to 420 MW/m2/K, with a negligible change in the corresponding NiOx thermal conductivity ~7 W/m/K. The contribution of the electronic component of NiOx thermal conductivity, calculated from the Wiedemann-Franz Law, remains negligible with treatment. With increased vacancy density at the interface, there is a decrease in the electrical and thermal contact resistance to the NiO films. This suggests that increased vacancy concentration in an oxide, as observed in a CF, enhances electronic and thermal conduction across the metal-oxide interface, in general. These results show that electronic and thermal energy transport can be tuned across interfaces of RRAM oxides by controlling the vacancy concentration, an important step in designing energy-efficient RRAM devices.
Ref: [1] H.S.P. Wong et al. Proc. IEEE 100, 1951 (2012); [2] C. Landon et al. Appl. Phys. Lett. 107, 023108 (2015); [3] S. Deshmukh et al. IEEE SISPAD, 281 (2015); [4] R Islam et al. ACS Appl. Mater. Interfaces 9, 20 (2017)

TP02.07.11
Thermal Characterization of High-Al Composition AlGaN High Electron Mobility Transistors Samuel H. Kim and Samuel Graham; Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

AlGaN-channel high electron mobility transistors (HEMTs) are promising candidates of ultra wide-bandgap transistors for power and RF applications. Their promise derives from the large breakdown field. The breakdown voltage of high-Al composition Al(x)Ga(1−x)N (x > 0.5) is expected to be about 3x higher than that of GaN. Also, thermal conductivity of AlN is 6x higher than sapphire, and 1.5x − 2x higher than GaN. These lead to significantly high power and RF figure of merit, especially at elevated temperatures, when Al(x)Ga(1−x)N (x > 0.5) channel layers are used instead of GaN in HEMTs. One study showed that, the 3 μm thick high quality AlN buffer layers over sapphire substrates provide excellent thermal conduction, enabling stable device operation with negligible drain-current degradation up to 250 °C. Unlike GaN/AlGaN HEMTs, however, there is no thermal characterization study reported for these ultra wide-bandgap transistors.

In this study, we investigate thermal response of high-Al composition AlGaN HEMTs. Thermal characterization techniques have been developed to evaluate the temperature distribution of wide band gap electronics that will be applied to these AlGaN HEMTs. We utilize Raman thermometry, IR thermal imaging, and transient thermoreflectance imaging to investigate the temperature distribution of these devices. Raman thermometry has been well established to be spatially and temperature accurate when monitoring the thermal response of devices under steady state DC biasing conditions. IR micro thermal imaging is a widely used tool to image temperature distributions of electronic devices. Lastly, transient thermoreflectance imaging will be used to not only monitor the formation of the hotspot under pulsed biasing, but also image temperature distribution across the channel.

SESSION TP02.08: Thermal Devices and Sensors
Session Chairs: Ming Su and Zichao Ye
Wednesday Morning, November 28, 2018
Sheraton, 3rd Floor, Fairfax AB

8:00 AM TP02.08.01
Development of *In Situ* High-Temperature High-Resolution Transmission Electron Microscopy Using a Picometer Scale Sample Manipulation System Manabu Tezura, Hideki Kobayashi, Takuya Okamoto, Koichi Murakami and Tokushi Kizuka; Division of Materials Science, Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Japan.

Heat resistant materials, which are subjected to high temperatures up to ~1700 K at strong external force, are key advanced structural materials. Microstructural dynamics of materials in phase transformation, precipitation, behavior of point defects, grain-boundaries, and interfaces at actual using environments should be investigated to design and improve such materials. *In situ* high-temperature transmission electron microscopy (HTTEM) can be applied to the observations of texture and deformation process at high temperatures [1]. However, in most of previous HTTEM, the observation was performed at conventional magnifications. In this study, we developed a new type of HTTEM for the investigation of microstructural dynamics during mechanical deformation using a piezodriving system [2–4].
A molybdenum mesh heater was mounted on a sample holder for HTTEM. A direct current was applied to the heater to increase its temperature due to Joule heating. The heater temperature while applying bias voltages was measured using a pyrometer. The heater temperature successfully increased up to the maximum temperature, i.e., approximately 2000 K [2]. *In situ* HTTEM observation was carried out with an acceleration voltage of 200 kV in a vacuum of 1×10^{-5} Pa. The fracture and deformation processes of gold nanocontacts at 930 K could be observed at the atomic resolution.

[1] M. Komatsu, H. Fujita, and H. Matsui, *Jpn. J. Appl. Phys.* **21**, 1233 (1982).
[2] T. Terasawa, S. Kikuchi, M. Tezura, and T. Kizuka, *J. Nanosci. Nanotechnol.* **17**, 2848 (2017).
[3] S. Kikuchi, M. Tezura, M. Kimura, N. Yamaguchi, S. Kitaoka, and T. Kizuka, *Scr. Mater.* **150**, 50 (2018).
[4] M.Tezura, K. Murakami, S. Kikuchi, T. Terasawa, and T. Kizuka, The 3rd Symposium on SIP-IMASM 2017.

8:15 AM TP02.08.02

A Study on the Thermal Coefficient of Resistance Dependency of Infrared Microbolometer <u>Jun Kyo Jeong</u>[1], Byeong Jun Jeong[1], Jaeseop Oh[2], Hi Deok Lee[1] and Ga Won Lee[1]; [1]Chungnam National University, Daejeon, Korea (the Republic of); [2]National Nanofab Center, Daejeon, Korea (the Republic of).

An uncooled infrared microbolometer is a principle that measures temperature changes due to infrared absorption as a change in resistance. Compared with the cooling type infrared microbolometer, the process is comparatively simple and can be manufactured with a high yield, and is advantageous in terms of packaging. This advantage is useful as a next-generation infrared sensor. The uncooled infrared microbolometer is fabricated as a focal plane arrays with high performance combined with the microbolometer and signal detection circuit fabricated using MEMS (Micro Electro Mechanical System) technology. In order to produce a high-performance infrared microbolometer, sensitivity and response speed must be improved. The main issues of infrared microbolometer are good thermal isolation, high absorption, good sensitive layer and good stability structure thermal transfer. In order to solve these problems, the application of the shape of the floating structure and the optimization of the geometry of the support structure to reduce the heat loss, High thermal coefficient of resistance (TCR) performance sensing membrane research for high sensitivity sensing, And stability for physical structure and simulation for optimizing heat transfer. In this paper, we have studied the temperature dependence of TCR, which defines thermal properties using COMSOL simulation for the fabrication of high performance uncooled infrared microbolometer. The structure of the uncooled infrared microbolometer designed in this study has an air-gap corresponding to λ/4 of the far-infrared wavelength, mainly 8 μm, that is to be detected. The structure consists of cantilever, absorption layer, resistance layer, and passivation layer. The uncooled infrared micrometer measures the current change due to the joule heating caused by the driving voltage and the incident infrared energy. simulations were conducted in COMSOL Multiphysics 5.3a software to verify and optimize the device design. The device was simulated as a 3D model using Electric Currents module, Heat Transfer in Solids. To improve the accuracy of the simulation, the TCR of the resistive layer a-Si was set as a function of temperature. In addition, the heat generation of the device is set to be the same as that of the actual device in consideration of heat loss to the outside. Although the TCR has been widely known as a parameter that greatly affects the characteristics of the bolometer, the influence of temperature dependence of the TCR on the device performance has not been fully considered. Through this study, we tried to show that the characteristics of the device can be more efficiently optimized by simulating the physical properties (resistivity, TCR, etc.) of the absorption layer and resistance layer of the uncooled microbolometer.

8:30 AM *TP02.08.03

Phase Change Nanoparticles for Biosensing, Barcoding and Enhanced Cooling <u>Ming Su</u>; Northeastern University, Boston, Massachusetts, United States.

Nanomaterials have been widely studied for their electronic, magnetic, mechanical, and chemical properties. We have studied the unique thermal properties of a new type of nanomaterials, nanoscale phase change materials (i.e., nano-PCMs). This group of materials may have any chemical composition, as long as there is a solid-liquid phase transition when temperature is changed. We have made a number of nano-PCMs and explored their applications in biosensing, barcoding, and enhanced cooling. Metallic nano-PCMs and organic nano-PCMs have been made with precise thermodyanmic properties (melting temperature and enthalpy) based on phase diagram knowledge. These nano-PCMs have been used to enhance heat transfer capability of a variety of fluids, to detect multiple molecular biomarkers of diseases, to create cover barcodes that can be added into objects, and to prevent catalytical reactors from thermal runaway.

9:00 AM TP02.08.04

Thermal Conductivity Measurement on Nanostructures in TEM <u>Hua Guo</u>[1], Panpan Zhou[2], Shuai Jia[1], Douglas Natelson[2] and Jun Lou[1]; [1]Department of Materials Science and NanoEngineering, Rice University, Houston, Texas, United States; [2]Department of Physics and Astronomy, Rice University, Houston, Texas, United States.

<!--![endif]----><!--![endif]----><!--![endif]---->As nanomaterials are blooming up in recent years, the properties of individual nanostructures have attracted a lot of interests, which were reported to be significantly distinct from their bulk counterparts in many cases [1-4]. Based on specific in-situ testing platforms, routine mechanical experiments [1,2], chemical/electrochemical reactions [3,4] can be carried out on micro/nanometer-scale specimens in SEM/TEM. Nevertheless, the thermal management of small specimens remains challenging. A few of solutions are available for nanothermometry. For instance, nanothermometers, like Ga in CNT were developed to measure temperature in TEM [5]. Nanometer-sized particles with low melting point were employed to indicate the temperature distribution of specimens irradiated by electrons [6]; VO2 nanowires were used to estimate the temperature of nanostructures [7]; Even the temperature distribution of Al foil was mapped directly by electron energy loss spectrum [8]. While to figure out heat transfer through nanostructures, MEMS devices have to be fabricated, and careful analysis of thermal circuit is necessary [9]. Recently, we developed a new method to investigate the thermal properties of nanostructures in TEM. In this study, we are introducing a new nanoscale heat flow meter based on an individual VO2 nanowire, which can be utilized to quantify the thermal conductivity of nanostructures. The thermal conductivity of SnSe was measured as 1.86±0.21. Wk-1m-1. According to literature, our measurement is close to the calculated value in the first-principles study, 1.55 Wk-1m-1 [10]. We believe that our platform will open an avenue to exploring thermal properties of nanostructures.
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9:15 AM TP02.08.05

A Micron Scale Nanosecond Resolution Temperature Probe for Sub-Second Processing of Thin Films <u>Letian Wang</u>[1], Zeqing Jin[1], Chuck Paeng[2], YS Kim[2] and Costas Grigoropoulos[1]; [1]Mechanical Engineering, University of California, Berkeley, Berkeley, California, United States; [2]Lam Research,

Fremont, California, United States.

Sub-second processing includes laser, flash lamp, spark plasma. thermal plasma jet and RTP furnace. Among them, flash lamp and pulsed laser processing of semiconductor material has been demonstrated in shallow junction doping, crystallization in industry. Recent development of nanotechnology, including nanowire, nanoparticle and 2D materials has inspired an increased number of light based processing including shaping, sintering, doping and phase transformation. Due to the nanoscale size effect, the processing temperature is however, not readily known, which impeded its integration on different substrate and volume manufacturing.

In this report, we will discuss the fabrication, calibration, and verification of a microscale resistive temperature sensor structure for light based processing. The sensor structure is target material-insulation-platinum-substrate. The 1um spatial resolution is resolved with pulsed laser trimming. An RF compatible circuit and an automated LabVIEW program are designed to record and interpret the transient temperature history. The rise time of whole system has been measured tas 10ns through ps laser heating.

The critical fabrication challenges lie on Pt's adhesion on substrates and insulation layer's robustness against irradiation. We first prove Pt has significant enhanced adhesion on sapphire, alumina coated quartz and poor adhesion on oxide thin film and bare quartz. The adhesion is improved with annealing and additional thin film deposition. The robustness of silicon nitride material is significantly higher than that of oxide. We further evaluated the minimum feature size and substrate effect on its stability and calibrated temperature coefficient of resistance(TCR). The sensor resistance is calibrated in-situ with tube furnace heating and cooling.

To verify the measurement, we successfully captured and measured the amorphous silicon and germanium melting upon ns laser irradiation. Combined with 1D heat transfer, the transient curve can be used to estimate the thermal contact resistance and/or estimate the thermal conductivity of targeted material. Different semiconductor material including amorphous Si, Ge and MoS_2 flake are tested.

Lastly, we discussed the application of this sensor for measuring peak temperature under different time scale of processing. For processing time scale t longer than 1us, the temperature is uniform across target material and Pt sensor layers. The typical case is CW laser heating and flash lamp processing. In this case, substrate properties will affect the possibility of applying the results to different systems. For t shorter than the thermal diffusion time of target layer (typically 2ns), the results will require additional simulation interpretation. However, the results can be directly applied to various substrates. It's ideal for research on heat affected zone for ps/fs machining. For the 2ns<t<1us, the results require interpretation and the application is subject to the substrate.

9:30 AM TP02.08.06
Integrated Thermal Flow Sensors for Microfluidic Interconnects <u>Boxue Chen</u>; Electrical and Computer Engineering, University of Texas-Austin, Austin, Texas, United States.

In recent years, novel materials processing techniques involving PDMS and paper materials have enabled revolutionary progress in performance and capability of chip-scale microfluidics. However, micro-fluidic systems remain largely single-chip constructs, and are far from the level of sophistication that is typically seen in multi-chip multi-board electronic systems. A major limitation lies in the fluidic chip-to-chip interconnects, where the simple tubing materials and structures lack the monitoring and pumping functionalities that are needed in reliable microfluidic systems.

In this context, we report the world's first fiber flow-rate sensor using new thermal sensing materials and device structures, both made possible by a novel multi-material fiber process, as a new form of chip-to-chip interconnects. In addition to the integrated flow-sensing capability, our device platform also resolves a fundamental trade-off between sensitivity, pressure drop, measurement range, and temperature rise in conventional thermal flow sensors. We develop a first-order one-dimensional heat-transfer model to establish the temperature response of ultra-long hot films in a fiber microfluidic channel. The improved flow sensing range in a multi-segment sensor, as predicted by the 1D analytical model, is corroborated by numerical simulations and experiments.

Record-setting flow-rate sensitivity was demonstrated in this work over an ultra-wide flow-rate range and unprecedentedly low pressure drop. The successful incorporation of high-TCR, high-resistance conductive polyethylene as the temperature-sensitive hot film yields a voltage response of 0.8 V/K and a flow-rate sensitivity of 384 mV/(uL*min^{-1}) between 0 and 20 μL/min. This ultrahigh voltage response allows the fiber sensor to operate with a maximum temperature rise of merely 20 °C, 5~10× smaller than that in typical MEMs sensors and important for handling biomedical samples. In addition, this ultrahigh voltage response enables ultralow pressure drop of 8 Pa at 100 μL/min, orders of magnitude lower than conventional MEMs thermal flow sensors. More importantly, we have realized a high-sensitivity measurement range of 5~200 μL/min through a multi-segment structure where each segment reaches its peak sensitivity at different flow rates.

Our work combines novel material systems and new device structures that deliver new functionality and significant improvements in performance. This unconventional form of flow sensors paves the way towards a complete functional overhaul of microfluidics feed lines needed in large-scale multi-chip integration in microfluidics and opens new possibilities in lab-on-fiber technologies.

9:45 AM TP02.08.07
Thermal Analysis of Nanophotonic Structures Using Noise Thermometry and the Thermoelectric Effect <u>Kelly W. Mauser</u>[1], Phillip Jahelka[1], Rebecca Glaudell[1], Michael Kelzenberg[1], Colton R. Bukowsky[1], Seyoon Kim[2], K. C. Schwab[1] and Harry A. Atwater[1]; [1]California Institute of Technology, Pasadena, California, United States; [2]ICFO–The Institute of Photonic Sciences, Barcelona, Spain.

Generating localized, high electric field intensity in nanophotonic and plasmonic devices has many applications, including enhancing chemical reaction rates, thermal radiation steering, chemical sensing, and photovoltaics. Along with a strongly localized electric field comes a temperature rise in non-lossless photonic materials, which can affect reaction rate, photovoltaic efficiency, and other properties of the system. Measuring temperature rises in nanophotonic structures is difficult, and methods commonly employed suffer from various limitations, such as low spatial resolution (Fourier transform infrared microscopy), bulky and expensive setups (scanning thermal microscopy), intrusive methods that interfere with nanophotonic structures (Pt resistive thermometry), or the need for specialized materials (temperature-dependent photoluminescence).
We overcome these limitations with the first-ever demonstration of temperature measurements of nanophotonic structures by employing both room temperature noise thermometry and the thermoelectric effect under ambient conditions without external probes, by utilizing the properties of the materials that make up the nanophotonic structure itself. We have previously estimated the ΔT in a nanophotonic device using the thermoelectric effect [1], but could not determine the absolute temperature of the system. In the application we will discuss, the absolute electron temperature of the nanophotonic material itself is measured. Because Johnson-Nyquist noise is material independent and is a fundamental measure of absolute temperature, there is theoretically no need for calibration as in the case of resistive thermometry. To measure the temperature rise of a nanophotonic resonant region remotely, the Seebeck coefficient of the material is first carefully measured using noise thermometry, then the thermoelectric voltage generated in the nanophotonic materials

themselves is measured from electrical leads spanning the resonantly excited region. To accomplish this, we have developed a metrology technique capable of simultaneously measuring electrical noise at two locations on the nanophotonic structure as well as the electrical potential between the two points, under chopped laser illumination that heats the structure via nanophotonic absorption, thus providing drift-corrected light-on/off temperature information. Furthermore, this method can be used to deduce thermal time constants of the system, which will be discussed. We have successfully measured temperature rises in a room-temperature guided mode resonant nanophotonic system using the described method from several degrees above ambient to 320 K with high fidelity and reproducibility, and these results show an excellent match to simulation.

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10:00 AM BREAK

10:30 AM TP02.08.08
Environment Sensing with Porous Photonic Structures Francisco Gallego-Gomez and <u>Cefe Lopez</u>; Consejo Superior de Investigaciones Científicas, Madrid, Spain.

Photonic colloidal crystals, also referred to as *artificial opals*, for their photonic properties, have wide applicability in many fields such as sensing, light harvesting, etc. Understanding of their ability to transduce fluids adsorption and confinement into a photonic response [1-3] allows to envisage new perspectives for integrated platforms for accurate control of liquid-solid interplay [4-5]. In particular, simple spectroscopic monitoring of the photonic bandgap allows to study vapor adsorption and condensation, wetting, imbibition and confined flow within their porous network. (Opals may offer a number of benefits compared to current devices. Beside the easy and versatile fabrication in different scales with diverse materials and post-manufacture treatments, the main advantage of artificial opals resides on the photonic nature of the output, which ensures high sensitivity and fast response, while no further sensors or imaging devices are required.)

Here we gather recent achievements that prove the potential of opals as photonic devices with extremely sensitive response to adsorption and condensation phenomena, both humidity and temperature dependent. On the one hand, water condensation in the nanoporous opal network under saturated vapor conditions was studied near the dew point [6]. As a particularly interesting feature, the photonic signal sharply changed at the onset of dew formation, and allowed in situ monitoring of the condensation process. As the dew point sensitively depends on both opal and atmosphere temperatures, the opal response can be employed for precise control of temperature in versatile situations. On the other hand, distinct opal response can be obtained from selective pore filling in a gaseous environment, as demonstrated in a hierarchically porous carbon opal [7]. Specifically, the photonic signal sharply reacts to the filling of microporosity, a fact that, for a given gas pressure, drastically depends on the thermal energy of the adsorbate molecules. Thus, we propose the unique photonic response of microporous opals as a novel, powerful means for thermal analysis.

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10:45 AM TP02.08.09
Effect of Band Parameters on Generation-Transport-Recombination (GTR) of Minority Carriers <u>Sadid Muneer</u>, Helena Silva and Ali Gokirmak; University of Connecticut, Storrs, Connecticut, United States.

For semiconductor devices under extreme electrical stress, substantial number of minority carriers are generated (G) at high temperature, are transported (T) under electric field, and recombine (R) at some place away from the generation location, creating an effective heat pump that adds to the symmetric joule heating, leading to an asymmetric thermal profile [1]. Our electrothermal finite element model captures the impact of the GTR process and shows the general trend of the correct asymmetry. However, the asymmetry observed in the experiments with silicon microwires is much stronger than the modeling results [1]. An alternative to better model the non-equilibrium processes that give rise to GTR is to use a semiconductor modeling approach. However, the conventional semiconductor models' transport and band parameters are not tailored for extremely high temperatures. As an example, the equilibrium carrier concentration for silicon near melting is predicted as $\sim 10^{20}$ cm^{-3} with conventional semiconductor physics instead of the melt concentration of $\sim 10^{22}$ cm^{-3} [2]. We have constructed a detailed non-equilibrium finite element semiconductor modeling platform, including electron and hole continuity equations, Poisson's equation for local potential calculation, and associated recombination mechanisms (SRH, Auger), to quantify and better understand the carrier-carrier and carrier-lattice interactions that gives rise to the GTR process and the consequent asymmetry [3],[4]. In the present work we specifically investigated temperature dependence of intrinsic carrier concentration [5], screening of Auger recombination at high carrier density [6], and collapse of bandgap near melting [7]. The results show that careful calibration of these parameters is essential to model GTR phenomenon and capture the correct direction and extent of the asymmetry.

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11:00 AM TP02.08.10
Morphology, Device Performance and Thermal Behavior of a Molecular Liquid Crystalline/Fullerene Blend <u>Alexander J. Bourque</u>[2], Chad Snyder[2], Sebastian Engmann[2], Lee Richter[2] and David Jones[1]; [1]The University of Melbourne, Melbourne, Victoria, Australia; [2]National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

The morphology and performance of thin-film photovoltaic devices comprising an active layer blend of a molecular liquid crystalline material (BQR) and a fullerene derivative (PC$_{70}$BM) were investigated here to assess the impact of thermal processing. In-situ grazing incidence x-ray scattering (GI-SAXS, GI-WAXS), differential scanning calorimetry (DSC) and photoluminescence spectroscopy (PL) were applied to study the active layer across a range of blend

compositions to correlate morphological changes, thermal behavior and photoactivity, respectively. Enhanced BQR crystallinity and phase purity was observed for increasing temperatures with optimal device performance peaking at 120°C; device performance suffered at progressively higher temperatures due to over-coarsening of acceptor/donor domains. DSC measurements were paired with in-situ GI-WAXS measurements subject to the same thermal history to identify multiple liquid crystal and crystalline transitions in the blend. Finally, melting point depression theory was applied to estimate the Flory-Huggins interaction parameter for the binary blend.

11:15 AM TP02.08.11
Micro-Thermocouples with Extreme Sensitivity <u>Daniel R. Assumpcao</u>[1], Shailabh Kumar[2], Vinayak Narasimhan[2] and Hyuck Choo[1, 2]; [1]Electrical Engineering, California Institute of Technology, Pasadena, California, United States; [2]Medical Engineering, California Institute of Technology, Pasadena, California, United States.

High-resolution detection of temperature changes in small scales could open up a new scientific vista by, for example, providing valuable intuition for energy distribution in nanophotonic structures or revealing functional details of cell biology based on subtle temperature differences [1]. Thermocouples are temperature-sensing devices that have been widely used in many applications for their simple fabrication, ease of measurements, and accuracy [2]. Micro-scale thermocouples made of IC-process-compatible metals such as Ni, Cr, or Au layers have been demonstrated for various applications [2], but they suffer from small Seebeck coefficients and consequently poor sensitivity, yielding temperature-sensing resolutions larger than 2 °C. The use of rare and expensive alloys such as bismuth and antimony telluride with high Seebeck coefficients could improve the sensitivity but requires sophisticated fabrication processes [3].

By taking the advantage of the high Seebeck coefficient of silicon, we have demonstrated a new approach for designing metal-on-silicon thermocouples with a noticeably high Seebeck coefficient of 9.17×10^{-4} V/°K and temperature-sensing resolution of 0.01 °K (theoretical limit: 0.00055 °K). We have also kept the device fabrication straightforward: it only involves photolithography and metal-liftoff on a silicon substrate because we chose materials with appropriate electronic properties and selectively formed Schottky barriers and Ohmic contacts to establish electrical isolations and conduction without adding fabrication steps. The Seebeck coefficient of our thermocouple is 30 times larger than values reported for standard thin metal-film thermocouples and comparable to Seebeck coefficients of rare alloy-based thin-film thermocouples that require sophisticated and costly fabrication processes. The temperature measurements were highly linear, with a linearity coefficient of 1. Our circuit analysis performed on the metal-on-silicon thermocouples shows that these devices can be further miniaturized down to a few micron size and arranged in a dense array format with an inter-device spacing of a micron without degrading the performance.

Furthermore, we applied this approach to demonstrate a highly flexible metal-on-silicon thermocouple with enhanced thermal sensitivity (bending radius: 1.51 cm). The outstanding performance of our thermocouples combined with an extremely thin profile, bending flexibility, and simple fabrication process will proliferate its use in diverse thermography applications in the micro- and nanoscales.

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11:30 AM TP02.08.12
Understanding the Superior Temperature Stability of Iridium Light-Emitting Electrochemical Cells Melanie Bowler, Tianle Guo, Anton Malko and <u>Jason D. Slinker</u>; The University of Texas at Dallas, Richardson, Texas, United States.

Single-layer light-emitting electrochemical cells with from ionic transition metal complexes (iTMCs) are relatively simple to construct and have great potential as cost effective emissive devices. Most studies to date have focused on iTMC devices from ruthenium and iridium chromophores. For practical applications, thermal stability is important for environmenal robustness, and little has been said about their relative thermal stabilty. Here, we studied the device performance of iridium and ruthenium ITMCs with temperature to directly compare their stabilities. The thermal onset of radiant flux loss is found to be 67 °C (152 °F) for iridium devices, 45 °C higher than ruthemium iTMCs, a show of its superior thermal stability. We subsequently used temperature-dependent electrochemical impedance spectroscopy, temperature-dependent photoluminescence spectroscopy, time resolved photoluminescence spectroscopy, and photoluminescence quantum yield measurements to understand the physical origin of this substantial temperature stability difference. Prior postulates suggested that films from iridium complexes would yield better thermal stability than those from ruthenium complexes due to details of the orbital energetics. Instead, it is found that this superiority is owed to the details of kinetic effects—the competing kinetics of multiple recombination pathways and the relative rates of radiative to nonradiative processes. Such information guides the design of iTMC emitters for superior light-emitting electrochemical cells.

11:45 AM TP02.08.13
Mechanics of Materials Interaction with Electromagnetic Wave <u>Diana Gamzina</u>, Emilio Nanni, Paul Welander and Sami Tantawi; Technology Innovation Directorate, SLAC National Accelerator Laboratory, Menlo Park, California, United States.

Advances in understanding RF breakdown have led to improvement in accelerator performance, but detailed knowledge of the temporal material changes due to its interaction with RF continues to be an unknown. It has been observed that an RF structure can be conditioned to handle significantly higher accelerating gradients by slowly ramping up RF power levels fed into the structure and that the RF breakdown rate can be reduced by utilizing copper with higher hardness numbers. While surface imaging post operation clearly show surface damage, the practical findings provide limited insight into material's behavior under RF loading. We evaluate the mechanics of material during its interaction with an electromagnetic (EM) wave. This analysis impacts the development of advanced RF accelerators and sources; it also informs the development of materials resistant to EM radiation damage and of material synthesis techniques that utilize EM fields for achieving far-from-equilibrium material states.
During RF heating, a sub-micron thick material surface layer is heated instantaneously creating steep and non-linear thermal gradients, which eventually (on sub-ms scale) evolve into linear thermal gradients. The transient thermal gradients and the boundary conditions imposed on the material cause the state of stress to temporally evolve. Furthermore, even though cubic material like copper has an isotropic coefficient of thermal expansion, its elasticity is highly anisotropic. Polycrystalline copper that is used for the manufacturing of RF cavities undergoes multiple high temperature thermal cycles that fully anneal the material so that the resulting material grain size is on the order of a few millimeters. As a result, local material response to the EM heating then also depends on the orientation of the crystal structure with respect to the material surface. It has been observed that highly compliant (100) direction oriented grains show significantly less damage than stiff (111) direction oriented grains; similar results were reported for laser induced damage in copper. Significantly higher stress levels are induced in the (111) grain when compared to the (100) grain for the same thermal strain values because of the

difference in the elastic moduli.

Conditioning of the RF structures is analogous to a strain-hardening process, but with temporally varying strain rate conditions. Similar to other strain hardening methods, the dislocation density eventually saturates with increasing strain values and, as a result, the RF structure reaches its peak RF operation gradient. Starting with a harder material (high dislocation density) allows one to jump to higher gradient levels (strain values) without generating additional dislocations. The evolution of the material surface during the interaction with the EM wave is still poorly understood, but we have started to provide analytic explanation to the collected experimental results.

SESSION TP02.09: Thermal Conductivity of Semiconductors
Session Chairs: Sukwon Choi and Ali Shakouri
Wednesday Afternoon, November 28, 2018
Sheraton, 3rd Floor, Fairfax AB

1:30 PM *TP02.09.01
Size Dictated Thermal Conductivities of GaN and AlGaN Thomas Beechem[1], Christopher B. Saltonstall[1], Hamidreza Seyf[2], Asegun Henry[2] and Andrew Allerman[1]; [1]Sandia National Laboratories, Albuquerque, New Mexico, United States; [2]Georgia Institute of Technology, Atlanta, Georgia, United States.

Gallium nitride (GaN) and its alloy AlGaN are being increasingly pursued for power electronics as their low specific resistivity, high mobility, and ultrawide bandgaps provide a pathway to smaller devices, a "smarter" grid, and better utilization of renewable energy sources. Per their moniker, power devices must handle—and dissipate—tremendous energy loads. These loads, in turn, can lead to self-heating sufficient to dampen both performance and reliability. To minimize self-heating, it is necessary to assess how the thermal properties of GaN and AlGaN are modified from their "textbook" value during device processing. Here, using a combination of time domain thermal reflectance (TDTR) measurements with material modeling, significant size-induced reductions in thermal conductivity are found in both GaN and AlGaN for layer thicknesses typical of devices. These reductions emerge from the low-frequency, long mean free path phonons that act as heat carrying tractor trailers, which "feel" boundaries even in the presence of significant disorder (e.g., alloying or doping). Size effects are thus inherent to the system and must be considered in predictions of performance or capability of devices.

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2:00 PM TP02.09.02
Electrical and Thermal Analysis of Vertical GaN-on-GaN P-N Diodes Luke Yates[1], Shigeyoshi Usami[2], Kentaro Nagamatsu[2], Georges Pavlidis[1], Yoshio Honda[2], Hiroshi Amano[2] and Samuel Graham[1]; [1]Georgia Institute of Technology, Atlanta, Georgia, United States; [2]Nagoya University, Nagoya, Japan.

GaN p-n diodes have demonstrated the potential to exceed silicon-based devices for a variety of power applications due to their low on-resistance and high breakdown voltage. While much effort goes into the electrical characterization of these devices, complete thermal characterization is lacking. The diodes used in this study consisted of a 420 µm n-GaN substrate on which MOCVD was used to grow 15 µm n⁻ GaN (Si), 500 nm p-GaN (Mg), and 30 nm p⁺-GaN (Mg). The completed chips consist of diodes with diameters of 100 µm, 300 µm, 500 µm, and 1000 µm. One set of devices was subjected to passivation with a polyimide film, while the other set of devices was non-passivated. Electroluminescence (EL) was performed on both sets of devices, and it was found that non-passivated devices demonstrated increased EL intensity at the mesa edges, most likely due to enhanced surface recombination, and subsequently showed IV characteristics that outperformed the passivated devices in terms of power handling capabilities at high forward voltages. When a high-power operating point is set for a diode, there can be a significant increase in temperature, which leads to thermal expansion, and other reliability issues inherent in the cyclic operation of a power device. To investigate the thermal response, we used time domain thermoreflectance (TDTR) to evaluate the thermal conductivity of a vertical GaN p-n diode as a function of depth. Transient thermoreflectance imaging was used to observe variations in heating profiles across devices of different diameters when operated at the same power densities, and to observe the transient temperature rise and fall for each of the diodes.

2:15 PM TP02.09.03
Thermal Analysis of GaN HEMTs Using Near Bandgap Thermoreflectance Imaging Georges Pavlidis[1, 2], Dustin Kendig[4], Luke Yates[1], Banafsheh Barabadi[3], Brian Foley[1] and Samuel Graham[1]; [1]Mechanical Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States; [2]CNST, National Institute of Standards and Technology, Gaithersburg, Maryland, United States; [3]Massachusetts Institute of Technology, Boston, Massachusetts, United States; [4]Microsanj LLC, Santa Clara, California, United States.

Transient thermoreflectance imaging (TTI) is a CCD based thermometry technique that can map the temperature distribution across a surface. For materials, such as gold, where the thermoreflectance signal has a strong linear temperature dependence, TTI has shown to have a high spatial (300 nm/pixel) and temporal resolution (50 ns). Consequently, the technique has been primarily used to monitor the gate metal temperature distribution in GaN High Electron Mobility Transistors (HEMTs) and enable characterization of the device's transient thermal dynamics. The origin of the extreme localized heating in GaN HEMTs, however, is known to be in the active GaN layer and thus accurate characterization of the temperature across the channel is necessary. Using a UV LED excitation source with a wavelength near the bandgap of GaN, TTI of the GaN channel in GaN HEMTs is presented and verified for the first time via the comparison of the gate metal temperature. A pixel by pixel calibration method is implemented to improve the spatial accuracy and account for any variability in the thermoreflectance coefficient across the device. Performing full transient scans, the time constants associated with the GaN region are found to be shorter than those measured via the gate metal. To ensure a strong thermoreflectance signal from the GaN surface, the importance of using an excitation wavelength near the bandgap of the GaN channel is highlighted. Through the analysis of HEMTs with different residual stresses in the GaN channel (engineered by using superlattice structures), the effect of the bandgap on the magnitude and the linearity of the thermoreflectance coefficient is presented and discussed. Overall, the improvements of TTI discussed in this study make the technique an accurate and effective method to measure the temperature distribution of both the gate metal and GaN.

2:30 PM BREAK

3:30 PM *TP02.09.04
Electro-Thermal Analysis of Ultra-Wide Bandgap Electronics <u>Sukwon Choi</u>; The Pennsylvania State University, University Park, Pennsylvania, United States.

To extend further the electrical performance envelope of wide bandgap (WBG) power and radio frequency (RF) electronics based on gallium nitride (GaN) and silicon carbide (SiC), device engineers are actively pursuing the development of generation-after-next ultra-wide bandgap (UWBG) devices. At the time being, aluminum gallium nitride (AlGaN), β-gallium oxide (Ga_2O_3), and diamond are technologically relevant UWBG materials that have bandgaps larger than that for GaN (3.4 eV).
While UWBG devices are built to operate under higher power densities compared to current state-of-the-art WBG counterparts, the thermal conductivities of AlGaN and Ga_2O_3 are lower than those for GaN and SiC by an order of magnitude. Therefore, self-heating is one major challenge for these UWBG devices. Electro-thermal interactions that lead to self-heating in AlGaN and Ga_2O_3 devices need to be accurately assessed and understood to accomplish the successful transition from WBG devices to the UWBG technology.
In this work, we will demonstrate the use of an integrated optical thermography scheme (Raman thermometry, thermoreflectance imaging, and infrared thermography) to study the steady-state and transient thermal characteristics of state-of-the-art AlGaN and Ga_2O_3 devices. These include AlGaN high electron mobility transistors (HEMT), Ga_2O_3 Schottky Barrier Diodes (SBD), and lateral Ga_2O_3 metal-oxide-semiconductor field-effect transistors (MOSFET). Results are validated through the use of coupled electro-thermal modeling. In addition, we will report our recent progress on the development of new optical temperature and stress metrology techniques suitable for UWBG electronics including "2-D transducer-assisted Raman thermography."

4:00 PM TP02.09.05
Spectral Focusing of Thermal Conductivity in GaN—A First Principles Study <u>Jivtesh Garg</u>; University of Oklahoma, Norman, Oklahoma, United States.

We find using first-principles analysis of thermal conductivity (k) in isotopically pure GaN that almost 60% of the heat is conducted by phonons in a very narrow frequency range of 5-7 THz (spanning only 9% of the frequencies in GaN). This spectral focusing of thermal conductivity is found to be due to a combination of two effects – large increase in lifetimes of phonons through suppression of anharmonic scattering in the 5–7 THz frequency range, coupled with a large phonon density of states at the same frequencies. Understanding of the effect is provided by solving the phonon Boltzmann transport equation in the single mode relaxation time approximation along with the use of harmonic and anharmonic force constants derived from density functional theory. The results can have important implications for engineering thermal performance of devices based on GaN.

4:15 PM TP02.09.06
Electron-Beam Probing of Vibrational Modes Across Semiconductor Interfaces with Nanometer Spatial Resolution <u>Zhe Cheng</u>[1], Juan Carlos Idrobo[2] and Samuel Graham[1]; [1]Georgia Institute of Technology, Atlanta, Georgia, United States; [2]Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

As the relentless miniaturization of microelectronics, thermal management becomes an integral challenge for sake of device reliability and safety. Due to the highly-scaled architecture of these electronic systems, heat dissipation can be significantly influenced or even dominated by interfaces. A fundamental understanding of vibrational modes near interfaces which contribute to interfacial heat transfer is still missing, especially at nanoscale spatial resolution. The development of a modern monochromated aberration-corrected scanning transmission electron microscopy (STEM)system makes it now possible to probe vibrational modes with a spatial resolution better than 1 nm and with an energy resolution better than 15 meV. In this work, a GaN+5 nm AlN+SiC interface sample was grown by molecular beam epitaxy and cut into a cross-section STEM sample (around 100 nm thick) using a Focused Ion Beam. Electron energy-loss spectroscopy (EELS) line profiles across the interfaces were collected. The spectra show vibrational peaks arising from SiC optical phonons (110 meV) across all data points. The detected SiC peaks in the AlN and GaN layers are long-range evanescent phonon fields (the *begrenzung*effect). Acoustic phonons are also detected in the energy range between 30-40 meV, which originate from GaN, AlN and SiC. The most interesting feature of EELS results is the presence of an enhancement of the phonon intensity near the interface for both optical and acoustic phonon modes. For three positions near the two interfaces (GaN/AlN and AlN/SiC), the phonon intensities are larger than those measured in the GaN and SiC layers, which may be attributed to surface phonon resonance or interface modes. Here, we will discuss our experimental results and present a theoretical understanding of the observed features in light of improving thermal management at the nanoscale. [1]

[1] The electron microscopy part of this research was conducted at the Center for Nanophase Materials Sciences, which is a Department of Energy Office of Science User Facility (JCI).This research was conducted, in part, 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.

4:30 PM *TP02.09.07
Advances in Sub-Micron and Nanosecond Resolution Thermal Characterisation of Wide Bandgap Semiconductor Devices and Materials James W. Pomeroy, Martin Kuball and <u>Bahar Oner</u>; University of Bristol, Bristol, United Kingdom.

GaN has transformed high-power, high-frequency RF amplifier and power switching technology, enabling more compact and efficient devices. Increasing the operating power density has enhanced device performance, although effective heat dissipation at the channel length scale becomes more critical. Concentrated Joule heating close to the gate generates large heat fluxes in GaN HEMTs: In extreme cases temperature gradients of 100°C/µm can be generated locally. Accurate temperature measurement in and around the transistor channel is essential to predict the meant time to failure (MTTF) and ensure reliability. Measuring the temperature distribution on this length scale also allows us to identify and improve any thermal resistance bottle-necks between the device channel and the heatsink. Conventional temperature measurement methods (e.g. IR thermography, Electrical) underestimate the channel temperature due to their limited spatial resolution, or in the case of pulsed operation, temporal resolution. The requirement for sub-micron spatial and nanosecond temporal resolution has driven the recent development of novel optical thermal characterisation techniques. We review a variety of techniques: Time resolved Raman thermography, including the application of solid immersion lenses for sub-micron resolution 3–D mapping; Raman nano-particle thermometry for surface temperature measurement on a variety of materials; UV transducer-less thermoreflectance. Hyperspectral Quantum-dot Thermal Imaging (HQTI) will be introduced – a very recently developement. The application of these techniques to aid the development of next-generation devices and materials is discussed, including GaN-on-diamond and other wide bandgap semiconductors.

SESSION TP02.10: Thermal Properties of Reactive Materials
Session Chairs: Jeffery DeLisio and Karsten Woll
Thursday Morning, November 29, 2018
Sheraton, 3rd Floor, Fairfax AB

8:00 AM TP02.10.01
Sample Controlled Thermal Analysis for Studying Energetic Materials Pierre-Henry Esposito[1], Renaud Denoyel[1], Thomas Neisius[2] and Marie-Vanessa Coulet[1]; [1]MADIREL - UMR, CNRS and Aix Marseille University, Marseille, France; [2]Féderation de Chimie, CNRS and Aix Marseille University, Marseille, France.

Among nanoenergetic materials, aluminum powders are at the center of numerous works since they remain an additive of choice in many energetic formulations [1]. In all those applications, it is the highly exothermic reaction of aluminum with an oxidant that confers to the powders their reactive and propulsive properties. The underlying idea of replacing micropowders by nanopowder is to take advantage of the enhanced reactivity that the nanoscale confers to the system.
Whatever the scale under consideration, any aluminum particle is covered by a thin alumina layer whose thickness does not vary much with the size of the aluminum core [2]. At low heating rates, the oxidation is controlled by a diffusion mechanism in which this alumina layer plays an important role due to its various polymorphic transitions [3,4]. The enhanced reactivity of aluminum nanopowders is thus linked to size reduction effects of the particles but also to structural changes of the alumina layer. Recently, morphology of the particles and grain nanostructuration of the aluminum core were also proposed as relevant parameters that could allow tuning the material properties [5].
In this contribution, we show that thermal analysis is a useful tool for understanding the oxidation mechanisms in aluminum powders. Powders with different morphology (sphere or flakes) and various sizes (from micro- to nano-scale) are compared. Firstly, it is shown that combined thermogravimetric (TG) and differential thermal analysis (DTA) performed up to 1500°C allows to establish reliable criteria of reactivity that can be extrapolated to realistic conditions. Secondly the oxidation mechanisms are studied using kinetically controlled thermal analysis [6]. In this mode where the oxidation rate is constant, the kinetics equations are simplified which facilitates the modeling of the experimental data. This modeling, together with ex-situ oxidation studies [7], enables to predict the oxidation behavior as a function of structural parameters such as specific surface area and morphology.

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8:15 AM TP02.10.02
Characterization of Cure of Polymeric Materials by Dielectric Analysis (DEA) Yanxi Zhang; Netzsch Instruments North America, LLC, Burlington, Massachusetts, United States.

A variety of questions may arise during the curing process. For example, at which temperature, or after how much time, does the resin begin curing? How high is the reactivity? When is curing complete? How can the curing cycle be optimized? Is there any potential for post-curing? The answers to questions such as these can be investigated by using Dielectric Analysis (DEA), not only in the laboratory environment, but also in-process.

Dielectric Analysis (DEA) allows for the measurement of changes in the dielectric properties of a resin during curing. This technique can be used in study of the curing behavior of thermosetting resins, adhesives, paints and coatings in nearly any application.

A sinusoidal voltage (excitation) is applied and the resulting current (response) is measured, along with the phase shift between voltage and current. These values are then used to determine the ion mobility (ion conductivity) and the alignment of dipoles. Of primary interest with regard to curing is the ion viscosity. This is the reciprocal value of the ion conductivity, which is proportional to the loss factor.

Various application examples about epoxy and other polymeric materials are included in the presentation, including heat cure and UV cure.

8:30 AM *TP02.10.03
Time-Resolved Speciation and Calorimetry of Reactive Nanolaminates at High Heating Rates Jeffery B. DeLisio[1], Feng Yi[2], David LaVan[2] and Michael R. Zachariah[1]; [1]Department of Chemistry and Biochemistry, University of Maryland, College Park, Maryland, United States; [2]National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

Sputter deposited reactive nanolaminates are of great interest for "on chip" energetic applications, but standard analytical techniques lack the ability to characterize these materials on timescales representative of a combustion event. In addition, the simple geometry at the fuel/oxidizer interface of multilayered nanolaminates provides an ideal system to further study the oxygen transport in thermite based reactions, making it possible to probe factors such as the influence of interface-to-volume ratio and its effect on ignition and energy release. Previously, temperature jump (T-Jump) time-of-flight mass spectrometry (TOFMS) was employed to characterize ignition/decomposition temperatures and gas phase speciation of these systems at high heating rates, but this system lacks the ability to measure the energetics of a reaction. Recently developed chip-based nanocalorimeters are capable of making thermal measurements at sufficient frequencies to characterize the energetics of these reactions. In this work, a chip-based nanocalorimeter developed at NIST was integrated with a TOFMS system to enable simultaneous measurement of temporal thermal dynamics and detection of evolved gas species at heating rates up to ~10^6 K/s. This integrated system was first tested by analyzing the decomposition of electrospray deposited salts and metal oxide particles. Reactive nanolaminates were then directly sputtered onto the nanocalorimeter sensors and the effect of bilayer number and thickness was characterized. For an aluminum/copper oxide (Al/CuO) reactive nanolaminate system, one reaction step was observed for a sample with a bilayer thickness of 33 nm. However, a two-step reaction mechanism was observed as the bilayer thickness was increased to 66 nm and beyond: solid-state reaction occurring at the interfaces of Al and CuO before the melting of Al and a much faster liquid−solid reaction right after the melting of Al. In addition, analyzing the measured power from

nanocalorimetry provides a more direct method, compared to optical emission and mass spectrometry based methods, for determining the ignition temperature while also being able to measure actual energy output from films with nanoscale thicknesses.

9:00 AM TP02.10.04
Tailoring the Microstructure of Metallic Thin Films Utilizing Heating Rate Effects on Phase Transformations in Reactive Al/Ru Nanolaminates <u>Karsten Woll</u>[1], Tobias Neuhauser[1], Christoph Pauly[2], Gemma Tinti[3], Nicola Casati[3] and Anna Bergamaschi[3]; [1]Karlsruhe Institute of Technology, Eggenstein-Leopoldsh, Germany; [2]Materials Science & Engineering, Functional Materials, Saarland Universtiy, Saarbruecken, Germany; [3]Paul Scherrer Institut, Villigen, Switzerland.

Reactive metallic nanolaminates or multilayers undergo exothermic runaway reactions when heated with rates larger than about 10^3 K/s. This behavior creates an interest of reactive nanolaminates for applications where local heat sources are required, e.g. in microscale-joining technology. The presented study considers another type of leveraging the reaction attributes. We address the question whether the exothermic phase transformations during ignition, that typically occur under high heating rates, can be utilized for microstructure tailoring of metallic thin films. From a fundamental point of view, the phase transformations occur at solid/solid or liquid/solid interfaces and are still an open field of research. As a model system, we chose Al/Ru nanolaminates and explore for subcritical heating how an increase in heating rate up to about 10^5 K/s affects the phase evolution and how this increase alters the properties of precipitating phases such as stoichiometry or morphology. In greater detail, we use conventional thermal analysis, namely differential scanning calorimetry, to reveal the phase transformations under slow heating and analyze the kinetics of the phase growth within a Johnson-Mehl-Avrami-type model. Complementary, in situ X-ray diffraction with synchrotron radiation enables us to determine the type of the growing phase and to corroborate the growth kinetics. In conjunction with the experiments, we apply classical nucleation theory combined with the diffusion kinetics to estimate the nucleation temperature observed during thermal analysis. The latter analysis protocol at low heating rates serves as reference for our high heating rate study. The advent of nanocalorimetry in the field of reactive materials enables us now to systematically analyze the transformational behavior under the rates of interest < 10^5 K/s. We perform experiments on Al-rich Al/Ru nanolaminates in the subcritical heating rate regime in combination with time-resolved X-ray diffraction using synchrotron radiation. In addition, we study the microstructure in the transmission electron microscope to correlate changes in the precipitating phase with the increase in heating rate. Eventually, we suggest pathways how the latter effects may help to tailor microstructures in thin films, e.g. to fabricate nanocomposites with optimized mechanical properties.

9:15 AM TP02.10.05
Frequency-Domain Thermal Conductivity Measurement for Reactive Solids and Melts at High Temperatures <u>Matthew Wingert</u>[1], Andrew Z. Zhao[1], Yasuhiro Kodera[1], Hongwu Xu[2], Stephen J. Obrey[2] and Javier E. Garay[1]; [1]University of California, San Diego, La Jolla, California, United States; [2]Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

High temperature materials and melts are increasingly being investigated for next generation energy technologies such as batteries utilizing molten compounds, and high temperature heat transfer fluids (HTFs), and thermal energy storage (TES) materials. Such systems aim to take advantage of the chemical and transport properties of the melts or the higher intrinsic thermodynamic efficiencies that come with higher temperature. To utilize such compounds for melt-based systems and as HTFs/in TES systems their thermal transport properties from the solid phase through the melt should be well characterized to understand how best to extract or retain heat and mitigate thermal design issues. Additionally, these materials can be highly corrosive or reactive at elevated operating temperatures and for specific material chemistries requiring that any thermal measurement technique can withstand harsh thermal and chemical sample environments in addition to being sensitive to the thermal properties under consideration. Here we describe a hot-wire geometry based thermal measurement system for accurate thermal conductivity measurements of solid compounds and melts. The chosen wire geometry is highly suitable for high temperature measurements of both solids and, particularly, liquids due to its relatively simple design and extensive working temperature range. Traditional hot-wire thermal measurement techniques pass a DC current through a thin resistive wire element suspended within a sample to induce a temperature rise. The thermal properties of that sample are then calculated based on the temporal evolution of measured temperature rise of the wire itself. This, however, requires careful calibration of the system and large volumes of sample material since the thermally probed volume increases with time and will at some time range include the system components and, for liquid or molten samples, convective flow. Here we instead utilize modulated heating of the hot-wire at fixed frequencies to limit the thermal penetration depth and time of the temperature signal. As opposed to measurements in the time-domain, performing the measurement in the frequency-domain increases measurement accuracy by limiting the thermally probed volume to the sample itself, eliminating the influence of external interfaces on the thermal signal. Additionally, limiting the time of the applied heat and resulting temperature pulse reduces the effects of convective transport in liquid/molten samples. Furthermore, by utilizing a modulated heat source for the probing signal, we can 'lock into' the harmonics of the thermal response of the hot-wire, which contain information on the thermal properties of the sample material while rejecting the influence of ambient temperature fluctuations on the probed temperature. Sensor fabrication and thermal sensitivity analysis will be presented alongside thermal measurements on solid and molten test compounds over a range of temperatures.

9:30 AM TP02.10.06
Inkjet-Assisted Nanocalorimetry for Optimization of Trace Detection <u>Feng Yi</u>, Jeffrey Lawrence, Matthew Staymates, Greg Gillen and David LaVan; National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

Nanocalorimetry is capable of generating rapid and arbitrary heating profiles to gather thermal and thermodynamic measurements with high sensitivity. Here, we are studying the dynamics of the heating cycle to optimize trace detection. For the sample preparation, Inkjet printing is used to pattern samples on the active area of the nanocalorimeters, and also allows for an estimate of the sample mass. Procedures have been developed to print *exemplar* trace materials onto nanocalorimeter sensors with precise control of position and sample mass. Nanocalorimetry results on several materials are shown to demonstrate the measurement capability.

9:45 AM TP02.10.07
Phase Evolution in Al/Ni Multilayer Thin Films Studied by Combined Nanocalorimetry and Sub-Millisecond X-Ray Diffraction <u>Tobias Neuhauser</u>[1], Gemma Tinti[2], Harald Leiste[1], Nicola Casati[3], Anna Bergamaschi[2], Michael Stüber[1] and Karsten Woll[1]; [1]IAM, Karlsruhe Institute of Technology, Eggenstein-Leopoldshafen, Germany; [2]OFLC/001, Paul Scherrer Institut, Villigen, Switzerland; [3]WLGA/229, Paul Scherrer Institut, Villigen, Switzerland.

High strength typically compromise deformability in metallic materials. To overcome this conflict, we strive to develop thin film nanocomposites where hard intermetallic phases are embedded in a ductile metallic matrix. Our approach considers metallic nanolaminates or multilayers as starting materials. PVD sputter deposited Al/Ni multilayers serve as model materials. To generate hard phases at the nanoscale, we utilize phase selection where intermetallic phases precipitate predominantly at interfaces and/or grain boundaries upon annealing. Based on theoretical calculations, the chosen heating rate up to values of about 10^5 K/s have an impact on the phase formation. However, when heated with an overcritical rate to a specific ignition temperature, these materials exhibit uncontrolled runaway exothermal reactions. Up to now, the phase formations driving the ignition are not yet understood. The challenging task in terms of investigation is the highly dynamic character of the reaction, where transformations occur within microseconds. Traditional

characterization tools operate at time scales that are too slow to reveal the individual transformations in detail. We developed an *in situ* technique where we combine chip-based nanocalorimetry and time-resolved X-ray diffraction with synchrotron radiation. Eventually, the achieved time resolutions of 50 μs enabling us to correlate the calorimetric information with the microstructure evolution during the reaction. In greater detail, we explore the role of interdiffusion, phase formation and melting for the runaway reaction initiation under high heating rates. Kinetic considerations are performed via nanocalorimetry with integrated pulse heating combined with *ex situ* X-ray diffraction. Effects of the high heating rates during ignition as well as the influence of the multilayer geometry on the early stages of phase formation are studied. Eventually, the elucidation of the transformations occurring at the threshold of ignition enables us to develop guidelines for microstructure development of nanocomposites.

10:00 AM BREAK

SESSION TP02.11: Thermal Properties of Solids I
Session Chairs: Lito De la Rama and Aditya Sood
Thursday Morning, November 29, 2018
Sheraton, 3rd Floor, Fairfax AB

10:30 AM TP02.11.01
New Family Memers in 2D Carbon Nitrides with Excellent Thermal Conductivity from First Principle Calculation Chi Zhang, Yuan Dong and Jian Lin; Mechanical and Aerospace Engineering, University of Missouri Columbia, Columbia, Missouri, United States.

Two novel structurally stable two-dimensional (2D) carbon nitrides are predicted by first-principles calculations (DFT). They are derived by extracting two adjacent atomic layers from cubic diamond or hexagonal diamond and then substituting the unsaturated C atoms with N atoms. The obtained 2D diamond-like carbon nitrides are named as 2D c-C_2N_2 and 2D h-C_2N_2. Their structural stability, electronic, mechanical, and thermal properties were systematicly explored by DFT. It is interesting to see that the c-C_2N_2 has a high thermal conductivity of 41200 W/m*K while the h-C_2N_2 has a thermal conductivity of 49500 W/m*K at 80 K. These values are several times of those of graphene and diamond at the same temperature. This work provides theoretic perspectives for exploring novel 2D carbon nitrides with extraordinary properties.

10:45 AM TP02.11.02
Mapping the Low Thermal Conductivity of Lead-Halide Based Perovskite Films with High Spatial Resolution Tobias Haeger, Maximilian Wilmes, Ralf Heiderhoff and Thomas Riedl; University of Wuppertal, Wuppertal, Germany.

Thermal management in hybrid halide perovskite thin film devices, like solar cells, light-emitting diodes, and lasers, is expected to be of outstanding importance for optimal performance and reliability [1]. As the thermal conductivity of perovskites is relatively low, it's experimental assessment is challenging, and only a few studies exist [2-4]. Recently, we reported on the thermal conductivity of methylammonium lead halide perovskite single crystals and thin films by means of dynamic Scanning Near-field Thermal Microscopy (SThM) [4]. The thermal conductivity of $CH_3NH_3PbX_3$ single crystals with X= I, Br and Cl, is found to be 0.34 ± 0.12, 0.44 ± 0.08 and 0.50 ± 0.05 W/(mK), respectively. Similar thermal conductivities are determined for the corresponding thin-film samples, which are treated by a planar hot pressing procedure to avoid topography artifacts (surface roughness <1 nm) [5]. Besides the influence of the choice of the halide, we will present the impact of a variation of the A-site cation (Cs vs. MA). An average thermal conductivity λ of 0.36 ± 0.08 W/(mK) is determined for cesium-lead-bromide perovskite thin films. These results fit very well with the data published for $CsPbBr_3$ single crystals [3]. We demonstrate, that the observed standard deviations of λ are attributed to high local variations of λ within the measured area. In order to determine the low thermal conductivity in perovskite thin films with high spatial resolution using the 3w-technique, we employ a thermal conductivity mapping in the frequency domain, for the first time. This technique allows us to detect simultaneously the topography, the local thermal conductivity, and the thermal diffusivity. Hereby, we will demonstrate that thermal conductivity variations between 0.33 to 0.38 ± 0.01 W/(mK) can even be found within one single crystal grain. The differences in thermal conductivity, even between the individual grains, are explained by different dimensionalities of Cs-based perovskites (3D: $CsPbBr_3$, 2D: $CsPb_2Br_5$), which are evidenced by X-ray diffraction to be present. The local differences in the product of the density and specific heat capacity are examined and will be discussed. The setup and properties of this system will be presented from the engineering point of view taking different mixing techniques into account. The advantage of our advanced measurement technique will be discussed with respect to phase separation analyses.

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11:00 AM TP02.11.03
Record-Low and Anisotropic Thermal Conductivity of Quasi-1D Bulk ZrTe₅ Single Crystal Jie Zhu[1], Tianli Feng[2,3], Scott Mills[4], Peipei Wang[5], Xuewang Wu[1], Liyuan Zhang[5], Sokrates Pantelides[2,3], Xu Du[4] and Xiaojia Wang[1]; [1]University of Minnesota Twin Cities, Minneapolis, Minnesota, United States; [2]Vanderbilt University, Nashville, Tennessee, United States; [3]Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; [4]Stony Brook University, Stony Brook, New York, United States; [5]Southern University of Science and Technology, Shenzhen, China.

Zirconium pentatelluride ($ZrTe_5$) has recently attracted renewed interest owing to many of its newly discovered extraordinary physical properties, such as 2D and 3D topological-insulator behavior, pressure-induced superconductivity, Weyl semimetal behavior, Zeeman splitting, and resistivity anomaly. The quasi-1D structure of single-crystal $ZrTe_5$ also promises large anisotropy in its thermal properties which have not yet been studied. In this work, by conducting time-domain thermoreflectance measurements, we discovered that single crystals of $ZrTe_5$ possess a record-low thermal conductivity along the *b*-axis (through-plane), as small as 0.33 ± 0.03 W m^{-1} K^{-1} at room temperature. This ultralow *b*-axis thermal conductivity is twelve times smaller than its *a*-axis thermal conductivity (4 ± 1 W m^{-1} K^{-1}) owing to the material's asymmetrical crystalline structure. We further conducted first-principles calculations to reveal the physical origins of the ultralow *b*-axis thermal conductivity, which can be attributed to: 1) resonant bonding and strong lattice anharmonicity induced by the electron lone pairs, 2) the weak interlayer van der Waals interactions, and 3) the heavy mass of Te atoms, which results in low phonon group velocity. This work sheds light on the design and engineering of highly effective thermal insulators for applications such as thermal barrier coating, thermoelectrics, thermal energy storage, and thermal management.
This work is supported by NSF DMR-1420013, National Natural Science Foundation of China (Grant No. 51336009), Department of Energy grant DE-

11:15 AM TP02.11.04
Impact of Ultrafine Nanostructuring on the Phonon Wave Transport of Si Phononic Crystals <u>Kouhei Takahashi</u>[1], Takashi Kawasaki[1], Naoki Tambo[1], Masaki Fujikane[1], Kunihiko Nakamura[1], Yasuyuki Naito[1], Yuxuan Liao[2], Makoto Kashiwagi[2] and Junichiro Shiomi[2]; [1]Panasonic Corporation, Kyoto, Japan; [2]Department of Mechanical Engineering, The University of Tokyo, Tokyo, Japan.

Phonon engineering has attracted much attention for developing new thermal transport properties in solids. In phonon engineering, nanostructuring plays an essential role. The effect of nanostructuring on the thermal transport is mainly twofold; (i) enhance diffuse boundary scattering of phonons, and (ii) change dispersion relation of phonons. The former mechanism is traditional which focuses on the particle nature of phonons. This has been demonstrated both experimentally and theoretically in various nanomaterials with increased surface boundaries. On the other hand, the latter mechanism focuses on the wave nature of phonons, in which the newly added interfaces of the nanomaterials provide a unique platform for the phonons to create new vibrational modes. Although theoretical studies predict intriguing thermal properties to be developed by the latter approach, we still lack experimental evidences that support the effectiveness of nanostructuring on modifying the phonon wave transport. Here, we report anomalous thermal transport properties of ultrafine Si phononic crystals, which can be correlated to the change in behavior of phonon waves. This is demonstrated in Si phononic crystal films with two-dimensional arrays of through-holes fabricated by ultrafine semiconductor nanofabrication technology. The pitch size of the through-holes of the phononic crystals examined here ranges widely from 34 nm to 2000 nm. Using time-domain thermal reflectance measurement, we found that thermal conductivity of Si reduces significantly with decreasing the phononic crystal pitch size. Particularly, the 34 nm-pitch phononic crystals exhibited nearly 50 times lower thermal conductivity than that of bulk Si. Monte-Carlo ray tracing simulation was conducted to investigate the contribution of boundary scattering on the reduced thermal conductivity. We found that thermal conductivity of Si phononic crystals with pitches larger than 300 nm can be reproduced well by this simulation model indicating that thermal conductivity reduction in these phononic crystals is within the scope of traditional boundary scattering of phonon particles. On the other hand, we found that thermal conductivity of phononic crystals with pitches smaller than 200 nm exhibit low thermal conductivities far below the values predicted by this phonon particle simulation model. We show experimental evidences that elastic properties are significantly modified from the bulk in the ultrafine phononic crystals indicating that the anomalous reduction in thermal conductivity is related to the change in group velocity of phonon waves. The present result provides an important insight into understanding the unusual thermal transport properties of phononic crystals.

11:30 AM TP02.11.05
Decoupling Thermal and Electrical Conductivity in a Single-Phase Epitaxial Tungsten Oxide <u>Shuai Ning</u>[1], Samuel Huberman[2], Gang Chen[2] and Caroline A. Ross[1]; [1]Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; [2]Department of Mechanical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Tuning the thermal transport properties in solid-state materials is of great interest for many technologies. Thermal conductivity is usually correlated to the electrical transport according to the Wiedemann-Franz law. Decoupling the thermal conductivity and electrical conductivity is highly desirable for thermoelectric energy conversion and thermal management, and quite challenging particularly in a single-phase material. Tungsten oxide (WO_3), which shows a perovskite-like structure with vacant A-sites, can accommodate a large number of defects and supports a significant structural distortion. It is thus a good prototype to investigate the dependence of thermal and electrical conductivity on the lattice and defects. In our work, oxygen pressure-dependent pulsed laser deposition (PLD) growth and ionic liquid (IL) gating experiments have been performed on epitaxial WO_3 thin films with a thickness of ~100 nm. The lattice parameters are strongly dependent on the interfacial strain from the substrate and on chemical strain from the defects. Specifically, the c/a ratio can be varied from 0.96 to 1.04. The room-temperature (RT) electrical conductivity characterized by van der Pauw method is drastically enhanced by both oxygen deficiency and intercalated protons, irrespective of lattice structure. indicating that donor defects play a determinative role in the n-type electrical conductivity. The RT through-plane lattice thermal conductivity analyzed by time-domain thermoreflectance (TDTR), however, is surprisingly found to be defect-insensitive, indicating phonon-phonon interaction dominates the thermal scattering. Furthermore, a strong correlation is observed between the lattice thermal conductivity and the out-of-plane lattice dimension such that the elongation of the out-of-plane lattice parameter can suppress the thermal conductivity from ~7.8 W/mK to ~1.2 W/mK. By engineering the lattice and defects, we successfully realized the selective and independent manipulation of the thermal conductivity (by ~7-fold) and the electrical conductivity (by ~5 orders of magnitude) in single-phase epitaxial WO_3 thin films. It not only enriches the functionalities of WO_3, but also sheds light on designing new thermoelectric and thermal interface materials.

11:45 AM TP02.11.06
Comprehensive T-Type Method for the Thermal and Thermoelectric Properties Measurement of Micro/Nano Wires and Ribbons <u>Shaoyi Shi</u>, Weigang Ma and Xing Zhang; Tsinghua University, Beijing, China.

Micro/nano wires and ribbons have large technological applications and new fundamental physical phenomena. Especially in nanoscale, the properties of nanowires and nano-ribbons may be significantly different from bulk, and the measurement method for bulk materials even cannot be applied. Development of the precise measurement method for micro/nano wires and ribbons is becoming the frontier research and has been attracting intense interest. We have developed an integrated T-type method for comprehensively measuring the thermal and thermoelectric properties of micro/nano wires and ribbons. In the T-type method, the dc heating-dc detecting, four probe, and ac heating-dc detecting modes are applied to measure the thermal conductivity, electrical conductivity and Seebeck coefficient, respectively.The thermal and thermoelectric properties can be comprehensively determined on the same sample in the same measurement configuration. By applying the T-type method, some typical micro/nano wires and ribbons, including graphene fiber and single bismuth sulfide nanowire, have been studied.

SESSION TP02.12: Thermal Properties of Solids II
Session Chairs: Lito De la Rama and Aditya Sood
Thursday Afternoon, November 29, 2018
Sheraton, 3rd Floor, Fairfax AB

1:30 PM *TP02.12.01
Advances in Ultrafast and Nanoscale Thermoreflectance Thermal Imaging <u>Ali Shakouri</u>[1], Kerry Maize[1], Sami Alajlouni[1], Amir K. Ziabari[1] and Dustin Kendig[2]; [1]Birck Nanotechnology Center, Purdue University, West Lafayette, Indiana, United States; [2]Microsanj LLC, Santa Clara, California, United States.

Static and dynamic hot spots and temperature non-uniformities limit the performance and reliability of electronic devices and integrated circuits. Here we review recent advances in transient thermoreflectance imaging to characterize temperature distribution in active devices. Imaging de-blurring techniques have been used to increase spatial resolution down to 100nm and temporal resolution is down to sub-nanosecond levels for full-field imaging and 100fs for single point measurements. While the lock-in or boxcar averaging techniques measure the change in surface or interface reflection coefficient very accurately, calibrating the thermoreflectance coefficient is essential to obtain absolute temperature profiles. A key challenge in thermal imaging of power devices is the separation of temperature induced change in reflected light due to thermal expansion. Both effects scale with the power dissipation in the device. Auto-focus and digital alignment can alleviate many of the edge effects in the thermal image, and multi-spectral thermoreflectance imaging can provide one of the most robust calibration methods to accurately obtain absolute temperature rise in power devices. Calibration of the thermoreflectance coefficient in micron-sized regions is further complicated due to sample movements when the stage temperature is changed. Here, we show that the transient temperature distribution can be used to calibrate thermoreflectance coefficient of unknown surfaces. Finally, semi-transparent coatings can create optical interferences in the reflected light which leads to a non-linear thermoreflectance coefficient. Methods to accurately extract the temperature in the presence of a non-linearity are presented. Several examples, including power GaAs, SiC, and GaN devices as well as through-the-substrate thermoreflectance imaging in silicon flip-chip bonded chips are presented. Finally, we briefly discuss the issue of defining temperature and what is actually measured in submicron regions. For Si, GaN, and many other semiconductors, Fourier law fails when the diameter of the heat source or the thermal penetration depth is less than a micron at room temperature.

2:00 PM TP02.12.02
Direct Imaging of Suppressed Thermal Transport near Individual Grain Boundaries in Polycrystalline Diamond Aditya Sood[1], Ramez Cheaito[1], Tingyu Bai[2], Heungdong Kwon[1], Yekan Wang[2], Chao Li[2], Luke Yates[3], Thomas Bougher[3], Samuel Graham[3], Mehdi Asheghi[1], Mark S. Goorsky[2] and Kenneth E. Goodson[1]; [1]Stanford University, Stanford, California, United States; [2]University of California, Los Angeles, Los Angeles, California, United States; [3]Georgia Institute of Technology, Atlanta, Georgia, United States.

Understanding the impact of lattice imperfections on nanoscale thermal transport is crucial for diverse applications ranging from thermal management to energy conversion. Grain boundaries (GBs) are ubiquitous defects in polycrystalline materials, which scatter phonons and reduce thermal conductivity (κ). Historically, their impact on heat conduction has been studied indirectly through spatially-averaged measurements, that provide little information about phonon transport near a single GB. Here, using spatially-resolved time-domain thermoreflectance (TDTR) measurements in combination with electron backscatter diffraction (EBSD), we make the first localized measurements of κ within few μm of individual GBs in boron-doped polycrystalline diamond. We observe strongly suppressed thermal transport near GBs, a reduction in κ from ~1000 $Wm^{-1}K^{-1}$ at the center of large grains to ~400 $Wm^{-1}K^{-1}$ in the immediate vicinity of GBs. Furthermore, we show that this reduction in κ is measured up to ~10 μm away from a GB [1]. A theoretical model is proposed that captures the local reduction in phonon mean-free-paths due to strongly enhanced phonon scattering near the disorder-rich grain boundaries. Our results provide a new framework for understanding phonon-defect interactions in nanomaterials, with implications for the use of high κ polycrystalline materials as heat sinks in electronics thermal management.

[1] A.Sood *et al.* ***Nano Lett.*** 18 (6), pp. 3466-3472 (2018).

2:15 PM TP02.12.03
Rethinking Phonons in Disordered Solids—Crystals with Defects/Impurities and Random Alloys Hamidreza Seyf and Asegun Henry; Georgia Institute of Technology, Atlanta, Georgia, United States.

Current understanding of phonons treats them as plane waves/quasi-particles of atomic vibration that propagate and scatter. The problem is that conceptually when any level of disorder is introduced, whether compositional or structural, the character of vibrational modes in solids changes, yet nearly all theoretical treatments continue to assume phonons are still waves. For example, the phonon contributions to alloy thermal conductivity (TC) rely on this assumption and are most often computed from the virtual crystal approximation (VCA). Good agreement is obtained in some cases, but there are many instances where it fails—both quantitatively and qualitatively. Here, we show that the conventional theory and understanding of phonons requires revision because the critical assumption that all phonons/normal modes resemble plane waves with well-defined velocities is no longer valid when disorder is introduced. Here we show, surprisingly, that the character of phonons changes dramatically within the first few percents of impurity concentration, beyond which phonons more closely resemble the modes found in amorphous materials. We then utilize a different theory that can treat modes with any character and experimentally confirm its new insights.

2:30 PM TP02.12.04
Effect of Quenched-in Vacancies on Precipitation in Aluminium Alloys Measured by Differential Fast Scanning Calorimetry Bin Yang[1, 2], Benjamin Milkereit[4, 2], Olaf Kessler[4, 2] and Christoph Schick[1, 2, 3]; [1]Institute of Physics, University of Rostock, Rostock, Germany; [2]Competence Centre CALOR, University of Rostock, Rostock, Germany; [3]Kazan Federal University, Kazan, Russian Federation; [4]Faculty of Mechanical Engineering and Marine Technology, University of Rostock, Rostock, Germany.

Quenched-in vacancies are point defects that can be present in materials after quench from high temperature. Quenched-in vacancies increase the rate of solute diffusion and therefore the kinetics of phase transformations. In this study different concentrations of vacancies were frozed-in by quenching from solution annealing temperature at different cooling rates up to 3×10^5 K/s by differential fast scanning calorimetry (DFSC). Then artificial aging at different temperatures and time followed by a differential reheating method (DRM) enables both time and temperature-dependent investigations of vacancy-induced precipitation in aluminium alloys. The method can potentially be transferred to similar systems or related solid-state phase transformation systems also beyond the particular system analysed in the present study.

2:45 PM TP02.12.05
Effect of Vacancies and Domain Walls on the Thermal Conductivity of PbTiO₃ Thin Films David Bugallo Ferrón[1], Elias Ferreiro-Vila[1], Eric Langenberg[1, 2], Gustau Catalan[3], Neus Domingo[3], Darrell G. Schlom[2] and Francisco Rivadulla[1]; [1]CiQUS-University of Santiago de Compostela, Santiago de Compostela, Spain; [2]Materials Science and Engineering, Cornell University, Ithaca, New York, United States; [3]Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC, Barcelona Institute of Science and Technology, Barcelona, Spain.

We report the effect of ferrolastic domain walls on the thermal conductivity of thin films of $PbTiO_3$. We fabricated a series of films by Molecular Beam Epitaxy on $SrTiO_3$ (001) substrates over a wide range of Pb/Ti ratio. X-ray diffraction and Piezoelectric Force Microscopy were used to correlate the thermal conductivity results with the distribution of ferroelectric domains as a function of Pb/Ti. Our results show that stoichiometric strained $PbTiO_3$ films shows an anomalously reduced thermal conductivity, comparable to that of highly defective samples. These results suggest that ferroelastic domain walls have a large effect on the thermal conductivity of this material, opening the possibility for reversible modulation of thermal conductivity by an external stimulus in ferroelectric oxides.

3:00 PM BREAK

3:30 PM TP02.12.06
Determining the Mechanical and Thermodynamic Properties of Iron Meteorites Below 300 K <u>Matthew Bonidie</u>[1], Christopher Noyes[1], Roy Forestano[1], Daniel Britt[2], Robert Macke[3], Guy Consolmagno[3] and Cyril Opeil[1]; [1]Boston College, Chestnut Hill, Massachusetts, United States; [2]Physics, University of Central Florida, Orlando, Florida, United States; [3]Specola Vaticana, Vatican City, Italy.

Iron meteorites are primarily kamacite or taenite based Fe-Ni polycrystalline alloys that solidify from planetary cores over a timespan of $t \geq 10^6$ years via thermal radiation into the vacuum of space. Depending on their Ni composition and cooling rates, iron meteorites crystallize into either fine octahedrite, coarse octahedrite, or hexahedrite crystal structures.

Through the use of resonant ultrasound spectroscopy, the elastic constants and Young's modulus were measured as a function of temperature from 10-300 K, allowing a comparison of how Ni percentage, crystallographic structure, and impact history effect the mechanical behavior of these meteorites. In addition, specific heat capacity, thermal conductivity, and thermal inertia of the iron meteorites will also be discussed.

3:45 PM TP02.12.07
Thermal and Phonon Spectral Transport Analysis for New High Thermal Conductivity Materials Joon Sang Kang, Man Li, Huuduy Nguyen, Huan Wu and <u>Yongjie Hu</u>; University of California, Los Angeles, Los Angeles, California, United States.

Understanding the origins of high thermal conductivity is of great important to thermal science and applications of thermal management and energy conversion, but remains a significant challenge in the field. Recent theoretical work including first-principles has predicted new class of thermal materials with high thermal conductivity beyond state-of-the-art materials and approaching that of diamond (> 1000 W/mK). However, experimental demonstration and understanding have been limited by materials synthesis, measurement accuracy, and theoretical toos. Here, we describe our current progress in developing high conducting thermal materials using advanced chemical synthesis approach to achieve high quality single crystalline crystals and analyzing the spectral phonon mode contributions using density functional theory and Botlzmann transport equations[1]. The heat conduction and phonon transport with size dependence are carried out by thermal mapping spectroscopy technique[2]. We investigate the effects to thermal conductivity from defects, interfaces, and grains. Our work aims for systematic investigation and material improvement for ultrahigh thermal conductivity and brings the promise of rational material design to achieve its theoretical limit. The significant impacts of this research in improving the efficiency of thermal energy conversion and management will also be illustrated.

References:
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[2] Hu et al., "Spectral mapping of thermal conductivity through nanoscale ballistic transport", Nature Nanotechnology 10, 701 (2015).

4:00 PM OPEN DISCUSSION

4:15 PM TP02.12.09
Thermal Conductivity Evaluation of Polymer Crystals—An *Ab Initio* Study <u>Keishu Utimula</u>[1], Tom Ichibha[2], Ryo Maezono[2] and Kenta Hongo[3, 4, 5]; [1]School of Materials Science, Japan Advanced Institute of Science and Technology, Nomi, Japan; [2]School of Information Science, Japan Advanced Institute of Science and Technology, Nomi, Japan; [3]Research Center for Advanced Computing Infrastructure, Japan Advanced Institute of Science and Technology, Nomi, Japan; [4]PRESTO, Japan Science and Technology Agency (JST), Kawaguchi, Japan; [5]Research and Services Division of Materials Data and Integrated System, National Institute for Materials Science, Tsukuba, Japan.

Lattice thermal conductivity (LTC) has been calculated mainly using linear lattice models or molecular dynamics simulations, but their theoretical reliability strongly depends on empirical parameters and choice of force field. With the advent of massively parallel computers, a more systematic and reliable approach to the evaluation of LTC has emerged, *i.e.*, *ab initio* anharmonic lattice dynamics calculations, where the linearized phonon Boltzmann equation is used to approximate a LTC formula, Peierls- Boltzmann equation, at the cubic anharmonic level. This approach has successfully reproduced LTC for several inorganic semiconductors in a wide range of LTC from ~1 to ~10^2 W/mK. However, few works have ever applied this approach to polymer systems, although the LTC of polymers is one of the most important quantities for industrial purpose. It is well known that higher crystallinity in polymers increases LTC, indicating that polymer crystals are expected to have the highest LTC. Experimentally, however, 'perfect' crystallizations are not realized for most polymers. Hence their upper limits of LCT are still unknown, though such values would provide useful guidelines for high-LTC polymer design. On the other hand, it is easy to model the polymer crystal structures and apply the simulations to calculate the LTC values, which are regarded as the theoretical upper limit of those of the polymers.
We have applied *ab initio* anharmonic lattice dynamics simulations to both chain and crystal polyethylene in order to evaluate their LTC values. It is established that their temperature dependences of LTC agree well with previous experiments. In addition, we found that polyethylene has comparatively long phonon lifetime, which mainly gives good LTC to the polymer. In this talk, we will report on not only these results but also several typical polymers such as polyethylene terephthalate and phenylene sulfide.

4:30 PM TP02.12.10
An Inverse Problem Framework for Extracting Phonon Properties from Thermal Spectroscopy Measurements Including Systems Featuring Interfaces with Unknown Properties <u>Mojtaba Forghani</u> and Nicolas G. Hadjiconstantinou; Massachusetts Institute of Technology, CAMBRIDGE, Massachusetts, United States.

Thermal spectroscopy has been established as a promising experimental method for characterizing the transport behavior of materials and as a useful alternative to density functional theory (DFT) calculations which are expensive and not always in agreement with real experimental measurements. While there have been significant advances enhancing the reliability and accuracy of this experimental technique, the inverse problem of extracting material properties from the experimental observations remains an open problem. In particular, it was recently shown [Forghani et al., Phys. Rev. B 94, 155439 (2016)] that techniques based on assuming validity of Fourier's law are invalid, unless a set of rather restrictive conditions are met.

We have recently proposed an inverse problem framework [Forghani and Hadjiconstantinou, Phys. Rev. B 97, 195440, (2018), Forghani et al., Phys. Rev. B 94, 155439 (2016)] that can be employed to extract mode dependent material properties, such as relaxation times or interface transmissivities, from

thermal spectroscopy measurements. The proposed technique solves the inverse problem by iterating between solutions of the forward (relaxation) problem and thus requires solutions that capture the mode-dependent physics; these solutions can be either analytical or numerical, including stochastic.

In this presentation we focus on applications of this technique to the extraction of phonon properties using deviational [Peraud and Hadjiconstantinou, Phys. Rev. B 91, 235321 (2015)] Monte Carlo simulations of the Boltzmann Transport Equation (BTE) to solve the forward problem. Specifically, we show that our method is able to reconstruct phonon free path distributions from experimental measurements obtained from a transient thermal grating setup. We also show that the proposed method can be used to extract phonon free-path distributions from systems featuring interfaces with unknown properties. We also discuss the extension of the method for reconstruction of the interface properties.

We expect that due to the generality of the proposed method, extension to other quantum mechanical particles, other material properties, and other numerically/analytically available algorithms for solving the forward problem, will be feasible.

4:45 PM TP02.12.11
Thermal Characterization of Sodium-Sulfides at High Temperature <u>Andrew Z. Zhao</u>[1], Matthew C. Wingert[1], Yasuhiro Kodera[1], Hongwu Xu[2], Stephen J. Obrey[2] and Javier E. Garay[1]; [1]University of California, San Diego, San Diego, California, United States; [2]Los Alamos National Laboratory, Los Alamos, New Mexico, United States.

Metal sulfides have a unique range of electronic and mechanical properties that has resulted in their exploration for next generation batteries, catalysts, semiconductors, and thermoelectrics. Many functional metal-sulfides must operate at high temperatures, but their thermal properties under extreme conditions have not been extensively studied and are not well understood. Measuring the thermal properties of highly reactive materials, such as metal-sulfides, has been challenging due to the corrosion and breakdown of sensor and containment materials at high temperatures. To advance the development of functional metal-sulfides, we seek to understand their structure and thermal properties at high temperatures. Here, we present a frequency-domain hotwire technique to measure the thermal conductivity of various sodium-sulfides at high temperatures. Unlike traditional hotwire measurement techniques, which apply a heat flux to a large sample volume to probe the temperature of the sample versus time, our custom system and sensor reduce the necessary sample volume to below 5 mL and probe the sample's thermal response in the frequency domain. Our system and sensor have been designed to survive corrosive chemical environments at temperatures up to 750 degrees Celsius. The thermal conductivity of sodium-sulfides at high temperatures have been measured for the first time and are presented here. The structure of the sodium-sulfides is examined using x-ray/neutron diffraction and electron microscopy; this approach helps provide structural insights into the experimental and theoretical thermal transport properties of sodium-sulfides.

SESSION TP02.13: Thermal Properties of Solids III
Session Chairs: Lito De la Rama and Aditya Sood
Friday Morning, November 30, 2018
Hynes, Level 1, Room 111

8:30 AM TP02.13.01
Lattice Dynamics Across the Temperature- or Pressure-Induced Structural Phase Transition in SnSe and SnS <u>Tyson Lanigan-Atkins</u>[1], Shan Yang[1], Jennifer Niedziela[2], Dipanshu Bansal[1], Tao Hong[2], Songxue Chi[2], Andrew May[2], Daniel Pajerowski[2], Georg Ehlers[2] and Olivier Delaire[1]; [1]Duke University, Durham, North Carolina, United States; [2]Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

SnSe and SnS are two promising thermoelectric materials, which have demonstrated outstanding figure-of-merits, but whose transport properties exhibit strong anisotropies tied to their layered crystal structure. At high temperature or high pressure, they undergo a continuous structural phase transition between a low-symmetry Pnma phase and a higher-symmetry Cmcm phase (SnSe: $T_c \sim 805K$ and $P_c \sim 10GPa$, SnS: $T_c \sim 880K$). In order to rationalize the strong anharmonicity and anisotropy in thermal conductivity, we have used time-of-flight (TOF) and triple-axis inelastic neutron scattering (INS) to map the phonon dispersions and density of states (DOS) of both compounds at high temperature across the phase transition. Our results show a striking, extended softening and broadening of phonon excitations with temperature and the soft mode character of this transition is clearly revealed. We extracted the phonon scattering rates by deconvoluting instrumental resolution effects, for both time-of-flight and triple-axis measurements. Scattering rates calculated from the two methods agree remarkably well. We performed systematic first-principles simulations of the temperature-dependent phonon dynamical structure factor, $S(\mathbf{Q},E)$, and scattering rates, which we compare with our experimental results. Furthermore, we have used TOF neutron diffraction, inelastic X-ray scattering and Raman spectroscopy to track the transition as a function of pressure finding good agreement with the previously reported transition pressure of ~10GPa. The projected DOS is tracked with pressure in order to follow the anisotropy of the lattice dynamics with pressure. We contrast some of the behaviors observed in our measurements and simulations with rocksalt chalcogenides (SnTe, PbTe, PbSe).
Funding from US-DOE/BES/MSED, Office of Science Early-Career-Award, and as part of the S3TEC-EFRC.

8:45 AM TP02.13.02
Thermal Stability Enhancement of Alpha Tin Films by Strain Engineering Jinshan Yao[1, 2], Huanhuan Song[1, 2], Shunji Xia[1, 2], Yu Gu[1, 2], Yuanfeng Ding[1, 2] and <u>Hong Lu</u>[1, 2]; [1]College of engineering and Applied Sciences, Nanjing University, Nanjing, China; [2]National Laboratory of Solid State Microstructures, Nanjing University , Nanjing, China.

Alpha tin (α-Sn, also known as gray tin), a metastable phase of tin, is a zero band gap semimetal with a diamond structure. Since Fu and Kane [1] predicted that alpha tin could be a topological insulator under certain strain, a lot of work have been done to study the topological properties of this material [2-4]. However, the growth of high quality alpha tin film remains challenging due to its low phase transition temperature and lack of appropriate substrates. We have successfully grown a series of alpha tin films on InSb (001) substrates by molecular beam epitaxy (MBE). The film thickness varies from 10 nm up to 400 nm. Atomic force microscope (AFM) shows a smooth surface morphology with roughness under a few nanometers. Transmission electron microscope (TEM) confirms the diamond structure of the alpha films.
It is known that bulk alpha tin is only stable up to 13.2 °C. Our interest is to utilize strain to enhance the thermal stability of alpha tin films, and the strain is tuned by varying the film thickness during the epitaxial growth process. The InSb substrate provides a compressive strain (0.14%). We have used temperature dependent XRD (T-XRD) and temperature dependent Raman for this study. The temperature range covers from -100°C to 250°C. The XRD results show the high crystalline quality of the alpha tin films. Clear thickness fringes are observed for all the samples, and reciprocal space mapping (RSM) shows that the alpha tin films are fully strained up to 400 nm. Temperature dependent results show that the phase transition temperatures of our

films can be increased to 120°C, and the transition temperature increases as the film thickness decreases. This enhancement is confirmed by both temperature-dependent XRD and Raman results. The linear thermal expansion coefficient of alpha tin film is extrapolated for the first time to be 7.14×10^{-6}/°C. Our study shows that strain is an effective way to engineer the thermal stability of the alpha tin films. The thermal stability enhancement ensures the reliability of all the following electrical and thermal characterizations above room temperature. We have observed magnetoresistance and superconductivity in these films.

9:00 AM TP02.13.03
Anisotropic and Quasi-Ballistic Thermal Transport in Nanostructure Embedded GaSb Thin-Film Semiconductors <u>Yee Rui Koh</u>[3, 2, 1], Hong Lu[5], Arthur Gossard[4] and Ali Shakouri[1]; [1]Purdue University, West Lafayette, Indiana, United States; [2]Birck Nanotechnology Center, West Lafayette, Indiana, United States; [3]Electrical and Computer Engineering, Purdue University, West Lafayette, Indiana, United States; [4]University of California, Santa Barbara, Santa Barbara, California, United States; [5]Nanjing University, Nanjing, China.

Gallium antimonite (GaSb) is a promising candidate for the high speed electronic and long wavelength photonic devices, e.g. infrared detectors, photovoltaic, diode lasers, etc. Previous measurements and theoretical studies focused on the bulk thermal conductivity of the GaSb. [1][2] For submicron devices or at high frequencies, it is important to study thermal transport in the GaSb thin films. Time-domain thermoreflectance (TDTR) is used to study thermal transport in 2μm thick GaSb film with embedded semimetallic ErSb nanoparticles. [3] We show that GaSb is among few non-alloy semiconductors showing the phonon quasi-ballistic effects. The apparent cross-plane thermal conductivity of pure GaSb thin film sample drops by ~15% when the pump laser modulation frequency is increased from 0.8 MHz to 10 MHz at room temperature. The frequency dependence of the cross-plane thermal conductivity disappears with the presence of 3%-20% ErSb nanoparticles. We also employed the beam reduction TDTR method [4] to study the anisotropic thermal transport in GaSb thin films. The ratio of cross- to in-plane thermal conductivity of the ErSb: GaSb samples vary from ~0.2 for pure GaSb to ~0.7 for GaSb with 20% ErSb nanoparticles volume concentration. Potential causes of the anisotropy from lattice mismatch with the substrate to self-organization of embedded nanoparticles in nanowire forms are discussed. Detailed temperature dependence measurements for both in-plane and cross-plane thermal conductivity of the ErSb:GaSb samples are also presented.

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[3] H. Lu, D. G. Ouellette, S. Preu, J. D. Watts, B. Zaks, P. G. Burke *et al.*, *Nano Lett.* (2014) **14**, 1107-1112.
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9:15 AM TP02.13.04
Thermal-Optical Readout of Multi-Level Thermal Emissivity $Ge_2Sb_2Te_5$ Patterns <u>Miao Wang</u>, Sichao Hou and Ming Su; Northeastern University, Boston, Massachusetts, United States.

$Ge_2Sb_2Te_5$ thin film (100 nm) can be patterned with multi-level crystalline and thermal emissivity states using laser in large scale. Various patterns can be fabricated by tuning laser power and speed. X-ray diffraction (XRD) and infrared analysis results show that $Ge_2Sb_2Te_5$ thin film has different thermal emissivity at different crystalline states. In-situ repeated heating of the $Ge_2Sb_2Te_5$ thin film confirms the tendency between crystalline and thermal emissivity change. Both the infrared image and thermal emissivity can be readout by infrared camera. The colorful infrared image enables easily identification of $Ge_2Sb_2Te_5$ crystallite change. The multi-level emissivity states of patterns produce multi-level optical data storage for future phase-change devices.

9:30 AM TP02.13.05
A Finite Element Model of Grain Boundary Melting in Phase Change Memory Devices Based on Thermodynamic Principles <u>Jake Scoggin</u>, Helena Silva and Ali Gokirmak; ECE, University of Connecticut, Storrs, Connecticut, United States.

Phase change memory (PCM) stores information in the phase (conductive crystalline or resistive amorphous) of glass forming materials, typically a chalcogenide. One of the largest hurdles for PCM is the tradeoff between data retention and switching speed. Wang *et al*. [1] demonstrated increased switching speed without decreased retention by reducing grain size in phase change materials. We propose grain boundary melting (GBM) as the mechanism behind this improvement. With nanocrystalline phase change materials, reset may be achieved with only partial amorphization of the active volume, leaving isolated crystalline nuclei. This decreases the volume of amorphization required for reset while providing multiple sites for simultaneous crystallization for set, reducing power and time requirements for both reset and set operations. Additionally, classical nucleation theory (CNT) predicts that the minimum stable grain size (r_c) increases with temperature, effectively lowering the melting temperature for smaller grains.
We model GBM based on thermodynamic properties of $Ge_2Sb_2Te_5$ (GST). We obtain phase and temperature dependent specific heats (C_p) as explained in our previous work [2] with an additional constraint of the specific heat difference for the liquid and crystalline phases ($\Delta C_{p,lc}$) at the glass transition extracted from the fragility [3] based on ultra-fast DSC measurements of GST [4]. We determine the temperature dependent r_c with CNT using free energy and entropy differences between phases (ΔG_{lc} and ΔS_{lc}) calculated from $\Delta C_{p,lc}$. Finally, we obtain temperature and size dependent GBM rates based on ΔG_{lc} and the kinetic growth velocity (U_{kin}) extracted from ultra-fast DSC measurements [4]. We incorporate GBM in our finite element phase change model ([5]–[8]) and simulate reset and set for reported device and grain sizes [1]. We show that GBM reduces set and reset times as grain sizes decrease and contributes to increased PCM variability due to device-to-device and cycle-to-cycle grain map changes.
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9:45 AM TP02.13.06
Cross Interface Model for Thermal Transport through Cross Contact <u>Xiaoxiang Yu</u>[1], Yucheng Xiong[2], Nuo Yang[1] and Dongyan Xu[2]; [1]Huazhong University of Science and Technology, Wuhan, China; [2]The Chinese University of Hong Kong, Hong Kong, China.

The van der Waals (vdW) contact has emerged as a growingly important role due to their extensive presence in nanostructured materials and systems, such as assembled nanostructure building blocks array and vdW heterostructure, which recently shows massive potential as various functional electronic and optoelectronic devices. These applications require a thorough understanding of thermal transport through the vdW cross contact to address the increasingly severe heat dissipation problem in electronics. Here, we report on a systematic study of thermal transport through the vdW cross contact between individual

copper phthalocyanine (CuPc) nanoribbons. We establish a brand new analytic model, cross interface model (CIM), for heat conduction across an interface with overlap, which is similar to to the two-temperature model and the two-channel heat transport model, and apply the model to our experiments and numerical simulations. The experimental results by suspended thermal bridge methods reveal that the interfacial thermal conductance per unit area (G_{CA}) between individual CuPc nanoribbons is on the order of 10^5 W/m^2-K, which is two to five orders of magnitude smaller than that of the conventional solid-solid interfaces. Molecular dynamics simulations reproduce well the experimental results and suggest that the small G_{CA} is ascribed to the weak adhesion strength and the large separation distance of cross contact between CuPc nanoribbons. This work gives an analytic model for heat conduction in cross contact interface and points out that the deteriorative interfacial thermal transport between small molecular nanostructures remains significant bottlenecks for heat dissipation in related electronic devices.

10:00 AM BREAK

10:30 AM TP02.13.08
Acoustic Phonon Spectra Modification and Light Emission Properties of Rare Earth Doped Polycrystalline Alumina Elias Penilla[1], Fariborz Kargar[2], Alexander A. Balandin[2] and Javier E. Garay[1]; [1]University of California, San Diego, La Jolla, California, United States; [2]University of California, Riverside, Riverside, California, United States.

The high thermal conductivity of Polycrystalline Alumina (PCA) make it a promising material for high power light emitting applications such as high energy lasers because deliverable power scales with thermal conductivity. Recently we have developed material processing methods that result in high optical quality PCA doped with higher than equilibrium concentrations of rare earth (RE) dopant atoms. We present photo luminescent (PL) spectroscopy and Brillouin—Mandelstam spectroscopy (BMS) studies of transparent PCA with RE doping levels sufficient for optoelectronic applications (0.1-0.5 at%). The PL results confirm RE incorporation and optical gain experiments demonstrate light amplification [1]. The BMS results show that this relatively low concentration of RE atoms incorporated into the PCA produces a significant change in the acoustic phonon spectrum. The velocity of the transverse acoustic phonons decreases by ~600 m/s at the RE density of only 0.1%. [2]. We discuss the results with regard to the tunability of the phonon spectrum and implications on solid state laser gain media.
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10:45 AM TP02.13.09
Thermal Analysis for Laser Scanning Pattern Evaluation in Laser Aided Additive Manufacturing Kai Ren[1], Youxiang Chew[2], Jerry Ying-Hsi Fuh[1], Yunfeng Zhang[1] and Guijun Bi[2]; [1]National University of Singapore, Singapore, Singapore; [2]Singapore Institute of Manufacturing Technology, Singapore, Singapore.

Laser Aided Additive Manufacturing (LAAM) is one of the key metal 3D printing technologies for surface cladding or fabrication of near-net shape parts. Its laser scanning pattern strategies can have significant effects on the temperature distribution for multi-bead, multi-layered additive manufacturing processes. Differences in thermal history would result in distinct residual stress distribution and substrate deformation. This paper proposed a laser scanning pattern evaluation frame to compare different scanning paths. In the frame, a novel efficient 3D thermo-history analysis finite element (FE) model was developed to predict temperature field evolution among the component for arbitrary scanning patterns during the whole deposition process. A thermo history evaluation method was designed to compare different scanning alternatives by selected criteria in homogeneity. The evaluation frame was validated by depositing a rectangular clad on a cuboid substrate with four different scanning patterns. The evaluation frame predicted the width-wise Zigzag scanning pattern would produce largest distortion. The distortion measurement outcomes agreed well with the predicting results.

11:00 AM TP02.13.10
Bi-Layered CVD Diamond—A New Thermal Solution for High Power Density Electronics Firooz Faili, Gruffudd Williams, Thomas Obeloer and Daniel Twitchen; Element Six, Santa Clara, California, United States.

High frequency RF, laser diodes and some silicon ASIC devices are a particular class of devices where power densities are pushing limits of kw/cm2. Many of these devices are now reaching the limit of current heat spreading technologies. Consequently, there is a continual need to improve thermal performance while reducing the cost.
To date, the integration of SiC (400 W/mK) substrates with GaN has provided the best option for GaN HEMT and MMIC technology for high power applications. However, despite the use of SiC substrate, adequate heat spreading is still the limiting factor in determining the maximum power dissipation for GaN based electronics. As such, the path to long-term reliability is often achieved by de-rating the maximum power dissipation. A far better heat spreading solution incorporating CVD diamond (2000 W/mK) has the potential for a factor of 3× or higher increase in power density relative to current state-of-the art GaN devices.
In this presentation we demonstrate success in integrating a thinner layer of very high thermal conductivity CVD diamond with lower thermal conductivity CVD diamond consistent with targeted thermal performance at lower cost. In the built of this hybrid material, the high thermal conductivity material will be the bonding interface to the RF/microwave device to enable immediate heat spreading. The lower thermal conductivity material will be the bonding interface to the heat sinking side, enabling cost effective heat transport. The integration of the layers is achieved through back to back deposition of the bi-layers. The challenge is to make the synthesis conditions conducive to achieving material quality and matching of the bi-layers mechanical properties to fabricate a robust final product.
The presentation will report on the analysis and results obtained by using Lee, S et al, to establish the limit of spreading layer thickness (layer 1). The model indicated that for a 100 mm x 100 mm hot spot, minimum thermal spreading resistance is achievable with minimum thickness of about 150-200 mm. The confirmation of a minimum spreading that would lead to minimum spreading resistance was verified for Biot numbers varying from <1 to >100. Required layer 2 thickness (low thermal conductivity material) to maintain lowest thermal resistance and maintaining mechanical integrity and thickness specifications was established by classical heat transfer solutions.
Additionally, an Abaquas model for typical multi-finger RF device with and without a diamond heat spreader was developed to compare the effect of graded concept where the thickness of high/low thermal conductivity is part of the sensitivity analysis and part of this presentation.
Three different techniques were used to judge the quality and success of the output material. These are through plane characterization using optical and thermal methods and in-plane measurement using heated bar and the results of those findings are a part of this presentation.