Nanometer-scale Science and Technology
Room: 12 - Session NS-ThM

Nanoscale Imaging and Microscopy
Moderator: N. Camillone, Brookhaven National Laboratory

8:00am **NS-ThM1 Spin Friction Observed on the Atomic Scale**, ***R. Wiesendanger****, B. Wolter, A. Kubetzka, K. von Bergmann, Y. Yoshida,* University of Hamburg, Germany*, S.-W. Hla*, Ohio University

With the advent of scanning probe microscopy techniques that involve a tip and a sample in relative motion in the contact or non-contact regime, the microscopic aspects of friction have become a major branch of research called nanotribology. A significant number of recent studies in this field have concentrated on the distinction between electronic and phononic contributions to friction. For the present study, we have used the combination of spin-polarized scanning tunneling microscopy [1] and single-atom manipulation in order to move individual magnetic atoms over a magnetic template [2]. By monitoring the spin-resolved manipulation traces and comparing them with results of Monte-Carlo simulations, we have been able to reveal the characteristic friction force variations resulting from the occurrence of spin friction on the atomic scale [3].

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[2] D. Serrate, P. Ferriani, Y. Yoshida, S.-W. Hla, M. Menzel, K. von Bergmann, S. Heinze,

A. Kubetzka, and R. Wiesendanger, Nature Nanotechnology 5, 350 (2010).

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Phys. Rev. Lett. (2012), in press.

8:20am **NS-ThM2 Observing Mineral Reactions in Supercritical Carbon Dioxide Utilizing High Pressure Atomic Force Microscopy**, ***A.S. Lea****, M. Xu, K.M. Rosso*, Pacific Northwest National Laboratory

Geologic sequestration of CO2 has become an emerging enterprise for reduction of greenhouse gas emissions. Because CO2 will be injected and stored in host rock at depths >800m, lithostatic pressure will cause the CO2 to remain in supercritical fluid state. Knowledge of mineral-fluid chemical transformation rates at geologically relevant temperatures and pressures is expected to be an important aspect of predicting reservoir stability. Many mechanisms of mineral transformation reactions where scCO2 is the dominant phase and water availability is low have so far remained unstudied. We have developed an atomic force microscope capable of observing in-situ mineral transformations under supercritical conditions (i.e., >72.8 atm and >304K) in real time.

Observations of the disappearance of a 1.5nm layer on the surface calcite is evident in anhydrous scCO2 are consistent with the dehydration of a hydrated calcium carbonate layer and is consistent with measurements from piezoelectric force microscopy. We have also followed the formation of a water film on the surface of geologically more relevant forsterite, which is deemed to be essential in the transformation of this silicate mineral into a carbonate, and have related film thickness to water content in the scCO2.

8:40am **NS-ThM3 Resolving Amorphous Solids - The Atomic Structure of Glass**, ***M. Heyde****, L. Lichtenstein, H.J. Freund*, Fritz-Haber-Institute, Germany **INVITED**

Vitreous silica is the basis of traditional glasses. Furthermore, it is the prototype oxide network former. Hence, it has been extensively investigated by diffraction methods, like X-ray and neutron scattering. Therefore, it is a great surprise how little is known about its atomic structure. It is impossible to directly extract ring statistics or local ring environments from diffraction. Theoretical structural models have been correlated to the diffraction data with reasonable agreement. Nevertheless, such agreement can never be unambiguously elucidate the structure of an amorphous material.

Modern imaging techniques render the investigation of two dimensional (2D) glass systems possible. Recently, we reported on the atomic structure of a thin metal-supported vitreous silica film on Ru(0001) using scanning tunneling microscopy (STM) [1]. For the first time, it was possible to verify Zachariasen's continuous random network [2] in real space. The existence of a 2D silica glass on a graphene support has been shown by scanning transmission electron microscopy [3] suggesting that further 2D glass systems may be prepared. The investigation of 2D glass models provides the unique possibility to study unexplored properties of amorphous materials.

Herein we report on the first non-contact atomic force microscopy (nc-AFM) images of a 2D silica glass grown on Ru(0001). We will present a thorough statistical analysis and a comparison to diffraction data of 3D silica glass as well as to theoretical models, hereby showing that a 2D thin film of vitreous silica can act as a model system for the amorphous 3D network.

[1] L. Lichtenstein, C. Büchner, B. Yang, S. Shaikhutdinov, M. Heyde, M. Sierka, R. W łodarczyk, J. Sauer, and H.-J. Freund, " The Atomic Structure of a Metal-Supported Vitreous Thin Silica Film", Angew. Chem. Int. Ed. **51**, 404 (2012).

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9:20am **NS-ThM5 Femtosecond Time-Resolved Scanning Tunneling Microscopy on Nanostructures**, ***H. Shigekawa***, University of Tsukuba, Japan

With the size reduction of structures in current electronic devices, differences in the electronic properties caused, for example, by the structural nonuniformity of each element have an ever-increasing effect on macroscopic functions. The study of nonequilibrium quantum dynamics in materials with small structures is of great importance not only from the fundamental viewpoint but also as a basis for the further development of functional devices. Real-space imaging of the transient carrier transport and transitions in nanostructures is desired to obtaine a deeper understanding of current semiconductor physics. Probing the effect of local electronic structures of nano-clusters on energy transfer is important for the analysis of chemical reactions in catalytic activities and also for the development of organic solar devices. To advance such studies, a method that enables the probing of local carrier dynamics with high spatial and temporal resolution is necessary.

Recently, femtosecond time-resolved scanning tunneling microscopy (STM), which enables ultrafast phenomena on a target material to be probed with the spatial resolution of STM, has been realized by the combination of STM with ultrashort-pulse laser technologies [1-4]. In time-resolved STM, the tunnel gap of STM is illuminated by a sequence of paired laser pulses, and the change in tunneling current ΔI is measured as a function of the delay time between the paired pulses (t_d). A high temporal resolution in the femtosecond range, which is limited only by the optical pulse width, is obtained simultaneously with the atomic spatial resolution of STM. This microscopy technique is applicable to systems in which the response of the tunneling current has a nonlinear dependence on the optical excitation intensity. I n the case of semiconductors, for example, the magnitude of ΔI obtained for a certain delay time t_d reflects the density of photogenerated minority carriers at t_d after the first pulse excitation, and the carrier decay processes can be observed by analyzing the delay-time dependence of ΔI. Using polarized light, spin dynamics can be probed, and the detection of signals such as phonons is also possible.

In this talk, I would like to introduce this new microscopy technique with some new results.

References

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9:40am **NS-ThM6 Unusual Island Formations of Iridium on Ge(111) Studied by STM**, ***M. van Zijll****, C. Mullet, B. Stenger, E. Huffman, D. Lovinger, W. Mann, S. Chiang*, University of California, Davis

We have used scanning tunneling microscopy (STM) to characterize the growth of iridium onto Ge(111). Iridium was deposited onto the Ge(111) c(2x8) surface at different coverages less than 1ML, and the samples were annealed to temperatures between 550K and 750K. A new form of growth was observed, consisting of pathways connecting larger iridium islands. As the annealing temperature increased, the iridium growth first formed unusual shapes with finger-like protrusions. Next, these shapes broke apart into smaller islands, which ultimately formed into larger islands at higher temperatures. High resolution images have been obtained, which allow insight into the atomic arrangements. We propose a model relating the activation energy of specific binding sites to the formation of various observed structures on the surface.

Funding from NSF CHE-0719504 and NSF PHY-1004848 (REU)

10:40am **NS-ThM9 Turning STM Images Into Chemical Understanding: Atomically Flat Si(100) Reveals the Mechanism of Silicon Oxidation**, ***M.A. Hines****, M.F. Faggin, K. Bao, A. Gupta, B.S. Aldinger*, Cornell University

Because of its technological importance, silicon oxidation has been studied intensely for decades; however, the disordered nature of the oxide makes these reactions notoriously difficult to understand. In this work, the oxidation reaction is coupled with a subsequent etching reaction, allowing oxidation to literally write an atomic-scale record of its reactivity into the etched surface — a record that can be read with scanning tunneling microscopy (STM) and decoded into site-specific reaction rates, and thus chemical understanding, with the aid of simulations and infrared spectroscopy. This record overturns the long-standing and much-applied mechanism for the aqueous oxidation of the technologically important face of silicon, Si(100), and shows that the unusually high reactivity of a previously unrecognized surface species leads to a self-propagating etching reaction that produces near-atomically flat Si(100) in a beaker at room-temperature — a long-standing technological goal. These findings show that, contrary to expectation, the low-temperature oxidation of Si(100) is a highly site-specific reaction and suggests strategies for functionalization by low-temperature, solution-based reactions.

11:00am **NS-ThM10 Spectroscopic Imaging of Silicon-Hafnia Interfaces**, ***C. Guedj****, H. Grampeix, C. Licitra, E. Martinez*, CEA, LETI, MINATEC Campus, France

New behavior and phenomena can emerge at oxide interfaces, and the nanocharacterization of these properties is a real challenge for the semiconductor industry [i] . To replace the conventional SiO_2 insulator, hafnium-based oxides have been introduced [ii],[iii] into advanced CMOS devices such as MOSFETs or memories [iv], but the nanometric control of their interfacial properties still remains a critical issue. For further industrial implementation of these oxides, it is necessary to obtain sufficiently high dielectric constants and bandgaps, good thermal stability on silicon, good scalability and sufficient reliability [v] at a reasonable cost. In this presentation, we have performed spectroscopic imaging of silicon-hafnia interfaces using energy filtered high-resolution transmission electron microscopy and valence electron energy loss spectroscopy (HRTEM-VEELS), coupled with X-Ray photoelectron spectroscopy (XPS), Reflection energy loss spectroscopy (REELS), UV photoelectron spectroscopy (UPS) and spectroscopic ellipsometry. Optical absorptions and bandgap profiles across the interface are obtained and novel ordering effects like axiotaxy are locally observed. An atomic-scale modelling is proposed, and the consequences in terms of device performances are detailed.

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[iii] M.H. Cho et al., Appl. Phys. Lett. 81, 1071 (2002)

[iv] B.Govoreanu et al., proc. IEEE IEDM , p 729 (2011)

[v] J. Robertson, Solid-state electron., Vol. 49, p 283-293 (2005)

11:20am **NS-ThM11 Atom Probe Tomography of AlInN/GaN based HEMT Structures**, ***N. Dawahre****, G. Shen, P. Tolmer, S.M. Kim, P. Kung*, University of Alabama, Tuscaloosa

Group III-Nitride semiconductors have been well known for their excellent optoelectronic properties associated with a wide direct bandgap, which has led to the emergence of blue and green lasers, ultraviolet-blue-green-amber and white light emitting diodes, and ultraviolet photodetectors. They are also rapidly becoming the material family of choice for next generation of RF-microwave devices, power amplifiers and high temperature electronics, thanks to high two-dimensional electron gas charge densities and high breakdown electric fields in these materials. GaN based materials are also more radiation resistant than conventional electronic materials, which makes them well suited for space electronics. Although less thoroughly investigated until now, lattice matched AlInN/GaN systems are promising to be a viable alternative to the current state-of-the-art strained AlGaN/GaN devices and their reliability issues.

In this work, we present the nanoscale characterization of AlInN semiconductors and AlInN/GaN high electron mobility transistor (HEMT) structures using a combination of transmission electron microscopy (TEM) and laser assisted atom probe tomography (APT), and correlate these with the structures' electronic and optical properties, as well as the effects of irradiation. APT is an emerging technique based on the field ion emission from a needle-shaped region of interest and is capable of yielding 3D chemical mapping with atomic sensitivity and sub-nanometer spatial resolution. We report here a study of the field evaporation mechanisms from wide bandgap AlInN and GaN using a visible ps laser during APT experiments and correlate them with APT experiments (e.g. laser pulse energy, …) in order to establish approaches for reliable chemical analysis at the nanoscale of AlInN compound alloys. We proceed to investigate the fundamental material characteristics of interest that can be extracted from a combined APT and TEM analysis, including indium segregation phenomena in AlInN, interdiffusion near the AlInN/GaN channel interfaces and interface roughness, as well as the effects of irradiation on the channel properties.

11:40am **NS-ThM12 Pit Initiation at MnS Nano-Inclusions in Carbon Steel under Exposure to Sulfate-Reducing Bacterium *D. alkanexedens***, ***J.S. Hammond***, Physical Electronics*, *B.H. Davis, Z. Suo,* Montana State University*, I. Beech,* University of Oklahoma*, D.F. Paul,* Physical Electronics*, R. Avci*, Montana State University

Cold rolled carbon steel (1018) is a commonly used structural material in various applications, including the construction of fuel storage tanks for naval ships. *Desulfoglaeba alkanexedens* (strain ALDCT) is a known fuel-degrading, anaerobic, sulfate-reducing bacterium (SRB) [1, 2] that thrives at fuel-water interfaces in marine environments and can influence the pitting corrosion of carbon steel. It has long been postulated that MnS inclusions in carbon steel can act as sites of pitting initiation [3]. The propagation of pitting corrosion is relatively well understood; however, the initiation of pits is still a subject of controversy [4, 5]. A careful study of pit initiation and propagation associated with sulfide inclusions, particularly as they relate to microbial influenced corrosion (MIC) under anaerobic conditions, has been lacking, partly because these inclusions are mostly submicron-sized and the evolution of their corrosion is difficult to monitor. The use of nanoprobes instead of microprobes is required to determine the elemental and chemical composition and to map out the elemental distributions at the submicron scale. Quantitative surface sensitive techniques such as Auger electron spectroscopy [4, 5] are essential for monitoring the nanoscale changes associated with surface-related phenomena, including MIC. This presentation will review the results of comprehensive and systematic studies of nano-inclusions on carbon steel surfaces prior to and following exposure of the steel to a solution of a mature ALDCT culture and to abiotic sulfide as a control. The nano-inclusions were carefully characterized using a field emission Auger nanoprobe with a spatial resolution of approximately 10 nm for imaging and spectroscopy and compared with results obtained using X-ray microprobes, which typically have a spatial resolution of around 1000 nm for spectroscopy and 10 nm for imaging. The study elucidates biologically driven corrosion reactions taking place in and around nano-inclusions. The impact of this fundamental analysis on the understanding of MIC phenomenon will be discussed.

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