Surface Science Division
Room 319 - Session SS+AS-WeA

Memorial Session in Honor of Patricia Thiel I

Moderators: Alex Belianinov, Oak Ridge National Laboratory, **Dapeng Jing**, Iowa State University

2:20pm **SS+AS-WeA-1 Assembly and Stability of Metal Nanoclusters at Surfaces: Modeling Inspired by Thiel-Group STM Studies***, **Jim Evans**, Y. Han,* Iowa State University*; D. Liu,* Ames Laboratory USDOE*; K. Lai,* Fritz Haber Institute of the Max Planck Society, Germany **INVITED**

STM studies by the Thiel group have characterized diverse non-equilibrium growth shapes for 2D metal nanoclusters (NCs) formed by deposition on strongly-binding metal surfaces, as well as the NC size and spatial distributions [1,2]. More recent work also considered deposition on a weakly-binding graphite substrate, producing not just supported 3D NCs, but also NCs intercalated beneath the top graphene layers [3]. These observations have guided development of predictive atomistic-level modeling of all aspects of the nucleation and growth process. For example, this modeling successfully captures the growth morphologies of individual NCs: fractals for limited periphery diffusion, height selected NCs due to quantum size effects; core-ring vs intermixed alloy structures for co-deposition; star-fish NCs on 5-fold quasicrystal surfaces; “squeezed” 3D NCs for intercalation, etc.

These arrays of supported metal NCs are metastable, and thus coarsen to fewer, larger NCs (reducing the energy cost of broken bonds at NC peripheries) on a time-scale typically significantly longer than that for deposition. In contrast to the expected Oswald Ripening (OR), the Thiel group showed for metal(100) homoepitaxy, coarsening was dominated by 2D NC diffusion and coalescence, i.e., Smoluchowski Ripening (SR) [4]. This observation has prompted extensive theory development for the NC size-dependence of diffusion (as this controls SR kinetics). For metal(111) homoepitaxy where OR occurs, the Thiel group explored the dramatic acceleration of OR due to even trace amounts of chalcogens due to the formation of metal-chalcogen complexes [4]. This work has also prompted extensive recent theoretical development.

[1] J.W. Evans, P.A. Thiel, M.C. Bartelt, *Surf. Sci. Rep*. **64** 1-128 (2006).

[2] T. Duguet, Y. Han, D. Jing, B. Unal, J.W. Evans, P.A. Thiel, *PNAS* **108** 989 (2011).

[3] A. Lii-Rosales, Y. Han, D. Jing,…K.C. Lai, J.W. Evans, P.A. Thiel, *Nanoscale* **13** 1485 (2021).

[4] K.C. Lai, Y. Han,… P.A. Thiel, D.-J. Liu, J.W. Evans, *Chemical Reviews* **119** 6670 (2019).

2:40pm **SS+AS-WeA-2 Stability and Dynamics of Sulfur-Metal Complexes on Coinage Metal Surfaces***, **Da-Jiang Liu,*** Iowa State University **INVITED**

Interactions between sulfur and other chalcogen atoms and metal surfaces are critical in areas such as heterogeneous catalysis, self-assembled monolayers, and 2D materials. Over the last decade, Prof Thiel's research group has conducted a systematic survey of adsorption of sulfur on various high symmetry surfaces of Cu, Ag, and Au using low temperature STM. A rich variety of sulfur-metal surface complexes have been observed, depending on the type of metal, the coverage of sulfur, and the surface orientation.

Identification of those complexes is facilitated by density functional theory (DFT) studies, which provide information regarding energies, geometries, and simulated STM images.

Those sulfur-metal complexes are crucial for mass transport that affects surface morphology. Molecular dynamics simulations using machine learning potentials trained from DFT calculations provide insights regarding the the role sulfur plays in enhancement of surface mass transport.

3:00pm **SS+AS-WeA-3 The Atomic of Structure of Surfaces: From Vacuum to Gas and Liquid Environments***, **Miquel Salmeron**,* Lawrence Berkeley National Laboratory **INVITED**

The development of spectroscopies (XPS, XAS) and microscopies (STM) that can operate in ambient gas pressures has revealed that the structure of material surfaces depends strongly on the environmental conditions of gas composition, pressure and temperature. Experiments have shown that adsorption of atoms and molecules can substantial restructure surfaces that are otherwise stable under vacuum conditions. Restructuring is manifested in the breaking on the initially flat crystalline surface by formation of nanoclusters from atoms detached from steps and other defects. In the case of alloys, adsorbed species change the surface stoichiometry by inducing segregation of alloy components. This restructuring is important because the catalytic activity and selectivity of catalyst surfaces can be strongly modified.

I will discuss the possible generality of this phenomenon by analyzing cases where atomically flat surfaces of many transition metals undergo such changes in the presence of CO even at cryogenic temperatures, while others remain unchanged

4:20pm **SS+AS-WeA-7 The Influence of Alloying on Surface Kinetics***, **Karina Morgenstern**,* Ruhr-Universität Bochum, Germany **INVITED**

The physical properties of nanoscale systems differ from those of macroscopic systems, making them attractive candidates to tune the electronic or optical properties of matter. However, nanostructures are thermodynamically only metastable, altering their shape and thus their properties even at room temperature [1]. Patricia Thiel and coworkers extended this work from vacuum to coarsening in the presence of chalcogens [2] and pioneered work for heteroepitaxial systems [3]. Following the latter, we use Ag/Cu(111) that serves, at a lattice mismatch of 13%, as a representative for a large deposit on a substrate with a small lattice constant. This large difference influences growth, induced growth, and decay of Ag nanoislands on Cu(111) as revealed by variable temperature scanning tunneling microscopy [3]. For natural growth, the dimensionality of the structures depends on temperature. A layer-by-layer growth at low temperature suggests that low-temperature growth might be an effective way to overcome the kinetic limitations of the step edge barrier for forming smoother interface layers. Similar, but not identical clusters can be induced from a 2D gas by scanning the surface at elevated voltages. The higher temperature islands exhibit a misfit dislocation pattern, which influences their decay. We relate specifically stable, magic island sizes to the complexity of the heteroepitaxial decay. Even more unusual is the decay of Cu-Ag core-shell islands, for which we discuss two qualitatively different types of decay mechanisms [5]. The implication of the kinetics. for the physicochemical properties of the nanoparticles are discussed in this talk.

[1]K. Morgenstern, phys. stat. sol. B 242, 773 (2005);P.A. Thiel, M. Shen, D.-J. Liu, J. W. Evans, J. Phys. Chem. C 113, 5047–5067 (2009);K.C. Lai, Y. Han, P. Spurgeon, W. Huang, P.A. Thiel, D.-J. Liu, James W. Evans, Chem. Rev. 119, 6670−6768 (2019).

[2]P.A. Thiel, M. Shen, D.-J. Liu, J.W. Evans, J. Vac. Sci. Technol. A 28, 1285 (2010).

[3]B. Unal, F. Qin, Y. Han, D.-J. Liu, D. Jing, A.R. Layson, C.J. Jenks, J.W. Evans, P.A. Thiel, Phys. Rev. B 76, 195410 (2007); Y. Han, B. Unal, F. Qin, D. Jing, C.J. Jenks, D.-J. Liu, P.A. Thiel, J.W. Evans, Phys. Rev. Lett. 100 (2008); Y. Han, D. Jing, B. Unal, P.A. Thiel, J.W. Evans, Phys. Rev. B 84, 113414 (2011).

[4]C. Sprodowski, K. Morgenstern, New J. Phys. 22, 063055 (2020); 9, 710 - 1-7 (2019); *ibid*J. Phys. Chem. C 123, 9846–9851 (2019);*ibid*Phys. Rev. B 100, 045402 - 1-8 (2019).

[5]C. Sprodowski, K. Morgenstern, Nanoscale 11, 10314 - 10319 (2019).

5:00pm **SS+AS-WeA-9 Cluster Superlattice Membranes***, **Thomas Michely**,* University of Cologne, Germany **INVITED**

Cluster superlattice membranes are a new type of a 2D material consisting of a two dimensional (2D) hexagonal lattice of similar-sized nanoclusters sandwiched between a single-crystal 2D layer and an embedding matrix material. The fabrication process involves three main steps, the templated self-organization of a cluster superlattice on the moiré of a 2D layer with a metal substrate, conformal embedding in a matrix, and subsequent lift-off from the metal substrate. The mechanical stability provided by the matrix of nm-thickness makes the membrane stable as a free-standing material and enables transfer to other substrates. The fabrication procedure is proposed to be applicable to a wide variety of cluster materials and cluster sizes from the single-atom limit to clusters of a few hundred atoms, as well as to several 2D layer/host matrix combinations.

In this talk we will exemplify the cluster superlattice membrane concept for Ir clusters on graphene or a monolayer of hexagonal boron nitride and embedded in a carbon matrix. The membrane fabrication process is characterized step-by-step using scanning tunneling microscopy and spectroscopy, x-ray photoelectron spectroscopy, optical and transmission electron microscopy, as well as Raman spectroscopy.

The versatility of the membrane composition, its mechanical stability, and the simplicity of the transfer procedure make cluster superlattice membranes a promising material in catalysis and magnetism, for which potential applications are outlined.

The contributions of Pantelis Bampoulis, Tobias Hartl, Moritz Will, Stefan Schulte, Kai Kämper, Davor Čapeta, Rajendra Singh, Daniel Scheinecker, Virginia Boix de la Cruz, Sophia Dellmann, Paolo Lacovig, Silvano Lizzit, Boris V. Senkovskiy, Alexander Grüneis, Marko Kralj, Jan Knudsen, and Jani Kotakoski to this work are gratefully acknowledged.

5:40pm **SS+AS-WeA-11 High Quality 2-D Materials Characterized Paradoxically from Broad Diffraction Features.***, Michael Tringides,* Iowa State University and Ames Laboratory US-DOE **INVITED**

Paradoxically a very broad diffraction background, named the Bell-Shaped-Component (BSC), has been established as a feature of graphene growth. Recent diffraction studies as a function of electron energy on Gr/SiC have shown that the BSC is not related to scattering interference. The broad background is in-phase with the Bragg component of both the (00) and Gr(10) spots. Instead textbook diffraction states it should be out-of-phase, since it should originate from destructive interference between adjacent terraces[1]. Additional experiments were carried out as a function of temperature over the range 1200° C-1300° C that single-layer-graphene (SLG) grows. Quantitative fitting of the profiles shows that the BSC follows the increase of the G(10) spot, proving directly that the BSC indicates high quality graphene[2]. The BSC has been also in graphene on metals including Gr/Ir(111)[3]. Recent experiments also show that the BSC is present in h-BN films grown on Ir(111)[3,4]. Its presence in such a wide range of 2-materials suggests its origin must be general and fundamental related to the unusual single layer uniformity common to these widely varying films. One possible explanation of the BSC relates to electron confinement within a single uniform layer which suggests that the BSC is an excellent measure of their uniformity. The confinement of the graphene electrons and the corresponding spread in their wavevector has been seen with ARPES[5]. The transfer of the large momentum spread to the diffracted electrons requires better theoretical understanding of the graphene electron-beam electron interaction.

On a personal note this was one of the last but very enjoyable scientific interactions I had with Pat. From the very beginning she was very enthusiastic and insightful about the problem. This was particularly important because the results were unintuitive and unexpected. This is a statement to her unusual combination of strengths: an extraordinary scientist with deep insights and a warm communicative friend.

In collaboration with P.A.Thiel (deceased), M. Horn von Hoegen , E. H. Conrad.

[1] S. Chen, *et al.Phys. Rev. B.* 100, 155307 (2019).

[2] S. Chen, *et al.J. Phys. Chem. Lett.* 11, 8937 (2020).

[3]K. Omambac *et al* , *Appl. Phys. Lett.* 118, 241902 (2021)

[4]M. Petrovic *et alNanotechnology* 32 505706 (2021)

[5] T. Ohta *et al.Phys. Rev. Lett.* 98, 206802 (2007).

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