

SYMPOSIUM CM02

Structure–Property Relations in Non-Crystalline Materials
November 26 - November 29, 2018

Symposium Organizers

Katharine Flores, Washington University
John Mauro, The Pennsylvania State University
Tanguy Rouxel, University de Rennes
Yunfeng Shi, Rensselaer Polytechnic Institute

* Invited Paper

SESSION CM02.01: Distinctions and Commonalities of Glasses
Session Chairs: Katharine Flores, John Mauro, Tanguy Rouxel and Yunfeng Shi
Monday Morning, November 26, 2018
Hynes, Level 2, Room 200

8:00 AM *CM02.01.01

The Continuous Random Network—A Review [Frans Spaepen](#); School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts, United States.

The continuous random network (CRN), introduced by Zachariasen for oxide glasses, became the paradigm for the structure of covalent, directionally bonded amorphous materials. Elemental amorphous Si and Ge, which form one of the simplest CRNs, have been studied for more than fifty years. We will review their structure, thermodynamic properties, phase transformations, flow and structural relaxation. We will revisit some striking features, such as their density being higher than that of the diamond cubic crystal, their negative activation volumes for crystallization, and the bimolecular kinetics of their structural relaxation.

8:30 AM *CM02.01.02

Understanding Indentation Behavior of Oxide Glass from Molecular Dynamics Simulation [Liping Huang](#); Rensselaer Polytechnic Institute, Troy, New York, United States.

To evaluate the damage resistance of glasses, instrumented indentation using sharp indenters is the method of choice, as it can mimic real-life damage incidents under controlled conditions. Furthermore, indentation provides a useful system to study crack initiation, as unstable crack propagation is prevented by the highly localized stress state. However, unravelling the nature of structural change under indentation is a formidable task in experiment because of the complexity that originates from the atomic-scale disorder of glass, and the experimental difficulties associated with the *in-situ* investigation at a local scale (tens of microns) under very high stresses. To this end, computer simulations can provide an important complement to experimental approaches. In this work, we carried out large scale molecular dynamics (MD) simulations to investigate the effect of quench pressuring during hot compression and chemical composition variation on the response of glass to nanoindentation. A rigid hollow Vickers indenter made of carbon atoms is used to indent the glass sample with a fixed loading rate, during which atoms in the indenter interact with the glass via a repulsive force field. To minimize the boundary condition effects in simulated nanoindentation tests, large samples of several hundred nm in lateral dimensions are used. The indenter angle is varied to study the effect of the indenter sharpness on the deformation of glasses, as what has been done in experiments. Short- and medium-range order of the plastically deformed glass are compared with those in the undeformed region. These simulated nanoindentation tests reveal how the stress field and glass structure evolve with the deformation underneath the indenter, which in turn shed light on the degree of densification and pile-up in different glasses.

9:00 AM *CM02.01.03

Connecting Mechanical Properties of Amorphous Polymers to Chain Alignment and Entanglements Marco A. Galvani Cunha and [Mark O. Robbins](#); Johns Hopkins Univ, Baltimore, Maryland, United States.

Polymer glasses are frequently used in a form of additive manufacturing called fused filament fabrication (FFF). Melts are extruded onto previous layers and form a weld before the temperature drops below the glass transition temperature. Extrusion is typically fast enough to produce significant chain alignment that affects the welds formed by diffusion between layers and leads to a strongly anisotropic amorphous structure. Improved understanding of the structure property relations in printed parts is essential to optimizing FFF for structure-critical parts and FFF offers unique opportunities to create non-crystalline materials with continuously tunable local alignment and entanglement densities.

We have used molecular dynamics simulations of a generic polymer model to examine the relaxation of aligned melts, including the evolution of alignment and the entanglement density in bulk regions and at the interfacial weld. The mechanical properties of the resulting structures are then studied under tensile and shear loading. Local structure determines the initial yield stress while entanglements lead to strain hardening and crazing that strongly affects the total fracture energy. Alignment of chains along the deposition direction means that there are more weak van der Waals bonds in the perpendicular directions. This reduces the yield strength for shear and tensile failure perpendicular to the deposition axis. Alignment and changes in entanglement density also produce profound changes in the strain to failure and ultimate fracture energy. Welded regions are most affected by diffusion during cooling and may be stronger than adjacent bulk material which has higher entanglement density than the weld but is also strongly aligned.

9:30 AM *CM02.01.04

Modeling Slip Statistics and Dynamics in Bulk Metallic Glasses, Granular Materials and Other Systems [Karin Dahmen](#)¹, Wendelin J. Wright²,

Dmitry Denisov³, Todd Hufnagel⁴, Peter K. Liaw⁵, Peter Schall³ and Jonathan Uhl⁶; ¹University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; ²Bucknell University, Lewisburg, Pennsylvania, United States; ³University of Amsterdam, Amsterdam, Netherlands; ⁴Johns Hopkins University, Baltimore, Maryland, United States; ⁵The University of Tennessee, Knoxville, Tennessee, United States; ⁶Los Angeles, Los Angeles, California, United States.

Slowly strained solids deform via intermittent slips that exhibit a material-independent statistics and dynamics. We compare predictions of a simple model for the plastic deformation, the slip statistics and dynamics, and time series properties to experiments on slowly deformed bulk metallic glasses and granular materials. We highlight measures that can be used to differentiate between different systems and explain connections to other systems with avalanches. Predictions for future experiments will be discussed. The results are important for transferring results across scales and material structures.

10:00 AM BREAK

10:30 AM *CM02.01.05

Tailoring Glass Structure to Break the Speed Record of Phase-Change Memory Evan Ma; Johns Hopkins University, Baltimore, Maryland, United States.

This talk describes our recent success (F. Rao *et al.*, Science 2017) in controlling the amorphous structure of chalcogenide Sc-Sb-Te glass to accelerate its crystallization, reaching an unprecedented operation speed for memory and switch applications. Specifically, we have designed a new phase-change memory alloy with drastically reduced crystal nucleation stochasticity from the parent amorphous phase. The ultrafast transition between the two metastable states accomplishes sub-nanosecond switching for cache-type phase-change random-access memory (PCRAM) technology. This is a milestone in memory materials, because operation speed is currently a key challenge in PCRAM technology, especially for achieving sub-nanosecond high-speed cache-memory (such as SRAM). The limiting factor in the commercialized PCRAM products is the writing speed (~currently several tens of nanoseconds), which originates from the stochastic crystal nucleation during the crystallization of the amorphous Ge₂Sb₂Te₅ glass. Here we use alloying into the parent glass to speed up the crystallization kinetics by orders of magnitude. The newly designed chalcogenide Sc-Sb-Te alloy enables a record-setting writing speed (as short as ~700 picoseconds) in a conventional PCRAM device, with no requirement for pre-programming or additional device design. This ultrafast crystallization stems from the reduced stochasticity of nucleation via geometrically matched and robust chemical bonds that stabilize crystal precursors in the amorphous state, which are found via *ab initio* simulations to exhibit long life-times, shortening the incubation time for crystallization. This discovery is an example of physical metallurgy principles in action, using atomic-scale insight into glass structures (bonding configurations and sub-critical nuclei) to control properties. For details, see F. Rao *et al.*, Science **358** (6369), 1423 (2017).

11:00 AM *CM02.01.06

The Interaction Between Stress, Light and Chemistry in Glass Josef Zwanziger; Chemistry, Dalhousie Univ, Halifax, Nova Scotia, Canada.

Application of mechanical stress to glass causes interesting changes in how it transmits light. This interplay is summarized by the elasto-optic tensor, the key metric for technological applications including zero stress-optic glass, and reduced stimulated Brillouin scattering glass. Fundamentally, these effects are controlled by the glass chemistry, and in particular the nature of the chemical bonds that make up the glass. We will summarize our approach to this problem, which is focused on both an empirical and *ab initio* approach to the structure-property relations governing the elasto-optic tensor. We will describe the control of the stress-optic response through judicious choice of glass chemistry, and also describe our current progress in understanding and developing glass with reduced stimulated Brillouin scattering. We will include discussion of both average properties and energy-dispersive effects. We will show how these effects may be computed *ab initio*, with a reasonable trade-off between accuracy and speed, and illustrate a bond-based model we are developing that attempts to put in simple terms the empirical relations we have discovered.

11:30 AM *CM02.01.07

Ductility and Residual Liquidity in Metallic Glasses Takeshi Egami^{1,2} and Wojciech Dmowski¹; ¹Univ of Tennessee, Knoxville, Tennessee, United States; ²Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

Lack of ductility is one of the major shortcomings of bulk metallic glasses which hamper their wide application as structural material. Ductility is a complex mechanical property which is difficult to characterize precisely. In a sense metallic glass is always microscopically ductile, because applied shear stress can locally liquefy glass. But it has no work-hardening, thus often local yielding results in catastrophic shear failure. In order to achieve macroscopic ductility glass must be able to relax local stress concentration before it starts macroscopic shear band or crack. In our view the key is the residual liquidity in glass. The structure of supercooled liquid is heterogeneous, and the frozen-in structure at the glass transition contains weak liquid-like and strong solid-like regions. It is difficult to assess such heterogeneity directly from the structure itself, but it is possible to characterize it through the structural response to applied stress. We determined the anisotropic pair-density function (PDF) of various metallic glass samples under uniaxial stress by high-energy x-ray diffraction using the spherical harmonics expansion of the structure function $S(Q)$ and the PDF. The measured anisotropic PDF at large distances agrees with the one expected for affine (uniform) deformation which determines the long-range strain e_x . However, at short distances it deviates from the affine deformation, and at the first neighbour the local strain, e_l , is smaller than e_x . The deviation from the affine deformation occurs because of local liquid-like regions, so that the ratio $G = e_l/e_x$, or $\Delta G = 1 - G$, characterizes the strength of residual liquidity in glass. We found that the ratio e_l/e_x is closely related to ductility. In particular, $G_c = 0.77$ is the threshold which separates brittle and ductile behaviors. If $G > G_c$ the samples are brittle, whereas if $G < G_c$ the samples are ductile. Thus we suggest that the percolation of the liquid-like regions results in ductile behaviour. This new parameter is compared to other criteria for ductility.

SESSION CM02.02: Structures of Glasses
Session Chairs: Katharine Flores and John Mauro
Monday Afternoon, November 26, 2018
Hynes, Level 2, Room 200

1:30 PM *CM02.02.01

Network Structures and Dissolution Behavior of Specialty Oxide Glasses Richard K. Brow; Department of Materials Science and Engineering, Missouri University of Science and Technology, Rolla, Missouri, United States.

Borate, phosphate, and borophosphate glasses have been developed for a variety of technological applications, including fast ion conductors, optical substrates, and biomedical devices. For the latter, compositions are often tailored to control the rate at which physiologically significant ions are released to induce the desired biomedical response. These reaction rates depend on the hydrolysis of bonds that link neighboring glass forming polyhedra as well as the hydration of bonds associated with other metal cations that modify the glass forming network, and so detailed understanding of the glass structure connects composition to design performance. For borate and borophosphate glasses, the network hydrolysis rates decrease with increasing fractions of tetrahedral borate. For phosphate glasses, hydrolysis is not significant in neutral pH physiological conditions, but the hydration rates of metal cations are faster when they are linked to chain-forming P-tetrahedra than when they are linked to a chain-terminating tetrahedron. Quantitative and qualitative structural information about Na-Ca-borate, phosphate, and borophosphate glasses, obtained by techniques like nuclear magnetic resonance spectroscopy, Raman spectroscopy, and ion chromatography, will be described and used to explain their bio-functionality.

2:00 PM CM02.02.02

Progress in Scattering with the Neutron Electrostatic Levitator (NESL) at the Spallation Neutron Source [Dante Quirinale](#); Neutron Technologies Division, Spallation Neutron Source, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States.

There is great interest in a developing understanding of the relationships between structures and dynamics in liquid and glassy systems. Metallic liquids, which exhibit a degree of short and medium range ordering, are well suited to scattering probes, but there are many difficulties associated with selecting the proper furnaces for such studies. The Neutron Electrostatic Levitator (NESL) [1] at the Spallation Neutron Source is a containerless environment developed for challenging systems, including high temperature alloys and undercooled liquids. It provides a high vacuum, high purity, non-contact environment for fundamental studies of materials at wide temperature ranges. Combined with x-ray scattering data and isotopic substitution, the system is well suited to structural characterization of liquids via pair distribution function analysis, as has been successfully demonstrated at the Nanoscale Ordered Materials Diffractometer (NOMAD) [2,3].

A series of upgrades has improved the stability of the levitator and enabled new avenues of exploration. Recently, the system has been operated at the Wide Angular Range Chopper Spectrometer (ARCS) [4] and is currently being commissioned at the Cold Neutron Chopper Spectrometer (CNCS) [5] for high resolution inelastic and quasi-elastic scattering, enabling non-contact probes of excitations in glass forming liquids as well as high temperature self-diffusion measurements. The current capabilities and characteristics of the levitation furnace, progress in inelastic scattering measurements, and early results from the commissioning at CNCS will be discussed.

[1] Mauro, N. A., A. J. Vogt, K. S. Derendorf, M. L. Johnson, G. E. Rustan, D. G. Quirinale, A. Kreyszig et al. "Electrostatic levitation facility optimized for neutron diffraction studies of high temperature liquids at a spallation neutron source." *Review of Scientific Instruments* 87, no. 1 (2016): 013904.

[2] Neufeind, Jörg, Mikhail Feygenson, John Carruth, Ron Hoffmann, and Kenneth K. Chipley. "The nanoscale ordered materials diffractometer NOMAD at the spallation neutron source SNS." *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 287 (2012): 68-75.

[3] Johnson, M. L., M. E. Blodgett, K. A. Lokshin, N. A. Mauro, J. Neufeind, C. Pueblo, D. G. Quirinale et al. "Measurements of structural and chemical order in Zr 80 P t 20 and Zr 77 R h 23 liquids." *Physical Review B* 93, no. 5 (2016): 054203.

[4] Abernathy, Douglas L., Matthew B. Stone, M. J. Loguillo, M. S. Lucas, O. Delaire, Xiaoli Tang, J. Y. Y. Lin, and B. Fultz. "Design and operation of the wide angular-range chopper spectrometer ARCS at the Spallation Neutron Source." *Review of Scientific Instruments* 83, no. 1 (2012): 015114.

[5] Ehlers, Georg, Andrey A. Podlesnyak, Jennifer L. Niedziela, Erik B. Iverson, and Paul E. Sokol. "The new cold neutron chopper spectrometer at the Spallation Neutron Source: design and performance." *Review of Scientific Instruments* 82, no. 8 (2011): 085108.

2:15 PM CM02.02.03

High-Resolution 3D Imaging for Drug Micro-Structure Characterization and Release Prediction [Zhen Liu](#); MRL, Merck & Co., Inc, West Point, Pennsylvania, United States.

Modern drug delivery increasingly relies on micro- and nano-structures to achieve specific release rate and therapeutic target. The delivery systems modulate drug release via engineering control of the API domain and pore size. Other approaches involve the use of functional coating or performance-enabling excipients. The small-scale nature of pores, drug domains, and delivery vehicles demands higher resolution technique to characterize. High-resolution image-based characterization has been broadly utilized in drug product development for fundamental understanding on the process-property-performance interplay and optimizing formulation process and design. It finds applications in various novel drug release systems such as tailoring rate-limiting film coat thickness where the pore formation is critical to control drug release and interrogating the underlying mechanism of in-situ drug nanoparticle formation from amorphous solid dispersions in dissolution media for solubility enhancement. 3D micro-imaging can qualitatively visualize micro-structures, quantify their spatial and chemical distribution, and predict release behavior. In recent years, the emerging image-based numerical simulation has received significant traction and plays an important role on predicting drug release performance. Information-rich 3D images can be converted to characteristic drug transport parameters through intelligent analysis and applied to numerical simulation models to predict release performance. This image-based simulation approach represents a potential paradigm shift in drug design and evaluation, with significantly reduced evaluation time, improved release performance, and lowered in-vitro and in-vivo experiment cost.

2:30 PM CM02.02.04

Nanoscale Imaging of Bulk Bottlebrush Polymers Using Helium-Ion Microscope [Nikolay Borodinov](#)¹, Alex Belianinov^{1,2}, Dongsook Chang¹, Jan-Michael Carrillo¹, Matthew J. Burch¹, Yuewen Xu³, Anton V. Ievlev^{1,2}, Bobby G. Sumpter¹ and Olga Ovchinnikova^{1,2}; ¹Center for Nanophase Materials Science, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ²Institute for Functional Imaging of Materials, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ³Kimberly-Clark Corporation, Irving, Texas, United States.

Recently, bottlebrush polymers have attracted significant interest due to their potential applications in drug delivery and electronics. The tunability of their properties, stemming from the diversity of sidechains and their spatial arrangement, have emphasized their industrial potential as compared to the linear macromolecules. In this context, the structural information and organization of these systems play a major role in the rational design of functional bottlebrush polymers. Specifically, direct observation of the molecular organization can reveal inter-chain interaction phenomena and explain the fundamental physical properties of these systems. Here, we report a new method to analyze bulk macromolecular chain arrangement of bottlebrush polymers based on Helium Ion Microscopy (HIM). By using the HIM we were able to quantify structural nematic-type ordering in an amorphous polymer bottlebrush system. High-resolution imaging coupled with data analytics has proven to highlight the location and distribution of the polymer backbones, after oxygen plasma-generated height contrast; as well as map changes in the backbone spatial arrangement as a function of thermal annealing. Our experimental findings are corroborated by the coarse-grained molecular dynamics simulations. Overall, this approach can generate clear insights on the internal structure of amorphous materials and provides a complimentary information channel to scattering techniques and theoretical modelling.

This work was performed at the Center for Nanophase Materials Sciences, a US Department of Energy Office of Science User Facility. This research used resources of the Oak Ridge Leadership Computing Facility, which is a DOE Office of Science User Facility supported under Contract DE-AC05-00OR22725. The authors acknowledge Scott Retterer at the Center for Nanophase Materials Science at Oak Ridge National Laboratory for helpful input

and discussion

2:45 PM CM02.02.05

Correlating Nanoscale Structural Heterogeneity to Glass Forming Ability and Mechanical Properties of Metallic Glasses Soohyun Im², Jared Johnson², Gabriel Calderon Ortiz², Menglin Zhu², Pengyang Zhao², Geun Hee Yoo¹, Eun Soo Park¹, Yunzhi Wang² and Jinwoo Hwang²; ¹Seoul National University, Seoul, Korea (the Republic of); ²Materials Science and Engineering, The Ohio State University, Columbus, Ohio, United States.

We determine the nano-to-mesoscale structural heterogeneity in metallic glasses (MGs) using 4-dimensional (4D) nanodiffraction in scanning transmission electron microscopy (STEM). Structural heterogeneity in MGs has been suggested by both experiments and simulations previously. The heterogeneity must involve local structural ordering at the nanoscale, commonly known as medium range order (MRO), some of which has been studied using small electron probes in the past. However, the statistically reliable information on how such MRO constitutes the heterogeneity has remained difficult to determine. Our new approach to determine the MRO and structural heterogeneity involves 4D-STEM, which uses a new-generation pixelated fast STEM detector that allows for the continuous collection of the diffraction patterns from a large area of the MG sample. Using angular correlation and intensity variance analyses, the diffraction patterns can then be converted to real space maps of the local ordering, which we use to precisely determine the type, size, distribution, and volume fraction of MRO. We will present two cases of how the heterogeneity affects the important properties of MGs, one is the glass stability in Ti-based MGs, and the other is the ductility of Zr-based MGs. To connect the structural heterogeneity to ductility, we use a new mesoscale simulation that incorporates the experimentally determined heterogeneity, which can simulate realistic shear band formation and overall deformation that match the spatial and temporal scales of the deformation of real MGs.

3:00 PM BREAK

3:30 PM *CM02.02.06

Structure is the Organization Plan of Glasses—But Dynamics Might Bring Deeper Insight Bernhard Frick¹, Henriette W. Hansen^{1,2,3} and Kristine Niss²; ¹Institut Laue–Langevin, Grenoble, France; ²Roskilde University, Roskilde, Denmark; ³Chalmers, Götheborg, Sweden.

It is well known that for a large number of glass forming liquids the static structure factor, $S(Q)$, shows no or only subtle changes when passing from the liquid into the glass. In contrast the dynamic structure factor $S(q,\omega)$ of simple or more complex glass forming liquids evidences in the GHz - THz frequency range and close to the glass transition clear and common signatures which have been addressed by several theories over the last decades. In spite of large experimental and theoretical activity in this field the glass transition is still not fully understood. Quasielastic neutron scattering plays a vital role for the experimental investigation of dynamic properties of disordered materials, glasses and undercooled liquids. We will give a brief overview over typical experimental findings near the glass transition and over recent instrumental progress on neutron spectrometers before presenting some examples. We then focus on our recent investigations on simple organic, hydrogen bonded and ionic liquids for which we have probed the dynamics near the glass transition by simultaneous dielectric and neutron spectroscopy. For these simultaneous experiments we have controlled both temperature and pressure which did allow us to map lines in the (P,T)-diagram along which the dynamics is unchanged and therefore is isochronous over a wide time range.

4:00 PM CM02.02.07

Spatially Heterogeneous Dynamics in Metallic Glass Nanowires Imaged by Electron Correlation Microscopy Debaditya Chatterjee¹, Pei Zhang¹, Jitisa Ketkaew², Jan Schroers² and Paul M. Voyles¹; ¹Department of Materials Science and Engineering, University of Wisconsin–Madison, Madison, Wisconsin, United States; ²Department of Mechanical Engineering and Materials Science, Yale University, New Haven, Connecticut, United States.

We have used electron correlation microscopy (ECM) to image the nanometer scale heterogeneities in the relaxation dynamics of the supercooled liquid of a metallic glass forming alloy [1]. The length and time scales of the heterogeneous dynamics are central to the glass transition and influence nucleation and growth of crystals from the liquid. Electron correlation microscopy (ECM) experiments use time-resolved tilted dark field transmission electron microscopy with sub-nanometer resolution for direct measurement of those length and time scales. ECM data on Pt-based metallic glass nanowires above the glass transition temperature (T_g) reveal a relaxation time scale that varies from a few seconds to hundreds of seconds and a length scale that varies from 0.8 to 1.4 nm. They also demonstrate the existence of a ~1 nm thick near-surface layer with an order of magnitude shorter relaxation time than inside the bulk which may influence crystallization of the wires. Additional measurements of the surface layer relaxation time below the bulk T_g , and its connection to enhanced surface diffusion in metallic glasses and surface crystallization will be discussed.

[1] P. Zhang, J. J. Maldonis, Z. Liu, J. Schroers, P. M. Voyles, Nat. Commun. **9**, 1129 (2018)

4:15 PM CM02.02.08

Kinetic Metallic Glass Evolution Model Thomas J. Hardin and Christopher A. Schuh; Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Metallic glass is a heterogeneous composite on the scale of a few nanometers; the structure of the glass on this scale governs its macroscopic thermo-mechanical response. This structure evolves in response to thermal and mechanical loading; this evolution is mediated by discrete kinetic events in which clusters of atoms locally rearrange themselves. We present a model of this structural evolution and mechanical response which consists of a thermodynamic state space, density of states, and models for relaxation and shear transformation events which move the glass through that state space. We implement this model in a homogenized statistical sense and compare to homogeneous relaxation and flow data previously in literature; we also implement it in a discrete mesoscale framework. We conclude with a discussion of gaps in the current understanding of the fundamental structure of metallic glass.

4:30 PM CM02.02.09

Atomic-Level Insight into Amorphous Aluminum Oxide Structure—Atomistic Simulation vs *In Situ* Experiment Marcela E. Trybula^{1,2}, Przemyslaw W. Szafranski³, Pavel A. Korzhavyi^{2,4}, Nikolay A. Vinogradov⁵ and Edvin Lundgren⁶; ¹Institute of Metallurgy and Materials Science Polish Academy of Sciences, Krakow, Poland; ²Department of Materials Science and Engineering, KTH-Royal Institute of Technology, Stockholm, Sweden; ³Department of Organic Chemistry, Faculty of Pharmacy, Jagiellonian University Medical College, Krakow, Poland; ⁴Institute of Metal Physics, Ural Branch of RAS, Ekaterinburg, Russian Federation; ⁵MAX IV Laboratory, Lund University, Lund, Sweden; ⁶Synchrotron Radiation Research, Lund University, Lund, Sweden.

Structural disorder in amorphous solids may depend on the method of their preparation. An easily-accessible method is electrochemical anodization of metal surface, which may result in formation of periodic voids, or pores, for example in a well-known Al anodization process [1,2]. These voids, or pores, are thought to derive from the morphological instabilities underlying the initial stage of oxidation [1]. Such nanostructuring can have a profound impact on local structural anisotropy or hierarchical ordering of atom clusters build-up in the structure of the amorphous Al oxide film.

In this contribution, we determine the structural and topological descriptors of bulk alumina to compare them with those obtained from *in situ* synchrotron-based experiment of porous anodic aluminum oxide scale growth. We also discuss the impact of self-assembling ring structure on chemical and topological short- and intermediate-range ordering in bulk alumina in the light of *in situ* oxide growth. The interpretation of our *in situ* X-ray diffraction data is supported by molecular dynamics simulations and DFT-based calculations. These allowed us to capture physical phenomena accompanying *in situ* anodic aluminum oxide growth. Obtained calculation results agree well with the available experimental [3] and computational data [4].

Literature:

- [1] K. R. Hebert, et al.: Nat. Mater. 2011, 11, 162–166.
- [2] N. A. Vinogradov et al.; ACS Appl. Nano Mater. 2018, 1, 1265-1271
- [3] P. Lamparter and R. Knieb Physica B 1997, 234-236, 405-406.
- [4] G. Gutierrez and Borje Johansson, Phys. Rev. B 65, 104202:1-9

4:45 PM CM02.02.10

Hierarchical Machine Learning to Decode Structural Origin of Heterogeneous Deformation in Disordered Materials Qi Wang and Anubhav Jain; Lawrence Berkeley National Lab, Berkeley, California, United States.

When subjected to external stimuli such as mechanical loading, atoms in disordered solids respond heterogeneously. Due to lack of representations to resolve the subtle packing difference around atom sites and approaches to deal with the long-range correlation involved, it is hard to quantitatively predict this heterogeneous, site-specific response solely from the structure. Here, by designing a robust hierarchical machine learning framework, we show that it is possible to predict the mechanical heterogeneity in disordered solids *a priori*, directly from the quenched structural state itself. We encyclopedically create a large pool of 810+ site descriptors, from 40+ sets of structural measures, spanning topological and chemical short- and medium-range order, and develop a novel hierarchical scheme to further extend the studied scale to an unprecedentedly long-range while still retaining good interpretability and generality. Impressive predictability is achieved in a fairly large strain regime, suggesting a long-lived inheritance of the quenched state until later obstructed by shear banding. The framework is robust over a range of compositions and processing conditions and can well detect the site environments tuned by these conditions. We also identify a bag of promising structural signatures unrevealed previously, with their predictability exhaustively benchmarked and discussed. This hierarchical learning framework is general and could potentially be applied to decode structural origin of any site-specific properties in the family of disordered materials.

SESSION CM02.03: Poster Session I: Structure-Property Relations in Non-Crystalline Solids
Session Chairs: Katharine Flores, John Mauro, Tanguy Rouxel and Yunfeng Shi
Monday Afternoon, November 26, 2018
8:00 PM - 10:00 PM
Hynes, Level 1, Hall B

CM02.03.01

Microstructure Design for Ductile Glass Composite Yanming Zhang, Binghui Deng, Liping Huang and Yunfeng Shi; Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States.

In this work we use molecular dynamics (MD) simulations to investigate glass composites constituted by two brittle model glasses with different stiffness. We show that tuning the stiffness ratio (SR), shape, volume fraction and distribution of the two brittle glass constituent can trigger a brittle to ductile (BTD) transition. Such composite glasses can exhibit high strength, remarkable toughness and some work hardening. The highest failure strain of 80% can be reached in composite glasses as compared to 7% in monolithic model glasses. We also found that mechanical properties of such glass composites will not be deteriorated by introduction of pre-notch. Excellent load redistribution capability introduced by structural heterogeneity is responsible for high ductility in our composite glasses. Through a systematic analysis, we unveil the design principles that lead to the aforementioned BTD transition. We believe the current approach could enhance ductility and broaden the application of glasses as enabling structural materials.

CM02.03.02

Molecular Modeling of Stress Corrosion Behavior Swastik Basu, Liping Huang and Yunfeng Shi; Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States.

Glass is well known to be susceptible to stress corrosion cracking caused by chemicals in the environment, a phenomenon that can cause delayed failure of glasses due to growth of pre-existing surface defects in the presence of humidity. The complex macroscopic effects of stress corrosion, like fracture, occur due to microscopic interactions, which demand a study to replicate the microstructural interactions within a model, which should reproduce the macroscopic behaviors. The purpose of this research is to study the stress corrosion behavior of a model metallic glass system with a view towards representing the underlying atomic level mechanisms using a molecular dynamics approach.

CM02.03.03

Liquid Metal Nanoscale Structures as Novel Platform for Characterization of Structural Relaxation of Metallic Glasses Ziyang He¹, Chen Liang² and Chenhao Qian³; ¹Economics Department, Columbia University, New York, New York, United States; ²Engineering Department, University of Liverpool, Liverpool, United Kingdom; ³Department of Mechanical Engineering, Jiangnan University, Wuxi, China.

This poster firstly introduces a new microfluidic method for preparing nanostructures of gallium-indium liquid alloy systems. Due to its smaller nanometer size (50-100nm diameter), good self-healing behavior, strong oxide layer formed by spontaneous oxidation, rich changeable nanomorphology driven by voltage variation and large undercooling range, the alloy system has become a good platform for studying amorphous structure transformation and internal structure of liquids using in-situ characterization technology under current conditions. We have successfully discovered the presence of secondary structures in this liquid metal system through in situ TEM lithiation experiments and subsequent nanomechanical and electrical experiments. By comparing the structural relaxation of the same kinetic fragility liquid with or without the oxide layer structure, we found that the oxide layer structure could guide the dynamic non-uniformity of the nano-amorphous system to some extent. At the same time, we are also actively exploring the future application of this alloy system in liquid metal self-healing electrodes, nano-heat pipes, nanoscale self-propelled robots and other industrial fields.

CM02.03.04

Self-Diffusion Mechanism of Atoms in Forsterite Glass Junya Nishizawa and Tomoko Ikeda-Fukazawa; Department of Applied Chemistry, Meiji University, Kawasaki-shi, Japan.

Forsterite glass exists as dust grains in interstellar molecular clouds and young stellar objects [1]. In interstellar molecular clouds, elements such as hydrogen, oxygen, carbon, and nitrogen deposit on dust grains, and form various molecules (e.g., H₂O, CO, CO₂, NH₃, CH₄, H₂CO, CH₃OH, and so on) [2]. These molecules undergo chemical evolutions to organic molecules through various processes on the surface of dust grains [2]. Dust grains are important materials governing the chemical and thermal evolutions in space. However, the transport coefficients of forsterite glass are less conclusive, because forsterite glass is easily to crystallize. To investigate the mechanism of self-diffusion of atoms in forsterite glass, molecular dynamics (MD) calculations were performed.

The MD calculations were performed using an atom-atom potential model with MXDORTO program [3]. The potential parameters were empirically determined by constraining the model to reproduce the experimental results of density, thermal expansion coefficient, and bulk modulus [4]. The transition point from glassy state of supercooled liquid state (T_g) for our potential model is 1567 K. A fundamental orthorhombic cell consisting of 160 Mg₂SiO₄ with three-dimensional periodic boundary conditions was used. The glass structure was prepared by quenching the liquid phase from 3000 K to 10 K with 0.4 K/ps in rate. The quenched glass was warmed to 3000 K with the same rate. The MD code was run with NTP ensemble. The pressure was kept at 0.1 MPa.

The self-diffusion coefficients of Mg, Si and O were calculated using mean-square displacement (MSD). To investigate the mechanisms of self-diffusion, the temporal variations of pair correlations functions for Mg were analyzed. The result shows that the jumping probability of Mg, which is located at a position with high Si and low Mg densities is high. Because of the strong Si–O bonds in the tetrahedral SiO₄ units, the jump of Mg atom (or MgO_x unit) was induced by structural distortion of the surrounded SiO₄ units. From analyses of spatial distribution of MSD, it was found that the MSD values of Mg are inhomogeneous at temperatures just below T_g . Because the self-diffusion coefficient of Si is significantly low at $< T_g$, the distribution of Si in forsterite glass is inhomogeneous. Therefore, the diffusivity of Mg depends on surrounded Si distribution.

Reference:

- [1] J. P. Bradley, L. P. Keller, T. P. Snow, M. S. Hanner, G. J. Flynn, J. C. Gezo, S. J. Clemett, D. E. Brownlee, J. E. Bowey, *Science*, **285**, 1716 (1999).
- [2] N. Watanabe, A. Kouchi, *Prog. Sur. Sci.*, **83**, 439 (2008).
- [3] K. Kawamura, MXDORTO, *Japan Chemistry Program Exchange*, #029 (1990).
- [4] T. Ikeda-Fukazawa, *J. Soc. Inorg. Mater. Jpn.*, **23**, 130 (2016).

CM02.03.06

Methods for Estimating Appearance of Metal-Like Plastic Sun Chul Jin, Hyungjin Roh, Kiyong Kim and Sunghawn Cho; Samyang, Daejeon, Korea (the Republic of).

A plastic has a lower specific gravity than glass or metal and has many advantages such as lightweight and good mechanical properties. These thermoplastics are rapidly replacing conventional glass and metal areas in fields such as electronic and automobile parts. Recently, as increasing need for environmentally friendly material, there is an increasing demand for plastic that can feel a metallic appearance similar to a metal without a spray process.

For the development of metal-feeling thermoplastics, it is well-known way to use metallic pigment. But because of difference in flowability between metal pigment and plastic, There is an appearance problem such as flow mark and weld-line. This is why metal-feeling plastic can't be expanded. In order to solve these problems, much research have been studied to control the shape and aspect ratio of metallic pigment and to improve the surface coating of it. However, it is limited to improve the appearance problems such as aggregation and orientation.

In addition, there is no effective method for objectively estimating the appearance of the metallic feeling except for flop index. But the flop index can evaluate only the metallic brightness and the degree of defects such as flow mark and weld-line caused by the metallic pigment could not be evaluated. As a result, there is no method of evaluating the appearance that can represent the overall phenomenon caused by the metallic pigment as an objective numerical value. In this research, development of method for estimating appearance of metal-feeling plastic is studied. Through correction of flop index, new index named as 'T/N_Flop_X' was developed. Using this index, it is available to objective evaluation and comparison of metal-feeling. And using the CCD camera, it was studied that correlation of sparkle effect, metallic pigment's orientation and weld-line.

Based on these studies, we found out sparkle index that could be explained about orientation and metal-feeling. Additionally we studied about control of metallic pigment for reduce an appearance problem. Orientation is important factor to determine weld-line degree and in a constant direction makes decrease it.

We found out factors that could control orientation especially additive having an affinity of polar and non-polar.

CM02.03.07

Amphiphilic Modification of PDMS Surface with PVA/PSBMA Zwitterionic Semi-Interpenetrating Hydrogel for Marine Antifouling Application Xingyang Xu, Rongrong Chen and Jun Wang; College of Material Science and Chemical Engineering, Harbin Engineering University, Harbin, China.

Marine biofouling is a highly complex process and a worldwide problem which involve a wide variety of species. The common techniques proposed include heavy metals (Cu₂O), or organic biocide, are bring potential harm to marine environment and ecosystem. Therefore, the nontoxic approaches, particularly silicone-included low-surface-energy Fouling Release Coatings (FRCs) may be the alternatives to chemically active coatings and more environmentally friendly AF strategies. In this study, a facile and versatile approach to the formation of amphiphilic marine antifouling is reported. The approach used boric acid (BA) to mediate the the plasma treated PDMS elastomer and subsequent immobilization of polyvinyl alcohol/poly (sulfobetaine methacrylate) (PVA/PSBMA) zwitterionic semi-interpenetrating hydrogel on solid substrates. PVA/PSBMA was immobilized on the PDMS surface via hydrogen bond and chemical bond. The resulting substrates were tested for the algae attachment test and protein adsorption assay, in which diatom and protein adhesion was significantly inhibited compared to PDMS. Advantageously, this approach allowed marine antifouling coatings to be prepared by a simple immersion process under environmentally friendly conditions.

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CM02.03.08

The Effect of Arm Segment Length on Thermally Induced Self-Healing Behavior of Supramolecular Star Poly(ϵ -caprolactone)s Network Woojin Lee¹, Dae-Yeon Won¹, Hyo-bin Wi¹, Jae Woo Chung² and Seung-Yeop Kwak¹; ¹Department of Materials Science and Engineering, Seoul National University, Seoul, Korea (the Republic of); ²Soongsil University, Seoul, Korea (the Republic of).

Supramolecular polymer is comprised of oligomers or polymers that are held together by reversible non-covalent supramolecular interactions. It is capable of responding to damage or crack and restoring the polymer's performance without affecting the initial materials properties. The healing property of supramolecular polymer network depends on two factors, that is, the first being the supramolecular interactions, and the second being the chain dynamics of the individual polymer chains. In this study, we synthesize the simple supramolecular network consisted of ureidopyrimidinone (UPy) ends functionalized 6-arm star poly(ϵ -caprolactone)s and investigate the effect of arm length on thermally induced self-healing behavior of the supramolecular star poly(ϵ -caprolactone) network. The resulting materials can be healed several times at 90C during 10 minutes, and even can be healed at 60C after 40 minutes. We find the compromise between number of tie points by supramolecular force and chain dynamics related to sufficient mobility of network. Both supramolecular end clustery crystal and main chain crystal might affect the mobility of network. For the efficient healing behavior, the crystalline domain of supramolecular polymer network should be collapsed. Thus, the sufficient thermally induced healing behavior can be achieved through the enhanced mobility of network.

CM02.03.09

Ab Initio Study of the Amorphous Cu-Bi System David Hinojosa-Romero¹, Isaías Rodríguez², Alexander Valladares², Renela M. Valladares² and Ariel A. Valladares¹; ¹IIM-UNAM, Mexico City, Mexico; ²Facultad de Ciencias-UNAM, Mexico City, Mexico.

As a pure element, bismuth is a semimetal which possesses several interesting physical properties, not all of them well understood. The recent discovery of superconductivity [1], as predicted by our group [2], and the increasing superconducting transition temperature as the pressure applied increases, are some examples of its particularities. Also, the fact that the amorphous phase is superconductive with a transition temperature several orders of magnitude larger than the crystalline at ambient pressure is unusual [2]. These phenomena have also motivated our predictions for the transition temperatures of Bi-bilayers [3] and the Bi-IV phase [4]. When mixed with other elements, bismuth seems to contribute to the superconducting character of the resulting material. Here we study the binary copper-bismuth amorphous system which is known to superconduct in diverse compositions [5]. Using *ab initio* molecular dynamics and the undermelt-quench method, we generate an amorphous structure for a 144-atom supercell corresponding to the Cu₈Bi₅₆ system. We shall report the calculated electronic and vibrational densities of states for this system and relate them to the superconducting properties of this alloy.

[1] O. Prakash, A. Kumar, A. Thamizhavel, S. Ramakrishnan. Evidence for bulk superconductivity in pure bismuth single crystals at ambient pressure. *Science* **355** (2017), pp. 52-55. DOI: 10.1126/science.aaf8227.

[2] Z. Mata-Pinzón, A. A. Valladares, R. M. Valladares, A. Valladares. Superconductivity in Bismuth. A New Look at an Old Problem. *PLoS ONE* **11** (2016), e0147645. DOI:10.1371/journal.pone.0147645.

[3] D. Hinojosa-Romero, I. Rodríguez, A. Valladares, R. M. Valladares, A. A. Valladares. Possible superconductivity in Bismuth (111) bilayers. Their electronic and vibrational properties from first principles. *MRS Advances* **3** (2018), pp. 313-319. DOI: 10.1557/adv.2018.119.

[4] A. A. Valladares, I. Rodríguez, D. Hinojosa-Romero, A. Valladares, R. M. Valladares. Possible superconductivity in the Bismuth IV solid phase under pressure. *Scientific Reports* **8** (2018) 5946 DOI:10.1038/s41598-018-24150-3.

[5] N. E. Alekseevskii, V. V. Bondar and Yu. M. Polukarov, *Zh. Eksperim. i Teor. Fiz.* **38** (1960), p. 294 [translation: *Soviet Phys. - JETP* **38** (1960), p. 213].

CM02.03.10

Structural Commonalities in Different Classes of Non-Crystalline Solids—A Pair Distribution Function Analysis Isaías Rodríguez², David Hinojosa-Romero¹, Renela M. Valladares², Alexander Valladares² and Ariel A. Valladares¹; ¹IIM-UNAM, Mexico City, Mexico; ²Physics, Faculty of Science, UNAM, Ciudad de México, Mexico.

In the past decades the research community has explored diverse structures and new fabrication methods of non-crystalline solids. Glassy materials that belong to the semiconductor realm and to the metallic type are the most studied both experimentally and simulationally. The present work investigates common structural trends whenever they exist and different trends among different classes. Amorphous semiconductors display Pair Distribution Functions (PDF) that are very similar among themselves and this indicates that these network forming materials have properties that are alike^[1]. Analogously metallic systems have comparable PDFs but different from the network forming materials, as it should be, since the properties between these two classes are very different^{[2][3]}.

Here we pay attention to the Short-Range Order (SRO) and Intermediate Range Order (IRO) of these two classes. In particular, the first peaks of the structures studied are contrasted, while the second peaks are shown to differ considerably. Whereas the semiconductor structures display a simple first and second peak with a near-zero value between them, the metallic systems have a very well defined non-zero value between the first and second peaks and they also display what we have come to identify as an “elephant” second peak^[4]. To manifest the uncommonalities with amorphous semimetals we recall calculations carried out by our group for bismuth where the elephant peak does not appear but the non-zero behavior between the first and the second peak is present^[5]. The Plane Angle Distribution (PAD) functions are also reported.

[1] A. A. Valladares, J. A. Díaz-Celaya, J. Galván-Colín, L. M. Mejía-Mendoza, J. A. Reyes-Retana, R. M. Valladares, A. Valladares, F. Alvarez-Ramirez, D. Qu and J. Shen, *New Approaches to the Computer Simulation of Amorphous Alloys: A Review*. *Materials*, **4**, 716-781 (2011).

[2] C.U. Santiago-Cortés, *Simulación de sistemas metálicos amorfos y porosos de elementos nobles*, Thesis (PhD), Universidad Nacional Autónoma de México, México (2011).

[3] I. Rodríguez, R. M. Valladares, A. Valladares, A. A. Valladares, to be published (2018).

[4] A. de Saint-Exupéry, *Le Petit Prince*, Reynal & Hitchcock, pp 1-2 (1943).

[5] Z. Mata-Pinzón, A. A. Valladares, R. M. Valladares, A. Valladares, *Superconductivity in Bismuth. A New Look at an Old Problem*. *PLOS ONE*, **11**(1): e0147645 (2016).

CM02.03.11

Dependence of Modulus on the Annealing Conditions of Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5} Bulk Metallic Glass Zheng Chen¹, Amit Datye¹, Jittisa Ketkaew¹, Sungwoo Sohn¹, Jan Schroers¹ and Udo Schwarz^{1, 2}; ¹Department of Mechanical Engineering and Materials Science, Yale University, New Haven, Connecticut, United States; ²Department of Chemical Engineering and Environmental Engineering, Yale University, New Haven, Connecticut, United States.

The mechanical properties of bulk metallic glasses are often tuned by annealing, which influences these properties by adjusting the relaxation or crystallization status of the glasses. Here, we studied the modulus of Pt_{57.5}Cu_{14.7}Ni_{5.3}P_{22.5} bulk metallic glass (Pt-BMG) annealed at different temperatures in the metastable regime by nanoindentation, where the annealing gives the BMG different fictive temperature and fractions of crystallization. We find the modulus of the investigated BMG samples exhibits a “V trend”: As the annealing temperature increases, we first observe a decrease that is followed by an

increase until saturation is reached. This phenomenon can be explained as a result of the combination of the glasses relaxation and the glasses crystallization: Relaxation caused by higher fictive temperatures lead first to higher free volumes, which leads to lower moduli, while past a specific temperature, crystallization generates new, denser phases with higher moduli. The latter finding is confirmed by nanoindentation measurements at which fully amorphous Pt-BMG samples with different fictive temperatures are compared with partially crystalline samples featuring the same fictive temperature.

CM02.03.12

Theoretical Support to Hydrogen Elimination Monitoring by Ultraviolet Photodissociation Mass Spectrometry Using Density Functional Theory Lindsay Morrison, Wenrui Chai, Jake Rosenberg, Graeme Henkelman and Jennifer Brodbelt; The University of Texas at Austin, Austin, Texas, United States.

Mass spectrometry (MS) has become an increasingly popular and useful in analyzing structures of proteins. Initially only information of low resolution and of the whole protein in general can be obtained. Many techniques that utilize property differences between parts of the protein to produce signature fragmentation patterns and products have been developed to gain more information on local geometry, such as collision induced dissociation (CID), electron transfer dissociation (ETD), electron capture dissociation (ECD) and ultraviolet photodissociation (UVPD). A new method called hydrogen elimination monitoring (HEM) was invented by Brodbelt et. al, to overcome disadvantage of other methods. For example, CID disrupts protein structure prior to fragmentation therefore higher order structural information is lost and ECD cannot differentiate highly ordered surface regions with internal buried regions. HEM aims finding out higher order structure anywhere in the protein by using hydrogen elimination information after fragmentation to determine the level of hydrogen binding prior to fragmentation, therefore determining local geometry. Experiments have demonstrated that hydrogen elimination correlates strongly to absence of backbone hydrogen bonding yet the underlying process and reason to this correlation is unknown. DFT studies of model peptides at ground state can help in illustrating the process and in providing theoretical support to HEM method.

In the computational study complementary to experimental findings, we used 3 structures of Ala₈ peptide models with increasing amount of hydrogen binding: an unstructured linear peptide, a hairpin turn and a helix, to study the thermodynamics as well as the kinetics of the fragmentation process, by finding out the enthalpy change of the fragmentation reaction and the minimum energy pathways (MEPs) for the processes. The thermodynamics show that fragmentation products without hydrogen elimination are much higher in energy compared to products with hydrogen elimination, and therefore extremely unfavorable. The MEPs revealed reasons why the thermodynamic favorable product may not always form. In the unstructured peptide, hydrogen elimination always take place at the same time as the C-C backbone is cleaved. In the hairpin turn and helix structure, however, the MEP show that C-C cleavage takes place first and produces spatial separation that could prevent hydrogen elimination. This finding shows the underlying principle of the correlation between hydrogen elimination and amount of hydrogen binding prior to fragmentation, and therefore supports HEM as an effective method for analyzing protein structure.

CM02.03.13

The Molecular Influence on High Strain Rate Microscale Impact Response of Synthetic Polymeric Materials Yuchen Sun^{1,2,4}, David Veysset¹, Alex Hsieh³, Steven Kooi¹, You-Chi M. Wu², John P. Mikhail⁵, A. A. Maznev^{1,2}, Jan W. Andzelm³, Gregory C. Rutledge⁵, Timothy M. Swager² and Keith A. Nelson^{1,2}; ¹Institute for Soldier Nanotechnologies, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ³U.S. Army Research Laboratory, RDRL-WMM-G, Aberdeen Proving Ground, Maryland, United States; ⁴Department of Material Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ⁵Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

The deformation of materials in extreme dynamical environments such as high-velocity microparticle impact is a challenge to understand though important for many areas of science and technology from space exploration to sand erosion. While impact dynamics of macroscale projectiles have been studied in real time using high-speed imaging, investigations of microscale impact have been essentially limited to post-mortem analysis of impacted specimens. Here, we present real-time observations of supersonic microparticle impacts using multi-frame imaging. In a laser-induced projectile impact test, a microparticle is accelerated by laser ablation from a sacrificial gold layer on a glass substrate. These particles can be accelerated into free space with controllable speeds up to 1.0 km/s depending on laser pulse energy and particle characteristics. The particles are monitored in flight and during impact with an ultra-high-speed camera that can record up to 16 images with a minimum interframe time of 3 ns. We investigated the high-velocity impact deformation response of elastomers to further the fundamental understanding of the molecular influences on high strain rate elastomeric response. The types of materials that were synthesized and tested are glassy polymers, graft copolymers, and other materials. We show the dynamic stiffening response of various elastomers including poly(urea urethane) upon impact at strain rates of $\sim 10^8$ s⁻¹ and demonstrate the significance of molecular constitution in the response. These results provide an impetus for modeling the molecular influence on high strain rate microscale impact responses in these polymeric materials.

CM02.03.14

Enhancing the Mechanical Properties of Biodegradable PLA using Ternary Polymer Blends Xianghao Zuo¹, Yuan Xue¹, Elena Urquiola², Ruilin Yin³, Jinghan Tang⁴ and Miriam Rafailovich¹; ¹Stony Brook University, Stony Brook, New York, United States; ²Hunter College High School, New York City, New York, United States; ³St. Anthony's High School, South Huntington, New York, United States; ⁴Mater Dei High School, Santa Ana, California, United States.

Acrylonitrile butadiene styrene (ABS) has a similar matrix structure to the styrene acrylonitrile copolymer but has additional distribution of polybutadiene which strengthens it and allows ABS to surpass the properties of traditional commercial polymers. PLA is a 100% biodegradable polymer which can be regarded as a replacement to many current commercial plastics. However, its brittleness limited its application in the industrial processing. Commonly, binary blends including PLA and another polymer additives are created to enhance the mechanical properties of PLA, but this has been found to be ineffective due to the poor interfacial reaction between the polymers. Previous studies have determined that a 70:30 PLA: ABS ratio effectively balances the bio-based properties of PLA with the exceptional mechanical properties of ABS. Many have observed that the binary PLA/ABS blend actually has worse mechanical properties than just the PLA alone. Therefore, an efficient compatibilizer with good affinity with both PLA and ABS is a key factor to solve this problem. In our previous work, we have certified that PMMA is miscible with PLA and considering the structure of ABS, we hypothesis PMMA should be an excellent compatibilizer to the blend.

To create the ternary blends, the polymers were added to a C.W. Brabender and then molded into the tensile and impact test shapes using a Carver Hot Press. The blends were also run through an extruder to create filaments for 3D printing. A 286% increase for the molded sample in the impact test was observed when 4% by weight PMMA was used with the 70PLA/30ABS blend. Mechanical tests also showed that this ternary polymer material can maintain high mechanical properties even when 3D printing, as the mechanical properties of the 3D printed surpassed the pure PLA sample and PLA/ABS binary blend by 24.3% and 55.5% respectively. SEM and TEM imaging were used to verify the location of PMMA phase. And contact angle tests show that ABS has a higher affinity with PMMA than PLA.

The ternary blends reached their peak mechanical properties with less than 5% by weight of compatibilizer added, suggesting the economic efficiency of this blend for industrial use. For future study, interfacial properties in the ternary blends could be investigated using secondary ion mass spectrometry (SIMS) analysis to reveal interactions that contribute to mechanical strength.

CM02.03.15

Enhancing Impact Resistance of Polymer Blends via Self-Assembled Nanoscale Interfacial Structures Xianghao Zuo, Yuan Xue, Yichen Guo and Miriam Rafailovich; Stony Brook University, Stony Brook, New York, United States.

We have designed and engineered ternary polymer blends with the mechanical properties comparable to high impact resistant conventional polymers under the guidance of the lattice self-consistent field model. Two formulas were used to study the mechanical properties. In one system, poly (methyl methacrylate) (PMMA) was used as the compatibilizer for the widely studied biodegradable polymer blend, poly (lactic acid) (PLA)/Poly (butylene adipate-co-butylene terephthalate) (PBAT) blend. We characterized the compatibility of those components and found PMMA was miscible with PLA and partially compatible with PBAT, which allowed it to self-assemble to a nanoscale interfacial layer on the PLA/PBAT interface. This PMMA layer can significantly decrease the interfacial energy and strongly entangle with either PLA or PBAT, resulting in the strengthening of the interface and dramatically enhancement of the impact resistance of the ternary blend. The optimal mechanical performance was achieved when the total PMMA concentration was less than 10 wt %. Higher PMMA content embrittled the blend since the additional PMMA did not contribute to the minimization of the interfacial energy but remained in the PLA phase, increasing the glass transition temperature of the matrix. In the other system, as in our previous study, PMMA is miscible with PLA and PS is totally miscible with styrenic polymers such as HIPS and ABS, therefore, PLA/Styrene Acrylic Copolymers (SMMA) with different styrenic polymers were blended during the study. SMMA will self-assemble to become an interfacial layer on the PLA/PS (or HIPS or ABS) interface at very low concentration (SMMA concentration less than 2%), and enhance the impact resistance of the ternary blend up to 50% compared to the binary blend of PLA/styrenic polymers. Increasing the SMMA concentration will form a third phase domain in the polymer matrix which will embrittle the whole system.

CM02.03.16

Electronic Transport in Aperiodic Labyrinth Lattices Vicenta Sanchez, Fernando Sanchez and Chumin Wang; Universidad Nacional Autonoma de Mexico, Mexico City, Mexico.

The search for a simple and direct relationship between atomic scale arrangement and macroscopic properties of a material constitutes a principal task of the materials science. For example, the Bloch theorem establishes extended electronic wavefunctions and then a ballistic conduction if the atoms of a crystalline material are periodically ordered. At the other extreme, one- and two-dimensional amorphous solids with randomly arranged atoms possess only exponentially localized eigenstates [1]. Nowadays, the study of electronic transport in artificial structures is of great importance in condensed matter physics, because such structures introduce many new physical properties essential for technological applications of atomic-scale devices. In this work, we report a new convolution theorem developed for the Kubo-Greenwood formula in Labyrinth tiling by transforming the original two-dimensional lattice into a set of independent chains with rescaled Hamiltonians [2]. Such transformation leads to an analytical solution of the direct-current conductance spectra, where quantized steps with height of $2g_0$ are found in Labyrinth tiling with periodic order along the applied electric field direction, in contrast to the step height of g_0 observed in the corresponding square lattices, being g_0 the conductance quantum. When this convolution theorem is combined with the real-space renormalization method [3], we can address in a non-perturbative way the electronic transport in macroscopic aperiodic Labyrinth tiling based on generalized Fibonacci chains [4]. Furthermore, we analytically demonstrate the existence of ballistic transport states in such aperiodic Labyrinth tiling. This finding suggests that the periodicity should not be a necessary condition for the single-electron ballistic transport even in multidimensional fully non-periodic lattices.

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[1] E. Abrahams, *et al.*, *Phys. Rev. Lett.* **42**, 673 (1979).

[2] F. Sánchez, V. Sánchez, C. Wang, *Eur. Phys. J. B* (2018) doi: 10.1140/epjb/e2018-90070-4.

[3] V. Sánchez and C. Wang, *Phys. Rev. B* **70**, 144207 (2004).

[4] F. Sánchez, V. Sánchez, C. Wang, *J. Non-Cryst. Solids* **450**, 194 (2016).

CM02.03.17

Fracture Tensile Test for Brittle Diamond-Like-Carbon at the Nanoscale Dahye Shin and Dongchan Jang; Korea Advanced Institute of Science and Technology, Daejeon, Korea (the Republic of).

Ceramics are well used in various fields as functional materials and their property range is a way more expanded these days by adding new nanoscale properties. Even though a number of studies have been achieved for investigating electronic, magnetic, optic properties etc. at nanoscale, the fracture behavior is not reached to the same level of evaluation. It is in need of investigating the fundamentals of fracture mechanics for nano-sized ceramic materials to guarantee the reliability of the systems adding to enjoy the newly enhanced nano-properties at the same time. Brittle failure of ceramics is usually mediated by a rapid crack propagation due to the lack of intrinsic crack tolerant mechanism which requires extremely high critical stress for its activation, usually never been reached before the total failure in bulk scale. However, in some theoretical studies, fracture of nanomaterials becomes insensitive to flaws when they shrink below a certain critical size and enables to reach almost theoretical strength of the material [1]. Getting ideas from this, here we present an unwonted roll of cracks at the nanoscale as an activator of a fracture resisting mechanism not as an enemy of brittle ceramics through nanoscale tensile experiments and finite element methods analysis. *In situ* SEM tensile fracture tests with different crack geometries were carried out. Diamond-like-carbon (DLC) was chosen to be conductive for SEM image quality, isotropic, and brittle material to eliminate any complicate material issues and to make the best focus on the mechanical analysis. Single-edge-notched-tension (SENT) and double-edge-notched-tension (DENT) samples with pre-notch size of 60 nm and thickness of 200 nm were fabricated in mushroom like shape with head size of $\sim 2 \mu\text{m}$ using Focused Ion Beam (FIB) on DLC film of $\sim 1.5 \mu\text{m}$ coated on Si wafer. The head part was grabbed and pulled by a self-produced claw-like tip. In short, we observed that the DENT samples were deviated from the expectations based on classical linear elastic fracture mechanics showing 150% higher fracture strength even with 60% of total crack length out of thickness. It is explained by the interaction between the two stress fields of each crack that activates additional fracture resisting mechanism in the neck region of the specimen preventing the whole sample from the failure.

[1] Gao, Huajian, et al. "Materials become insensitive to flaws at nanoscale: lessons from nature." *Proceedings of the national Academy of Sciences* 100.10 (2003): 5597-5600.

CM02.03.18

Studies of Photo-Thermal Dual Curing Behaviors of Acrylate Monomers with FTIR and Photo-DSC Hyuck Sik Wang, Seung Hyuk Lee, Seok Hyung Bu and Kigook Song; Kyung Hee University, Yongin-si, Korea (the Republic of).

The photo-curing behaviors of acrylate monomers capable of urethane thermal reaction were investigated using time-resolved FTIR spectroscopy and photo-DSC (Differential Scanning Calorimetry). Faster photo-reaction and lower conversion of acrylate reactions were observed in the thermal-photo dual curing process compared to the photo-curing only process. In the case of the acrylate system with long chain oligomers, faster photo-reaction was also observed in the dual curing process although no difference was found in the degree of conversion of acrylates between two photo-curing processes. The photo-curing process of three acrylate monomers was investigated using ATR-FTIR spectroscopy with a deuterated acrylate compound. In the free-radical terpolymerization, the conversion of three acrylate monomers into terpolymer as a function of time was monitored by observing the characteristic FTIR peaks of each component. In order to identify the acrylate components involved in the free-radical terpolymerization, careful peak assignments were made for the acrylate terpolymer such that characteristic FTIR bands from different monomers chosen for quantitative analysis should not overlap with one another. The use of deuterium substituted acrylate monomer as an aid in the interpretation of the FTIR spectra of three component systems has been demonstrated in this study.

CM02.03.19

Fluorescent Carbon Particles Formed from Concentrated Glucose Solutions Tomilola Obadiya, Harsh Uppala and David Sidebottom; Creighton University, Omaha, Nebraska, United States.

Carbon dots (C-dots) are a class of low-dimensional carbon-based particles which exhibit a signature photoluminescence (PL) consisting of a red-shifted emission when irradiated with uv-visible light. This Photoluminescence (PL) has been explained as either the effects of quantum confinement, or of energy traps on the particle surface. Recently, several groups have reported the synthesis of C-dots directly from the thermal treatment of aqueous solutions of simple sugars (e.g., glucose, sucrose) either in a conventional autoclave or in a microwave oven. These studies have looked exclusively a preparation from low concentration (less than 10 wt% sugar) solutions reacted at rather high temperatures (between 160 to 200 °C). We report the synthesis of fluorescent carbon particles produced from viscous glucose solutions of a much higher concentration heated at much lower temperatures. Analysis by photon correlation spectroscopy (PCS) reveals the particles form immediately with a size (approximately 300 nm) that is nearly 100 times larger than the precursor clusters of sugar but which decrease slightly in size with additional heating. Despite their larger size, PL shows emission similar to that of smaller C-dots but with clear indications of fine structure suggesting a set of discrete surface energy levels likely associated with different functional groups attached to the particle's surface.

CM02.03.20

Modeling of the Resistance Drift Phenomenon in Chalcogenide-Based PCMs Kazimierz J. Plucinski; Military University of Technology, Warsaw, Poland.

Chalcogenide phase change materials (PCM), such as those based on Ge-Sb-Te alloys, have been shown to have unique properties that have been used for a long time in optical memories (DVD), and, more recently, in non-volatile resistive memories [1, 2].

Nonetheless, several challenges must be overcome if PCM memory technology is to enter the market. The most critical of these challenges is that the resistance of the PCM amorphous phase increases with time (so-called "resistance drift phenomenon") due to the ageing of the material, and this drift has a negative effect on the storage of information.

The basic physical mechanisms underlying drift phenomena are still unclear and are currently the subject of intense discussion. Different and sometimes contradictory mechanisms have been proposed, such as [1]: increasing [3] or reducing [5, 4] disorder during drift; increase [6] or decrease [7] density of defect states during drift; impact [8] or no effect [9] of stress on drift.

Despite all the recent research efforts, we do not yet have a clear picture of the structural mechanism of relaxation occurring during the ageing of the amorphous PCM phase, and further research is needed.

Discussion and analysis of different mechanisms proposed for increasing of the resistivity of the chalcogenide based PCM amorphous phase with time is presented – taking into account recent reported results of measurements and concepts, eg: clustering of Ge atoms in the amorphous phase of GeTe during ageing [10]; thermal excitations of electrons trapped in defect states within the electronic gap [4]; correlation between drift coefficient and activation energy [15]; increasing of the band gap during ageing [11]; increase in the proportion of homopolar Ge-Ge bonds with ageing [10]; densification of the films during ageing [12]; localization of the gap states during ageing [13, 14]; formation of Ge-Ge bonds upon ageing in thin films [10].

Structural and quantum chemical analysis was carried out using modified procedures described eg in [16].

References:

[1] Noé P et al 2018, *Semicond. Sci. Technol.* **33**, 013002; [2] Kolobov AV et al 2017, *Semicond. Sci. Technol.* **32**, 123003; [3] Fantini P et al 2012, *Appl. Phys. Lett.* **100** 213506; [4] Ielmini D et al 2009, *Microel. Eng.* **86** 1942; [5] Gopalakrishnan K et al 2010 *Symp. on VLSI Tech. Dig.* pp 205; [6] Pirovano A et al 2004, *IEEE Trans. El. Dev.* **51** 714; [7] Ielmini D et al 2008, *Appl. Phys. Lett.* **92** 193511; [8] Mitra M et al 2010, *Appl. Phys. Lett.* **96** 222111; [9] Rizzi M et al 2011, *Appl. Phys. Lett.* **99** 223513; [10] Noé P et al 2016, *J. Phys. D: Appl. Phys.* **49** 035305; [11] Mitrofanov K V et al 2014, *J. Appl. Phys.* **115** 173501; [12] Kalb J et al 2003, *J. Appl. Phys.* **94** 4908; [13] Gabardi S et al. 2015, *Phys. Rev. B* **92** 054201; [14] Sosso G et al 2012, *Phys. Stat. Sol. B* **249** 1880; [15] Luckas J et al 2013, *J. Appl. Phys.* **113** 023704; [16] Plucinski K J et al 2015, *Mat. Sci. in Sem. Proc.* **38**, 184-187.

CM02.03.21

The Relationship between Photoluminescence and Short-Range Order Structure in SrTi_{1-x}Al_xO₃ Amorphous Compounds Valmor R. Mastelaro¹, Yajaira D.R. Jerez¹, Lauro Maia³ and Alain Ibanez²; ¹Physics Institute of Sao Carlos, University of Sao Paulo, Sao Carlos, Brazil; ²Institut NÉEL - CNRS, Grenoble, France; ³Physics Department, Federal University of Goias, Goiania, Brazil.

Although compounds exhibiting the perovskite structure, and particularly SrTiO₃, have been very well studied concerning their photoluminescence (PL) properties, to our knowledge, the effect of water purity used and the addition of aluminum substituting partially titanium atoms on the PL properties have not yet been studied. To complete the previous studies, samples of SrTi_{1-x}Al_xO₃ composition with x ranging from 0.005, 0.01, 0.03 and 0.05 were prepared by the modified polymer precursor method under different water purity. SrTi_{1-x}Al_xO₃ (STAO) composition samples with the amounts of aluminum equal to x = 0.005, 0.01, 0.03 and 0.05 were synthesized by the modified polymer precursor method. The obtained resins were subsequently thermally treated at 250 °C at a heating rate of 10 °C/min for 4h under air atmosphere and subsequently ground to obtain fine black amorphous powders. Different temperatures of heat treatments between 450 ~ 500 °C were selected as well as different calcination times between 2h and 8h. XANES spectra were collected at Ti K-edge using the transmission mode at the XAFS2 beam line of Brazilian storage ring. The pre-edge region of the XANES spectra on the Ti K-edge presents four transitions. They were attributed to a quadrupolar excitation of the 1s electron level to the octahedron t_{2g} orbitals; a transition of the 1s

electron to unoccupied 3d level; transitions attributed to the dipole excitation of the 1s electron level to the t_{2g} and e_g orbitals of the neighboring octahedron. Significant differences in the intensity of the pre-edge transition for samples containing 3% and 5% of aluminum were observed indicating that in these samples the local symmetry around titanium presents a greater distortion or a greater degree of disorder. This distortion or disorder may originate from the existence of sites with titanium pentacoordinate (^{5}Ti) or hexacoordinated (^{6}Ti). The comparison of the intensity of the transition present in the pre-border region of the XANES spectra of the samples versus the value of the PL intensity area, in agreement with literature data, shows a clear evolution of PL emission with the relative proportions / amounts of pentacoordinate and hexacoordinated symmetries and also the PL decreasing with the beginning of the crystallization process.

CM02.03.22

Modifier Cations in Silicate Glasses—Possible Changes of the Local Structures During the Very Early Stages of Crystallization Valmor R. Mastelaro¹ and Edgar D. Zanotto²; ¹Physics Institute of Sao Carlos, University of Sao Paulo, Sao Carlos, Brazil; ²Materials Engineering, Federal University of São Carlos, Sao Paulo, Brazil.

Crystallization is a key issue in understanding glass and plays a fundamental role in the development of advanced glass-ceramics. In the absence of catalyzing agents, most supercooled liquids crystallize heterogeneously from the external surfaces; only a few systems crystallize homogeneously in the interior. It is essential to follow the formation of the first nuclei. **Is the whole local structure around the cations modified well before crystallization is completed?** The precise role of nucleating agents in glass-ceramic formation will likely only be understood by investigating the very first stages of crystallization with a strictly local structural probe having atomic selectivity. The X-ray Absorption Fine Structure (XAFS) technique is quite appropriate to characterize the local structure of specific cations present in glassy samples from the earliest stage of crystal nucleation. In this work, partially crystallized and fully crystallized samples were obtained after treatment at temperatures and times defined in previous studies. The XANES and EXAFS spectra of selected cations ions in the BaO-SiO₂, Ba₂TiSi₂O₇, CaMgSi₂O₆ - 9 mol% Fe₂O₃, MgO-SiO₂, 1NaO-2CaO-3SiO₂ and 2NaO-1CaO-3SiO₂ glassy systems were collected at room temperature by using the transmission and total electron yield modes. A preliminary analysis of the data indeed showed modifications in the local order around some cations as the time of crystallization increased. The results will be fully discussed.

CM02.03.23

Shear Band Nucleation and Propagation in Metallic Glass Matrix Composites Jonathan Gentile¹, Douglas Stauffer² and Jason R. Trelewicz¹; ¹Stony Brook University, Stony Brook, New York, United States; ²Bruker Nano, Minneapolis, Minnesota, United States.

Metallic glass matrix (MGM) composites combine high-strength amorphous metals with ductile crystalline inclusions to overcome the inherent brittleness of metallic glasses. While the crystalline heterogeneities have been shown to influence the process of shear localization, the underlying mechanisms are not well understood especially since they seemingly operate at disparate length scales. To explore the role of crystalline inclusions in the process of strain delocalization, we employ instrumented nanoindentation, which is particularly suited to study the deformation physics of these composite materials due to its ability to detect individual shear band propagation events and its precise control over plastic zone size. Using nanoindentation, we focus on elucidating three specific phenomena including the onset of plasticity through the formation of shear bands, the propensity for shear localization and its dependence on indentation strain rate, and the nature of shear band propagation. In this presentation, we describe instrumented Hertzian contact experiments that provide quantitative evidence for enhanced shear band nucleation as the shear band trajectory evolves with indentation depth to encompass the crystalline phase. Additionally, by measuring the fraction of discrete plastic events deriving from shear band plasticity during loading, we outline a transition from discrete to continuous deformation with increasing indentation strain rate, which is consistent with the behavior of monolithic metallic glasses. Through comparison of the propensity for shear localization with microstructural length scales of the MGM composites, we show that the presence of amorphous-crystalline interfaces simultaneously limit shear band propagation and promote a more homogeneous response through the partitioning of shear strain to the crystalline phase.

CM02.03.24

Revealing β -Relaxation Mechanism Based on Energy Distribution of Flow Units in Metallic Glass Zhen Lu¹, Wei Hua Wang² and Hai Yang Bai²; ¹Mathematics for Advanced Materials Open Innovation Laboratory (MathAM-OIL), Sendai, Japan; ²Institute of Physics, Beijing, China.

The β -relaxation, which is the source of the dynamics in glass state and has practical significance to relaxation and mechanical properties of glasses, has been an open question for decades. Here, we performed stress relaxation experiments under isothermal and linear heating modes and molecular dynamics simulations to investigate the different β -relaxation behaviors of various metallic glasses and the correlation between β -relaxation and flow units based on the activation energy distribution of flow units. We show that the β -relaxation originates from the flow units in metallic glasses, and the activation energy distribution of flow units modulates the β -relaxation modes such as excess wing, shoulder and peak in their dynamic spectra. A clear picture on the structural origin of β -relaxation and the correlation between activation energy distribution of flow units and β -relaxation behaviors in metallic glasses is proposed, which might be helpful to understand the nature of glasses and glass dynamics.

CM02.03.25

Diffusion and Avalanches in a Mesoscopic Model of Amorphous Plasticity Botond Tyukodi^{1,2}, Kareem Khirallah¹, Damien Vandembroucq² and Craig E. Maloney¹; ¹Northeastern University, Boston, Massachusetts, United States; ²PMMH, ESPCI, Paris, France.

Plastic deformation of amorphous materials around the yielding point shows critical properties such as avalanches, diverging correlation lengths and finite size effects. While this criticality is captured by various models, there is less consensus regarding the degree at which critical exponents are robust to the details of the particular system. Here we focus on the robustness of fluctuations in these systems to the details of the main ingredients of amorphous plasticity: elastic interactions and structural disorder. We find that, at short times, neither the details of the elastic interaction kernel, nor the type of the disorder are important when it comes to the critical properties. We find a short term diffusive behavior in our model and the associated diffusion coefficient shows the same finite size scaling as previous particle simulations. We connect the scaling of the diffusion coefficient to the scaling of avalanche sizes and we show that avalanches are essentially system spanning slip lines. Long term diffusivity is sensitive to the construction of the elastic kernel and shows a less trivial finite size scaling.

CM02.03.26

Atomistic Simulation of Nearly Defect-Free Models of Amorphous Silicon—An Information-Based Hybrid Approach Dil K. Limbu¹, Raymond Atta-Fynn² and Parthapratim Biswas¹; ¹Department of Physics and Astronomy, The University of Southern Mississippi, Hattiesburg, Mississippi, United States; ²Department of Physics, The University of Texas at Arlington, Arlington, Texas, United States.

We present an information-based total-energy optimization method to produce nearly defect-free structural models of amorphous silicon. Using geometrical, structural and topological information from tetrahedral networks, we have shown that it is possible to generate structural configurations of amorphous silicon, which are superior than the models obtained from conventional reverse Monte Carlo methods involving structural constraints and total-

energy optimization. The new static (i.e. relaxation-based) approach presented here is capable of producing atomistic models with structural properties which are on a par with those obtained from the modified Wooten-Winer-Weaire (WWW) models of amorphous silicon. Structural, electronic, and vibrational properties of the hybrid models are compared with the best dynamical models obtained from using machine-intelligence-based algorithms and efficient molecular-dynamics simulations, reported in the recent literature. We have shown that, together with the WWW models, our hybrid models represent one of the best static models so far produced by total-energy-based Monte Carlo methods in conjunction with experimental diffraction data of amorphous silicon.

CM02.03.27

Metastable Hydrogenated Amorphous Silicon (a-Si:H) as Reversible Programmable Photonic Material Mahir A. Mohammed^{1,3}, Ripalta Stabile^{1,3}, Jimmy Melskens^{2,3}, Wilhelmus (Erwin) Kessels^{2,3} and Oded Raz^{1,3}; ¹Electrical Engineering, Eindhoven University of Technology, Eindhoven, Netherlands; ²Applied Physics, Eindhoven University of Technology, Eindhoven, Netherlands; ³Institute for Photonic Integration, Eindhoven University of Technology, Eindhoven, Netherlands.

Hydrogenated amorphous silicon (a-Si:H) is known to exhibit light-induced metastable properties that are reversible upon annealing. Although these metastable properties suggest the existence of reversible optical properties of a-Si:H as well, very little is known about this effect. If indeed properly identified and characterized, such reversible optical properties may find application in the reversible programmable photonic integrated circuits (PICs) that can enable multiple functionalities on the same chip, similar to field-programmable gate arrays (FPGAs). However, the required reversible effective refractive index change due to light soaking and annealing has not been reported yet nor has it been thoroughly investigated. Therefore, the effects of prolonged high intensity light soaking and annealing on a-Si:H on the near infrared (NIR) optical properties are studied in this work. A thin-film interferometric technique was developed to detect minute changes probed using a NIR laser source (1465-1575 nm). Using this approach, an increase in refractive index resulted in a red shift of the sharp reflection minimum and a blue shift for the decrease in refractive index. To detect the changes in optical properties more precisely, double-layered thin films were used: a-Si:H was deposited by inductively coupled plasma-enhanced chemical vapour deposition (ICP-PECVD) on SiO₂, which was in turn deposited by PECVD on a crystalline silicon substrate. The a-Si:H deposition temperature was set to 80 °C and 300 °C, such that significantly different structural properties, e.g. hydrogen content and density, could be achieved. An irreversible blue shift was observed during the first cycle of annealing and light soaking after the deposition. However, from the second cycle onwards, a red shift of the spectrum due to light soaking, i.e. reversal of the annealed state was observed. It appeared that the initial irreversible changes are inevitable and only after these changes reversibility is observable. The reversibility was sustained after further cycles of annealing and light soaking. The reversibility appears for both a-Si:H deposited at 80 °C and 300 °C. However, the magnitude of the reversibility for a-Si:H deposited at 80 °C is significantly larger when compared to a-Si:H deposited at 300 °C. This suggests a correlation of the metastable properties of a-Si:H on the hydrogen content and density of the material, i.e. porous films (deposited at 80 °C) are more susceptible to light-induced change than dense films (deposited at 300 °C). The magnitude of the reversibility in refractive index for a-Si:H deposited at 80 °C is estimated to be around 0.03%. Although small, this metastable change should be sufficient for an application in reversible programmable optical switch. These results therefore indicate that a-Si:H has potential in enabling reversible programmable PICs and work to implement this material in a photonic device is currently ongoing.

CM02.03.28

Ag⁺ Ion Emission from Sharp-Edged Ag⁺ Ion Conducting Glasses and Two Emission Mechanisms Yusuke Daiko, Hiroki Mori, Sawao Honda and Yuji Iwamoto; Nagoya Institute of Technology, Nagoya, Japan.

Ion implantation is an effective method for surface modification of materials, and that has been used in various fields such as the semiconductor and metal industries, and bio-technology. In general, a discharged plasma (gas) or liquid (e.g., liquid Ga for a focused ion beam) is used as the ion source so far. However, in these cases, side reactions (generation of radicals or various ions with different mass, e.g. in the case of H⁺ emission, H₂⁺ and H₃⁺ etc. are also generated) are unavoidable. Also, ion accelerators are huge and expensive.

On the other hand, ion emissions from high ion conducting solid electrolytes have also been investigated because in a good solid electrolyte the mobile ions can move almost as freely as those in a liquid. The emission of O⁻ ions from O²⁻-ion-conducting yttria-stabilized zirconia (YSZ) was first reported in 1997. Similarly, continuous Ag⁺ ion emissions for a few days were reported using Ag-ion-conducting (AgI)_{0.5}(AgPO₃)_{0.5} or RbAg₄I₅ [8,9]. For 12CaO-7Al₂O₃(C12A7) clathrate crystals, it was found that not only electrons but also ions such as O⁻, H⁺, and F⁻ ions can incorporate inside cages, and emissions of these anions from C12A7 pellets were also observed. In this ion emission method, a plasma is not required for ionization and the ion emission apparatus becomes simple.

We have studied ion emissions from various types of ion-conducting glasses [1-3]. One advantage of utilizing glass is its formability for tip sharpening because the electric field strength is proportional to the inverse of the curvature radius of the tip. Here we report Ag⁺ ion emission from a sharpened Ag⁺ ion conducting glasses. An aluminum phosphosilicate glasses Ag₂O-Al₂O₃-P₂O₅-SiO₂ show Ag⁺ ion conductivity of 3×10⁻³ S/cm at 300 °C, and an ionic current of Ag⁺ ion emission was successfully observed at 300 °C and 1×10⁻⁵ Pa. A good linear correlation is obtained between the log(current) and the square root of the acceleration voltage, suggesting the emission of Ag⁺ ion from the tip of glass fiber is expressed by Schottky model similar to a thermionic electron emission. On the other hand, in the case of AgI-B₂O₃-Ag₂O glasses known as a super-ion-conducting glass, an Ag⁺ ion conductivity was higher than 5×10⁻³ S cm⁻¹ at room temperature, and Ag⁺ ion emission was observed for the first time at room temperature and non-vacuum atmosphere. The relationship between the emission current and voltage is expressed by space-charge limited current model, in which the current is proportional to the (voltage)^{3/2}. Ag⁺ ion emission mechanisms are discussed in relation with these two models. We also tried a cell adhesion test using the palm-sized Ag⁺ ion emission gun as a first step of an application for a bioengineering field.

[1] Y. Daiko et al., *J. Sol-Gel. Sci. Technol.*, **83**(2017) 252-258. [2] Y. Daiko et al., *Solid State Ionics*, **322**(2018) 5-10. [3] Y. Daiko et al., *Adv. Eng. Mater.*, **20**(2018) 1800198.

CM02.03.29

Enhancement of Creep Deformation Induced via Proton Implantation for Phosphate Glasses Monitored Utilizing an Electrochemical Indenter Yusuke Daiko, Sawao Honda and Yuji Iwamoto; Nagoya Institute of Technology, Nagoya, Japan.

Intermediate temperature fuel cells (IT-FCs) operating around 400-500 °C have attracted much attention as next-generation energy source owing to their high conversion efficiency and low fabrication cost. Our group successfully prepared a fast proton conducting phosphosilicate glass using conventional melting method, and we confirmed fuel cell operation using H₂ and O₂ at the intermediate temperature (~5 mW/cm²) [1,2]. Similar to typical oxide glasses, our glass has quite few H⁺ (OH groups) just after quenching the melt. However, based on originally developed in-situ FTIR measurement, we found a proton implantation into the phosphosilicate glass occurs under fuel cell operating condition [3]. We anticipated such proton implantation affects mechanical properties of glass. In this study, creep behavior of proton conducting glass in fuel cell atmosphere is reported.

A new electrochemical indentation apparatus was developed, in which we can control measuring conditions including atmosphere (H₂, N₂, air and relative humidity), temperature, and electrical field. A spherical Inconel 625 indenter was used as an electrode simultaneously, and we evaluated in-situ creep behavior under the proton implantation. Proton conducting glass was prepared by conventional melting method with composition of 7.5Na₂O·7.5K₂O·

35P₂O₅·50SiO₂ (mol%). After polishing the glass with ~1 mm thickness, Pt ring-electrode was sputtered on a side of the glass plate. Atmosphere was controlled by flowing a humidified H₂ gas (4%H₂-96% Ar), heating up to 200 °C, and applying DC 5 V between the Pt ring and Inconel electrodes. This condition is similar to the anode reaction of fuel cell (H₂ → 2H⁺ + 2e⁻), and proton implantation occurs. We conducted an indentation creep experiment under the reaction. We also carried out same experiments in N₂ atmosphere as comparison. Humidity effects were also investigated using humid gas (relative humidity ~1%).

The phosphosilicate glass showed typical creep behavior in N₂ atmosphere at 200 °C. Interestingly, the creep displacement increases remarkably in H₂ atmosphere, and we obtained a longer relaxation time for creep in H₂ atmosphere compared with that in N₂. These results suggest that proton implantation affects significantly for mechanical properties of glass. Results including Raman spectroscopy will be shown and discussed at the presentation.

[1] Y. Daiko, et al., *Electrochem.SolidState Lett.* **14**, B63 (2011) [2] Y. Daiko, et al., *Electrochemistry*, **82**, 901 (2014) [3] Y. Daiko et al., *J. Ceram. Soc. Jpn.*, **121**, 539 (2013).

CM02.03.30

State of Water Absorbed in Epoxy with Voids Fatmaelzahraa I. Abdelmola and Leif A. Carlsson; Ocean and Mechanical Engineering, Florida Atlantic University, Boca Raton, Florida, United States.

Polymer resins are used for numerous applications, for example as matrix materials for high performance fiber-reinforced composites. Such structures operate in humid air and liquid water, which may cause swelling and degradation of the material. Because of imperfections in the chain structure such as chain ends, glassy polymer contain molecular sized voids called “free volume”. In addition, macroscopically sized voids are commonly found in polymers. When polymers absorb water, differential scanning calorimetry (DSC) studies have shown that the absorbed water may be classified as free water and bound water. Free water state is when the water molecules occupy free volume and voids. Bound water state exists when the water molecules interact with the polymer chains and form hydrogen bond.

In order to examine the influence of voids on water uptake, and the state of water in epoxy, foaming agents were utilized to produce a controllable amount of voids (void contents from 0 to about 50%). Epoxy specimens containing voids and void-free were prepared. Water uptake experiments were conducted by immersing specimens with and without voids in distilled water at 40 °C. The moisture content was monitored by gravimetric measurements. To examine the state of absorbed water, DSC analysis of dry and water saturated epoxy specimens without and with voids was conducted over a temperature range from -80 °C to room temperature. DSC data was recorded during both the cooling and heating cycles. The state of water absorbed was determined based on analysis of the appropriate transitions recorded.

The free and bound water phase transitions were absent in the dry void-free specimen. In the water saturated void-free specimen, most the moisture absorbed was non-freezable water. In the water saturated medium and high void content specimens, peaks attributed to free and bound water were observed. The contents of free and bound water were estimated from the exothermic peaks in the DSC curves. The bound water peak was much smaller than the free water peak, and decreased with increasing the void content. The area under the free water peak increased with increasing void content.

CM02.03.31

Thermal Stability and Nucleation Dynamics by Flash DSC in Zn-Based Metallic Glass Meng Gao and John H. Perepezko; Department of Materials Science and Engineering, University of Wisconsin–Madison, Madison, Wisconsin, United States.

Zn-based metallic glasses (Zn₄₀Mg₁₁Ca_{31-x}Yb_{18-x}, x=0-4) are strong glass forming alloys with low glass transition temperatures that enable metallic plastic behaviors. While the crystallization onset temperature is also low, the crystallization kinetics have not been examined and analyzed quantitatively. In this work, for one Zn-based metallic glass of Zn₄₀Mg₁₁Ca₃₁Yb₁₈, the thermodynamic properties and nucleation dynamics have been determined based on the application of the novel Flash DSC with ultrafast heating and cooling rate. The critical cooling rate range for glass formation was measured along with the critical heating rate for preventing crystallization and the kinetic fragility. A unique double-nose-shaped temperature-time-transformation (TTT) diagram between the glass transition temperature and the melting temperature was obtained by isothermal tests and it was verified to be induced by two different nucleation sites for the same crystallization products. To further investigate the properties of the two nucleation sites, a heterogeneous nucleation model was developed to simulate the experimental TTT diagram and reveal the novel nucleation pathway of Zn-based metallic glasses. This study provides a novel insight in the influence of spatial heterogeneity on crystallization dynamics in amorphous materials.

CM02.03.32

Interface Behavior Characterization during Bonding of Al₂O₃ to Titanium Using a Ni_{76.5}Fe_{4.2}Cr₁₃B_{2.8}Si_{4.5} Metallic Glass Foil Quetzalmaflore Miranda-Hernández¹, José Lemus¹, Leonel Ceja-Cardenas² and Jorge A. Verduzco¹; ¹Instituto de Investigación en Metalurgia y Materiales, Universidad Michoacana de San Nicolás de Hidalgo, Morelia, Mexico; ²Ingeniería Mecánica, Instituto Tecnológico de Morelia, Morelia, Mexico.

One of the advantages of using metallic glass foils as joining element of materials over other filler elements such as pasts obtained from powders using agglutinants, is that the liquid former can fill more efficiently the surfaces to bond; phosphorous, boron, nickel and/or iron metallic foils have raised their use for joining applications. Due to the rapid solidification technologies, it is possible to produce ribbons or foils directly from the liquid state, obtaining a number of alloys able to be used as the joining element of several materials.

This work studied the microstructure behavior of the interface formed during joining of samples combinations like sandwich of Al₂O₃/Ti using a Ni_{76.5}Fe_{4.2}Cr₁₃B_{2.8}Si_{4.5} metallic glass foil, of 38 μm thick, as the joining element using the brazing process. Al₂O₃ was produced in cylindrical shape, with diameter of 11 mm and thickness of 3 mm, by sintering powder at 1550°C. Al₂O₃/metallic glass foil/Ti combinations were joined under argon atmosphere, using different joining times and temperatures varying from 10, 20 and 30 minutes, and 1150°C and 1160°C, respectively. Successful bonding of Al₂O₃ to Ti was observed at both bonding temperatures, 1150°C and 1160°C studied. Scanning electron micrographs (SEM) of the reaction layer show the growth of the reaction zone increasing with an irregular thickness, with both, bonding temperature and time. The joining process induced an inter-diffusion of alloy elements from the Ti and ceramic material to the amorphous foil, conveying to the formation of intermetallic and second phases at the joining interphase, as was observed by SEM. Residual porosity was observed at the joining zone near to the Al₂O₃ bonding line. The results revealed too, the formation of an interface zone similar to composite material with Al₂O₃ fiber inside of a metallic matrix composed mainly by the glass foil, Ni, Fe, and Cr, as well as Ti. TiNi intermetallic phase was observed in the joining interface.

CM02.03.33

Stress-Induced Martensitic Transformation of Cu₅₀Zr₅₀ Shape Memory Alloy Optimized Through Microalloying and Co-Microalloying Francois de Luca², Paul S. Nnamchi¹, Abdurauf Younes¹, A. T. Fry² and Sergio G. Sanchez¹; ¹Northumbria University, Newcastle upon Tyne, United

Kingdom; ²National Physical Laboratory, Middlesex, United Kingdom.

The stress-induced martensitic transformation of Cu₅₀Zr₅₀ at. % shape memory alloy was controlled through microalloying and co-microalloying and the performance compared at macro and nano scale. Nanoindentation (P/h)-h curves indicate that there is a change in deformation mode from dislocation slip to martensitic transformation during the loading. This change in mode is demonstrated from the change in slope at the initial stages of deformation. The maximum slope of 1.24 is attained for Cu₄₉Zr₅₀Ni₁ at. % compared to about 1.07 for the parent Cu₅₀Zr₅₀ alloy and 0.48 for Cu₄₉Zr₅₀Co₁ at. % thus suggesting that 1 at. % Ni promotes the martensitic transformation while 1 at. % Co decreases the effectiveness of the transformation compared to that of the parent alloy. For the co-microalloyed composition, Cu₄₉Zr₅₀Co_{0.5}Ni_{0.5} at. %, the slope is about 0.88 and therefore intermediate. A similar trend is obtained by measuring the plasticity index values obtained from the ratio of plastic deformation area and total area under the P-h curves since it is minimum for the alloy with 1 at. % Ni (i.e., 0.49) and maximum for 1 at. % Co (i.e., 0.54) compared to that of Cu₅₀Zr₅₀ (i.e., 0.52). The effect of the microalloying elements on the twinning propensity of the parent alloy has also been assessed from measurements at macroscale from differential scanning calorimetry (measuring the shift of the transformation temperatures) and X-ray diffraction (relative intensity change of austenite and martensite peaks before and after pre-compression) studies.

CM02.03.34

Exploring Load, Velocity and Surface Disorder Dependence of Friction with One-Dimensional and Two-Dimensional Models Omur E. Dagdeviren; McGill University, Montreal, Quebec, Canada.

The effect of surface disorder, load, and velocity on friction between a single asperity contact and a model surface is explored with one-dimensional and two-dimensional Prandtl-Tomlinson (PT) models [1]. We show that there are fundamental physical differences between the predictions of one-dimensional and two-dimensional models. The one-dimensional model estimates a monotonic increase in friction and energy dissipation with load, velocity, and surface disorder. However, two-dimensional PT model, which is expected to approximate a tip-sample system more realistically, reveals a non-monotonic trend, i.e. friction is inert to surface disorder and roughness in wearless friction regime. The two-dimensional model discloses that the surface disorder starts to dominate the friction and energy dissipation when the tip and the sample interact predominantly deep into the repulsive regime. Our numerical calculations address that tracking the minimum energy path and the slip-stick motion are two competing effects that determine the load, velocity, and surface disorder dependence of friction. In two-dimensional model, the single asperity can follow the minimum energy path in wearless regime; however, with increasing load and sliding velocity, the slip-stick movement dominates the dynamic motion and results in an increase in friction by impeding tracing the minimum energy path. Contrary to two-dimensional model, when one-dimensional PT model is employed, the single asperity cannot escape to minimum energy minimum due to constraint motion and reveals only a trivial dependence of friction on load, velocity, and surface disorder. Our computational analyses clarify the physical differences between the predictions of one-dimensional and two-dimensional models and open new avenues for disordered surfaces for low energy dissipation applications in wearless friction regime.

[1] O.E. Dagdeviren, *Nanotechnology* 29, 315704 (2018).

CM02.03.35

Non-Contact Sub-Micron Infrared Spectroscopy of Non-Crystalline Materials Using Visible Probe Detection Eoghan Dillon¹, Craig Prater¹ and Curtis Marcott²; ¹Photothermal Spectroscopy Corp, Santa Barbara, California, United States; ²Light Light Solutions, Athens, Georgia, United States.

Infrared microspectroscopy is a powerful technique for obtaining unique chemical information from a variety of biological systems. In general, spatial resolutions are limited by the Abbe diffraction laws to $\sim \lambda/2$ (3-10 μm). In recent years, the development of the AFM-IR technique has allowed for overcoming these diffraction limitations by using an AFM probe as the detector for IR absorption. Using a quantum cascade IR laser (QCL), the molecular vibrations in a sample are excited, leading to thermal expansion of the surface, which is monitored using an AFM cantilever. This technique reduced the spatial resolution of < 10 nm, however, in certain cases this high resolution is not required and the size of an image in AFM-IR is limited by the piezo stage to sub 100 μm .

A new technique has been developed that fills the gap between IR microspectroscopy and AFM-IR. This is an optical based technique that still beaks the diffraction limits associated with conventional IR microspectroscopy, and provides sub-micron spatial resolution. Taking advantage of the same fundamental principles that govern AFM-IR, the thermal expansion of a sample surface induced by a QCL IR laser is monitored using a visible probe laser, instead of an AFM probe. This unique technique provides transmission like IR spectra while operating in a reflective regime. The spatial resolution is limited by the diffraction limit of the visible probe laser, while also being independent of the IR wavelength used. This talk with focus on the use of optical based photothermal IR spectroscopy to characterize a variety of materials.

CM02.03.36

Near-Field Correlative Nanoscopy Accesses Physical Constants in Complex Functional Materials Stefan Mastel and Tobias Gokus; Neaspec GmbH, Martinsried, Germany.

Nanoscale characterization methods play a key role in the analysis, development and optimization of nanoscopic materials and devices. Often several characterization techniques are required to gain a comprehensive understanding of the various material properties of such complex functional materials. Here we introduce the combined analysis of complex nanoscale material systems by correlating infrared scattering-type Scanning Near-field Optical Microscopy (s-SNOM) [1] and nanoscale Fourier Transform Infrared (nano-FTIR) spectroscopy [2] with information obtained by other Scanning Probe Microscopy (SPM) based techniques. For example, the material-characteristic nano-FTIR absorption spectra of a phase-separated PS/LDPE polymer blend identifies sharp material interfaces between the two materials by measuring a line profile across a ca. 1 μm sized LDPE island inside the PS matrix. Near-field reflection/absorption imaging at 1500 cm^{-1} of the only 50 nm thin film allows to selectively highlight the distribution of PS in the blend, while selective atomic force microscopy (AFM) modes simultaneously map the mechanical properties like adhesion of the different materials [3,4]. Further, results will be presented that correlate the nanoscale near-field optical response of semiconducting samples like graphene (2D) or functional SRAM devices (3D) in different frequency ranges (mid-IR & THz) to Kelvin Probe Force Microscopy (KPFM) and Electrostatic Force Microscopy (EFM) measurements. Thus, neaspec s-SNOM systems represent an ideal platform to characterize complex material systems by different near-field optical and SPM-based mechanical and electrical methods at the nanoscale.

[1] F. Keilmann, R. Hillenbrand, *Phil. Trans. R. Soc. Lond. A* **362**, 787 (2004).

[2] F. Huth, et al., *Nano Lett.* **12**, 3973 (2012).

[3] B. Pollard, et al., *Beilstein J. of Nanotechnol.* **7**, 605 (2016).

[4] I. Amenabar, et al., *Nature Commun.* **8**, 14402 (2017).

CM02.03.37

Extending the Limits of Performance Materials in an HTHP Environment Rostyslav Dolog, Valery Khabashesku and Qusai Darugar; Baker Hughes, a

GE Company, Houston, Texas, United States.

Materials technology propelled the oil and gas industry forward for decades, meeting its critical needs for performance materials in increasingly demanding high-temperature/high-pressure (HTHP) conditions and enabling breakthroughs from the introduction of specialty materials. Our objective is to demonstrate a novel composite material design approach for oil and gas applications.

Conventional composite technology has fulfilled increasing materials property requirements by using expensive high-end performance polymers and fillers. Our goal is to demonstrate novel approaches to extend the performance limits of organic and/or inorganic composites to high-temperature applications of up to 400° F, without relying on costly high-end raw materials. Commercial low-cost materials were used to develop high-strength performance composites by extensive application of advanced processing techniques. In addition, we studied the potential applications of developed composites for downhole completions applications through prototype testing.

Material properties were assessed within the 300 to 400° F temperature range by using a compressive strength test, Dynamic Mechanical Analysis (DMA), Differential Scanning Calorimeter (DSC), and Thermo-gravimetric Analysis (TGA). Furthermore, test coupons were aged in water and downhole fluids to evaluate the effect of prolonged exposure to downhole conditions on mechanical properties. Implementation of out-of-the-box approaches enabled development of low-cost, high-performance systems capable of achieving compressive strengths over 20 ksi at temperatures over 300° F. In-depth processing optimization enabled further improved composite properties. The practical implications of the experiments enabled covering a large number of conventional and unconventional fillers for organic and/or inorganic matrices.

We demonstrated the development of high-strength organic and/or inorganic composites based on low-cost raw materials for high-temperature applications. This novel material-design approach was investigated with advanced material analysis techniques.

CM02.03.38

High Pressure-High Temperature Phase Diagram Using Electrical Resistance Measurements in a “Paris-Edinburgh” Large Volume Press [Moran Emuna](#)¹, [Yaron Greenberg](#)², [Eyal Yahel](#)² and [Guy Makov](#)¹; ¹Materials Engineering, Ben-Gurion University of the Negev, Beer Sheva, Israel; ²Physics, NRCN, Beer-Sheva, Israel.

We present a novel experimental design for high sensitivity measurements of the electrical resistance of samples at high pressures (0-6GPa) and high temperatures (0-1000K) in a 'Paris-Edinburgh' type large volume press. Uniquely, the electrical measurements are carried out directly on a small sample, thus greatly increasing the sensitivity of the measurement. The sensitivity to even minor changes in electrical resistance can be used to clearly identify phase transitions in material samples. Electrical resistance measurements are relatively simple and rapid to execute and the efficacy of the present experimental design is demonstrated by measuring the electrical resistance of Pb, Sn and Bi across a wide domain of temperature-pressure phase space and employing it to identify the loci of phase transitions. Based on these results, the phase diagrams of these elements are reconstructed to high accuracy and found to be in excellent agreement with previous studies. In particular, by mapping the locations of several well-studied reference points in the phase diagram of Sn and Bi, it is demonstrated that a standard calibration exists for the temperature and pressure, thus eliminating the need for direct or indirect temperature and pressure measurements. The present technique will allow simple and accurate mapping of phase diagrams under extreme conditions and may be of particular importance in advancing studies of liquid state anomalies.

CM02.03.39

Structure, Curing Dynamics and Performance of Phthalonitrile Resins [Boris Dyatkin](#)¹, [Stephen M. Deese](#)¹, [Tristan Butler](#)¹, [Naresh C. Osti](#)², [Madhusudan Tyagi](#)³ and [Matthew Laskoski](#)¹; ¹Chemistry, U.S. Naval Research Laboratory, Washington, District of Columbia, United States; ²Neutron Scattering Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ³Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, Maryland, United States.

High-temperature polymer matrix composites (PMCs) allow great control over various intrinsic properties (e.g. oxidative stability, mechanical toughness, thermal conductivity, etc.) that tailor these lightweight materials for numerous emerging applications. Despite many available formulations, conventional epoxies and phenolics, which form the matrix backbones of most thermoset composites, require high processing temperatures and cannot adequately withstand fire damage or high temperatures. Our efforts have recently yielded several types of thermosetting polymer resins called phthalonitriles, which are synthesized *via* a two-step, one-pot nucleophilic displacement reaction between dihaloaromatic compounds and bisphenols, followed by end-capping with 4-nitrophthalonitrile. Several backbone structure varieties are available for this resin system, and all of them offer low gelation (150 °C) and final curing temperatures (350 °C). In addition to low processing costs, the resulting thermosets offer high strength and exceptional fire resistance (up to 700 °C). However, existing research efforts have not adequately described the curing process and associated monomer dynamics for these resins; nor have they correlated them with structures and performance of resulting composites. Given that the backbone chemistry of each resin system significantly influences cross-linking and material properties, this information is essential to further optimize materials processing of high-performance phthalonitrile-based PMCs.

We have correlated the microscopic dynamics of three different phthalonitrile resin monomers during different thermal conditions with the morphologies, chemistry, and properties of resulting thermosets. The systems used a resorcinol backbone, a bisphenol A (PEEK™-like) backbone, and a resveratrol backbone. We measured the temperature-dependent monomer dynamics by conducting quasi-elastic neutron scattering measurements of each resin at room temperature, at 135 °C (at the T_g), during the gelation transition, and at 257 °C (fully cured systems), and correlated the extracted mobility and diffusion transformations with rheometry-derived viscosity changes to fundamentally probe the curing process of each system. In turn, these insights provided a proper explanation of the resulting morphology and, in turn, the oxidative stability and tensile strength of each resin system. Our efforts have established greater processing controls over high-performance phthalonitrile thermosets and facilitated their implementation in fiber-reinforced composites, flame-retardant panels, and lightweight airframes.

CM02.03.40

Porous-Carbon Nanotube Aerogels for Ultrafast Charging Supercapacitors and Potassium-Ion Batteries [Wenqi Zhao](#)^{2,1}, [Yibin Li](#)² and [Anyuan Cao](#)¹; ¹Peking University, Beijing, China; ²Harbin Institute of Technology, Harbin, China.

Energy storage systems with ultrafast charging properties have become a hot topic in recent years along with the increased life rhythm. Supercapacitors are energy storage systems capable of fast charging and discharging, thus generating superior power density. Potassium ion batteries (PIBs) possess a series of advantages as the next generation energy storage systems, such as low cost, large reserves compared to lithium, and high energy density. Porous carbon with high surface area and tunable pore size represents a promising candidate to construct ultrafast supercapacitors; so far most of porous carbon-based electrodes can only be charged to a moderate current density (100-200 A/g), also with significant capacitance loss at increasing rate. Here, we show that a three-dimensional (3D) aerogel consisting of interconnected 1D porous-carbon nanotubes (PCNs) could serve as a freestanding supercapacitor electrode with excellent rate performance (62% retention at 1000 A/g) and high power density (265 kW/kg). The aerogel is formed through a combination

of nitric acid doping and controlled air-etching processes. Mechanism study reveals favorable kinetics including a low and linear IR drop, about 85% contribution from electrical double layer capacitance, a very small time constant (0.057 s) and a metallic feature of 1D PCNs by theoretical calculation. The development of rechargeable batteries using potassium ions has recently attracted considerable attention. Here, we chose carbon nanotube (CNT) sponges as scaffolds to load nitrogen doped porous carbon (NDPC) and form hierarchical structures. The obtained 3D CNT/NDPC sponges can work as freestanding electrodes with significantly increased potassium storage capacity and compressive properties. The hybrid sponges achieve high capacity of 420 mAh/g as PIB electrodes, excellent rate capability and stable cyclic performance.

In conclusion, we demonstrated controlled fabrication of 3D freestanding porous electrode materials with ultrafast charging properties in supercapacitors and PIBs. Our pore-creation method, by combining HNO₃-doping and air-etching processes, could be extended to other N-containing precursors to fabricate various porous-carbon structures with tunable hierarchical pores. The highly porous 1D nanotube structure has the potential to develop microelectronic and power-supply devices that require fast charging/discharging capability (e.g. within 0.1 seconds).

References

Wenqi Zhao, Hui Zhang, Jie Liu, Lu Xu, Huaisheng Wu, Mingchu Zou, Qian Wang, Xiaodong He, Yibin Li, Anyuan Cao. Controlled air-etching synthesis of porous-carbon nanotube aerogels with ultrafast charging at 1000 A/g. *Adv. Energy Mater.*, under review.

Wenqi Zhao, Anyuan Cao, Yibin Li. Carbon nanotube/nitrogen doped porous carbon sponges with high performance for potassium ion batteries. Prepared.

CM02.03.41

Mechanically Strong and Thermally Conductive Ultra-High Molecular Weight Polyethylene Sheets [Shenqiang Ren](#); University at Buffalo, The State University of New York, Amherst, New York, United States.

Ultra-high molecular weight polyethylene (UHMWPE) is of great interest as a next-generation body armor material due to its superior mechanical properties. However, such unique properties depend critically on its microscopic structure characteristics, including the degree of crystallinity, chain alignment and morphology. Here we present a highly aligned UHMWPE and of its composite sheets containing uniformly dispersed boron nitride (BN) nanosheets. The dispersion of BN nanosheets into the UHMWPE matrix increases its mechanical properties over a broad temperature range. Experiments and simulation confirm that the alignment of chain segments in the composite matrix increases with temperature, leading to an improvement in mechanical properties at high temperature. Together with the large thermal conductivity of UHMWPE and BN, our findings serve in expanding the application spectrum of highly aligned polymer nanocomposite materials for ballistic panels and body armor over a broad range of temperatures.

CM02.03.42

Microcellular Materials with Stress-Activated Pores Exhibiting Opto-Mechanical Properties [Bilal Abdul Halim](#), Sheikh Rasel, Reza Rizvi, Navid Namdari and Emran Hossain; Polymer and Inorganic Composites, Structures and Surfaces Lab, Toledo, Ohio, United States.

Microcellular (1-30 μ m) and Nanocellular (<1 μ m) polymers have significantly lower densities relative to the base polymer resulting in improved specific mechanical properties as well as increased impact absorption and thermal insulation. Batch micro- and nano-cellular processes are generally well suited for low volume lab-based studies. The gas sorption within the polymer system tends to swell the polymer, resulting in increased free volume, higher chain mobility and a depressed glass transition temperature (T_g). These porous polymers acquire a static porosity, not quite as applicable or interesting as those with a dynamic porosity. Such a characteristic enables the polymer to mimic several stimuli activated porous systems found in nature, which exist at all length scales. For instance, the regulation of what enters and exits the cell (including oxygen, carbon dioxide, and other molecules and ions) cannot transpire if the cell membrane wasn't permeable (porous). Another example is the ability of the cuttlefish to use its cuttlebone, which is not exactly a bone, but a calcium carbonate like material that is almost 90% porous. Disjoined from the fish, the cuttlebone floats on water, however, the cuttlefish is able to control the flow of water in and out of the cuttlebone which helps with its buoyancy and structure.

Synthetic attempts at systems with dynamic porosity have focused mainly at the molecular-scale and nano-scale. No proven examples of dynamic porosity exist at the micron-scale. This study introduces a fundamental examination of foams composed of the triblock copolymer styrene-ethylene-butylene-styrene (SEBS) which was prepared using batch foaming, where the polymer is put in a pressure chamber using CO₂ as the blowing agent, and were then quenched at different temperatures (30C, 50C, 70C, 90C). These foams exhibit pores that shrink under stress and remain stable with an internal vacuum. Now, the reduced pore size fails to act as a light-scattering site, turning the polymer transparent and recovering back to an almost neat SEBS film. Different characterization techniques were done on foams before and after applying stress, using Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC), and X-Ray Diffraction (XRD). The opaque to transparent transition (OTT) was studied using an in-situ optomechanical setup comprised of an LED and a photoresistor while under a dynamic load using a universal testing machine. Each foam at different quenching temperature undergoes OTT at different loads and remains transparent. However, collapsed pores can be re-foamed which was demonstrated through saturating the almost-recovered SEBS for many cycles whilst getting density measurements and electron microscopy images at each cycle. This behavior can be instrumental in making pressure sensitive films.

CM02.03.43

Unraveling the Solution-State Supramolecular Structures of Donor-Acceptor Polymers and Their Influence on Solid-State Morphology and Charge-Transport Properties [Yuqing Zheng](#)¹, Jian Pei¹, Jie-Yu Wang¹ and Lin Zou²; ¹Peking University, Beijing, China; ²Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang, China.

Polymer self-assembly in solution prior to film fabrication makes solution-state structures critical for their solid-state packing and optoelectronic properties. However, unraveling the solution-state supramolecular structures is challenging, not to mention establishing a clear relationship between the solution-state structure and the charge-transport properties in field-effect transistors. Here, for the first time, it is revealed that the thin-film morphology of a conjugated polymer inherits the features of its solution-state supramolecular structures. A "solution-state supramolecular structure control" strategy is proposed to increase the electron mobility of a benzodifurandione-based oligo(*p*-phenylene vinylene) (BDOPV)-based polymer. It is shown that the solution-state structures of the BDOPV-based conjugated polymer can be tuned such that it forms a 1D rod-like structure in good solvent and a 2D lamellar structure in poor solvent. By tuning the solution-state structure, films with high crystallinity and good interdomain connectivity are obtained. The electron mobility significantly increases from the original value of 1.8 to 3.2 cm² V⁻¹ s⁻¹. This work demonstrates that "solution-state supramolecular structure" control is critical for understanding and optimization of the thin-film morphology and charge-transport properties of conjugated polymers.

CM02.03.44

Toughening PDMS Through Entanglements [Deborah Ehrlich](#), Junpeng Wang and Jeremiah Johnson; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

There is a need for tough PDMS that maintains its optical clarity and high temperature resistance. Fillers increase the modulus, toughness, and tear resistance of PDMS, but diminish optical clarity. Entanglements can be used to improve the mechanical properties of PDMS, without impacting desirable properties. By enhancing entanglements, we can further increase the modulus, toughness, and tear resistance of PDMS elastomers while maintaining optical clarity and high temperature resistance. Here we discuss our efforts to synthesize novel PDMS network architectures with entanglement promoted

toughness.

CM02.03.45

Combining Raman Spectroscopy with Rheology to Correlate Physical and Chemical Properties of Polymers [Richard A. Larsen](#)¹, Frederik Fleissner², Boris Wezislá², Georg Krenn³ and Katharina Napp²; ¹Anton Paar, Ashland, Virginia, United States; ²Anton Paar OptoTec, Seelze-Letter, Germany; ³Anton Paar GmbH, Graz, Austria.

During chemical reactions such as polymerizations, the physical as well as chemical properties of a material change. While the viscoelastic properties usually can be characterized with a rheometer, no chemical information is obtained by the mechanical testing. The interpretation of rheometric results often relies on empirical models and a more phenomenological approach. For directly relating the changes in rheological behavior to chemical changes, Raman spectroscopy is employed in-situ with rheology. Raman is a spectroscopic technique based on inelastic light scattering from the sample molecules. By measuring the presence and intensities of molecular vibrations, Raman spectroscopy provides information on the chemical composition and structure of the sample. Furthermore, the Raman spectrum reflects internal molecular parameters such as bond strengths and the structural arrangement of the molecules within the material.

The combination of both techniques enables the simultaneous correlation of the mechanical properties and the molecular structure to obtain a better understanding of the sample.

The Anton Paar MCRxx2 (Modular Compact Rheometer) series of rheometers can be easily combined with the Anton Paar Cora Raman spectrometers via an optical fiber probe. For the applications presented here, a high temperature probe with an extended working distance of 10 mm was used to obtain measurements through the lower measurement plate of the rheometer system. To demonstrate the possibilities of a combined Rheo-Raman system, we investigated resin hardening as well as the melting behavior of polyethylene. First, the hardening of an epoxy resin was monitored providing insight into the chemical and physical changes during the reaction. Specifically, the reaction induced changes in the flow characteristics over time were characterized. In the Raman spectrum, the chemical changes can be found in the decrease of vibrational bands belonging to the epoxy group of the reaction component. Secondly, the phase transition from the crystalline to amorphous state in HDPE (High Density Polyethylene) was monitored while the polymer was heated. This resulted in a higher viscosity as well as alteration of vibrational bands in the Raman spectrum reflecting the conversion from a crystalline to an amorphous structure.

Having both viscoelastic and spectroscopic information on a sample allows a more detailed characterization of the observed sample. As a result, sample behavior can be analyzed in all its facets for better quality control as well as optimizing the process properties of materials.

CM02.03.46

A Compressive-Sensing Pixelated Direct Detector for 4D-STEM Benjamin Bammes, Robert Bilhorn and [Robert Monteverde](#); Direct Electron, LP, San Diego, California, United States.

Use of a pixelated detector in scanning transmission electron microscopy (STEM) enables the simultaneous acquisition of both the conventional annular dark-field (ADF) signal and the coherent bright-field (BF) diffraction pattern at every probe position. By detecting the scattering angle of nearly all the primary electrons that interact with the specimen, this “4D-STEM” technique promises to provide much more information about the specimen than conventional STEM using only an ADF detector.

An acute challenge for acquisition of 4D-STEM data is the relatively slow speed of pixelated detectors for capturing the coherent BF signal. Slow acquisition of STEM data introduces deleterious artifacts from specimen drift and thus forces users to acquire a severely limited field-of-view—a significant problem for non-crystalline specimens.

One strategy to improve the speed of these detectors, is to reduce the number of pixels in the pixel array. However, this strategy prevents acquisition of the low- and medium-angle DF signal on the pixelated detector and it may also undersample the BF diffraction pattern and reduce its usefulness for differential phase contrast (DPC) or ptychography. This is especially problematic for complex specimens, such as specimens containing light atoms.

To address this challenge, we have implemented a new compressive-sensing readout mode—called Arbitrary Kernel Row Addressing (AKRA)—on our DE-16 direct detection camera. In AKRA readout mode, the user can specify any arbitrary combination of kernel rows from the detector to readout; all other kernel rows are skipped. By reading out fewer pixels, the detector framerate can be increased, enabling STEM imaging of a larger field-of-view. But since the “missing” pixels are scattering across the detector, the pixelated detector still captures a large area of the BF diffraction pattern and surrounding DF signal, with the “missing” pixels reconstructed using compressive-sensing algorithms. Therefore, AKRA enables fast 4D-STEM acquisition with a large pixelated detector so that rich structural information can be collected for large regions-of-interest of complex specimens.

CM02.03.47

Size-Dependent Properties of Nano-Crystalline Oxides [Siu-Wai Chan](#); Columbia University, New York, New York, United States.

A number of oxides, when prepared in nano-scale crystallites, exhibit a larger than bulk lattice parameter. A couple of these nano-oxides also show decreasing thermal expansion as well as stiffness constants as crystal-size goes beyond 10nm. We will discuss the physics and the materials science behind such an extraordinary behavior and the implications for solid-state chemistry and physics in nanoscale.

CM02.03.48

Fluorinated Polyurethane Resin with Fold Shape Structure and the Cavitation Erosion Resistance Performance [Haocheng Yang](#), Rongrong Chen, Jun Wang, Xuejie Guo and Kazunobu Takahashi; Materials Science and Engineering, College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin, China.

Cavitation erosion is a common mode of propeller surface damage, which seriously affects the hydrodynamic performance of propeller. In industrial applications, it is a surface treatment technology can effectively improve the cavitation erosion resistance performance by spraying elastomer organic coating on hydraulic components. Fluorinated polyurethane is a good elastomer which not only has excellent mechanical properties, but also has good ability of anti-biofouling. Herein, hydrophobic fluorinated polyurethanes (FPU), which combination of cavitation erosion resistance and biological fouling resistance coating were prepared by using the method of introducing fluorine with perfluoroalkyl ethanol (TEOH-10) for modification of isophorone diisocyanate (IPDI) and controlling the IPDI adding dosage and time. The chemical structure of FPU was investigated by Fourier transform infrared

spectroscopy (FT-IR), nuclear magnetic resonance spectrum (NMR) and gel permeation chromatography (GPC). The bonding strength between top coating and metal interlayer is significantly excellent (>4 MPa). Cavitation erosion tests were performed on Ultrasonic bubble generator for 10h. The mass loss of different cavitation time was examined by balance analysis. Surface morphology of the specimens was observed by Contour GTX and scanning electron microscope (SEM), respectively. Six-months marine field test in the Yellow Sea revealed that the FPU coatings exhibited excellent antifouling/fouling release performance. (This paper is funded by the International Exchange Program of Harbin Engineering University for Innovation-oriented Talents Cultivation.)

CM02.03.49

Cryo-EM Characterization of Chalcogenide Glass Solution Structure [Nikita Dutta](#) and Craig B. Arnold; Princeton University, Princeton, New Jersey, United States.

The unique optical properties of solution-processed chalcogenide glasses have long been of interest for photonic devices; a common test system is arsenic (III) sulfide (As_2S_3) in amine solvents. It is widely accepted that As_2S_3 takes on nanoscale structures in solution, and our ability to control properties when processing for devices is limited by our lack of a full understanding of these structures and the factors that influence them. This, in turn, is limited by the difficulty of characterizing the material in its dissolved state. This is a challenge faced commonly in structural biology, where cryo-electron microscopy (cryo-EM) has become the method of choice for determining the structure of hydrated biological molecules. We adapt this novel characterization technique for the chalcogenide samples and employ it alongside liquid cell electron microscopy and other more traditional methods to explore the in-solution structure of As_2S_3 in *n*-propylamine. Our results provide the first visuals of a long hypothesized structure and begin to reveal its dependence on core processing parameters like solution concentration and solvent type.

CM02.03.50

Interfacial Structure and Dynamics of Tetrahedral Amorphous Carbons in Room Temperature Ionic Liquids [Kirti Bhardwaj](#) and Greg Swain; Michigan State University, East Lansing, Michigan, United States.

Nitrogen incorporated tetrahedral amorphous carbon (*ta*-C: N_x) is diamond-like carbon composed of a mixture of sp^2 - (graphite-like) and sp^3 -bonded carbon. It can be deposited at room temperature and makes a great electrode material because of its remarkable microstructural stability, high inertness, wide potential window, mechanical strength, low-temperature deposition (<100 °C), tunable doping level and surface chemistry. Research is needed to better understand how growth parameters like dopant concentration, substrate etc. affect the electrode properties i.e. electrical conductivity, microstructure, surface chemistry, and interfacial capacitance.

The goal of this work is to progress the current understanding of structure-property relationships of amorphous carbons. This presentation will review some of the basic properties of these advanced carbons, investigated using Raman, X-ray reflectivity, AFM, XPS, and SEM. Structure and dynamics of interface between *ta*-C: N_x and RTILs will be investigated using cyclic voltammetry and electrochemical impedance spectroscopy. RTILs are solvents composed entirely of ions. They have great potential to replace conventional organic solvent/electrolyte systems in energy storage devices because of their remarkable properties like wide electrochemical potential window (> 4V), environmentally-benign characteristics (non-volatility, non-toxicity) and excellent thermal and electrochemical stability. To optimally harness the properties of *ta*-C: N_x and RTIL-based devices, a comprehensive fundamental understanding of their electrochemical behavior is critical.

CM02.03.51

Extensive Plastic Deformation in Vitreous Silica in Micropillar Compression Tests Zachary W. Rouse¹, [Shefford P. Baker](#)¹, Sanjit Bhowmick² and Syed Asif²; ¹Department of Materials Science and Engineering, Cornell University, Ithaca, New York, United States; ²Bruker Nano Surfaces Division (formerly Hysitron Inc.), Minneapolis, Minnesota, United States.

Pure SiO₂ glass is generally considered to be brittle, yet it is known that it can be deformed plastically in indentation or scratch tests. Understanding this plastic deformation is important in the development of devices with improved resistance to mechanical failure, but very little is known about the atomic scale mechanisms that control plasticity. Most work in this area has depended on indentation experiments, where complex inhomogeneous stress state makes interpretation difficult. To study plastic deformation quantitatively, we have developed silica glass micropillars having highly ideal geometries and tested them in compression in-situ in a scanning electron microscope. We characterized yield behavior, strain hardening, and strain rate sensitivity. Many behaviors are evident that are not accessible in indentation tests, including strain softening. Extremely large plastic strains were observed. Plastic deformation mechanisms and the possible role of electron illumination in plasticity is elucidated.

SESSION CM02.04: Deformation of Glasses I
Session Chairs: John Lewandowski and Yunfeng Shi
Tuesday Morning, November 27, 2018
Hynes, Level 2, Room 200

8:00 AM *CM02.04.01

Fracture Toughness of Modern and Ancient Glasses as Measured by the SCF and SEPB Methods [George D. Quinn](#)¹ and Jeffrey Swab²; ¹Materials Measurement Science Division, National Institute of Standards and Technology, Gaithersburg, Maryland, United States; ²U.S. Army Research Laboratory, Aberdeen Proving Ground, Maryland, United States.

The fracture toughness of eight glasses was measured by the surface crack in flexure (SCF) and single-edged precracked beam (SEPB) methods. These include four soda lime silicas including a common plate glass form, two low iron modern forms, and one ancient Roman glass, a fused silica, a borosilicate crown (BK-7) optical glass, and two other borosilicate glasses for armor applications. The historical soda lime silica glass was made in an ancient Roman glass factory that operated in Palestine until 383 AD. This glass was exposed to the environment for almost sixteen centuries. The two SCF and SEPB methods have different susceptibilities to environmentally-assisted slow crack growth, that can be a major interference in measuring fracture toughness in ambient testing environments. A new definition for fracture toughness of glasses is proposed.

8:30 AM CM02.04.02

Fracture Toughness and Atomic Bonding Character in Glass Tanguy Rouxel, Fabrice Celarie and Theany To; Glass and Mechanics, UMR 6251 IPR, University de Rennes 1, Rennes, France.

The fracture surface energy (γ) and the fracture toughness (K_{Ic}) of glass were estimated from the nominal composition by means of a simple approach to the structure at the atomic scale. The theoretical values are compared with the experimental ones, as obtained by means of self-consistent methods such as the Single Edge Pre-crack Beam (SEPB) and Chevron Notch (CN) ones, when available. A remarkable agreement is observed for ionocovalent glasses. In comparison, indentation cracking methods are found to mostly overestimate K_{Ic} by up to 50 %. In the case of metallic glasses, the theoretical values are much smaller than the experimental ones, which supports the occurrence of crack tip plasticity and shielding effect. Toughness (or ductility) is chiefly governed by the average coordination number, the bond directionality, and the atomic packing density.

8:45 AM CM02.04.03

Intrinsic Ductility of Glassy Solids Yunfeng Shi; Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States.

Glasses are usually brittle, seriously limiting their practical usages. Recently, the intrinsic ductility of glass was found to increase with the Poisson's ratio (ν), with a sharp brittle-to-ductile (BTD) transition at $\nu_{BTD}=0.31-0.32$. Such a correlation between far-from-equilibrium fracture and near-equilibrium elasticity is unexpected and not understood. Via force-field tuning technique, metallic glasses, amorphous silicon, silica glasses, and polymeric glasses have been investigated, showing BTD transition accompanied by an increase in their Poisson's ratio. Interestingly, beyond monolithic glasses, the Poisson's ratio of glassy composites embedded with crystallites also correlate to the intrinsic ductility. The Poisson's ratio, although defined elastically, reflects the bonding covalency and structural disorder, as well as microstructure heterogeneity.

9:00 AM CM02.04.04

Stresses and Strains in Colloidal Glass J. Zsolt Terdik¹, David Weitz^{1,2} and Frans Spaepen¹; ¹SEAS, Harvard University, Cambridge, Massachusetts, United States; ²Department of Physics, Harvard University, Cambridge, Massachusetts, United States.

Micron-sized hard-sphere colloidal particles can be used to form dense amorphous packings. Due to the large size and slow dynamics of colloidal particles, confocal microscopy can be used to investigate the 3D structure and dynamics of these glasses at the particle level. Previous studies have directly visualized both the inhomogeneous particle level strains in deformed colloidal glasses (i.e. STZs), and surrounding continuum strain fields. Measuring the *stress* in colloidal glasses during deformation, however, is a significant challenge; due to the large size and thermal interaction energies, colloidal solids have very small elastic moduli, on the order to 10-100mPa. We introduce a new technique, traction force rheology, to directly measure the mechanical response of colloidal glasses while simultaneously visualizing the microstructure using a confocal microscope. The method consists of a bilayer of colloidal glass atop a well calibrated soft polymer gel of slightly greater shear modulus. The composite bilayer is sheared and the shear stresses are inferred from the displacement of embedded tracer particles in the calibrated polymer gel. Using these stress measurements, we show that under cyclic applied shear the colloidal glass goes through a sequence of reversible and irreversible microscopic rearrangements which are related to the spatially correlated heterogeneities in the stress field.

9:15 AM CM02.04.05

High Strain Rate Compression Testing of Amorphous Silica Micropillars Rajaprakash Ramachandramoorthy¹, Jakob Schwiedrzik¹, Laszlo Petho¹, Damian Frey², Jean-Marc Breguet² and Johann Michler¹; ¹EMPA, Thun, Switzerland; ²Alemnis, Thun, Switzerland.

Mechanical testing of bulk materials at high strain rates is a well-established field of research over the past multiple decades. Recently in the past decade, the field of micromechanics has been established and it is now recognized that a reduction in sample dimensions to the micro- and nano- scale leads to enhanced material properties such as strength and ductility. Until now, the micromechanical experiments such as indentation and micropillar compression has been conducted only at quasi-static strain rates. This limitation of low strain rate testing ($<0.1/s$) at the microscale arises primarily due to the lack of high strain rate testing platforms capable of simultaneous high-speed actuation and high-speed sensing of microscale displacements and millinewton loads. Thus, the micromechanical properties and the deformation mechanisms for almost every material at strain rates above $0.1/s$ remains largely unknown. This presentation will report, for the first time, a piezo-based experimental methodology for conducting high strain rate *in situ* micropillar compression testing at rates upto $\sim 1000/s$ inside a scanning electron microscope. The strain rate achieved in this study is an increase of approximately four orders of magnitude compared to the current state-of-the-art micromechanical testing. The advantages and unique challenges of conducting micromechanical testing at high strain rates, with a particular focus on wave phenomena, inertia and sample recovery capability at particular strain, will be compared against traditional macroscale high strain rate tests conducted using kolsky bars. Subsequently, a case study on the high strain rate micromechanical characterization of amorphous silica or glass, a commercially relevant classic material, will be presented. The rate dependent mechanical properties of $\sim 1\mu m$ diameter amorphous silica micropillars will be presented as a function of strain rate across eight orders of magnitude, from $0.0001/s$ to $1000/s$. Remarkably, the amorphous silica micropillars undergo a unique ductile-brittle-ductile transition in failure mechanism as the strain rate is increased from quasi-static to $1000/s$. The stress-strain curves become serrated at strain rates between 0.01 and $10/s$, a typical mechanical response of amorphous materials. Using the extracted velocities of the load drops in the serrated stress-strain curves, analytical calculations based on adiabatic heating and atomistic simulations reported in literature, an explanation for the anomalous plasticity behavior of amorphous silica at different strain rates will be presented. Also, it will be shown, for the first time, that the yield stress increases as the strain rate is increased till $10/s$ and then saturates as the strain rates are increased further till $1000/s$. Finally, a comparison between the macro-scale and micro-scale mechanical response of amorphous silica at high strain rates will be used to demonstrate their startling differences.

9:30 AM *CM02.04.06

Effect of Aging and Cryogenic Temperatures on the Mechanical Response of Sputtered Zr-Ni-Al Metallic Glass Nano Structures Julia R. Greer¹, Rachel Lontas², Anthony Kwong¹ and Yongwei Zhang³; ¹California Institute of Technology, Pasadena, California, United States; ²Intel Corporation, Portland, Oregon, United States; ³HPC, Fusionopolis, Singapore.

Brittleness of metallic glasses (MGs) is a major drawback for their structural use at bulk scale. It has been shown that when reduced to $\sim 100nm$, some metallic glasses undergo a brittle-to-ductile transition and become plastically deformable. To harness this ductility emergent only at nano-scale and proliferate it onto materials with macroscale dimensions, we produced hollow-tube octet-truss nanolattices made out of sputtered NiAlZr with median wall thicknesses of ~ 10 to $\sim 100nm$, which results in a relative density of $\sim 5\%$ and renders them to be 20x lighter than their bulk counterparts. In-situ uniaxial compression experiments conducted inside an SEM reveal a transition from brittle, catastrophic failure in thicker-walled nanolattices (>60 nm) to deformable, gradual, layer-by-layer collapse in thinner-walled nanolattices (<40 nm). We explain the brittle-to-deformable transition as wall thickness decreases in terms of the "smaller is more deformable" material size effect that arises in nano-sized MGs. We further irradiated ZrNiAl nano-architectures with 12 MeV Ni⁴⁺ ions and found that the thickest-walled nanolattices (~ 88 nm) withstood irradiation; all other substantially shrunk and collapsed. *In-situ* nanomechanical experiments reveal significant improvement in mechanical response upon irradiation, with a $\sim 36\%$ increase in average

yield strength and enhanced deformability. Irradiated nanolattices deformed via a layer-by-layer collapse in contrast to catastrophic failure in equivalent as-fabricated samples.

Shortage of literature on mechanical properties and structural analysis of sputtered MGs motivated fundamental study of NiAlZr. We measured as-sputtered thin film to have a Young's modulus of 70 GPa and a yield strength of 1.8 GPa and discovered that room temperature aging for three years increased modulus by ~15% and yield strength by ~25%. In-situ tensile experiments on individual nano-samples uncovered their ductility to be larger than reported for other MGs, reaching >10% engineering strains, >150% true strains, and necking down to a point in relatively large, 150nm-wide, samples. Ductility was dependent on specimen size and annealing conditions, with highest ductility of ~150% true strain in ~90 nm wide samples; all annealed specimens of equivalent dimensions were substantially less ductile. We present molecular dynamics simulations, TEM microstructural analysis, and synchrotron XRD characterization to explain observed mechanical behavior in the framework of β -relaxation, free volume reduction and a concomitant increase in short- and medium- range order upon annealing and aging. These findings illustrate key role of the presence and distribution of free volume in governing mechanical deformation of MGs. Our work demonstrates the importance of sample dimensions, fabrication method (sputtering), post-processing conditions (annealing, aging, and irradiation), as well as nano-architecting, in tuning mechanical properties of MGs.

10:00 AM BREAK

10:30 AM *CM02.04.07

Mechanical Glass Transition Revealed by the Fracture Toughness of Metallic Glasses Jan Schroers¹, Jittisa Ketkaew¹, Eran Bouchbinder² and Takeshi Egami³; ¹Yale University, New Haven, Connecticut, United States; ²Weizmann Institute of Science, Rehovot, Israel; ³The University of Tennessee, Knoxville, Knoxville, Tennessee, United States.

The fracture toughness of glassy materials, despite its central role in glass science and technology, remains poorly understood. In large part, this is due to the disordered, intrinsically non-equilibrium nature of the glass structure which challenges its theoretical description and experimental determination. By meeting some of these challenges, we show that the notch fracture toughness of metallic glasses exhibits an abrupt toughening transition as a function of a well-controlled fictive temperature T_f , which characterizes the glass structure. The ordinary temperature, which has been previously associated with a ductile-to-brittle transition, is shown to play a minimal role. The observed transition is interpreted to result from a competition between the T_f -dependent plastic relaxation-rate and an applied strain-rate. Consequently, a similar toughening transition as a function of strain-rate is predicted, which is demonstrated experimentally here. The observed mechanical toughening transition bears strong similarities to the ordinary glass transition and explains previously reported large scatter in fracture toughness data and ductile-to-brittle transitions.

11:00 AM CM02.04.08

Cyclic Shear in a Mesoscopic Model of Amorphous Plasticity Kareem Khirallah, Botond Tyukodi and Craig E. Maloney; Mechanical and Industrial Engineering, Northeastern University, Boston, Massachusetts, United States.

We present results of a mesoscopic model of amorphous plasticity in which the material is subject to oscillatory shear. We show the existence of a threshold amplitude of the shear. Below this threshold amplitude, eventually all plasticity is exhausted and the material shows a fully elastic response under the periodic shear. The time necessary to reach this fully elastic state diverges as one approaches the critical amplitude. Above the critical amplitude we observe a hysteresis in the stress response. After several cycles the hysteresis reaches a steady state, showing that plasticity never vanishes above the threshold amplitude. Right above the critical amplitude, we observe a strong localization of plastic activity and a diffusive increase of strain and displacement fluctuations. Our results are in good agreement with several recent particle simulation observations.

11:15 AM CM02.04.09

Topological Origin of Strain Induced Damage of Elastomers by Bond Breaking Yikai Yin, Nicolas Bertin, Yanming Wang, Zhenan Bao and Wei Cai; Stanford University, Stanford, California, United States.

Elastomers that can sustain large reversible strain are essential components for stretchable electronics, which enables novel wearable and biological applications. The stretchability and mechanical robustness of unfilled elastomers can be enhanced by adding breakable cross-links, which also causes stress-strain hysteresis indicating strain-induced damage in the elastomer network. However, it remains unclear whether the breaking of the cross-links follows a predictable pattern that can be used to understand the evolution of damage with strain. Through coarse-grained molecular dynamics simulations and topology analyses, we find that bond breaking events are controlled by the evolution of shortest paths between well-separated cross-linkers. We show that the average length of the shortest paths, which is both anisotropic and hysteretic with strain, is the microstructural parameter responsible for damage evolution. These findings provide an explicit connection between the microscopic molecular structures and the macroscopic mechanical behaviors of elastomers, thereby paving the way to the development of physics-based models of elastomers, and providing guidelines for the molecular design of mechanically robust soft materials.

11:30 AM *CM02.04.10

Effects of Stress State on Flow and Fracture of Metallic Glasses John Lewandowski; Department of Materials Science and Engineering, Case Western Reserve University, Cleveland, Ohio, United States.

The processing and subsequent mechanical behavior of a variety of commercially important materials are affected by the imposed stress state. An earlier review* has summarised the experimentally documented effects of superimposed pressure on deformation under quasi-static conditions, following the classic work of P.W. Bridgman at Harvard University. This will be used to put the effects of superimposed pressure on metallic glasses into perspective. It will be shown that the pressure response of a variety of materials exhibit distinct differences, including metallic glasses, and the potential reasons for these differences will be presented. If time permits, the relevance of such deformation and fracture studies to deformation processing will be overviewed.

*JJ Lewandowski and P Lowhaphandu, International Materials Reviews, 43(4), pp. 145-188, 1998.

1:30 PM *CM02.05.01

A Study of Shear Band Broadening in Simulated Glasses Darius Alix-Williams and [Michael L. Falk](#); Johns Hopkins University, Baltimore, Maryland, United States.

Two models are proposed to predict the evolution of shear band width as a function of applied strain for simulated glasses mechanically deformed in simple shear. The first model arises from dimensional analysis and an assumption that band broadening is controlled by the strain rate inside the shear band. The second model describes the shear band as a pulled front propagating into an unsteady state, the dynamics of which are described using the effective temperature shear transformation zone (ET-STZ) theory. Both models are compared to three simulated systems: a two-dimensional binary Lennard-Jones glass, a Cu₆₄Zr₃₆ glass modeled using an embedded atom method (EAM) potential, and a Si glass modeled using the Stillinger-Weber potential. Shear bands form in all systems across a variety of quench rates. Depending on the case these bands either appear to broaden indefinitely or to saturate to a finite width. The shear band strain rate model appears to apply only when band growth is unconstrained, indicating the dominance of a single time scale in the early stages of band development. The front propagation model, which reduces to the other model in the early stages of band broadening, also applies to cases in which the band width saturates, suggesting that competition between the rate of shear-induced configurational disordering and thermal relaxation set a maximum width for shear bands in a variety of materials systems.

2:00 PM *CM02.05.02

Dynamic of Shear Bands Initiation in Metallic Glasses—Analysis of a Mg-Based Alloy Using Nano-Indentation [Yannick Champion](#); Centre National de la Recherche Scientifique, St Martin D'heres, France.

Deformation in metallic glasses occurs by initiation and propagation of multiple thin shear bands. This mode is rather difficult to analyse since a single band propagates early and to a large extent in the specimen leading to catastrophic failure. Exception is for example in confined deformation tests. We used instrumented nano-indentations to perform series of independent experiments at room temperature on a Mg₆₅Cu_{12.5}Ni_{12.5}(Ce₇₅La₂₅)₁₀ metallic glass. Loading part of curves shows serrations which size and duration were measured using an automated procedure. To make analyses consistent, data were considered only in the domain with similar strain rates, in the range of 1 to 0.3 s⁻¹. Times between successive serrations follow a normal distribution that suggests a random occurrence of serrations in the glass. It was then conjectured, that (i) serration occurs through activation of appropriate zone in the glass that should naturally scale with a multiple of an elementary domain size characterizing the deformation mechanism. (ii) As activated zones leading to serration are very few in the glass, the process should fit with rare event dynamics. Actually, serration sizes are well fitted by a Poisson distribution. The model predicts an elementary size which scale with that of the activation volume of 3 atoms, measured from nano-indentation creep tests at constant load in the same series of experiments (Thurieu et al, J. Appl. Phys. 2015). Dynamic of shear bands initiation is then analyzed using statistical approach based on the method proposed by Adam and Gibbs (J. Chem. Phys. 1965).

2:30 PM CM02.05.03

Insight into Shear-Band Affected Zone in Metallic Glasses Through the Measurement of Magnetic Domains [Lai Quan Shen](#) and Wei Hua Wang; Institute of Physics, Chinese Academy of Sciences, Beijing, China.

Plastic deformation of metallic glasses (MGs) has long been considered to be confined in nanoscale shear band, which usually leads to catastrophic failure and limits their potential applications. Recently, it was found that an affected zone is also involved upon shear banding. Yet, due to technical limitations, the shear-band affected zone (SBAZ), which is critical for understanding shear banding and thus the design of ductile MGs, remains to be precisely identified. Here, by taking magneto-elastic coupling induced magnetic domains as a probe with sufficiently high sensitivity and spatial resolution, we unveil the structure of SBAZ in much more detail. We demonstrate that shear banding is composed of a nanoscale core surrounded by a micron-scale SBAZ with gradient in the strain field, and multiple shear bands interact through the superimposition of the SBAZs. There even exists super long-range gradual elastic stress field extending hundreds of micrometers away from the shear-band core. Our method and findings enable a visualized insight into SBAZ and provide a comprehensive picture on shear banding, which are important for elucidate the micro-mechanisms for plastic deformation of glasses.

2:45 PM CM02.05.04

Understanding the Mechanisms of Amorphous Plasticity through Molecular Simulation [Penghui Cao](#), Michael Short and Sidney Yip; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Using a meta-dynamics method of sampling activated state pathways we study two related plastic responses of a model metallic glass at experimental strain-rate levels beyond the reach of traditional molecular dynamics simulations. The problems are (1) discrete stress relaxation (slip avalanches) in the onset of yielding and subsequent strain evolution, and (2) stress effects on creep rate. In (1) we quantify the yielding response and the role of major and minor avalanches in sustaining serrated plastic deformation. In the case of deformation under a constant stress, problem (2), we demonstrate a nonlinear interplay between non-affine atomic displacement and cooperative shear transformation distortion of local atomic clusters that provides a molecular explanation of the familiar behavior of creep-rate upturn beyond a stress threshold, as well as a mechanism map delineating the effects of stress and temperature. Collectively these findings lead to an understanding of the elementary processes governing deformation and flow of disordered materials and the effects of thermal and stress activations.

3:00 PM BREAK

3:30 PM *CM02.05.05

Improving the Ductility of Metallic Glasses by Heterogeneities [Jurgen H. Eckert](#)^{1,2}; ¹Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria; ²Materials Physics, Montanuniversitaet Leoben, Leoben, Austria.

Significant progress has been made in recent years in how to optimize processing conditions for glass formation, net-shape forming and property rejuvenation. However, the details of the correlation between composition, atomic structure, defects and thermo-mechanical treatments for structure modification and their impact on shear banding behavior and failure mechanisms for achieving macroscopic ductility are still not well-understood. Recent work suggests that the intrinsic properties of metallic glasses and composites are strongly affected by the details of short- and medium-range order arrangements and their response to external fields like mechanical deformation or temperature cycling causing heterogeneous stress and strain variation on different length-scales.

This talk explores the diversity that can be achieved in metallic glasses and composites considering structure changes, recovery and rejuvenation mechanisms when the materials are subjected to different casting conditions or thermo-mechanical cycling. The findings will be discussed with respect to short- and medium-range order modulation, local stress and strain states, defect generation and annihilation, and precipitation of secondary phases. The

structure changes will be correlated with plastic deformability and failure mechanisms, and the effectiveness of composition tuning and thermo-mechanical processing for plasticity improvement will be discussed to derive guidelines for property optimization.

4:00 PM *CM02.05.06

Spatial-Temporal Characterization of Shear Band in Bulk Metallic Glasses Xie Xie¹, Yu Chieh Lo², Tong Yang³, Junwei Qiao⁴, Gongyao Wang¹, Shigenobu Ogata⁵, Hairong Qi¹, Karin Dahmen⁶, Yanfei Gao^{1,3} and Peter K. Liaw¹; ¹University of Tennessee, Knoxville, Tennessee, United States; ²National Chiao Tung University, Hsinchu, Taiwan; ³Oak Ridge National Laboratory, Oak Ridge, Tennessee, United States; ⁴Taiyuan University of Technology, Taiyuan, China; ⁵University of Illinois at Urbana-Champaign, Urbana, Illinois, United States; ⁶Osaka University, Osaka, Japan.

Recent research shows that temperature is an important factor for the shear-band operations in bulk metallic glasses (BMGs). Thus, the characterization of shear bands through thermal imaging provides a way to study BMG deformation. Based on recent reports and research progress, the present work develops a kinetic Monte Carlo (kMC) model to investigate and simulate the initiation and propagation of shear bands, which correlates well with the thermograph-imaging results. These findings are expected to reveal the hidden statistical characteristics during the BMG deformation and advance the basic understanding of the BMG deformation mechanism.

Acknowledgements: we would very much appreciate the supports from (1) the Department of Energy (DOE), Office of Fossil Energy, National Energy Technology Laboratory (DE-FE-0011194) with the program manager, Dr. J. Mullen, (2) the U.S. Army Research Office project (W911NF-13-1-0438) with the program managers, Dr. M. P. Bakas and Dr. D. M. Stepp, and (3) the support from the National Science Foundation (DMR-1611180) with the program directors, Drs G. Shiflet and D. Farkas.

4:30 PM CM02.05.07

Local Yield Stress Analysis in Simulated 3D Glasses Dihui Ruan¹, Sylvain Patinet² and Michael L. Falk¹; ¹Johns Hopkins University, Baltimore, Maryland, United States; ²ESPCI, Paris, France.

The 'Local Yield Stress' (LYS) method is applied to an atomistic model of as-quenched glasses by shearing local regions. By probing the structure in local shear modes, the LYS method measures the local yield stress as the incremental stress at the onset of a plastic instability. This method has been upgraded to a three-dimensional version with variations in orientations, rotations and triaxiality when locally deformed. This analysis is then utilized to identify the population of 'Shear Transformation Zones' (STZs), defined as local atomic clusters that rearrange cooperatively when the material is subjected to shear. These STZs are present in the as-quenched material structure. The population of STZs is correlated with the plastic events observed during a molecular dynamics simulation in which the glass is subjected to shear at the boundaries in order to assess the predictive capability and persistence of the derived STZ population while the material undergoes deformation.

4:45 PM CM02.05.08

Atomic-Scale Homogeneous Plastic Flow of Bulk Metallic Glass Jiaxin Yu^{1,2}, Amit Datye², Zheng Chen², Chao Zhou², Omur E. Dagdeviren², Jan Schroers² and Udo Schwarz^{2,3}; ¹Key Laboratory of Testing Technology for Manufacturing Process, Ministry of Education, Southwest University of Science and Technology, Mianyang, China; ²Department of Mechanical Engineering and Materials Science, Yale University, New Haven, Connecticut, United States; ³Department of Chemical and Environmental Engineering, Yale University, New Haven, Connecticut, United States.

The onset of yielding and the local plastic flow mechanism of bulk metallic glasses (BMGs) at room temperature have not been fully understood at atomic scale. Further reducing the stressed volumes of BMGs during mechanical testing can decrease the amount of activated shear transformation zones (STZs) under shear stress, which is expected to provide direct insight into the onset of plastic deformation and the material's atomic-scale flow behavior. In this work, we employed thermoplastic forming to produce atomically flat Pt-based BMG surfaces, whose yield stress, the onset of yielding, and plastic flow at the atomic scale were subsequently studied using atomic force microscopy (AFM)-based nanoindentation. The experiments revealed a much higher yield stress compared to the value obtained by conventional nanoindentation testing, which indicates that the yield stress of BMG strongly depends on the stressed volume in the test, with a smaller stressed volume causing a higher yield stress. Differing from control experiments performed on Pt(111), the plastic flow of Pt-BMG is homogeneous, and no pop-in events are observed. Moreover, the plastic response of Pt-BMG does not exhibit any loading rate dependence, but needs a constant stress to sustain flow. These atomic-scale results are contrasted to the larger-scale model that explains plastic deformation of BMG as originating from the finite STZs activation.

SESSION CM02.06: Poster Session II: Structure-Property Relations in Non-Crystalline Solids

Session Chairs: Katharine Flores, John Mauro, Tanguy Rouxel and Yunfeng Shi

Tuesday Afternoon, November 27, 2018

8:00 PM - 10:00 PM

Hynes, Level 1, Hall B

CM02.06.01

Real-Time Observation of Thermally-Induced Structural Changes of Poly(Lactic Acid) Thin Film by Terahertz Spectroscopy Madoka Nakamura, Makoto Okano and Shinichi Watanabe; Keio University, Yokohana, Japan.

Polymeric materials exhibit intriguing temperature-dependent structural transitions, such as a glass transition at T_g , and a crystallization phase transition at T_c . Since some polymers have relatively low T_g and T_c , the structural change might occur during the productive processes. Since the structure of polymers affects their optical, electrical, and mechanical properties, it is important to characterize them *in-situ* during the productive processes. Recently, it has been demonstrated that the terahertz time-domain spectroscopy (THz-TDS) is a powerful tool to evaluate the structure of polymeric materials[1-5]. In contrast to the conventional methods such as X-ray diffraction, THz-TDS has some clear advantages: (i) Nondestructive and contactless inspection. (ii) Evaluation of T_g [1,3] (iii) Detection of both the amorphous and the crystalline phases[5]. (iv) Prompt measurement within 1 ms. These features allow us to real-time monitor the structural change of the polymeric products. Here, we demonstrate a real-time sensitive monitoring of the thermally-induced structural changes of poly(lactic acid) (PLA) using THz-TDS. PLA is one of the most promising biodegradable polymers for industrial polymer products. Because the PLA has relatively low T_g (~60°C) and T_c (~120°C), its structure easily modified by the heating. Thus, the PLA is a suitable material for investigating the structural changes by the heating with the THz-TDS.

By real-time monitoring the terahertz optical responses of the PLA during the heating, the complicated temperature dependence of the complex dielectric function ($\epsilon = \epsilon' + i\epsilon''$) of the PLA was observed. To clarify the structural change of the PLA, we focused on the spectral shape of ϵ' , especially the absolute

value of the slope, $|\Delta\epsilon'|$, at 0.5-1.0 THz. We found two characteristic behaviors of $|\Delta\epsilon'|$ regarding the structural changes of the PLA: (i) Existence of the inflection point at T_g . (ii) Drastic decrease around T_c . Our findings are well explained by the classical Lorentz oscillator model[5]. The former behavior results from the broadening of the vibration mode due to the change in the free volume from the glass to the rubber states[1,3]. The latter one is attributed to the blueshift of the vibration mode accompanied by the phase transition from the amorphous to the crystalline phases[2,5]. Our novel analytical procedure that is based on the Lorentz oscillator model and utilizes $|\Delta\epsilon'|$ as an indicator to evaluate the structure clearly reveals the structural change in the PLA compared with the previous reports [1-5]. Thus, we conclude that our method is promising for proving the structural change of polymeric materials in the productive processes.

[1] S. Wietzke *et al.*, *Opt. Express* **17**, 19006 (2009).

[2] N. Fuse *et al.*, *Jpn. J. Appl. Phys.* **49**, 102402 (2010).

[3] M. Komatsu *et al.*, *J. Appl. Phys.* **117**, 133102 (2015).

[4] H. Li *et al.*, *Polym. Test.* **57**, 52 (2017).

[5] H. Iwasaki *et al.*, *J. Phys. Chem. B* **121**, 6951 (2017).

CM02.06.02

Beneficial Effects of Oxygen Addition on Glass Formation in a High-Entropy Bulk Metallic Glass Di Cao, Zhaoping Lu and Yuan Wu; University of Science and Technology Beijing, Beijing, China.

Glass-forming ability (GFA) is one of critical scientific problems for the field of bulk metallic glass (BMGs), and how to facilitate glass formation is always a central yet important research theme for this field. Compared with conventional BMGs in the same alloy system, newly developed high-entropy BMGs (HE-BMG) usually show much enhanced thermal stability, but appreciably reduced GFA. In contrast to the conventional wisdom, we found that GFA of the Zr₂₀Cu₂₀Hf₂₀Ti₂₀Ni₂₀ HE-BMG could be enhanced by oxygen microalloying. The underlying mechanism was explored from both thermodynamic and kinetic point of view, and our analysis indicates that the high packing density resulted from addition of small oxygen atoms is responsible for the beneficial effect of oxygen. The current findings not only shed new insights into understanding of glass formation, but also broaden the view for exploring new kinds of HE-BMGs with enhanced properties and low manufacturing costs.

CM02.06.03

ToF SIMS Characterization of Polymer Thin Films—Impact of Molecular Weight Amal Ben Hadj Mabrouk^{1,2,3}, ¹University Grenoble Alpes, Grenoble, France; ²CEA-LETI, Grenoble, France; ³Sorbonne Universités, Paris, France.

Organic materials have risen to great importance in the world of electronics. Especially polymers have brought new possibilities to the field. With their numerous advantages like thermal stability, etch resistance and flexibility [1], organic compounds are growingly being studied and used for conductive layers, high resolution lithographic and packaging applications. In order to understand the logic behind the development and selection of such materials, it is fundamental to acquire a basic familiarity with the relationships between their structural parameters and physicochemical properties. Chemical depth profiling techniques like time-of-flight secondary ion mass spectrometry (ToF-SIMS) can help identify the relationship between the polymer chemical behavior when being bombarded by primary ions and their structural parameters. ToF-SIMS depth profiling of organic materials has developed rapidly and has been improved by using mainly the “Dual beam” technique which allows the precise tracking of characteristic chemical fragments and the suppression of the accumulated damage during the etching process [2].

In this work we present the characterization of Poly (methyl methacrylate) and Polystyrene thin films with varying molecular weights ($2-9.9 \times 10^5 \text{ g}\cdot\text{mol}^{-1}$) by ToF-SIMS measurements. It focuses on the in-depth investigation of the influence of the molecular weight of the mentioned polymers on the efficiency of the sputtering process, at different energies. The characterization was carried out using monoatomic Cesium sources with different energies for sputtering and Bismuth ion sources for analysis. Additionally, roughness measurement using Atomic Force Microscopy (AFM) were performed because the surface topographic change during sputtering is known to be one of the most important factors to affect depth resolution. The experiments show an inversely proportional relationship, with different orders of magnitude, between the sputtering yield volume ($\text{nm}^3/\text{primary ion}$) and the molecular weight M_w . This tendency can be related whether to the studied polymers glass transition temperature (T_g) or to the initial solution viscosity.

This work was carried out in the Nano-Characterization Platform (PFNC) at the CEA Grenoble

[1] J.M. Rooney, (1984) "Microelectronic Applications for Polymers: Structure Property Relationships", *Microelectronics International*, Vol. 1 Issue: 4, pp.32-35, <https://doi.org/10.1108/eb044142>

[2] Ninomiya, S., Ichiki, K., Yamada, H., Nakata, Y., Seki, T., Aoki, T. and Matsuo, J. (2009), Precise and fast secondary ion mass spectrometry depth profiling of polymer materials with large Ar cluster ion beams. *Rapid Commun. Mass Spectrom.* **23**: 1601-1606. Doi:10.1002/rcm.4046

CM02.06.04

Highly Processable Work-Hardenable Zr-Based Metallic Glass Composites Reinforced by Continuous TiNi Fiber Jie Zhou, Zhaoping Lu and Yuan Wu; University of Science and Technology Beijing, Beijing, China.

Bulk metallic glasses (BMGs) have attracted considerable research activities because of their unique mechanical properties, such as high strength, large elastic limit and high hardness. However, room-temperature brittleness and strain-softening limited their structural applications. Up to now, it has been proved that enhanced plasticity and strong work-hardening ability could be achieved by introducing the concept of transformation-induced plasticity (TRIP) into Zr-based or Ti-based bulk metallic glass composites (BMGCs). Most currently developed TRIP-reinforced BMGCs are fabricated with in-situ formed second phase method, in which homogeneous formation of austenitic phase is a big challenge.

To produce work-hardenable BMGCs in a processable way, we designed a series of BMGC reinforced by introducing ex-situ continuous TiNi fibers, which can bring in martensitic transformation (MT) and TRIP effect and eventually leads to the combination of pronounced plasticity and considerable work-hardening ability under both quasi-static and dynamic compressive loading.

In this talk, preparation, microstructure characteristics, mechanical properties and deformation mechanism of BMGCs reinforced by TiNi fibers will be discussed.

CM02.06.05

Combinatorial Temperature Resistance Sensors for the Analysis of Phase Transformations Haitao Zhang¹, Yong Xiang¹ and Joost J. Vlassak²; ¹University of Electronic Science and Technology, Chengdu, China; ²Harvard University, Boston, Massachusetts, United States.

In this work, we describe a sensor array that can effectively measure the resistance of thin films as a function of temperature and composition. The sensor is fabricated in very simple micro fabrication steps. Detailed FEM simulation indicates that the sensor has very high temperature uniformity, which leads to

extreme sensitivity and thus the ability to detection of subtle structure change of materials. We have used the sensor to observe structural relaxation, the glass transition, and crystallization of PdSiCu metallic glasses. We also find that the ratio of the resistance of crystallized to as-deposited material is correlated with the glass-forming ability for both PdCuSi and NiZr-based alloys, potentially providing an avenue to the fast screening of good glass formers in complex material systems.

CM02.06.06

How Alkaline and Earth-Alkaline Elements Can Change Role in Glasses and Melts? Implication for Nucleation Processes and Redox Change? Daniel R. Neuville and Maria Rita Cicconi; IPGP-CNRS-USPC, Paris, France.

Alkali and alkaline earth can behave as network modifier or as charge compensator of AlO_4^- in aluminosilicate glasses and melts. As a function of the role, density, molar volume, viscosity, liquidus and glass transition temperature and more generally, macroscopic properties, can change significantly. But how evaluate or prove this change of role? Recently, Helhen and Neuville (2014) have shown by comparing Raman in VV and VH polarization, that a new band appears in the VH Raman spectra when the role of Ca(Na, Mg) changes from charge compensator to network modifier. Furthermore, we have shown in the XANES spectra at the Ca K-edge, important differences in the Ca pre-edge peaks as a function of this same change of role. Similar behaviour were observed on the Calcium K-edge via XANES spectroscopy (Cicconi et al., 2016) and on the Na, via NMR (Le Losq et al., 2014). During this presentation, we plan to show some new results on XANES, Raman, NMR.

To conclude, by looking at the role of alkaline earth elements in glasses and melts, it is possible to have a better knowledge of the structure of glasses and melts, but also to better understand their influence on redox and nucleation processes.

Reference :

Le Losq Ch., Neuville D.R., Florian P., G.S. Henderson and Massiot D. (2014) *Geochimica Cosmochimica Acta*, 126, 495-517.

Helhen B. and Neuville D.R. (2015) *The Journal of Physical Chemistry B*, 119, 4093-4098.

Cicconi M.R., de Ligny D., Gallo T.M., Neuville D.R. (2016) *American Mineralogist*, 101, 1232-1236.

CM02.06.07

Short Range Order in Fluorine Containing $\text{CaO-SiO}_2\text{-CaF}_2$ Glasses from NMR, Neutron Diffraction, and X-Ray Absorption Spectroscopy Laura A. Swansbury^{1,2} and Gavin Mountjoy¹; ¹University of Kent, Canterbury, United Kingdom; ²Morgan Advanced Materials, Bromborough, United Kingdom.

The glass system $\text{CaO-SiO}_2\text{-CaF}_2$ has been studied to help elucidate the structure of more complex $\text{CaO-SiO}_2\text{-P}_2\text{O}_5\text{-CaF}_2$ fluorine-containing bioactive glasses. The $\text{CaO-SiO}_2\text{-CaF}_2$ glass series was synthesized and the glass transition temperature decreased linearly with increasing CaF_2 concentrations. Compositional analysis revealed that fluorine losses occurred due to fluorine volatilisation during synthesis. The chemical shift positions in the ^{19}F MAS-NMR spectra became more negative with increasing CaF_2 concentrations, becoming more similar to that of pure CaF_2 . By studying the calcium environment using neutron diffraction and x-ray absorption spectroscopy at the Ca K-edge, reasonably consistent values for Ca-F and Ca-O nearest neighbour distances of approximately 2.3 Å and 2.4 Å (respectively) could be obtained. However, it was challenging to establish the coordination numbers and disorder in distances of such nearest neighbours.

CM02.06.08

Structure-Property Relations in Amorphous Polymer Derived Ceramics for Electronic Applications Mehrdad Abbasi¹, Soohyun Im¹, Jared Johnson¹, Gabriel Calderon Ortiz¹, Menglin Zhu¹, Nathan A. Oylar², Michelle M. Paquette², Paul Rulis², Ridwan Sakidja³ and Jinwoo Hwang¹; ¹The Ohio State University, Columbus, Ohio, United States; ²University of Missouri – Kansas City, Kansas City, Missouri, United States; ³Missouri State University, Springfield, Missouri, United States.

We develop a novel methodology for accurate design and fabrication of complex disordered solids using a combination of advanced experimental and computational techniques. Complex disordered solids are non-crystalline materials for which the fundamental building blocks are typically molecules or molecule fragments, and therefore they have great potential for tunable structure and properties for various applications. However, the complexity and high degree of freedom in their structure impose substantial challenges to the design and optimization of these materials. This presentation will focus on the structural characterization of polymer derived amorphous hydrogenated boron carbide thin films using 4-dimensional scanning transmission electron microscopy (4D-STEM). The 4-D STEM utilizes electron nanoprobe and the new-generation fast pixelated STEM detector, which records the diffraction patterns from individual nanoscale volumes of the material. The fluctuation and angular correlation analyses of the diffraction patterns can provide the unprecedented details of the structural heterogeneity, including the size, distribution, connection, and volume fraction of medium range ordering (MRO). We show that the MRO in amorphous hydrogenated boron carbide can be comprised of the connection and networking of the icosahedral short-range clusters, and the MRO can directly affect the important physical and electrical properties of the films. Our finding is promising as it could greatly expand the breadth of materials-by-design approaches by flexibly tuning the structure of disordered materials to achieve desired properties.

CM02.06.09

In Situ Observation of Shear-Driven Amorphization Process in Silicon Crystals Scott X. Mao¹, Yang He¹, Chongmin N. Wang² and Ting Zhu³; ¹University of Pittsburgh, Pittsburgh, Pennsylvania, United States; ²Pacific Northwest National Laboratory, Richland, Washington, United States; ³Georgia Institute of Technology, Atlanta, Georgia, United States.

Amorphous materials are used for both structural and functional applications. An amorphous solid usually forms under driven conditions such as melt-quenching, irradiation, shock loading or severe mechanical deformation. Such extreme conditions impose significant challenges on the direct observation of the amorphization process. Various experimental techniques have been used to detect how the amorphous phases form, including synchrotron X-ray diffraction, transmission electron microscopy (TEM) and Raman spectroscopy, but a dynamic, atomistic characterization has remained elusive. Here, by using in-situ high-resolution TEM, we show the dynamic of the amorphization process of silicon nanocrystals during mechanical straining at the atomic scale. We find that shear-driven amorphization occurs in a dominant shear band starting with the diamond-cubic (dc) to diamond-hexagonal(dh) phase transition and then proceeds by dislocation nucleation and accumulation in the newly formed dh-Si phase. The process then leads to the formation of an amorphous Si (a-Si) band, embedded with dh-Si nanodomains. The amorphization of dc-Si via an intermediate dh-Si phase is a previously unknown pathway of solid-state amorphization.

CM02.06.10

Mineralogical Characterization and Quantification of a Complex Natural Mineral Containing Diatomite after Thermal Treatment Carolina Cárdenas-Ramírez^{1,2}, Franklin Jaramillo Isaza¹ and Maryory Gomez Botero¹; ¹Universidad de Antioquia, Medellín, Colombia; ²Sumicol S.A.S, Medellín, Colombia.

In the present work, a thermal treatment of a complex natural mineral containing diatomite was carried out to investigate the effect on its phase transitions and, moreover, to properly identify and quantify such phases. Diatomite is a type of hydrated amorphous biogenic siliceous mineral, primarily opal, from geological deposits and possesses unique properties as highly porous structure, excellent absorption capacity and thermal stability. One of the major problems is distinguishing crystalline cristobalite from some forms of opal which have similar diffraction patterns, the opal phases significantly contain water and these phases are not crystalline in the classical sense, therefore as no long-range ordering exists, it is difficult to identify such phases through conventional XRD techniques. The characterization is even more difficult as typical natural minerals are not pure diatomite. The sample studied for this investigation was calcined in a muffle furnace at temperatures of 600°C, 900°C and 1100°C. The phase evolution and microstructure of the sample were investigated by X-ray fluorescence (XRF), thermogravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDXS) and transmission electron microscopy (TEM). Through Rietveld refinement method the phases were quantified. The results showed that the clay minerals in the raw material were kaolinite, quartz, illite and a great amount of amorphous (presumably diatomite). The calcination at 1100°C allowed to crystallize most of the phases other than diatomite, allowing to quantify the amount of diatomite present in the material when compared with the raw sample. No crystallization of diatomite was observed at any of the evaluated temperatures. Besides, it was found by HRTEM that diatomite has a short-range ordering, d-spacings were measured and correlated with possible crystalline phases showing cristobalite/tridymite-like crystals, even in the raw sample, these crystalline phases correspond to cryptocrystals. These findings allow to improve the understanding of complex natural minerals containing diatomite through the implementation of a systematic use of different characterization techniques for its adequate phase determination and quantification.

CM02.06.11

Amorphous Germanium Material Evaluation for Evanescent Wave Sensors for MWIR and LWIR Sensing Applications Eveline Postelnicu¹, Peter Su¹, Danhao Ma¹, Ruitao Wen¹, Raturaj Pujari¹, Ryan Kosciolk¹, Venita Boodho¹, Ron Synowicki², Jurgen Michel¹, Lionel C. Kimerling¹, Kazumi Wada¹ and Anuradha Agarwal¹; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²J.A. Woollam Company, Inc., Lincoln, Nebraska, United States.

Room temperature deposited amorphous germanium (Ge) material has been evaluated for evanescent sensing applications in the Midwave and Longwave infrared regions (MWIR and LWIR). The advantage of amorphous Ge is that it can be used to sense a wide variety of organic molecules for both biomedical and environmental sensing and its room temperature processing is very economically efficient. Thin films of amorphous Ge were obtained using various processing approaches: Sputter Deposition, Electron Beam Evaporation (E-beam), and Physical Vapor Deposition (or thermal evaporation). Films were characterized using X-Ray Diffraction (XRD), Fourier Transform InfraRed (FTIR) Spectroscopy, Wavelength-Dispersive (Electron) Spectroscopy (WDS), Hall Effect measurements, and Ellipsometry. It was shown that Electron Beam Evaporation yielded the purest material, with 96% Ge and 4% carbon contamination, while thermal evaporation showed only around 70% Ge and 30% of the film containing contaminants from the evaporation chamber. Ellipsometry performed on the amorphous Ge samples at a wavelength range of 1.5 to 15 microns showed that the index of refraction, n , of sputtered Ge had a lower range (2.9 – 3.4) than that of E-beam Ge (4 – 4.5). The extinction coefficients for both sputtered Ge and E-beam Ge are in a comparable range, 0 to 0.4, for the same measured wavelength range (1.5 to 15 microns), indicating low absorption losses within the material. X-Ray Diffraction confirmed the amorphous nature of the deposited Germanium. Waveguides utilizing this low loss amorphous Ge within a Si-CMOS-compatible platform will be presented.

CM02.06.12

Structural Variation of (Hydrogenated) Amorphous Silicon with Density—A Classical Monte Carlo Study Enrique Guerrero and David A. Strubbe; Physics, University of California, Merced, Merced, California, United States.

We present computational generation of hydrogenated (a-Si:H) and non-hydrogenated (a-Si) amorphous silicon structures for use in studying the electronic properties of thin-film solar cells, such as "heterojunction with intrinsic thin-layer" (HIT) cells with a-Si:H and c-Si layers. We generate structures using the Wooten-Winer-Weaire (WWW) classical-potential Monte Carlo method using our CHASSM (Computational Hydrogenated Amorphous Semiconductor Structure Maker) code, which implements a WWW scheme that can take into account Si-H bonds. We create structures of various densities and study the effect on structural parameters including bond lengths, bond angles, dihedral angles, and radial distribution functions. Abrupt transitions occur at certain critical densities (different depending on hydrogen content) which suggest crossover between different types of amorphous structures, perhaps even different phases. We investigate mechanical and spectroscopic consequences of these changes. At low densities, voids form, which are likely to constitute defects limiting carrier mobilities and may be implicated in light-induced degradation (the Staebler-Wronski effect). We mathematically characterize the voids using Voronoi polyhedra and persistent homology. We show some refinements of the Monte Carlo randomization process needed to avoid ending in crystalline structures or a class of unphysical excessively coordinated structures.

CM02.06.13

Insight into the Mechanism of Damage Initiation and Fracture of Conductive Polyurethane Nanocomposites Spencer A. Hawkins⁴, Evan Sullivan⁵, Alireza Sarvestani^{1,2}, Hilmar Koerner³ and Dhriti Nepal³; ¹Ohio University, Athens, Ohio, United States; ²Mechanical Engineering, Mercer University, Macon, Georgia, United States; ³Wright-Patterson Air Force Base, Air Force Research Laboratory, Dayton, Ohio, United States; ⁴Universal Technology Corporation, Beavercreek, Ohio, United States; ⁵University of Kentucky, Kentucky, Kentucky, United States.

Polyurethane (PU) is a functional copolymer whose properties bridge the gap between rubber and thermoplastics. Their excellent physical properties, such as flexibility and abrasion resistance along with their high temperature plasticity have made them an ideal structural material for application in aerospace structures, automobiles, electro-machinery vocation, etc. In an attempt to promote the formation of a conductive network within PU, we have developed an experimental technique to decorate carbon nanofibers (CNFs) with silver (Ag) nanoparticles and subsequently blended them with PU. Introduction of a small amount of CNF (coated with Ag) into the PU matrix produced a conductive nanocomposite with higher stiffness and strength compared to that of pure PU but substantially reduced the fracture toughness of the material. Here, we present a systematic and comprehensive study to understand the mechanism of damage nucleation and fracture evolution in Ag-CNF-PU nanocomposites. By mapping the surface of samples using AFM-IR, the onset of damage was monitored prior to realization of plastic deformation during in situ tensile testing. Coupled with the results of DMA analysis, we concluded that strain induced crystallization in PU and polymer debonding from CNF surface are the most detrimental mechanisms that control the fracture toughness of PU nanocomposites. These conclusions were used to develop a model that predicts the mechanical behavior of PU nanocomposites at finite deformations.

CM02.06.14

Mechanical Behavior of Highly Rejuvenated Bulk Metallic Glasses Jie Pan and Yi Li; Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China.

Rejuvenation of metallic glasses, bringing them to higher-energy states, is of interest in improving their plasticity. However, how to achieve significant

flow and rejuvenation throughout a deformed metallic glass remains challenging, and the mechanical behavior of the highly rejuvenated bulk metallic glasses is unexplored. In this presentation, we will reveal the significant improvement in compressive plasticity in a Zr-based bulk metallic glass (BMG) by structural rejuvenation, which is in stark contrast to the ageing induced brittleness. Upon constrained compression on the BMG rods at room temperature, extreme rejuvenation occurs in a large volume of BMG specimens, accompanied with a considerable amount of free volume generation, reduced hardness, Young's modulus. As a result, shear transformation zones will be easily activated, giving rise to reduced yield strength of 1.37 GPa, much improved compressive plasticity, as well as more homogeneous deformation. The present work reveals the correlation between the deformation behavior and energy state in metallic glasses, which will help us to understand the deformation mechanism of metallic glasses, even disordered systems.

CM02.06.15

Atomistic Modeling of a Photovoltaic Material—Hydrogenated Amorphous Silicon [Raymond Atta-Fynn](#)¹, [Harsh Arya](#)¹, [Somilkumar Rathi](#)² and [Parthapratim Biswas](#)³; ¹Physics, Univ of Texas-Arlington, Arlington, Texas, United States; ²Eugenus Inc., San Jose, California, United States; ³Physics, University of Southern Mississippi, Hattiesburg, Mississippi, United States.

Hydrogenated amorphous silicon (*a*-Si:H) is an important electroactive and photovoltaic material of technological importance that can be quite difficult to model accurately, particularly on a large scale for electronic structure analysis. In this work, we present a novel and efficient approach which couples accelerated classical molecular dynamics with *ab initio* relaxation to model high-quality, large atomistic models of *a*-Si:H. Specifically systems containing 10,000 Si atoms and H atomic concentration of 9%-18% were simulated. The models are nearly free of coordination defects and their structural, electronic and nuclear magnetic resonance properties of the model are in good agreement with experimental data. The approach paves the way for the generation of realistic device-size atomistic networks of *a*-Si:H. Furthermore, the approach can be readily generalized to produce a variety of binary and ternary amorphous networks in two and three dimensions, and amorphous/crystalline heterojunctions to address the physics of photovoltaic devices.

CM02.06.16

Extreme Energy Absorption Through High Rate Deformation of Freestanding Glassy Polymer Thin Films [Jinho Hyon](#)¹, [Ye Eun Song](#)¹, [Edwin L. Thomas](#)¹, [Jason Streit](#)² and [Richard Vaia](#)²; ¹Material Science and NanoEngineering, Rice University, Houston, Texas, United States; ²Materials & Manufacturing Directorate, Air Force Research Laboratory, Dayton, Ohio, United States.

Of all materials, only polymers exhibit a strongly dissipative melt state. If a set of deformation processes can lead to strong heating of an initially glassy polymer material, large amounts of kinetic energy can be absorbed. Normally at room temperature, glassy polymers undergoing rapid tensile loading craze, crack and then fracture with little overall energy absorption. Here we exploit the higher mobility and lower entanglement density of the chains near the free surfaces of ultrathin films to induce extensive crazing and consequently adiabatic heating by imposing a very high strain rate ($\sim 10^7/s$) using a micro-projectile ballistic test. The near-surface thin film effects not only dramatically increase the number of crazes nucleated, but assist their subsequent growth, impingement and the accompanying large adiabatic temperature rise of the deforming film. We employ 3.7 micron diameter spherical silica projectiles propelled at incident velocities ranging from 350-800 m/s to investigate the kinetic energy (KE) absorption. Homopolymer polystyrene (PS) films with different molecular weights and film thicknesses and single component nanocomposite PS grafted nanoparticle (PSgNP) films ($\sim 1\%$ v/v NPs with 100's of chains covalently anchored to each NP) show extraordinary high KE absorbed per unit mass of the target film (on the order of several MJ/kg, comparable to the energy density of TNT). Use of a glassy-glassy microphase separated lamellar diblock copolymer (PS-*b*-P2VP) to create films comprised of just a few parallel lamellae allows strong alteration of the polymer chain conformations while keeping the overall molecular weight (MW) and glass transition temperature (T_g) comparable to the PS homopolymer and grafted NP films. A block copolymer offers the additional energy absorption mechanism required for block mixing if heating takes the sample above the order to disorder transition temperature.

CM02.06.17

Evaluation of Amorphous Alumina as Effective Hydrogen Resistive Coating for Ferritic Steel [Xiahui Yao](#), [Vrindaa Somjit](#), [Ju Li](#) and [Bilge Yildiz](#); Department of Nuclear Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Hydrogen gas (H_2) as a promising energy storage media and a clean fuel, plays a central role in future low-carbon infrastructure. Yet the storage and transportation of hydrogen gas is cumbersome due to its high diffusivity, low density and poor compressibility. Long range hydrogen delivery exploiting the existing natural gas pipeline network has been proposed and found feasible when the volume ratio of hydrogen is below 15%. But the high diffusivity of hydrogen results in nearly seven times higher permeation loss than natural gas. At the same time, the notorious hydrogen embrittlement effect is expected to degrade the mechanical performance of the steel and bring safety concerns. To improve the tolerance of existing pipeline steels toward high concentrations of hydrogen, as in direct transportation of hydrogen gas in these pipelines, a low-cost and effective hydrogen resistant coating is desired to be applied on the inner surface of the steel pipelines. α - Al_2O_3 is one of the best materials to reduce the permeation of hydrogen. But the formation of crystalline α - Al_2O_3 requires processing temperatures beyond the tolerance of pipeline steel. In this work, we developed two conformal coatings of amorphous Al_2O_3 on the surface of ferritic steel with mild formation temperature and evaluated their effectiveness as a hydrogen permeation barrier. An electrochemical testing approach was adopted for this evaluation to mimic the operation condition of hydrogen pipeline, which is featured by the ambient temperature but high H_2 activity (equivalent to a high H_2 pressure of 30~70 MPa). We found that amorphous Alumina also provides excellent barrier characteristics. Over 200 times permeation reduction factor was found for the coating with only 1/300 of steel thickness. The micro-structure of the two coatings were also compared and found to be critical in the permeation performance. Currently, we are systematically assessing the effect of the microstructure, controllable by synthesis and post-anneal conditions, on the resistance of these layers against hydrogen entry and diffusion. Our result suggests that by properly managing the microstructure of the coating layer, it is possible to utilize the low temperature derived amorphous alumina as an effective hydrogen barrier coating.

CM02.06.18

Ultra-High Strength Above 10 GPa and Short-Range Atomic Order of Amorphous Boron [Jessica M. Maita](#), [Gyuho Song](#), [Mariel Colby](#) and [Seok-Woo Lee](#); University of Connecticut, Storrs, Connecticut, United States.

Amorphous boron fiber has been widely used as a reinforcement filler in aerospace resin-matrix composites due to its high strength and high elastic modulus. However, its mechanical properties have not been measured accurately due to its intrinsic issues during fabrication. Amorphous boron is usually produced in single-filament reactors by chemical vapor deposition of boron on tungsten wire, and the final product is a core-shell wire with a tungsten boride core and amorphous boron shell. The diameter of this composite fiber is approximately 100 micrometers, and the thickness of the boron-shell is 40 micrometers. Traditionally, wire tension tests of the composite fiber or hollow amorphous boron fiber have been conducted but would underestimate the strength due to the greater probability of defects that exist along the long wire. Therefore, it is necessary to perform reliable mechanical tests at small length scales. Recent developments in micropillar compression and tension testing enable us to probe mechanical properties of small materials accurately. In addition, the local atomic arrangement in amorphous boron has not been clearly understood because of the complexity in its amorphous structure. Therefore, it is necessary to conduct advanced transmission electron microscopy (TEM) to analyze the local structure at atomic resolution.

In this presentation we will discuss microstructural and mechanical characterization of amorphous boron with high resolution TEM and in-situ scanning selection microscopy (SEM) micropillar compression results. TEM diffraction patterns show a unique set of three halo rings while an amorphous material usually has a single halo ring. The three halo rings imply amorphous boron would consist of the random distribution of crystallites. Fast Fourier transform (FFT) was used to confirm these crystallites consist of short-range ordered boron clusters. We will also discuss micropillar compression results, the yield strength as a function of micropillar diameter. Its ultra-high strength (~13 GPa) will be discussed in terms of its unique microstructure and the intrinsically strong atomic bonding of metalloid materials. Our results help to provide a deeper understanding of plasticity and fracture processes in amorphous boron and will be useful in the development of mechanically robust boron-fiber composites.

CM02.06.19

Mass and Thermotransport in Liquid Ni-Al-Co Alloys Tanvir Ahmed³, William Yi Wang¹, Zi-Kui Liu², Irina Belova³ and Graeme Murch³; ¹School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an, China; ²Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States; ³School of Engineering, The University of Newcastle, Callaghan, New South Wales, Australia.

Mass and thermotransport properties in liquid Ni-Al-Co alloys are studied over a wide temperature and concentration range by using molecular dynamics (MD) simulations. The calculations are performed by means of equilibrium MD simulations in conjunction with the Green-Kubo formalism and an embedded-atom method (EAM) potential for this system developed by Pun *et al.* [1]. Results of simulations also allow the description of the temperature and concentration dependence of the thermodynamic factor. Furthermore, the simulations permit analysis of the heat of transport as a function of temperature and composition as well. The complete range of the diffusion properties including Onsager off-diagonal terms and partial properties are estimated for the considered temperature and concentration ranges. Overall, results of this study agree well with previous published experimental and simulation data where available. In addition, for liquid Ni-Al alloys, the calculations are also carried out with a potential [2] for comparison purposes.

References

- [1] Purja Pun, G. P., Yamakov, V., and Mishin, Y., "Interatomic potential for the ternary Ni-Al-Co system and application to atomistic modeling of the B2-L1₀ martensitic transformation", *Modelling Simul. Mater. Sci. Eng.*, 23(6), 065006, 2015. DOI: <http://dx.doi.org/10.1088/0965-0393/23/6/065006>
[2] G.P. Purja Pun and Y. Mishin, "Development of an interatomic potential for the Ni-Al system", *Phil. Mag.* 89, 3245, 2009. DOI: <http://dx.doi.org/10.1080/14786430903258184>

CM02.06.20

Mobility of Proton Carriers in Proton Conducting Phosphate Glasses Takahisa Omata¹, Takuya Yamaguchi², Tomohiro Ishiyama², Satoshi Tsukuda¹, Junji Nishii³, Toshiharu Yamashita⁴ and Hiroshi Kawazoe⁴; ¹Tohoku University, Sendai, Japan; ²National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Japan; ³Research Institute for Electronic Science, Hokkaido University, Sapporo, Japan; ⁴Kawazoe Frontier Technologies Corporation, Yokohama, Japan.

Proton conduction in phosphate glasses is a historical topic in solid state ionics and glass chemistry because of their potential applications of electrolytes in various devices. A lot of studies have focused on to understand and to improve their proton conductivity. In previous proton conducting phosphate glasses, because the proton carriers were supplied from the residual water that was vaporized and come away from the melt during melting at the temperatures higher than 1000 °C, the proton carrier concentration was limited to 10¹⁹~10²⁰ cm⁻³. We recently developed a proton injection technique that is electrochemical substitution of alkali ions with protons termed as APS. APS enables to achieve extraordinary high proton concentration such as 10²² cm⁻³; therefore, to achieve high proton mobility is strongly desired in order to realize high proton conductivity.

In this study, we studied the influences of the polymerization degree of phosphate glass network and kinds of alkaline-earth oxides that are typical glass network-modifiers on the proton mobility. As a result, we found that the proton mobility increases with the decreasing polymerization degree of glasses; however, the proton mobility start to decrease when pyrophosphate ions, P₂O₇⁴⁻, become major component in phosphate network, because the protons are deeply trapped in pyrophosphate ions rather than metaphosphate ions, (PO₃)_n. Regarding to the kinds of alkaline-earth oxide modifiers, the proton mobility was higher in the glass containing BaO than the glass containing MgO. The higher proton mobility in the Ba-glass than the Mg-glass was attributed to higher ionicity of the Ba-O bond than the Mg-O bond based on P 2p and O 1s core-level XPS spectra.

Based on these understandings, we designed a glass, 36HO_{1/2}-4NbO_{5/2}-2BaO-4LaO_{3/2}-4GeO₂-1BO_{3/2}-49PO_{5/2}, and it was prepared by APS using 36NaO_{1/2}-4NbO_{5/2}-2BaO-4LaO_{3/2}-4GeO₂-1BO_{3/2}-49PO_{5/2} glass as a precursor glass. The proton conductivity of the glass was 1×10⁻³ Scm⁻¹ at 280 °C in dry 5% H₂/N₂, and it was almost constant during keeping at 280 °C over 500 hours. It was also shown that the glass is stable under the condition of fuel cell operation. These properties are favored for the electrolyte in the intermediate temperature fuel cell.

CM02.06.21

Structural Characterization of Oxide Glass-Ceramic Scintillators for Radiation Detection Sarah Lombardo^{1,2} and Jason Nadler¹; ¹Georgia Tech Research Institute, Atlanta, Georgia, United States; ²Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, United States.

Glass-ceramic nanocomposite scintillators have become an attractive option as radiation detection materials. These materials provide radioisotope detection capabilities at lower cost with improved scalability, stability and mechanical robustness. However, light output required for proper energy resolution is proven a challenge as a result of light scattering from varying refractive indices and crystallite agglomeration present within the non-crystalline glass matrix. Understanding the structure-property relations of oxide glass-ceramic scintillator compositions is crucial for enhancing resolution, as these relations pertain to processing and performance. Analysis of the structure-property relations of oxide glass-ceramic scintillators has been achieved by employing techniques such as scanning and transmission electron microscopy, X-ray diffraction, and energy-dispersive X-ray spectroscopy for structural characterization. In addition, photoluminescence and radiation spectroscopy are employed for characterization of performance. These techniques allow for the identification of light output and resolution obtained as a result of heterogeneity, crystal structure, and phase composition present within these non-crystalline materials.

CM02.06.22

Fabrication of High-Dispersed Strawberry-Like P(St-co-MAA)/SiO₂ Composite Microspheres and Their Applications in Cementitious Materials Guanzhi Cheng^{1,2}, Yongjiang Xie^{1,2}, Xinguo Zheng^{1,2}, Huajian Li^{1,2}, Quanxiao Dong^{1,2} and Shida Li^{1,2}; ¹Railway Engineering Research Institute, China Academy of Railway Sciences, Beijing, China; ²State Key Laboratory of High Speed Railway Track Technology, Beijing, China.

Silica nanoparticles (SiO₂ NPs) can be used in cementitious materials to improve their workability and mechanical properties. But avoiding the agglomeration of SiO₂ NPs within the cementitious matrix are still the challenges to play the role of them effectively. In this work, the poly(styrene-co-methyl acrylic acid) (P(St-co-MAA)) latex particles with hydrophilic carboxylic chains grafted from the surface were first fabricated via soap-free emulsion polymerization, and then high-dispersed strawberry-like composite microspheres were prepared with the P(St-co-MAA) latex partially covered by SiO₂ NPs through lay-by-layer (LBL) assembly process. The effects of such composite microspheres on the properties of cementitious materials were

investigated afterwards.

The surface carboxylic content of P(St-co-MAA) latex particles was measured by conductometric titration. The morphologies of the latex particles and P(St-co-MAA) / SiO₂ composite microspheres were characterized by transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Thermogravimetric analyzer (TGA) and dynamic light scattering (DLS) were employed to characterize the composition and the dispersibility of the composite microspheres, respectively. After adding the composite microspheres into cementitious matrix, the hydration process of the fresh mixture was monitored by cement hydration heat analyzer. Its workability and mechanical properties were tested via conventional methods. The porosity of the hardened specimens was characterized by mercury injection method.

The results show that the surface carboxylic content of P(St-co-MAA) latex was about 1.5×10^{-4} mol/g. For the P(St-co-MAA) / SiO₂ composite microspheres, SiO₂ NPs with the mass ratio about 5.0 wt% were anchored on the latex surface, leaving above 50 % area of the surface uncovered. Such strawberry-like composite microspheres could be easily dispersed in aqueous phase without further treatment where the poly-dispersity index (PDI) was about 0.3. The composite microspheres had no obvious effects on the fluidity of the mortar and the water absorption of the hardened specimen. But it could promote the condensation of the mortar and improve their early compressive strength and flexural strength. Compared to the blank control, the 3d compressive strength of the specimens in which the mass of composite microspheres was 4 wt % of the cement was 5 MPa higher, and the flexural strength of those was 1 MPa higher. The modified mechanism of the composite microspheres for mortar was proposed.

CM02.06.23

Calorimetric Studies of a New La-Based Metallic Glass Jie Shen and Wei Hua Wang; Institute of Physics CAS, Beijing, China.

We have prepared a La-based MG which exhibits an unique exothermic peak occurring after the glass transition and before the onset of crystallization. The enthalpy change of the La-based MG is large, ~ 17% of the heat of fusion. Such a large enthalpy change enables the La-based MG to have an increase in the glass transition temperature and the β -relaxation temperature of 17 K and 30 K respectively, and a remarkable increase of the activation energy for the β -relaxation of 71%. The La-based MG exhibits an abnormal α -relaxation which shows no decrease of loss modulus at high temperature. In the stress relaxation and creep measurements, the MG gets a strong retardation with relaxation time extending from 54 s to 480 s and only 2% decrease in length after a high-temperature creep. These thermo-mechanical responses demonstrate the strong nature of its liquid: the fragility index m of the new metallic glass is only 22. The development of this new MG may provide us a new model system for investigating some fundamental issues in glassy field.

CM02.06.24

Amorphous Carbon for Hard Mask with High Etch Resistance Through Bonding Control with Various Doping Elements Min-Woo Jeong, Kun-Tae Kim, Kyung-Tae Jang, Miyoung Kim and Young-chang Joo; Seoul National Univ, Seoul, Korea (the Republic of).

As the area shrinkage of semiconductor devices for high memory density, the high aspect ratio pattern is needed such as 3D NAND flash. To create a vertical pattern with a mask, mask is needed to be thicker for etching it longer. However, a thick mask distorts the shape of the pattern with a shadowing effect. Therefore, it is necessary to have a hard mask that can be made thinner. The vertical structure is fabricated by plasma based dry etching process with hard masks, which have superior etch resistance. Therefore, it is necessary to study the properties of hard mask materials for deeply patterned devices. The hard mask should have higher etch resistant to plasma reactive gas than conventional organic soft mask for deeper patterning. It must also be easily removed after the etching process. These conditions are well satisfied with amorphous carbon, which is the most promising material for hard mask.

Carbon has various atomic bonds like sp^3 of diamond and sp^2 of graphite. The difference in carbon bond between the two materials greatly affects the properties such as mechanical and electrical properties. Amorphous carbon is known that the kind of bonding is changed according to doping element and composition. In this study, we have studied how the etch characteristics change with the change of bonding nature of amorphous carbon according to various metal element doping.

Amorphous Carbon (a-C) was deposited on SiO₂/Si substrate by DC magnetron sputter system using graphite solid target for higher purity and lower roughness than commercial CVD process. Metal element doping was proceeded by using 10 wt% of Si and W pre-doped target. The thin film was analyzed by Raman spectroscopy, XPS and etch characteristics were investigated by ICP etcher. We also examined the mid-range order of the a-C through the radial distribution function (RDF) using the diffraction pattern through TEM analysis.

The content of Si and W in a-C was measured by XPS results, 7.39 wt% and 12.2 wt% respectively. As a result of Raman spectroscopy and XPS of doped a-C thin film, the ratio of D peak and G peak (I_D/I_G) and sp^3 bonding increased, which means the increase disordered hexagonal graphite structure. Moreover, the I_D/I_G value was further increased when the heat treatment was performed up to 500 °C, which is because carbide is generated more by heat treatment. Because the Si and W form the carbide in a-C film, the degree of disorder increased. In addition, when the structure of the thin film was analyzed with RDF, it was confirmed that the sp^3 bond was increased with formation carbide. The increased sp^3 bonding portion in amorphous C improved etch resistance, which is consistent with the tendency with mechanical performance of diamond like carbon (DLC) having high sp^3 bonding. The relationship between mid-range order of doped a-C and its property was confirmed by the microstructure analysis and the measured etch resistance with various doping elements.

CM02.06.25

A String Model for the Boson Peak and Inelastic X-Ray Scattering Data of Amorphous Materials Ernesto Bianchi and Fernando Lund; Univ of Chile, Santiago, Chile.

In a continuum, solid mechanics, approximation, THz vibrations in glasses can be understood as the normal modes of vibrating strings with fixed ends on top of the Debye approximation modes. These strings scatter acoustic waves and, in a multiple scattering formulation, generate an effective (complex) index of refraction, thus describing dispersive, damped waves [1]. The attenuation and velocity dispersion as a function of frequency are qualitatively similar to that observed in glasses through Inelastic X-ray Scattering (IXS): For very low frequencies attenuation grows like frequency squared, consistent with Akhiezer damping. As frequency grows, a frequency to the fourth power behavior takes over, consistent with scattering from small objects (in this case, the strings). Finally, as frequencies around the Boson peak are reached, a new frequency squared behavior appears. The phase velocity is a decreasing function of frequency for low frequencies, and switches over to an increasing function at frequencies around the Boson peak.

The dynamic structure factor $S(k,w)$ corresponding to these acoustic waves is calculated as an explicit function of two variables, wave vector k and frequency w . The resulting formulae provide a specific functional relationship between the Boson peak data and the IXS data. It should be possible to directly test these results, for example with glycerol glass data [2].

[1] F. Lund, Phys. Rev. B 91 (2015) 094102.

[2] G. Monaco and V. M. Giordano, PNAS 106 (2009) 3659-3663.

CM02.06.26

Cation Glass, Anion Crystal—Disorder and Order in Metal-Sulfide Thin Films Kevin Ye and Rafael Jaramillo; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Structural disorder in semiconductors is important to characterize reliably because it strongly affects materials performance, for instance by introducing potential fluctuations and electron-hole recombination sites. In a multicomponent material the differing contrast of different elements to particular characterization techniques can lead to misleading and contradictory conclusions about the nature of disorder and even the existence of crystalline volumes. We present a study of highly-disordered Cu-Zn-Sn-S (CZTS) films, deposited by physical vapor deposition at low temperature and post-annealed at different temperatures. We previously reported synchrotron x-ray absorption spectroscopy (XAS) data showing that deposition at low temperature kinetically stabilizes single-phase compositions that are well outside of the narrow solid solution of CZTS at equilibrium [1]. Here we use complementary characterization techniques to understand and quantify structural disorder: XAS (XANES and EXAFS), x-ray diffraction, and transmission electron microscopy. By combining all three techniques and numerical simulations we reach quantitative conclusions about the nature of cation disorder and the kinetics for recrystallization. We find that cations in highly-disordered CZTS are distributed nearly at random while the sulfur anions remain in a well-defined lattice. This phenomenon of cation glass, anion crystal is important to recognize for its signature in different characterization techniques. For optoelectronic devices it may be useful to design light absorbers and windows with widely varying absorption edge energy.

[1] S. C. Siah *et al.*, *IEEE J. Photovolt.* **5**, 372-377 (2015).

CM02.06.27

Thermo-Physical Properties of SrO-Al₂O₃ Binary System Yongxiao Gao¹, Zhitao Shan¹, Bowen Ruan¹, Zhe Zeng¹, Haizheng Tao¹, Xiujian Zhao¹ and Yuanzheng Yue^{1,2}; ¹State Key Laboratory of Silicate Materials for Architectures, Wuhan University of Technology, Wuhan, China; ²Department of Chemistry and Bioscience, Aalborg University, Aalborg, Denmark.

Owing to the heterogeneous nucleation at the melt-crucible interface, when using the conventional evaluating methods, such as rotating cylinder and maximum bubble pressure method, it is difficult to access the thermo-physical properties in the super-cooled region for poor glass formers. To avoid this phenomenon, here we use the containerless aerodynamic levitator laser-heated technique to measure the thermo-physical properties, i.e., density and viscosity of xSrO-(100-x) Al₂O₃ (35≤x≤75) binary system in the metastable super-cooled and equilibrium states. According to the average coefficient of thermal expansion (CTE) of melts calculated from the densities, we noticed that the average CTE shows a non-linear and non-monotonic tendency with increasing the content of SrO. In addition, the average CTE of these aluminate melts exhibit two local minimum at the corresponding compositions with the minimum eutectic temperature. At the same time, these eutectic compositions exhibit local maximum of glass forming ability judging from their bigger ratio values of T_g/T_m and higher viscosity at their corresponding melting points.

CM02.06.28

Structural Origin of Mixed Modifier Effects in Aluminosilicate Glasses Zhitao Shan¹, Bowen Ruan¹, Yongxiao Gao¹, Haizheng Tao¹ and Yuanzheng Yue^{1,2}; ¹Wuhan University of Technology, Wuhan, China; ²Aalborg University, Aalborg, Denmark.

While the mixed modifier effect that the dynamic properties, i.e., the enthalpy, electric conductivity, glass transition temperature (T_g) and the hardness exhibit relatively deviations from linearity, has been known for decades, yet it is still drawing significant attention in the glass community. Although, many proposed models can explain parts of the mixed modifier effect reasonably well, none can explain all of anomalous behaviors. To understand the behavior of mixed modifier effect it is important to reveal the relation between glass structure and properties. There has recently been some progress in understanding such relation [1-3]. It is well known that the cation can play the role of network-modifier, pseudo network-former and charge balancer in the network. In the present work, we report our findings about the mixed modifier effects as network-modifier, pseudo network-former and charge balancer in aluminosilicate glasses fabricated by the aerodynamic levitation technique and/or traditional melt-quenching method. The results show that the hardness exhibiting a negative deviation from linearity as the network modifier, a positive deviation from linearity as pseudo network-former and a near-linear trend as the charge balancer. Different with the previous reports about the mixed modifier effect, the glass transition temperature (T_g) show a positive deviation from linearity when the modifier play the role of the pseudo network-former. We have revealed the structural origin of some dynamic properties, such as the hardness and T_g , by means of combined techniques such as calorimetry, viscometer, Raman spectroscopy and nuclear magnetic resonance.

Reference

1. J Kjeldsen, M M. Smedskjaer, J C. Mauro, Y Z. Yue, Hardness and incipient plasticity in silicate glasses: Origin of the mixed modifier effect, *Applied physics letters*, 2014.
2. Z T. Shan, C J. Li, H Z. Tao, Mixed alkaline earth effect on the mechanical and rheological properties of Ca-Mg silicate glasses. *Journal of the American Ceramic Society*, 2017.
3. Z T. Shan, S J. Liu, H Z. Tao, Y Z. Yue, Mixed effect on mechanical and rheological performances in aluminate glasses. *Journal of the American Ceramic Society*, under review.

CM02.06.29

Design of Non-Oxide Nanocomposite Ceramic Materials with High Fracture Toughness for Extreme Applications Kaijie Ning, Priyatham Tumurugoti, Kade A. McGarrity and Holly Shulman; Inamori School of Engineering, Alfred University, Alfred, New York, United States.

Ceramic materials can possess properties that withstand extreme environments, such as high temperatures, extreme abrasion, ablation, and corrosion. Strong directional bonding, which brings about high elastic moduli and high theoretical strength, also causes these materials to be sensitive to flaws that produce catastrophic failure. The lack of fracture toughness prevents accessing high strength, preventing use of many promising ceramics in load bearing and wear applications. There are a variety of mechanisms that can be implemented to increase fracture toughness. In our work, we focus on developing novel non-oxide nanocomposite ceramic materials targeting improvement of fracture strength through atomic process control of additives, microstructural design, and an advanced 3D reconstruction technique. The boundary phase control, grain shape modification, and second phase reinforcement are of interest for sintering novel structural nanocomposites in order to reveal toughness mechanism from different scale levels. Preliminary results of powder processing, sintering, microstructural and mechanical characterization of SiC/Si₃N₄ nanocomposites are reported here. It is expected that the novel designed nanocomposite ceramics would achieve much improved fracture strength compared to the traditional ceramic matrix.

CM02.06.30

Origin of Negative Strain Rate Dependency of Metallic Glass Flow Stress Akio Ishii¹, Tomoaki Niiyama², Takahiro Hatano³, Tomotsugu Shimokawa² and Shigenobu Ogata¹; ¹Osaka University, Toyonaka, Japan; ²Kanazawa University, Kanazawa, Japan; ³The University of Tokyo, Bunkyo-ku, Japan.

It is reported that negative or no strain rate dependency of the flow stress of metallic glasses appears at high strain rate or low temperature condition[1][2]. We reveal that this curious strain rate dependency is strongly related to the timescale of glass relaxation process from a rejuvenated glass state induced by activation of shear transformation. We use a constitutive model which estimates average residence time of thermal activation process [3]. In the model we

assume the relaxation process recovers the activation energy of shear transformation. Our model successfully reproduces the experimental strain rate dependency of flow stress over the wide strain rate and temperature ranges. The negative or no strain rate dependency appears when the timescale of the activation of shear transformation approaches the characteristic timescale of glass relaxation process.

- [1] J. Lu, *et al.*, *Acta Mater.* 51 (2003)
- [2] A. Dubach, *et al.*, *Phil. Mag. Lett.* 87 (2007)
- [3] F. Yue, *et al.*, *Phys. Rev. Lett.* 109 (2012)

SESSION CM02.07: Glasses at the Nanoscales
Session Chairs: Julia Greer and Robert Maass
Wednesday Morning, November 28, 2018
Hynes, Level 2, Room 200

8:00 AM *CM02.07.01

History-Independent Cyclic Response of Nanotwinned Metals Qingsong Pan², Haofei Zhou¹, Lei Lu² and Huajian Gao¹; ¹Brown University, Providence, Rhode Island, United States; ²Institute of Metal Research, Chinese Academy of Sciences, Shenyang, China.

Nearly 90 per cent of service failures of metallic components and structures are caused by fatigue at cyclic stress amplitudes much lower than the tensile strength of the materials involved¹. Metals typically suffer from large amounts of cumulative, irreversible damage to microstructure during cyclic deformation, leading to cyclic responses that are unstable (hardening or softening) and history-dependent. Existing rules for fatigue life prediction, such as the linear cumulative damage rule, cannot account for the effect of loading history, and engineering components are often loaded by complex cyclic stresses with variable amplitudes, mean values and frequencies, such as aircraft wings in turbulent air. It is therefore usually extremely challenging to predict cyclic behavior and fatigue life under a realistic load spectrum. Here, through both atomistic simulations and variable-strain-amplitude cyclic loading experiments at stress amplitudes lower than the tensile strength of the metal, we report a history-independent and stable cyclic response in bulk copper samples that contain highly oriented nanoscale twins. We demonstrate that this unusual cyclic behavior is governed by a type of correlated 'necklace' dislocation consisting of multiple short component dislocations in adjacent twins, connected like the links of a necklace. Such dislocations are formed in the highly oriented nanotwinned structure under cyclic loading and help to maintain the stability of twin boundaries and the reversible damage, provided that the nanotwins are tilted within about 15 degrees of the loading axis. This cyclic deformation mechanism is distinct from the conventional strain localizing mechanisms associated with irreversible microstructural damage in single-crystal, coarse grained, ultrafine-grained and nanograined metals.

8:30 AM *CM02.07.02

The Interpretation of Apparent Ductility of Nanosized Glasses at Low Temperature Ju Li; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Recent experiments have shown ductile deformation of nanoscale metallic and oxide glasses [Nano Lett 18 (2018) 2492; Nano Lett 16 (2016) 105; Scripta Mat 98 (2015) 40]. Due to the lack of strain-hardening mechanism, such ductility is not material-intrinsic and depends on the geometry and other mechanical boundary conditions. Based on atomistic and kinetic Monte Carlo simulations, we comment on the extended defects, "ideal strength" and actual strengths, extreme-value statistics and damage in finite-sized glasses. [Acta Mat 73 (2014) 149]

9:00 AM CM02.07.03

Structure and Properties of Amorphous Thin Films Vary with Nanometric Thickness Boaz Pokroy, Yael Etinger Geller and Alex Katsman; Technion-Israel Institute of Technology, Haifa, Israel.

Amorphous materials, in contrast to crystalline ones, lack long-range order. Its order decays rapidly with the distance and while the local environment for a particular type of atom is quite similar, it is not identical; these fine changes in the atomistic structure of the materials lead to new and very interesting phenomena which are unique for amorphous materials. Although many aspects of science and technology rely on amorphous materials, much less research is conducted about their structure than on their crystalline counterparts.

In nature there are many organisms that use crystallization via an amorphous phase in order to achieve controlled mineralization. One of the main advantages of this method is that it enables the organism to exert control over the resulting polymorph, which is not necessarily the thermodynamically-stable one, by first controlling the short-range order in the amorphous phase.

In this research we draw inspiration from nature and study the ability to control various structural aspects of amorphous materials via nanometer size effects. We chose atomic layer deposition (ALD) as our material deposition method, since it is a technique that can provide extremely precise, sub-nanometric, thickness control and can deposit conformal and pinhole-free amorphous films of various materials.

Amorphous thin films of aluminum oxide deposited by atomic layer deposition method were found to vary structurally as a function of size; thinner films, as predicted previously, exhibited more 4-coordinated Al sites. These atomistic alterations were expected to change the amorphous thin film's average density, and indeed it was found to vary with the alumina layer thickness. This effect is explained in terms of the deposition process, where each newly deposited layer is a new surface layer that 'remembers' its structure, resulting in thin films of substantially lower density. This further encouraged us to study the effect of size on different density-dependent properties and it was indeed found that the refractive index and dielectric constant of these layers also change with the thin films' thickness. We believe that the ability to tune one property or another solely by size, according to a specific requirement, can open new possibilities for materials selections and applications, in science and technology.

References:

- [1]. Y. Etinger-Geller, A. Katsman, B. Pokroy, *Chem. Mater.* 2017, 29, 4912-4919.
- [2]. L. Bloch, Y. Kauffmann, B. Pokroy, *Cryst. Growth Des.* 2014, 14, 3983-3989.

9:15 AM CM02.07.04

Sample-Size and Temperature Effects in Deformation Behavior of Bulk Metallic Glasses Chandra Sekhar Meduri and Golden Kumar; Texas Tech University, Lubbock, Texas, United States.

Bulk metallic glasses (BMGs) deform plastically through localized shear bands at room temperature. It is well established that shear banding process in

BMGs depends on multiple parameters such as, the elastic constants, the sample size and processing, and the testing conditions (temperature, strain-rate, and loading geometry). Studying the effects of these variables and linking them to a unifying flow model is critical for fundamental understanding and potential applications of BMGs. In this work, we study the effects of testing temperature and sample size on nucleation and propagation of shear bands and the fracture surface through bending and tensile testing. Bending experiments show an increase in number of shear bands and plasticity with decreasing temperature. Analysis of fracture morphologies from the high-throughput tensile tests show an increasing contribution of thermal softening (through shear offset) and decreasing contribution of defect development (through coalescence of nanovoids and formation of microcracks) to the final fracture as sample size and/or temperature decreases. The results are discussed in terms of existing models for shear band formation and fracture of BMGs.

9:30 AM CM02.07.05

Addressing the Achilles' Heels of Amorphous Carbon with Doping—Mechanisms of Thermal and Oxidative Degradation—From Earth to the International Space Station Filippo Mangolini¹, Brandon Krick², Tevis Jacobs³, Subarna Khanal³, Frank Streller⁴, J. Brandon McClimon⁴, James Hilbert⁵, Somuri Prasad⁶, Thomas Scharf⁷, James Ohlhausen⁶, Jennifer Lukes⁵, W. Gregory Sawyer⁸ and Robert Carpick⁵; ¹Texas Materials Institute, Department of Mechanical Engineering, The University of Texas at Austin, Austin, Texas, United States; ²Department of Mechanical Engineering and Mechanics, Lehigh University, Bethlehem, Pennsylvania, United States; ³Department of Mechanical Engineering and Materials Science, University of Pittsburgh, Pittsburgh, Pennsylvania, United States; ⁴Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania, United States; ⁵Department of Mechanical Engineering and Applied Mechanics, University of Pennsylvania, Philadelphia, Pennsylvania, United States; ⁶Sandia National Laboratories, Albuquerque, New Mexico, United States; ⁷Department of Materials Science and Engineering, University of North Texas, Denton, Texas, United States; ⁸Department of Mechanical and Aerospace Engineering, University of Florida, Gainesville, Florida, United States.

Amorphous carbon materials are used as protective coatings in a wide range of applications owing to their unique mechanical, electrical, and optical properties. However, they suffer from two key environmental limits: insufficient thermal stability, and high reactivity in oxidizing environments. This inhibits their use in many harsh-environment technologies, such as protective coatings for aerospace components, automotive components, advanced manufacturing tools, and next-generation magnetic storage devices. Here we show that doping hydrogenated amorphous carbon films with silicon and oxygen can overcome these environmental limits and we explain the mechanisms by which these benefits occur through fundamental studies, including experiments conducted on the International Space Station.

The thermally-induced structural evolution of silicon- and oxygen-containing hydrogenated amorphous carbon (a-C:H:Si:O) was investigated *in situ* by X-ray photoelectron and absorption spectroscopy, as well as molecular dynamics (MD) simulations^{1,2}. The spectroscopic results indicate that upon high-vacuum annealing, two thermally-activated processes occur in a-C:H:Si:O: 1) ordering/clustering of sp² carbon; and 2) conversion of sp³- to sp²-bonded carbon. The experimental results are in qualitative agreement with MD simulations performed using the ReaxFF potential. MD simulations also indicate that the higher thermal stability of a-C:H:Si:O compared to hydrogenated amorphous carbon (a-C:H) derives from the lower fraction of strained carbon-carbon sp³ bonds in a-C:H:Si:O compared to a-C:H, which are more likely to break at elevated temperatures.

Exposing a-C:H:Si:O to elevated temperatures under aerobic conditions or to the harsh low Earth orbit (LEO) conditions (aboard the International Space Station during the seventh Materials International Space Station Experiments mission) leads to carbon volatilization limited to the near-surface region with the formation of a silica surface layer³. This prevents the remaining underlying carbon phase from volatilization by reaction with oxygen and/or water in the environment. The incorporation of silicon and oxygen in a-C:H thus enhances the thermo-oxidative stability and resistance to the LEO conditions via a self-protecting route for carbon oxidation by creating an oxygen diffusion barrier.

These findings provide a novel physically-based understanding of the superior stability of a-C:H:Si:O in harsh environments compared to a-C:H.

(1) Mangolini, F.; Hilbert, J.; McClimon, J.B.; Lukes, J.R.; Carpick, R.W. *Langmuir* **2018**, *34*, 2989-2995.

(2) Hilbert, J.; Mangolini, F.; McClimon, J.B.; Lukes, J.R.; Carpick, R.W. *Carbon* **2018**, *131*, 72-78.

(3) Mangolini, F.; Krick, B.A.; Jacobs, T.D.B.; Khanal, S.R.; Streller, F.; McClimon, J.B.; Hilbert, J.; Prasad, S.V.; Scharf, T.W.; Ohlhausen, J.A.; Lukes, J.R.; Sawyer, W.G.; Carpick, R.W. *Carbon* **2018**, *130*, 127-136.

9:45 AM CM02.07.06

Effect of Deposition Rate and Substrate Temperature on Structure and Properties of Sputtered Metallic Glass Thin Films Sachin V. Muley¹, Debaditya Chatterjee¹, Felix P. Lu² and Paul M. Voyles¹; ¹Materials Science and Engineering, University of Wisconsin Madison, Madison, Wisconsin, United States; ²Grainger Institute for Engineering, University of Wisconsin–Madison, Madison, Wisconsin, United States.

Physical vapor deposition offers a route to synthesizing glasses with a wide range of thermodynamic and kinetic stability. We have studied the structure and properties of Zr₆₅Cu_{27.5}Al_{7.5} thin films deposited by single target magnetron sputtering as a function of the deposition rate, substrate temperature, and residual pressure of oxygen and water vapor. Films grown starting with a base pressure of 2×10⁻⁸ Torr and low partial pressures of oxygen of 2×10⁻¹⁰ Torr and water vapor of 5×10⁻⁹ Torr exhibited a phase boundary between amorphous and crystalline states as a function of deposition rate and substrate temperature. At a deposition rate of 0.22 nm/s in 3.8 mTorr of process gas (Ar) the films were crystalline at high substrate temperatures (458K, 0.67×T_g/T_g – 498K, 0.73×T_g/T_g), but amorphous at lower substrate temperatures. At a deposition rate of 1.57 nm/s in 3.8 mTorr of Ar, the films were amorphous up to a substrate temperature of 483K (0.70×T_g/T_g). Optimizing over deposition rate and substrate temperature increased the films' modulus by 34% and hardness by 11% as compared to liquid-quenched ribbons with same composition, consistent with increased density and improved stability. Fluctuation electron microscopy (FEM) experiments show that the glasses with improved mechanical properties have increased icosahedral medium range structural order. Films grown starting from poorer vacuum (base pressure - 5×10⁻⁷ Torr) with higher partial of oxygen (2×10⁻⁸ Torr) and water vapor (5×10⁻⁸ Torr) at 0.22 nm/sec in 3.8 mTorr of Ar were amorphous at substrate temperatures from 295K (0.43×T_g/T_g) to 518K (0.76×T_g/T_g). These observations suggest that enhancing properties and stability in PVD metallic glasses requires optimization of both deposition rate, which governs monolayer residence time, and substrate temperature, which influences surface diffusivity. They reiterate evidence from bulk synthesis that glass forming ability is sensitive to incorporation of oxygen. Calorimetric assessment of stability also will be presented.

10:00 AM BREAK

10:30 AM *CM02.07.07

Fast Dynamics of Metallic Glasses at Low Dimensions Wei Hua Wang; Institute of Physics, Beijing, China.

The dynamics of metallic glasses at low dimensions such as in surface, ultrathin films, nano-scale particles were measured and studied. The dynamics and diffusion with the value of more than 10⁵ times faster than that of bulk are found far below glass transition temperature. The fast dynamics induces some interesting phenomena, such as a fast crystallization below glass transition temperature at the free surface which is more than 100 times faster than that in bulk, higher electrocatalytic activity and unique self-stabilizing catalytic performance over a long-cycling life than the commercial Pt/C catalysts in Pd-based MGs, and generation of the modulated superlattice-like nanostructure modulated nanostructure from the surface to interior, are found. The fast dynamics can be applied to form ultrastable metallic glasses with unique properties at room temperature. The observations have implications for

understanding the glassy dynamics, and pave a way for controllable fabrication of unique and sophisticated nanostructure on glass to realize the properties modification.

11:00 AM CM02.07.08

Interfacial Plasticity and Strain Delocalization in Metallic Nanoglasses [Jason R. Trelewicz](#) and Bin Cheng; Stony Brook University, Stony Brook, New York, United States.

The ductility and toughness of metallic glasses are classically limited by plastic flow localizing into shear bands, a process which is augmented by the introduction of structural inhomogeneities to produce a more homogenous plastic response. For example, in metallic glass matrix composites, ductility enhancements have been attributed to the presence of crystallites in the amorphous matrix, although the mechanisms of delocalization relating to shear band nucleation and propagation are still an active area of research. A new class of amorphous alloys that contain amorphous grains separated by “interfaces”, referred to as metallic nanoglasses, have also exhibited the ability to delocalize plastic strain and believed to result from the interfacial regions distributing shear band nucleation. Using molecular dynamics simulations, we explore the process of strain delocalization in nanoglass models produced via high pressure consolidation of amorphous nanoparticles. Interfaces are identified in the consolidated structures using a new volumetric strain threshold criterion, and generally exhibit a larger free volume and reduced full icosahedral fraction relative to the cores of the amorphous spheres. Uniaxial tensile simulations are conducted on the nanoglasses with amorphous grain size and relaxation temperature systematically varied to study the conditions for effective delocalization. We find that the presence of interfaces promote distributed plasticity with a grain size effect deriving from preferential localization transpiring within the interfacial regions containing greater excess free volume. Interfacial structural state also plays an important role where relaxation at higher temperatures initiates rejuvenation and in turn, enhanced localization that manifests in the flow curves as a stress overshoot upon the formation of a dominant shear band. Our results demonstrate that finer amorphous grain sizes and interfacial regions with enhanced disorder promote a more homogenous plastic response, thus providing insights into nanoglass deformation that can be translated to alloy design through the consolidation of nanometer-sized glassy particles.

11:15 AM CM02.07.09

Dynamic Mechanical Analysis on the Effect of Room Temperature Aging on Sputtered $Zr_{55}Ni_{25}Al_{20}$ Metallic Glass [Anthony Kwong](#), Miranda Schwacke and Julia R. Greer; California Institute of Technology, Pasadena, California, United States.

Compared to bulk metallic glasses, the free- volume content is higher in sputtered metallic glasses due to the high cooling rate of the magnetron sputtering fabrication technique. This excess free volume accommodates larger amounts of local shear during deformation and improves the material’s ductility. However, not much research has been done on understanding the impact of room temperature aging on the size and distribution of free volume in sputtered metallic glass.

In our research, we sputtered five μm - thick Zr-Ni-Al onto a Si substrate and used focus ion-beam (FIB) milling to fabricate micro- and nano- sized pillars. The diameter of the pillars ranged from 300 nm to 1.3 μm with heights ranging from 900 nm to 3.9 μm , respectively. Uniaxial pillar compressions were performed on the as- sputtered Zr-Ni-Al. The elastic modulus and yield strength were measured to be 75.5 ± 12 GPa and 2.49 ± 0.24 GPa, respectively. The as-sputtered Zr-Ni-Al was aged at room temperature in a nitrogen dry box for three years and new pillars were fabricated using FIB milling and then, tested under uniaxial compression. After aging, the elastic modulus and yield strength increased to 82.5 ± 4.1 GPa and 2.73 ± 0.09 GPa, respectively. To provide insight into this increase in mechanical property, we performed dynamic mechanical analysis (DMA) to determine the storage and loss modulus of the as-sputtered and aged Zr-Ni-Al.

For the DMA experiments, new pillars were fabricated on both the as- sputtered and aged Zr-Ni-Al. These pillars were tested at room temperature at frequencies between 3 and 700 Hz. The peak of the loss modulus corresponds to the activation of β relaxations in the material. For the as- sputtered and aged Zr-Ni-Al, this occurred at a frequency of 440Hz and 450 Hz, respectively. The higher frequency of the aged metallic glass indicates that the activation energy of the β relaxations is larger. As expected, room temperature aging redistributed the free volume to a more energetically favorable configuration. Thus, even higher energy is required to relax the aged metallic glass. In addition, the magnitude of the loss modulus increased as a function of pillar diameter. The loss modulus ranged from 20 GPa to 100 GPa for pillar diameters ranging between 300 nm to 1.3 μm , respectively. The total free volume in large pillars is greater than that in small pillars, thus resulting in increased loss modulus. The cooperative shear model (CSM) demonstrated that β relaxations are associated with the transition of shear transformation zones (STZs) in an elastic matrix. Utilizing CSM, the volume and activation energy of the STZs can be calculated. These findings elucidate the effect of room temperature aging on sputtered metallic glass and pave the road for future work on quantifying the activation energy and volume of STZs, the rearrangement of which is the mechanism of deformation in metallic glass.

11:30 AM CM02.07.10

Microstructure and Mechanical Properties of Metallic Nanoglasses Prepared by Nanoparticle Consolidation [Omar Adjaoud](#) and [Karsten Albe](#); TU Darmstadt, Darmstadt, Germany.

Metallic nanoglasses are amorphous materials with microstructural features analogous to nanocrystalline materials, which consist of glassy grains connected by glass-glass interfaces. They can be produced by cold-compaction of glassy nanospheres which are prepared by inert-gas condensation [1,2]. The interfaces are characterized by an excess volume [3], a lack of short range order [4], and a different composition than the glassy grains [5,6].

In this contribution, we present a detailed analysis of microstructure formation of metallic nanoglasses by molecular dynamics simulations. We analyze the atomic structure of the glassy grains and glass-glass interfaces during the consolidation process. Moreover, we discuss the thermodynamics and kinetic stability of anoglasses, structural features of the interfaces, segregation effects and the mechanical response in uniaxial tensile tests. Finally, the computational results are put in the context of experimental findings.

[1] J. Jing *et al.*, *J. Non-Cryst. Solids*, 113 (1989) 167-170.

[2] J.X. Fang *et al.*, *Nano Lett.*, 12 (2012) 458-463.

[3] D. Sopy *et al.*, *Appl. Phys. Lett.*, 94 (2009), p. 191911.

[4] Y. Ritter *et al.*, *Acta Mat.*, 59 (2011) 6588-6593.

[5] O. Adjaoud *et al.*, *Acta Mat.* 113, 284-292 (2016).

[6] O. Adjaoud *et al.*, *Acta Mater.* 145 (2018) 322-330.

11:45 AM CM02.07.11

Dispersive Diffusion Fit to Heavy-Tail Relaxation in Amorphous Semiconductors and Disordered 2D Materials [Matthew Grayson](#), Jiajun Luo and Lintao Peng; Northwestern University, Evanston, Illinois, United States.

Dispersive diffusion occurs when the diffusion "constant" in the diffusion equation obeys a power law in time. Remarkably, such processes are successful in describing diverse phenomena from dielectric relaxation in glasses to creep in strained polymers to earthquake aftershocks. In the present work two different disordered semiconductor systems -- amorphous indium-gallium-zinc-oxide (a-IGZO) and exfoliated 2D black phosphorus (BP) are shown to both obey a variety of dispersive diffusion behaviors, depending upon doping and disorder strength. Transient responses in a wide range of disordered condensed matter systems show a heavy-tail relaxation behavior: the decay time constant increases as time increases, revealing a spectral distribution of time constants. However, the asymptotic behavior of such transients is notoriously difficult to measure due to the extremely rapid decay at short times and the extremely slow and decreasing decay rate at long times. This work introduces a generalized analysis method for arbitrary heavy-tail transients, which accurately fit a finite experimental dataset to one of a continuum of candidate heavy-tail functions. By plotting the transient response versus log-time and taking the derivative, a simple half-maximum line-width analysis of the derivative is shown to predict the asymptotic value within less than 1%. The dispersive diffusion transient fit is a generalized fit that includes the stretched exponential as a limiting case. The line fits and asymptotic predictions are demonstrated using experimental transient responses from historical data on amorphous silicon and amorphous InGaZnO. The remarkable ability to fit heavy-tail transients in the 2D material black phosphorus implies that the low-dimensionality of such crystalline 2D systems suffer from poor screening such that the disorder potential results in behavior that is more akin to dynamics found in amorphous materials.

SESSION CM02.08: Transformations Relevant to Glasses
Session Chairs: Himanshu Jain and Edgar Zanotto
Wednesday Afternoon, November 28, 2018
Hynes, Level 2, Room 200

2:00 PM *CM02.08.01

Sequences of Metastable Phase Formation Determined via Ultrafast Calorimetry Jörg F. Löffler; Laboratory of Metal Physics and Technology, Department of Materials, ETH Zurich, Zurich, Switzerland.

Initial phase formation via nucleation and growth plays an important role in the microstructure evolution upon melt solidification. I will report on novel chip-based fast differential calorimetry (FDSC) to determine thermophysical properties at rates of several 10^5 K/s and thus to reveal the sequence of metastable phase formation during rapid solidification. In such a way we were able to determine new phase transition paths, such as solid-solid phase transformations via melting for a Au-based glass [1]. In addition, with FDSC it is possible to interrupt rapid cooling after a phase transition and then to "up-quench" the frozen structure via heating at ultrafast rates. Using this strategy, we were able to demonstrate for a Mg-based alloy that a transient quasicrystal (QC) phase nucleates first from the melt and then transforms into an equilibrium approximant phase [2]. We assume that such a transition path, which minimizes the free-energy barrier for nucleation, is likely to be a general mechanism for metastable QC-forming systems. We were also able to completely melt the QC phase mixture via suppressing the metastable-to-stable phase transition. In general, FDSC with the corresponding strategy of "up-quenching" a previously frozen structure can generate the discovery of hidden transient phases and thus the construction of metastable phase diagrams. I will show that such studies are not only key to the understanding of crystallization in metallic materials, but are also of great interest in determining nucleation mechanisms in polymeric materials, biological systems, and pharmaceutical substances.

[1] S. Pogatscher, D. Leutenegger, J. Schawe, P. J. Uggowitzer, J. F. Löffler, 'Solid-solid phase transitions via melting in metals', *Nature Comm.* 7:11113, doi:10.1038/ncomms11113 (2016).

[2] G. Kurtuldu, K. F. Shamlaye, J. F. Löffler, 'Metastable-quasicrystal-induced nucleation in a bulk glass-forming liquid', *PNAS*, doi:10.1073/pnas.1717941115 (2018).

2:30 PM BREAK

3:30 PM *CM02.08.03

Fundamental Nature of the Light-Induced Restructuring and Modification of Properties of Glass Himanshu Jain; Lehigh University, Bethlehem, Pennsylvania, United States.

Glass is a metastable material that can be stimulated to transform toward stable crystalline state continuously or discretely by providing sufficient external energy. Irradiating a glass with a light beam, typically but not necessarily, a laser of suitable energy can produce this transformation in a narrowly focused region. Depending on glass composition and laser beam characteristics (such as wavelength, intensity, exposure duration, total dose and polarization), various chemical (such as etching rate in a solvent), and physical (e.g. optical, electrical) properties have been modified, while rest of the glass remains unaffected. Thus, through a controlled movement of the sample under fixed laser beam, one can modify the structure of glass to the desired extent in a pre-determined region and fabricate 1D, 2D or 3D micro-architecture of remarkably different properties within uniform glass matrix. This strategy of glass restructuring in oxide and chalcogenide glasses has been exploited in the fabrication of micro-optic Fresnel elements, grayscale lithography, information storage, active single crystal waveguides, microfluidic devices, etc. In this presentation, we will examine the fundamental nature of such restructuring, which can be traced in the changes of electronic defects, coordination defects, atomic configurations and/or local chemical composition.

4:00 PM CM02.08.04

Are Hints about Glass Forming Ability Hidden in the Liquid Structure? Juan Wang¹, Ryogo Suzuki¹, Anupriya Agrawal^{1,2} and Katharine Flores^{1,2}; ¹Mechanical Engineering and Material Science, Washington University in St. Louis, St. Louis, Missouri, United States; ²Institute of Materials Science and Engineering, Washington University in St. Louis, St. Louis, Missouri, United States.

There has been concerted effort to correlate high temperature structure and dynamics of liquids with glass forming ability of alloys. Despite intense interest, identifying the structural origin of glass forming ability in metallic alloys remains a challenge due to the difficulty of describing the evolution of the long-range disordered structure from the liquid. Here, we report the cluster variance in the liquid as a potential parameter to predict glass formation. We have used molecular dynamics simulations with embedded atom method (EAM) potentials to simulate the quenching of metallic liquids resulting in crystalline, glassy or composite phases. We observe that variance in cluster fraction correlates with crystallization and hence with glass forming ability. We will show that this correlation persists in multiple binary and ternary systems. Further, it is independent of the dominant cluster type as well as the type of EAM potential used. Moreover, EAM potentials used were not custom fitted to get accurate liquid properties.

We also validated our molecular dynamics prediction of glass forming compositions with experiments. Using a high-throughput, direct laser deposition processing method to experimentally evaluate glass formation, the glass forming ability of Zr-Cu, Zr-Ni-Al, Zr-Cu-Al, and Zr-Cu-Ti was consistently found to be greatest where the variance in the fraction of the dominant cluster in the simulated liquid is minimized. The laser deposited alloy libraries further enabled an investigation of the mechanical behavior across the composition range using nanoindentation. Correlations of these properties with the

simulated structures will also be discussed.

4:15 PM CM02.08.05

In Situ Observation of Spinodal Decomposition Process in Silicate Glass Katsuaki Nakazawa¹, Shin-ich Amma² and Teruyasu Mizoguchi¹; ¹The University of Tokyo, Meguro-ku, Japan; ²New Product R&D Center, Asahi Glass Co., Ltd., Yokohama, Japan.

Mechanical and optical properties of glasses can be modified by phase separation phenomena. The number of phases, sizes of phases and especially morphologies of phases affect those properties. Morphologies of phases deeply depend on the volume fractions of the separated phases. If the volume fractions of two phases are equal, interconnected structures are fabricated, whereas non-equal volume fractions fabricate the droplet structures. The morphologies of the interconnected and droplet structures can be clearly discriminated. The interconnected structure is composed of two tubular phases which three-dimensionally entangle. The droplet structure is composed of spherical minor phases dispersed in the major phases.

The process of phase separation is divided into three stages; initial, middle and final stages. In the case of spinodal decomposition, interconnected and droplet structures are fabricated in the middle stage of phase separation. Thus, the phase-separated structures are same at the initial stage of phase separations.

Phase separation phenomena have been mainly researched by scattering methods. Scattering methods don't possess high spatial resolution and can't observe local composition. Thus, the formation processes of the two structures haven't been revealed.

Here, we used high-resolution STEM (Scanning Transmission Electron Microscopy) and in-situ heating TEM holder to overcome above problem. HAADF (High Angle Annular Dark Field)-STEM possesses high spatial resolution and can detect local composition. We selected 20.0CaO-10.0Al₂O₃-70.0SiO₂ as a sample which is known to occur spinodal decomposition and separate into major Ca-rich phases and minor Si-rich phases [1]. This sample was heated up by the in-situ heating holder to observe formation process of droplet structure. As a result, temporal changes of the compositional fluctuation, temporal changes of volume fractions of Si-rich phases and Ca-rich phases and temporal change of morphologies of phase-separated structures were clearly observed. Two novel mechanisms of phase coarsening were also observed, evaporation-condensation mechanism and migration-collision mechanism. We analyzed the causes of two coarsening mechanisms. We revealed that coarsening mechanisms were decided by compositional distribution. Phases migrated along compositional distribution. Si-rich phases migrate along Si-rich phases and vice versa. Migration along composition was only observed in the middle stage.

The details of the temporal changes and the coarsening of those phases will be discussed in my presentation.

[1] K. Nakazawa et al., Scripta Mater. 154 (2018) 197

4:30 PM CM02.08.07

Theoretical Study on Polymorphic Transformations in Amorphous Ice Rodion Belosludov¹, Kirill Gets², Ravil Zhdanov², Vladimir Belosludov² and Yoshiyuki Kawazoe³; ¹Institute for Materials Research, Tohoku University, Sendai, Japan; ²Nikolaev Institute of Inorganic Chemistry, SB RAS, Novosibirsk, Russian Federation; ³New Industry Creation Hatchery Center, Tohoku University, Sendai, Japan.

Polymorphism, i.e. the presence of more than one amorphous state or phase in amorphous solids and liquids, is of fundamental importance in materials science [1]. Experimental and theoretical studies on very-high-density (VHDA), high-density (HDA) and low-density (LDA) ices have raised questions regarding the nature of the transformation between the amorphous forms of ice. One of the main questions is whether the amorphous ices are thermodynamically continuously connected with liquid states and can be regarded as vitrified liquids (glassy states) or distorted crystalline phases (crystal-like states) [2]. In most cases, classical molecular dynamics (MD) simulations are able to reproduce qualitatively many of the transformations between ice, amorphous ice, and liquid water observed in experiments. However, amorphous ices are quantum systems and therefore the zero-point vibration free energy is large and at low temperatures, it should be taken into account in free energy calculations. The description of various amorphous phases of ices has been performed on a molecular level in order to study the nature of amorphous polymorphism in a water system [3]. The models of very high-, high- and low-density amorphous (VHDA, HDA and LDA, respectively) ices have been modelled and the pressure-temperature phase diagram was constructed for water in the low temperature region using the combination of MD and lattice dynamics (LD) approaches. It was shown that the transformation between the amorphous phases (at positive pressure LDA → HDA, LDA → VHDA, and at negative pressure HDA → VHDA) is sharp and is a real phase transition in the classical sense at low temperatures. At positive pressure the transformation from the metastable phase HDA to the thermodynamically stable phase VHDA is a continuous transition due to kinetic impediment.

REFERENCES

- [1] M.C. Wilding *et al.* Chem. Soc. Rev. **35** (2006) 964.
- [2] T. Loerting *et al.* J. Non. Cryst. Solids **407** (2015) 423.
- [3] R. V. Belosludov *et al.* J. Alloys Compd. **707** (2017) 108.

SESSION CM02.09: Relaxation of Glasses
Session Chairs: A. Lindsay Greer and Robert Maass
Thursday Morning, November 29, 2018
Hynes, Level 2, Room 200

8:00 AM *CM02.09.01

Metallic Glasses—Relating Mechanical Properties to the Relaxation Spectrum A. Lindsay Greer; Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom.

Thermomechanical processing (TMP) of metallic glasses (MGs) [1] can take them to states of higher or lower energy, describable in terms of higher or lower fictive temperature T_f . Recently, there has been particular interest in achieving extremely high values of T_f , as the corresponding glasses are expected to show increased plasticity [2]. This presentation moves on to consider how T_f itself is an inadequate measure. Glasses show a *relaxation spectrum* as a function of temperature on heating, seen, for example, in the shape of the energy-absorption peaks in dynamic mechanical analysis, or of the sub- T_g (glass-transition temperature) exothermic peaks in differential scanning calorimetry. In this spectrum, α -relaxation relates to the formation of different glassy states on cooling at different rates, and describes processes occurring near T_g ; β -relaxation occurs below T_g ; and there are yet further processes at lower temperature [3]. We examine how the shape of the relaxation spectrum can be tailored by TMP, and how this affects the properties of MGs. We show that, for MGs with a relatively low T_g , and comparing near-ultrastable with higher-energy states, the distinction between α -relaxation and sub- T_g β -relaxation can become blurred. By combining processing techniques, for example annealing with cryogenic thermal cycling [4], one can find that a glass is

simultaneously more and less relaxed: with higher hardness, yet easier onset of plastic flow. Such combinations are of clear interest in achieving more uniform plastic flow, one of the most important aims for MGs. In explaining such combinations, it is relevant to consider the heterogeneity of the MG, possibly describable as *soft-spots* in a comparatively rigid matrix. We consider how novel TMP may improve the properties of MGs. We consider how state-of-the-art structural characterization and atomistic modelling can assist in developing a fundamental understanding of how MG properties can be changed by TMP. And we make comparison with other families of glassy materials.

[1] YH Sun, A Concustell, AL Greer, Thermomechanical processing of metallic glasses: extending the range of the glassy state. *Nature Rev. Mater.* **1**, (2016) 16039.

[2] J Pan, YX Wang, Q Guo, D Zhang, AL Greer, Y Li, Extreme rejuvenation and softening in a bulk metallic glass, *Nature Comm.* **9** (2018) 560.

[3] P Palomino Rico, DG Papageorgiou, AL Greer, GA Evangelakis, The atomistic mechanism of fast relaxation processes in $\text{Cu}_{65}\text{Zr}_{35}$ glass, *Acta Mater.* **135** (2017) 290–296.

[4] SV Ketov, YH Sun, S Nachum, Z Lu, A Checchi, AR Beraldin, HY Bai, WH Wang, DV Louzguine-Luzgin, MA Carpenter, AL Greer, Rejuvenation of metallic glasses by non-affine thermal strain, *Nature* **524** (2015) 200–203.

8:30 AM CM02.09.02

Topological Control on Glass Relaxation Xin Li¹, Yushu Hu¹, John C. Mauro², Morten Smedskjaer³ and Mathieu Bauchy¹; ¹University of California, Los Angeles, Los Angeles, California, United States; ²Department of Materials Science and Engineering, The Pennsylvania State University, University Park, Pennsylvania, United States; ³Department of Chemistry and Bioscience, Aalborg University, Aalborg, Denmark.

Understanding, predicting, and controlling glass relaxation is of primary importance for the manufacturing of substrate glasses used in display applications, as any small variation in volume can result in undesirable pixel misalignment. However, no clear atomistic mechanism of structural and stress relaxation is available to date, which limits our ability to identify optimal glass compositions featuring low relaxation. Here, based on molecular dynamics simulations, we study the relaxation of a series of alkali-free calcium aluminosilicate (CAS) and sodium silicate (NS) glasses with varying compositions. We observe that selected glass compositions exhibit minimal relaxation. We investigate the structural origin of this behavior by means of topological constraint theory. Based on this analysis, we demonstrate that minimal relaxation is achieved for isostatic glasses, which are both free of eigenstress and floppy modes. This highlights the crucial role of the atomic topology in controlling the propensity for relaxation.

8:45 AM CM02.09.03

Elastic Properties and Structural Relaxation of a Chain Like Polymer Manon Heili and John Kieffer; University of Michigan, Ann Arbor, Michigan, United States.

We investigate the structural reorganization process in a chain-like polymer, polyvinylidene fluoride (PVDF). A unique optical setup is used combining a miniature tensile tester placed into the optical path of a Brillouin light scattering (BLS) system, to probe the elastic properties of a sample while it is uniaxially strained. BLS yields the adiabatic moduli of the materials, while their isothermal moduli are derived from the measured stress-strain curves. This two-pronged probing approach yields data, which upon detailed analysis provides for unprecedented insights into the distribution of relaxation times associated with various Maxwell elements, as well as evidence for visco-elastic property changes that require descriptions beyond these simple models.

Upon straining, elastic moduli of the polymer drop instantaneously. However, while maintained at a constant strain, the material undergoes stress relaxation during which the load necessary to maintain this elongation decreases. During stress relaxation, both the adiabatic and isothermal moduli reconstitute, leaning towards the unstrained values. The structure indeed rearranges to optimize molecular packing and maximize the non-bonding interactions. A thermodynamical approach is proposed to correlate the relaxational modulus with the entropic aspects of the structural changes for this polymer.

9:00 AM CM02.09.04

A Microscopic Description of the Anelastic and Structural Relaxation of Metallic Glasses Tianjiao Lei¹, Luis Rangel DaCosta¹, Yonghao Sun^{3,2}, A. Lindsay Greer³, Ming Liu², Zhen Lu², Wei Hua Wang² and Michael Atzmon^{1,4}; ¹Materials Science and Engineering, University of Michigan-Ann Arbor, Ann Arbor, Michigan, United States; ²Institute of Physics, Chinese Academy of Sciences, Beijing, China; ³Department of Materials Science and Metallurgy, University of Cambridge, Cambridge, United Kingdom; ⁴Nuclear Engineering and Radiological Sciences, University of Michigan-Ann Arbor, Ann Arbor, Michigan, United States.

Metallic glasses (MGs) possess high strength and elastic limit, but they also exhibit little macroscopic ductility due to shear band formation. Because of the disordered atomic structure, it is challenging to define defects that accommodate deformation in MGs. From observations in physical analogs, these defects have been identified as shear transformation zones (STZs), which are dissipative and thermally activated [1]. At small strains, STZs are isolated and can be reversed due to back-stress in the elastic matrix upon removal of the applied stress, which results in anelastic behavior. Recently, Ju *et al.* obtained a quantized hierarchy of STZs for an Al-based MG from quasi-static anelastic relaxation measurements [2]: the volume difference between STZs corresponding to adjacent peaks in the time-constant spectrum equals that of one Al atom. The volume fraction of potential STZs, i.e. atomic clusters capable of shear transformation, increases with size. After annealing at 110 °C for 1 hour, the number of potential STZs decreases, but the corresponding time constants remain unchanged [3].

The common observation of a main (α) relaxation, and high-frequency (β) relaxation in mechanical spectroscopy is readily explained in molecular glasses, but its microscopic nature in MGs is still under debate. It has been shown that the relative intensity of the β relaxation in MGs correlates with ductility [4]. The purpose of the present work is to use anelasticity to characterize the STZ spectra of La-based MGs with and without pronounced β relaxation, and to study the effect of structural relaxation from a microscopic view. $\text{La}_{55}\text{Ni}_{20}\text{Al}_{25}$ and $\text{La}_{70}(\text{Ni}_x\text{Cu}_{1-x})_{15}\text{Al}_{15}$, $x=0,1$ were investigated. Two regimes of volume increment are observed, suggesting a size dependence of STZ composition. Room-temperature structural relaxation only affects the larger/slower STZs -- the number of corresponding potential STZs decreases, while their time constants increase. Notably, a detailed description of structural relaxation emerges: its dominant effect is on the largest, and therefore slowest, STZs. Cycling to liquid-nitrogen temperature, observed to induce rejuvenation [5], only leads to subtle changes in the anelastic behavior. The effect of the composition x above will be discussed in the context of observations on its effect on ductility [4].

[1] Argon, *Acta Metall.* **27**, 4758 (1979).

[2] Ju *et al.* *J. Appl. Phys.* **109**, 053522 (2011).

[3] Atzmon and Ju, *Phys. Rev. E* **90**, 042313 (2014).

[4] Yu *et al.* *Phys. Rev. Lett.* **108**, 015504 (2012).

[5] Ketov *et al.*, *Nature* **524**, 200 (2015).

9:15 AM CM02.09.05

β -Relaxation and Its Correlations with Properties in Metallic Glasses Hai Yang Bai, Peng Luo and Wei Hua Wang; Institute of Physics, Chinese

Academy of Sciences, Beijing, China.

Metallic glasses (MGs) with structures viewed approximately as dense random packing of hard spheres offer a simple but effective model system for the study of relaxations and related issues in glass science. β -relaxation in MGs has been found to be closely bound up with the structural characteristics, formation, glass transition, deformations or flow behaviors, physical and mechanical properties, crystallization, and stability of MGs. We present the state of the art research on various aspects of the β -relaxations in model metallic glass systems and demonstrate the critical importance of these fast relaxation behaviors in understanding deformation, flow behavior, aging and rejuvenation, mechanical and physical properties of metallic glasses. We illustrate that it is an attractive prospect to incorporate the dynamic relaxations insights into the design of MG materials with extraordinary properties.

Reference

- [1] Z. Wang, K. L. Ngai, W. H. Wang, S. Capaccioli. Coupling of caged molecule dynamics to Johari-Goldstein β -relaxation in metallic glasses. *J Appl. Phys.* 119, 024902 (2016)
- [2] H. B. Yu, X. Shen, Z. Wang, L. Gu, W. H. Wang, H. Y. Bai, Tensile plasticity in metallic glasses with pronounced β relaxations. *Phys. Rev. Lett.* 108, 015504 (2012).
- [3] Z. Wang, B. A. Sun, H. Y. Bai and W. H. Wang. Evolution of hidden localized flow during glass-to-liquid transition in metallic glass. *Nature Communications* 5, 5823 (2014).
- [4] Z. Lu, W. Jiao, W. H. Wang, and H. Y. Bai. Flow unit perspective on room temperature homogeneous plastic deformation in metallic glasses. *Phys. Rev. Lett.* 113, 045501 (2014).
- [5] H. B. Yu, W. H. Wang, H. Y. Bai and K. Samwer. The β relaxation in metallic glasses. *National Science Review* 1, 429-461(2014).
- [6] P. Luo, Y. Z. Li, H. Y. Bai, P. Wen and W. H. Wang. Memory effect manifested by boson peak in metallic glass. *Phys. Rev. Lett.* 116, 175901 (2016)

9:30 AM CM02.09.06

Limitations on Localized Motions in Glass-Forming Liquids—A Dynamic Light Scattering Study [David Sidebottom](#); Creighton University, Omaha, Nebraska, United States.

The structural relaxation in glass-forming liquids is characterized by a two-step decay process. A rather fast initial relaxation (often referred to as the β -relaxation) occurs at early times as a result of localized motions that are globally restricted. As a result of this partial decay, the dynamic structure factor displays an intermediate plateau known as the non-ergodic level. At a longer timescale, the remaining structure is able to relax globally through the so-called α -relaxation whose relaxation times scales with the liquid's viscosity.

Here, we review dynamic light scattering measurements of the dynamic structure factor in a variety of glass-forming liquids spanning a wide range of fragility indices, both fragile molecular liquids and strong network-forming oxides for which a careful determination of the non-ergodic level has been made. We show that this plateau level increases with decreasing fragility implying that strong network-forming liquids tend to experience less localized structural arrangements than their molecular liquid counterparts.

9:45 AM CM02.09.07

The Formation of Ultrastable Metallic Glasses on Cold Substrates [Peng Luo](#), Hai Yang Bai and Wei Hua Wang; Institute of Physics, Chinese Academy of Sciences, Beijing, China.

Vitrification from physical vapor deposition is known to be an efficient way for tuning the kinetic and thermodynamic stability of glasses and significantly improve their properties. There is a general consensus that preparing stable glasses requires the use of high substrate temperatures close to the glass transition one, T_g . Here, we challenge this empirical rule by showing the formation of Zr-based ultrastable metallic glasses at room temperature, i.e., with a substrate temperature of only $0.43T_g$. By carefully controlling the deposition rate, we can improve the stability of the obtained glasses to higher values. In contrast to conventional quenched glasses, the ultrastable MGs exhibit a large increase of T_g of ~ 60 K, stronger resistance against crystallization, and more homogeneous structure with less order at longer distances. Our study circumvents the limitation of substrate temperature for developing ultrastable glasses, and provides deeper insight into glasses stability and their relaxation dynamics.

References

- [1] P. Luo, P. Wen, H. Y. Bai, B. Ruta, and W. H. Wang. Relaxation decoupling in metallic glasses at low temperatures, *Physical Review Letters* 118, 225901 (2017).
- [2] P. Luo, C. R. Cao, F. Zhu, Y. M. Lv, Y. H. Liu, P. Wen, H. Y. Bai, G. Vaughan, M. di Michiel, B. Ruta, and W. H. Wang. Ultrastable metallic glasses formed on cold substrates, *Nature Communications* 9, 1389 (2018).

10:00 AM BREAK

SESSION CM02.10: Novel Fabrication of Glasses
Session Chairs: A. Lindsay Greer and Robert Maass
Thursday Morning, November 29, 2018
Hynes, Level 2, Room 200

10:30 AM *CM02.10.01

Recent Insights into Thermo-Mechanical Energy Storage in Metallic Glasses [Robert Maass](#); Department of Materials Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois, United States.

Macroscopic properties of metallic glasses, such as Young's modulus, plastic strain at failure, fracture toughness, corrosion resistance, or the magnetization behavior depend on the structural state of the glass. This has inspired intense research efforts focusing on the control of structural modifications in glasses that are often quantified by the stored excess enthalpy relative to an as-cast reference, rather than by the precise changes of the atomic structure.

Particularly, high enthalpy states have attracted strong interest since they improve the commonly limited room temperature ductility of metallic glasses. In this talk, we will highlight our recent efforts in this topic, paying attention to three different methods on how to store excess enthalpy in monolithic metallic glasses, including a mechanical, thermo-mechanical, and a purely thermal method. Specifically, this means we will discuss 1) how an alternating elastic load leads to energy storage and how this translates to nanoscopic property fluctuations, 2) how alternating elastic loading during cooling to cryogenic temperatures reveals a low temperature loss process that is accompanied by energy storage, and 3) how ultra-fast heating can lead to significant enthalpy

storage of initially very relaxed glasses. The latter approach will be combined with in-situ x-ray measurements and atomistic simulations. Our results are discussed in terms of possible underlying mechanisms reflected in the global response.

11:00 AM CM02.10.02

Monatomic Metallic Glasses Processed through *In Situ* Ultrafast Liquid Quenching Scott X. Mao, Li Zhong and Yang He; University of Pittsburgh, Pittsburgh, Pennsylvania, United States.

It has long been conjectured that any metallic liquid can be vitrified into a glassy state provided that the cooling rate is sufficiently high. Experimentally, however, vitrification of single-element metallic liquids is notoriously difficult. True laboratory demonstration of the formation of monatomic metallic glass has been lacking. Here we report an experimental approach to the vitrification of monatomic metallic liquids by achieving an unprecedentedly high liquid-quenching rate of 1014Ks. Under such a high cooling rate, melts of pure refractory body-centred cubic (bcc) liquid tantalum and vanadium, and fcc Ni under H₂ environment are successfully vitrified to form metallic glasses through liquid/solid interface driven process. Combining in situ transmission electron microscopy observation and atoms-to-continuum modelling, we investigated the formation condition of the monatomic metallic glasses as obtained. The availability of monatomic metallic glasses, being the simplest glass formers, offers unique possibilities for studying the structure and property relationships of glasses. The interface-driven technique also shows great control over the reversible vitrification–crystallization processes, suggesting its potential in micro-electromechanical applications. The ultrahigh cooling rate, approaching the highest liquid-quenching rate attainable in the experiment, makes it possible to explore the fast kinetics and structural behaviour of supercooled metallic liquids within the nanosecond to picosecond regimes.

11:15 AM CM02.10.03

Spray Drying of Amorphous Nanoparticles Mathias Steinacher and Esther Amstad; EPFL, Lausanne, Switzerland.

Amorphous materials can have distinctly different properties compared to their crystalline counterparts. These include different dissolution rates or higher catalytic activity. Additionally, amorphous materials can serve as transient precursors for the formation of certain crystalline materials such as CaCO₃. Certain materials have a low propensity to crystallize and hence, they can easily be processed into amorphous structures. Other materials have a high propensity to crystallize and are therefore extremely difficult to process into amorphous structures. To process these materials into amorphous structures without using large quantities of crystallization inhibitors, their crystallization must be kinetically arrested during early stages of their formation. This can for example be achieved through rapid cooling of melts. However, this method cannot be employed to process thermally labile substances that decompose before they melt. To overcome this limitation, we developed a microfluidic spray drier that produces small drops that possess a very high specific surface area and hence dry very quickly. We use surface acoustic waves to produce droplets in the range of 1-10 μm. The atomizer can process aqueous and non-aqueous solutions containing organic and inorganic reagents. The aerosol droplets are rapidly dried in a dedicated drying unit and the dry particles are subsequently deposited on a substrate to analyze the influence of the processing parameters on their structure and morphology.

In this talk, I will demonstrate that materials can be made amorphous if processed in sufficiently small drops that dry quickly, even if the material possesses a high propensity to crystallize and even if it is processed from low viscosity solutions where the mobility is high. I will present the influence of the formation time and processing conditions on the structure and composition of different amorphous materials, including drugs, and inorganic materials and how this knowhow can be used to produce materials with unusual structures and compositions.

11:30 AM CM02.10.04

Processing-Property Relationship for Additive Manufacturing of Metallic Glasses Punnathat Bordeenithikasem and Douglas Hofmann; NASA Jet Propulsion Laboratory, Pasadena, California, United States.

Additive manufacturing (AM) or 3D printing is a disruptive technology that is revolutionizing the manufacturing industry. Metallic glasses (MGs) are considered for use in metal AM due to their desirable mechanical properties and high cooling rates achieved through the printing process. To ensure that printed MG parts are suitable for their intended applications, a more robust understanding of the processing-property relationship for AM of MGs must be developed by the scientific community. In this presentation, the influences from feedstock purity, oxidation, and printing parameters on the mechanical and wear properties of printed MG parts are discussed, with direct comparisons to cast MG samples.

11:45 AM CM02.10.05

Atomic Imprinting into Metallic Glasses Rui Li, Zheng Chen, Amit Datye, Georg Simon, Jittisa Ketkaew, Emily Kinser, Ze Liu, Chao Zhou, Omur E. Dagdeviren, Sungwoo Sohn, Jonathan P. Singer, Chinedum Osuji, Jan Schroers and Udo Schwarz; Yale University, New Haven, Connecticut, United States.

Molding and imprinting, which are among the oldest and most widely used manufacturing techniques, have recently regained scientific interest with the demonstration of nanomolding and nanoimprinting as surface functionalization methods. Typically, imprinting involves the embossing of a hard mold into a soft material. Due to the convenient adjustability of their degree of softening, thermoplastic polymers had been the material class of choice for most imprint procedures. Metallic glasses, however, have recently been identified as ideal moldable materials, gaining popularity since they combine favorable mechanical and electrical properties. They are particularly promising for small features sizes since their lack of intrinsic structural order with potentially atomic-sized flow units suggests that they may have the ability to conform to a mold's shape even on atomic length scales. In this presentation, we demonstrate that thermoplastic imprinting of a metallic glass can reproduce surface features with sub-ångström accuracy through the replication of terraces from a strontium titanate single crystal surface separated by steps of unit cell height as template. The molded metallic glass replicates the 'atomic smoothness' of the strontium titanate, with identical roughness to the one measured on the mold even after multiple usages of the mold and with such molded metallic glass surfaces exhibiting an exceptional long-term stability of years. By providing a practical, reusable, and potentially high-throughput approach for atomic imprinting, our findings may open novel applications similar in magnitude to the development of nanoimprinting two decades ago.

1:30 PM CM02.11.01

Computational Design of Lightweight Structural Materials with Triply Periodic Minimal Surfaces [Zhao Qin](#) and Markus Buehler; Massachusetts Institute of Technology, Cambridge, Massachusetts, United States.

Structural materials found in nature, such as wood, bone, insect forewings, bee hive and bird beak, synergistically combine strength, stiffness and toughness with lightweight. In contrast, most manmade engineering materials do not have such multifunctional features. Among many biological materials, the ones with lightweight foam structures serve good examples to provide a variety of mechanical supporting, thermal conservation and impact shielding functions in the animal body and their external protections. Many of the basic building blocks of these lightweight, elastic, and highly dissipative materials can be categorized by triply periodic minimal surfaces (TPMS), such as structures so-called gyroid and Schwarz' diamond, etc. TPMS have the symmetries in a similar way as crystals but they are composed of a single surface instead of 3D blocks, making their structure and mechanics unique. We try to explore the general mathematical function of TPMS and quasi-TPMS structures and use them as the input geometry to generate solid materials with innovative lattice structures. We theoretically investigate the mechanical property of these structures by using finite element method and molecule dynamics at the different scale levels and combine the modeling work with 3D printing to develop a technique that is capable of producing materials with lightweight TPMS structures with highly predictive material functions in a consistent and reproducible way. We discover that the structural geometry plays a dominating role in governing the scaling laws of the mechanics as a function of the material density. Our study suggests that these structures can be used as templates to design and make the 3D forms of many 2D materials including graphene, yield structures of 4.6% the density and 10 times the strength of mild steel. We expect such TPMS structures to have high stiffness, toughness, thermal conservation and impact tolerance, as well as lightweight, giving the material a full potential for protection with energy efficiency for production and transportation.

1:45 PM CM02.11.02

Soft Fibrous Materials with Inter-Fiber Adhesion Catalin Picu, [Vineet Negi](#) and Ahmed Sengab; MANE, Rensselaer Polytechnic Institute, Troy, New York, United States.

Many soft materials of biological and industrial interest are composed from nanofibers. In such cases, inter-fiber adhesion may produce fiber bundling and organization on scales larger than that of individual components. A type of network structure, entirely stabilized by adhesion, which was not described previously in the literature, emerges. We describe such structures and identify the range of system parameters in which they are expected to occur. Further, we study their mechanical behavior and observe a broad range of tunable properties, including softening in tension, large strain range in which the structure responds linearly to applied strains, and adhesion-dependent elastic moduli. We consider systems with permanent cross-links and systems in which fibers are not cross-linked but interact adhesively and by excluded volume interactions. The application of these results to collagen structures and carbon nanotube buckypaper are discussed.

2:00 PM CM02.11.03

Theoretical and Experimental Investigation of Haze in Transparent Aerogels [Lin Zhao](#)¹, Elise M. Strobach¹, Bikram Bhatia¹, Sungwoo Yang², Arny Leroy¹, Lenan Zhang¹ and Evelyn N. Wang¹; ¹Massachusetts Institute of Technology, Cambridge, Massachusetts, United States; ²The University of Tennessee at Chattanooga, Chattanooga, Tennessee, United States.

Transparent aerogel materials integrated in high-performance glazing units hold great promise to reduce building heat loss and improve indoor thermal comfort because of their ultra-low thermal conductivity. One of the primary challenges preventing the adoption of aerogels in windows is their poor visual experience. While the inherent porous structure is vital to suppress heat loss, the refractive index mismatch between the solid skeleton and air causes visible light to scatter and give rise to haze that degrades the contrast of an image when viewed through the aerogel. Previous studies on haze in aerogels relied on direct experimental characterization with little understanding of the underlying mechanisms. In this work, we investigate the haze of transparent silica aerogels using experimental measurement as well as theoretical modeling. We developed a radiative transfer model that can predict the diffuse transmittance, total transmittance, and haze of an aerogel based on its physical properties, i.e., density, mean particle size, and thickness. To validate the model, we fabricated aerogel samples with two different chemical precursors with a wide range of transparency and haze. Comparison of model predictions with experimental results measured using a UV-Vis spectrophotometer showed good agreement across the entire visible spectrum. We then used the validated model to perform a parametric study of haze and found that the haze is most sensitive to the mean particle size. Smaller particle size not only reduces the haze at a given aerogel thickness but also weakens its dependence on thickness. In addition, we developed a complementary approach that prescribes the set of aerogel properties required to achieve certain haze/transmittance targets. We believe this work advances the fundamental understanding of haze in a wide range of transparent porous materials and could help guide material development to achieve optimal optical performance.

2:15 PM CM02.11.04

On the Shape and Size of Voids in Ultra-Large Models of Hydrogenated Amorphous Silicon—A First-Principles Study [Durga P. Paudel](#)¹, Raymond Atta-Fynn², David Drabold³ and Parthapratim Biswas¹; ¹Department of Physics and Astronomy, The University of Southern Mississippi, Hattiesburg, Mississippi, United States; ²Department of Physics, University of Texas, Arlington, Arlington, Texas, United States; ³Department of Physics and Astronomy, Ohio University, Athens, Ohio, United States.

We present an *ab initio* study of hydrogen microstructure in pure and hydrogenated amorphous silicon with particular emphasis on the shape and size of voids and the dynamics of hydrogen atoms inside the voids. By using ultra-large models of *a*-Si, obtained from classical molecular dynamics simulations, with a realistic volume density of voids of 0.1%–0.3%, the dynamics of Si (and H) atoms on the surface of the cavities are studied and their effects on shape and size of the voids are examined using first-principles density-functional calculations. The resulting changes (from the *ab initio* calculations) are compared with the corresponding data obtained from total-energy relaxation using the Stillinger-Weber potential. The size and shape of the voids are analyzed by examining the three-dimensional distributions of Si/H atoms on the surface of voids using the convex-hull approximation of the void regions and computing the radius of gyration of the corresponding convex-hull regions. A comparison of our results with those obtained from the small-angle x-ray scattering (SAXS) measurements of *a*-Si/*a*-Si:H in the Guinier approximation is also discussed.

2:30 PM CM02.11.05

Recent Advances in Thermoplastic Fabrication of Metallic Glasses Golden Kumar and [Zhonglue Hu](#); Texas Tech University, Lubbock, Texas, United States.

Thermoplastic embossing with metallic glasses is considered as a solution for scalable manufacturing for metallic micro- and nano-structures. Despite its potential, embossing faces major challenges such as, limited aspect-ratio, expensive and non-reusable templates, inability to transfer nanostructures to materials other than metallic glasses etc. Significant advances have been made in recent years to overcome these barriers. For example, by reversing from embossing to drawing, assembled nano-tips, nano-wires, and nano-tubes with aspect-ratios exceeding 1000 can be fabricated inexpensively. These nanostructures can be transferred to plastics, semiconductors, quartz, or other metals. Macroscopic structures obtained by machining can be downsized to nanoscale features without using lithography by manipulating the viscous, capillary, and adhesive stresses. The templates can be non-destructively

separated from metallic glasses by minimizing the thermal expansion mismatch. Drawing approach can be readily adapted for high-throughput fabrication and testing of nanoscale test specimens, enabling rapid screening of size-effects in mechanical, thermal, and electrical behavior. Recent progress and future directions in thermoplastic fabrication and nanoscale testing of metallic glasses will be discussed.

2:45 PM CM02.11.06

Atomistic Simulations of Amorphous Functional Materials by Combining Machine Learning and DFT Volker Deringer; University of Cambridge, Cambridge, United Kingdom.

Understanding the links between atomic structure, chemical bonding, and macroscopic properties in amorphous materials is a formidable task. Quantum-mechanical atomistic simulations, prominently based on density-functional theory (DFT), have played important roles in this - but are computationally expensive, and can describe complex solids only in small model structures. Novel interatomic potentials based on machine learning (ML) have recently garnered a lot of attention in the computational physics community, as they achieve close-to DFT accuracy but at only a fraction of the cost.

In this talk, I will argue that ML-based interatomic potentials are particularly useful for studying amorphous solids, and that they can be combined with established DFT methods for gaining new insight into this important materials class. I will first describe a Gaussian Approximation Potential (GAP) for amorphous carbon [1], with a brief introduction to the underlying theoretical framework [2], and a special view on what is needed to validate potentials for the amorphous state. I will then present an application to porous and partly "graphitized" carbon structures, which are relevant for applications in batteries and supercapacitors [3]; this includes a new ML strategy for simulating the movement of Li-ions in such materials [4]. Finally, I will present very recent work on amorphous silicon (*a*-Si), another prototypical non-crystalline material, where ML-driven large-scale simulations have allowed us to generate structural models in good agreement with experimental findings [5], again making steps toward the routine and realistic atomistic modeling and understanding of the amorphous state.

[1] V. L. Deringer, G. Csányi, *Phys. Rev. B* **95**, 094203 (2017).

[2] A. P. Bartók, M. C. Payne, R. Kondor, G. Csányi, *Phys. Rev. Lett.* **104**, 136403 (2010).

[3] V. L. Deringer, C. Merlet, Y. Hu, T. H. Lee, J. A. Kattirtzi, O. Pecher, G. Csányi, S. R. Elliott, C. P. Grey, *Chem. Commun.* **54**, 5988 (2018).

[4] S. Fujikake, V. L. Deringer, T. H. Lee, M. Krynski, S. R. Elliott, G. Csányi, *J. Chem. Phys.* **148**, 241714 (2018).

[5] V. L. Deringer, N. Bernstein, A. P. Bartók, R. N. Kerber, L. E. Marbella, C. P. Grey, S. R. Elliott, G. Csányi, *J. Phys. Chem. Lett.* **9**, 2879 (2018).

3:00 PM BREAK

SESSION CM02.12: Exotic Glasses
Session Chairs: Tanguy Rouxel and Yunfeng Shi
Thursday Afternoon, November 29, 2018
Hynes, Level 2, Room 200

3:30 PM *CM02.12.01

Unique Polymer Nanocomposites with Thermally Stiffening Behavior Rahmi Ozisik; Department of Materials Science and Engineering, Rensselaer Polytechnic Institute, Troy, New York, United States.

Viscoelastic properties of grafted particle nanocomposites are known to be influenced by the mixing and demixing of grafted chains with the matrix. In the current study, we show that low-mobility, glassy brushes adsorbed/tethered onto nanoparticles that are dispersed within a high-mobility, liquid-like polymer matrix can significantly tune the overall viscoelastic and dynamic properties of the whole nanocomposite system. This work was inspired by recent work performed at the Akcora group at Stevens Institute of Technology showing a reversible thermal stiffening was observed in nanocomposite polymers, in which the matrix and surfactant polymer chains had a glass transition temperature (T_g) difference of 200 degrees. Using molecular dynamics, we simulated a composite system containing nanoparticles grafted with high glass transition temperature polymer chains that are dispersed in a low- T_g matrix polymer. We considered two main (and extreme) conformational states for the high- T_g grafted chains: collapsed (grafted chains are strongly adsorbed onto the nanoparticle, and therefore, phase-separated from the matrix) and stretched (grafted chains extend into the matrix). We found that when the grafted chains were stretched out, the nanocomposite had significantly greater storage modulus than the system having collapsed grafted chains. Detailed analysis showed that the stretched conformational state of grafted chains reduced matrix chain mobility, which leads to the thermal stiffening effect. Finally, by simulating structures with a range of grafted chain conformations bounded by fully collapsed and fully stretched states, we demonstrated that grafted chain conformation could be used to control the viscoelastic response of the whole nanocomposite system.

4:00 PM CM02.12.02

Prediction of Amorphous Structure and Stability of P-N and N-CO Extended Solids Under Pressure Iskander G. Batyrev; U.S. Army Research Laboratory, Aberdeen, Maryland, United States.

The structure and vibrational properties of P-N extended solids at 50 GPa were predicted using density functional theory (DFT) and evolutionary algorithms employing variable and fixed concentrations of components. The amorphous structure of the compound with stoichiometry N9P was found to be dynamically stable (no imaginary frequencies in phonon dispersion curve), but unstable relative transformation to solid nitrogen with an R-3C space group and phosphorus with a CMMM space group, according to convex hull calculations. The amorphous structure of the N-CO extended solid was obtained with various concentrations of N atoms (37.5%, 50%, and 90.625%) under isotropic compression up to 50 GPa calculated using DFT. The presence of CO is found to significantly lower the pressure required to form an amorphous covalent N-C-O network consisting of chains and a cage of the network. Upon lowering the pressure and decomposition of the compressed extended solid, N atoms are disconnected first from the ends of polymeric chains. Results of calculation of IR and Raman spectra are compared with available experimental results.

4:15 PM CM02.12.03

Electride Glass—Effect of Electron Anion on Structure and Property of Host Glass Hideo Hosono¹ and Peter V. Sushko²; ¹Tokyo Institute of Technology, Yokohama, Japan; ²Pacific Northwest National Laboratory, Richland, Washington, United States.

Electride is a compound in which electrons serve as anions and was first reported in 1983 by J.Dye who succeeded in obtaining this crystal by dissolving metal cesium into crown-ether solution. Since electride may be regarded as a crystal of solvated electron, it attracted attention as an exotic material. However, material research was not advanced because of its extremely high sensitivity to air and heat. In 2003 we first realized RT / air stable electride C12A7:e employing 12CaO7Al₂O₃ crystal (C12A7:O²⁻) accommodating O²⁻ in the crystallographic cages as a counter anion by replacing the O²⁻ with electron applying a chemical treatment (Science 2003). Resulting C12A7:e containing anionic electron of 2x10²¹cm⁻³ exhibits metallic conductivity with conductivity of 1500 Scm⁻¹ (Nano Lett.2006) and superconductivity at low temperatures (JACS 2007). The present research was motivated by a question of "what happens when C12A7:e become amorphous?". The results obtained are summarized as below:

1. Bulk glass is easily obtained for C12A7 (64CaO-36Al₂O₃) by conventional melt-quenching, while no such a glass formation was impossible for C12A7:e.
2. C12A7:e glass could be prepared by twin-roller quenching. The resulting glass kept the almost the same anionic electron concentration and exhibited semiconducting nature, which differs from the metallic conducting in crystalline C12A7:e.
3. T_g (730C) of C12A7:e is distinctly lower than that (830C) for electron-free C12A7 glass. This extent of T_g reduction is larger than that (DeltaT_g=50C) in CaO-Al₂O₃ glasses with different CaO content (45-70%) and increases with electron concentrations.
4. The electrical conductivity in C12A7:e glass is enhanced over 5 orders of magnitude by annealing around T_g. No such a pronounced conductivity change has been reported as far as we know.
5. The work function of C12A7:e glass measured by UPS was 3.0eV, which is comparable to metal Li and Ca, but chemically stable.
6. No significant difference in X/neutron RDFs was noted between e-free C12A7 and e-doped C12A7 glasses but striking difference was observed by Resonance Raman scattering.

We explain some of these results by ab initio MD simulation (PNAS 2016) and propose electride glass is a novel type amorphous semiconductor.

4:30 PM CM02.12.04

Exploring Structure-Fragility Relationships in Polyrotaxane Glasses Karan V. Dikshit and Carson J. Bruns; University of Colorado Boulder, Boulder, Colorado, United States.

In this work we characterize the viscoelastic properties of a new class of thermoplastics called polyrotaxane glasses. The polyrotaxane glass macromolecules comprise a polyethylene glycol (PEG) chain threaded by many α -cyclodextrin beads displaying modifiable organic functional groups. X-ray diffraction and calorimetry studies confirm the amorphous nature of these materials. Above the glass transition temperature (T_g), the local cooperative motions of the polyrotaxanes can be probed by various rheological and mechanical techniques. These local motions appear to cease on experimental time scales at T_g, yet secondary relaxations persist even in the apparently frozen state as the material continues to reduce free energy away from equilibrium. We elucidate the effect of chain length and bead density on the fragility and glassy dynamics of these polyrotaxane materials. The fragility of the glasses, which is determined by the extent to which viscosity deviates from the ideal Arrhenius temperature relationship due to the ceasing of local motions as T_g is approached, is characterized by rheological studies above the T_g. Below the T_g, information about the secondary relaxations is obtained by dynamic mechanical analysis. These studies bring us closer to realizing applications for these systems by expanding the scope of our understanding of their mechanical behaviour across a wide range of temperatures and frequencies.

4:45 PM CM02.12.05

Influence of Organic Bridging Groups on the Mechanical Properties of Organosilica Materials Douglas A. Loy; University of Arizona, Tucson, Arizona, United States.

Organosilica with bridging organic groups are of great interest in constructing porous materials for liquid chromatographic supports, catalysts, and adsorbents for hazardous materials, non-porous coatings to protect against corrosion or permeation, modified surfaces for composites, and even sunscreens based on nanoparticles bearing bridging organic chromophores to absorb ultraviolet light. While much has been learned of the influence of the bridging group on porosity, far less is known of its effect on the mechanical properties of the amorphous materials. To this end, we have prepared a wide range of organosilica materials as monolithic forms that permit their analysis by mechanical characterization using a Universal testing apparatus and thermal-mechanical properties by dynamic mechanical analyses. Organosilicas with bridging groups that include rigid aromatics, flexible alkylenes, and heteroatom functionalized bridges were prepared by sol-gel polymerizations and air dried to afford monolithic xerogels for mechanical testing.