MM 14: Liquid and Amorphous Materials I

Time: Tuesday 11:30–12:45 Location: SCH/A315

MM 14.1 Tue 11:30 SCH/A315

Shining Light on Gold-in-Gallium: DFT Insights into Photocatalytic Benzyl Alcohol Oxidation — •Oliver Conquest[1], Chung Nguyen[2], Sarina Sarina[2], and Catherine Stampfl[1] — [1]School of Physics, The University of Sydney, Sydney, Australia — [2]School of Chemical and Biomolecular Engineering, The University of Sydney, Sydney, Australia

Recent experimental results have shown that pure liquid Ga with an oxide later does not perform well as a photocatalyst for Benzyl alcohol conversion to Benzaldehyde. When Au nanoparticles (Au NP) are introduced into the system, it emerges as an excellent Benzyl alcohol conversion photocatalyst. The Au NP develop an ultra-thin amorphous-GaO_x (a-GaO_x) skin when placed in liquid Ga, the a-GaO_x in the presence of Au is expected to play an important role in the photoreaction. Therefore, understanding the reaction mechanism requires atomic level investigation into the a-GaO_x/Au(111), and Au(111)/a-GaO_x/Ga interfaces. We perform molecular dynamics and density functional theory (DFT) calculations to provide insight into the charge and photoexcited properties of the Au(111)/a-GaO_x/Ga heterostructures with a careful emphasis on the a-GaO_x layer. The DFT calculations of the a-GaO_x/Au(111) interface demonstrate the charge transfer characteristics between the Au(111), a-GaO_x Ga-liq layers and provide a new detailed understanding of the photocatalytic mechanisms at play.

MM 14.2 Tue 11:45 SCH/A315

Reactive Edges and Inevitable Adsorption in Carbon Nanomembranes — •Levin Mihlan[1], Filip Vuković[2], Andrei Postnikov[3], Verena Müller[4], and Jürgen Schnack[1] — [1]Universität Bielefeld, Germany — [2]TU Wien, Austria — [3]Université de Lorraine, France — [4]Friedrich-Schiller-Universität, Germany

Carbon nanomembranes (CNMs) are nanometer-thin materials synthesized via electron-induced crosslinking of aromatic self-assembled monolayers. These membranes can be functionalized for various applications, initially serving as molecular filters. In addition to their internal structure, the precise elemental composition is not yet fully understood [1]. Therefore a first-order prediction for ultraviolet photoelectron spectroscopy (UPS) was developed based on DFT-calculated densities of state. Combined with theoretical carbon-only CNM model structures and an analysis of the near-zero binding-energy region, this approach enables statements regarding the saturation of different regions as well as the presence of reactive edges and dangling bonds. Since these regions are highly unstable under ambient conditions, physisorption and chemisorption of elements such as hydrogen and oxygen are to be expected. In this work, various CNM model structures are systematically investigated using this methodology, ultimately supporting the presence of such depositions, provided that other observations are valid.

[1] Dementyev, Petr, et al. "Carbon Nanomembranes from Aromatic Carboxylate Precursors" ChemPhysChem 21.10 (2020): 1006

MM 14.3 Tue 12:00 SCH/A315

Volume increase of silica glass due to water intercalation and silanol group formation — Manuel Enns[1], Wolfgang Körner[1], Christian Elsässer[1,2], and •Daniel F. Urban[1,2] — [1]Fraunhofer Institut für Werkstoffmechanik IWM, Freiburg, Germany — [2]Freiburger Materialforschungszentrum FMF, Albert-Ludwigs-Universität Freiburg, Germany

We present a theoretical study on the change of volume of silica glass due to the intercalation of molecular water and the formation of silanol groups. By a statistical representative set of density functional theory calculations, we obtained a volume increase per mole of molecular water in amorphous SiO_2 of 2.5 cm^3/mol. In comparison, for the reaction of water to silanol groups we found on average a 3.5 times larger volume increase of 8.7 cm^3/mol. Our results show that the exothermic dissolution of H_2O into silanol pairs is not restricted to small rings of size three and four. We find an equal distribution of reaction energies over all ring sizes which we explain by the structural relaxation and the related energy gain of the entire amorphous neighbourhood. Statistically, most exothermic dissolution of H_2O may happen at five-membered rings since they outnumber the three- and four-membered rings in amorphous SiO_2. Our findings shed new light on the underlying mechanisms and the size of the volume change of the water intercalation in silica glass and we discuss our findings with respect to previous experimental and theoretical work.

MM 14.4 Tue 12:15 SCH/A315

Insights into the interplay of relaxation and crystallization of Vit106a glass — •Lukas Musiol[1], Merlin Kempf[2], Lukas Musiol[1], Remi Daudin[2], and Gerhard Wilde[1] — [1]Institute of Materials Physics, University of Münster, Wilhelm-Klemm-Str. 10, 48149 Münster, Germany — [2]Université de Grenoble Alpes, CNRS, Grenoble INP, Laboratoire SIMaP, Grenoble, France

Metallic glasses are metastable systems that show relaxation behavior towards a local energy minimum and crystallize when heated sufficiently above their glass transition temperature (Tg). Different modes of relaxation can be accessed by varying the combination of relaxation time and temperature. At temperatures significantly lower than Tg only β-relaxation is expected, corresponding to local rearrangements of few atoms. For temperatures close to Tg and for long times only α-relaxation is observed which corresponds to collective rearrangements in the glass. While these two relaxations are often considered independent, a growing body of evidence shows that they are linked [J. Phys. Chem. Lett., 3 (2012), 735; Intermetallics, 93 (2018), 101]. Additionally few attempts have been made to understand how structural changes during relaxation influence crystallization behavior.

Vit106a as a model system of bulk metallic glasses has been investigated concerning the relaxation dynamics and changes in crystallization behavior using conventional scanning calorimetry correlated to strutural analyses using transmission electron microscopy-based methods.

MM 14.5 Tue 12:30 SCH/A315

Unraveling the Correlation Between Populated Site Energies, Activation Barriers and Saddle Point Energies in Solid Ion Conductors — •Martin Schäfer[1], Mohammad A. Badragheh[2], Michael Vogel[2], and Karl-Michael Weitzel[1] — [1]Universität Marburg, Marburg, Germany — [2]T.U. Darmstadt, Darmstadt, Germany

Transport phenomena in disordered materials are governed by a complex potential energy landscape that includes a distribution of local energy minima (sites), saddle point energies and local energy barriers. An understanding of the connection of these properties is essential to unravel the transition between local hops and long-range transport.

In this work, the populated site energy distribution (PSED) is experimentally determined by the Charge Attachment Induced Transport (CAIT) technique that yields concentration dependent diffusion coefficients and activation energies by comparison of measured concentration depth profiles to calculated profiles gained by Nernst-Planck-Poisson modeling [1]. The distribution of local barriers is probed through Nuclear Magnetic Resonance (NMR) measurements [2]. For Li3B7O12, the FWHM of the PSED is determined to be 250 meV while the activation energies show a FWHM of about 440 meV suggesting that the apparent energy distribution of saddle points must be significantly broader than the distribution of site energies.

[1] V.H. Gunawan, M. Schäfer, and K.-M. Weitzel, Phys.Chem.Chem.Phys., 26, 14430 (2024)

[2] M.A. Badgragheh, E. Winter, M. Vogel, unpublished results