

O 82: Nanostructure at Surfaces: Dots and Clusters

Time: Thursday 10:30–13:30

Location: MA 043

O 82.1 Thu 10:30 MA 043

CO₂ Activation on ultra-small Au particles on MgO Thin Films — ●CHRISTIAN STIEHLER¹, FLORENCIA CALAZA¹, MARTIN STERRER¹, NIKLAS NILIUS², and HANS-JOACHIM FREUND¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany — ²Carl von Ossietzky Universität Oldenburg, Institut für Physik, D-26111 Oldenburg, Germany

Metal particles exhibit favorable catalytic properties that are unknown for the respective bulk metals [1]. Although several reasons are discussed in the literature, the true origin for their enhanced activity remains unknown. Electron quantization and the associated band-gap opening at the Fermi level are certainly involved in the unusual catalytic response of the nano-islands. In this talk, we discuss the electronic structure of Au clusters that contain 50-200 atoms and are of monolayer height [2,3]. Simultaneously, we have probed the ability of the particles to bind and activate carbon dioxide (CO₂), by using STM, XPS, TPD and IRAS measurements. The molecules preferentially bind along the cluster edge, at which a charge transfer from the electron-rich perimeter into the adsorbates takes place. Our talk addresses possible interrelations between the CO₂ adsorption behavior and the quantized electronic structure of the gold islands.

[1] M. Valden et al., *Sci* 281, 1647 (1998)[2] X. Lin et al., *PLR* 102, 2068011 (2009)[3] C. Stiehler et al., *PRB* 88, 115415 (2014)

O 82.2 Thu 10:45 MA 043

Ripening mechanisms of supported size-selected clusters — ●FABIAN KNOLLER, MICHAEL KÖNIG, YVES FUKAMORI, FRIEDRICH ESCH, and UELI HEIZ — Technische Universität München, Chair of Physical Chemistry, Lichtenbergstr. 4, 85748 Garching, Germany

Truly monodisperse clusters give an unprecedented access to the investigation of ripening in the non-scalable size regime. Here, the ripening dynamics of individual Pd₁₉ clusters have been studied on a strongly interacting Rh(111) surface and on a weakly interacting supported, periodically wettable Moiré-graphene film [1]. Whereas on the former substrate Ostwald ripening is observed in series of STM images at room temperature, the latter shows Smoluchowski ripening at slightly elevated temperatures of about 323 K. In both cases, the lateral resolution is sufficient to detect isomerization processes that influence the ripening kinetics: shape-dependent atom detachment linked to atom diffusion, respectively height fluctuations linked to cluster diffusion. These movements act intermittently, on much faster time scales than the mean ripening process. We try to tackle this experimental problem by two additional STM measurement techniques, implemented by one electronic device: With FastSTM, time series with a temporal resolution of up to now 10 frames/s have been gained, while Atom Tracking allows for lateral and vertical determination of the cluster maxima with a time resolution down to 5 ms and a lateral resolution below atomic dimensions.

[1] Y. Fukamori, M. König, B. Yoon, B. Wang, F. Esch, U. Heiz and U. Landman, *ChemCatChem* 5 (2013) 3330-3341

O 82.3 Thu 11:00 MA 043

STM and STS study of Tb induced magic clusters on Si(111)7x7 — ●JAN GROSSE, MARTIN FRANZ, and MARIO DÄHNE — Institut für Festkörperphysik, Technische Universität Berlin, 10623 Berlin, Germany

Surface clusters constitute a promising new research field in solid state physics due to their interesting quantum properties and possible future applications in nanodevices and catalysis. In this work, scanning tunneling microscopy (STM) and spectroscopy (STS) was used to study Tb induced clusters on the Si(111)7x7 surface. The samples were prepared by molecular beam epitaxy using submonolayer Tb coverages and annealing at moderate temperatures. It was found that the self-organized growth of clusters occurred in the center of the 7x7 half unit cells. These clusters have a triangular shape, but do not show the mirror symmetry of the half unit cell, thus they form one of the two equivalent rotated configurations. Furthermore, the ability of tip-induced switching between these two configurations was demonstrated. From atomically resolved STM images a structure model explaining nicely our observations could be developed. Additionally, STS measurements were performed in order to compare the electronic structure of the

centered clusters with the surrounding Si(111)7x7 surface.

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O 82.4 Thu 11:15 MA 043

Simulation of AFM-images for Fe-clusters on Cu(111) — ●SVITLANA POLESYA¹, SERGIY MANKOVSKY¹, DIEMO KÖDDERITZSCH¹, JAN MINÁR¹, HUBERT EBERT¹, and FRANZ GIESSIBL² — ¹LMU München, Dept. Physikalische Chemie, München, Germany — ²Institut für Experimentelle Physik, Univ. Regensburg, Germany

The present work is motivated by a study on small Fe_n-clusters ($n = 1, 2$, and 3) on Cu(111) surface using Atomic Force Microscopy (AFM) at subatomic level. The first part of the work is devoted to the investigation of the ground state properties of deposited Fe clusters by means of DFT calculations. The crucial role of the relaxation of the Cu surface for the equilibrium position of Fe atoms is demonstrated. The effect of electronic correlations on the equilibrium positions have been investigated within the LSDA+U calculations using different U values. In the second part of the work the forces on the tip approaching the Fe/Cu(111) surface are studied. The tip was modeled by a single atom of inert gas as well as by an H atom. The dependence of the AFM image on the tip-cluster distance is shown that is in agreement with the experimental findings.

O 82.5 Thu 11:30 MA 043

Structure of graphene/Ir(111) supported Pt/Rh clusters — ●DIRK FRANZ^{1,2}, NILS BLANC^{3,4,5}, JOHANN CORAUX^{3,4}, HESHMAT NOEI², ROMAN SHAYDUK², and ANDREAS STIERLE^{1,2} — ¹Universität Hamburg, D-20355 Hamburg, Germany — ²DESY NanoLab, D-22607 Hamburg, Germany — ³Université Grenoble Alpes, Inst NEEL, F-38042 Grenoble, France — ⁴CNRS, Inst NEEL, F-38042 Grenoble, France — ⁵CEA-UJF, INAC, F-38054 Grenoble, France

Ultrasmall metallic nanoparticles exhibit altered structural, chemical and magnetic properties as compared to their bulk counterparts making them attractive for applications as highly active heterogeneous catalysts or high storage density magnetic media. To pinpoint structure-functionality relationships for systems containing nanoparticles with diameters smaller than 2 nm an atomic scale understanding of their structure is mandatory.

It was previously shown that different 2D metal cluster arrays can be grown using the moiré of graphene/Ir(111) as a template [1]. We have employed several surface sensitive techniques (SXRD, XRR, GISAXS, XPS) to investigate the structure and composition of Pt/Rh particles (shape, epitaxy, strain) with less than 50 atoms grown on a graphene/Ir(111) support. SXRD and GISAXS essentially benefit from the ordered arrangement of the clusters and are able to reveal the average atomic structure of these small clusters [2].

[1] A. T. N'Diaye, et al., *New J. Phys.* 11, 103045 (2009).[2] D. Franz, et al., *Phys. Rev. Lett.* 110, 065503 (2013).

O 82.6 Thu 11:45 MA 043

Activation Energies for Chemical Reactions of size-selected Cobalt Oxide Clusters determined by Electron Diffraction — ●STEPHAN BARTLING, INGO BARKE, and KARL-HEINZ MEIWES-BROER — University of Rostock, Institute of Physics, 18051 Rostock, Germany

Size-selected cobalt oxide clusters deposited on different substrates can act as selective and efficient nanocatalysts [1]. In this contribution we present a new setup for determination of kinetic reaction parameters (i.e. apparent activation energy) of metal clusters using reflection high energy electron diffraction (RHEED) under reactive conditions. Soft-landed Co clusters of sizes in the range of 6 to 17 nm are exposed to oxygen or hydrogen and heated during the experiment. The evolution of RHEED patterns reveals significant changes of the particle structure during the treatment (cf. [2]). Analysis of the temperature dependence yields the effective activation energy E_a for CoO oxidation and Co₃O₄ reduction. The results for different cluster diameters are discussed in view of size dependence and the role of cluster morphology.

[1] E.C. Tyo et al., *ACS Catalysis* 2 (11), 2409 (2012)[2] A. Kleibert, *Phys. Status Solidi B* 247, 1048 (2010)

O 82.7 Thu 12:00 MA 043

Photoelectron spectroscopy of nearly free C₆₀ fullerenes on noble gas layers (Ar/Kr/Xe): Dependence of the HOMO peak position on the noble gas electron affinity — ●DOMINIK WOLTER, CHRISTOPH SCHRÖDER, and HEINZ HÖVEL — Fakultät Physik / DELTA, Technische Universität Dortmund, 44221 Dortmund, Germany

We have investigated C₆₀ deposited on argon (Ar), krypton (Kr) and xenon (Xe) layers, with ultraviolet photoelectron spectroscopy (UPS). The noble gas layers are intended to decouple the C₆₀ fullerenes from the underlying substrate. As substrates we used copper(111), silver(111) and gold(111) single crystals covered with 60 monolayers (ML) of Xe and optional additional 10 ML of Kr or Ar on top of the Xe films. The first ML of each gas was adsorbed at slightly higher temperatures than the following ones to get a well ordered surface. To extract the signal of nearly free fullerenes we measured the spectra for the noble gas covered substrate before C₆₀ deposition and subtracted them from measurements after the C₆₀ deposition. Compared to the expected position we were able to observe a shift of the C₆₀ signal, which is identical to the electron affinity of the noble gas layers. This is of importance for the interpretation of UPS on mass selected metal clusters on similar surfaces.

O 82.8 Thu 12:15 MA 043

XANES measurements and corresponding FEFF simulations on Ag clusters deposited in PDMS and silica aerogel — ●STEFANIE ROESE, DAVID ENGEMANN, and HEINZ HÖVEL — Fakultät Physik / DELTA, Technische Universität Dortmund

The knowledge of the geometric structure, size and electronic properties is essential for many applications of clusters.

Ag clusters produced in a supersonic expansion can be deposited without coalescence into matrix materials like silica aerogel or PDMS.

In addition to optical measurements X-ray absorption near edge structure spectroscopy (XANES) has developed as a powerful tool to determine geometric and electronic information about the sample. The measurements were carried out at the synchrotron radiation sources ESRF and DELTA.

The experimental data are compared to ab initio multiple scattering calculations (FEFF) [1] for different cluster sizes and structures like icosahedra and cuboctahedra. The comparison between the measured data and the simulations yields information about the geometric and electronic structure of the deposited clusters as well as about the influence of chemical environments. With the aid of the FEFF simulations the cluster aggregation process due to high deposition amounts can be visualized. Further, the reaction of the clusters with oxygen in the x-ray beam can be modeled.

[1] J. J. Rehr et al., Phys. Chem. Chem. Phys., 12, 5503-5513 (2010)

O 82.9 Thu 12:30 MA 043

Deposition of Ti nanoclusters by Gas Aggregation Source and HiPIMS — ●OLEKSANDR POLONSKYI, WAQAS SADDIQUE, ALEXANDER HINZ, THOMAS STRUNSKUS, and FRANZ FAUPEL — Institute for Materials Science, Chair for Multicomponent Materials, Christian-Albrechts University at Kiel, Kaiserstr. 2, 24143 Kiel, Germany

Metal nanoparticles have been of high scientific interest in the last decades as they are intermediate objects between single atoms or molecules and solid matter and have unique chemical, physical, electrical, magnetic and optical properties. Nanocluster and nanoparticle production in the gas phase and their deposition have been extensively investigated within the last three decades using various cluster sources. In our work we focus on deposition of Ti (TiOx) nanoparticles using magnetron based Gas Aggregation cluster Source (GAS) in combination with High Power Impulse Magnetron Sputtering (HiPIMS) discharge. First, Ti sputtering at relatively high working pressure (100-200Pa) using HiPIMS was studied in details. With regard to nanoparticles deposition, it was observed that the utilization of HiPIMS discharge allows, at certain window parameters, generation of pure Ti nanoparticles without oxygen admixture, what was not possible with conventional DC magnetron sputtering. The purity of prepared films was studied by XPS immediately after deposition. In case of reactive HiPIMS, high deposition rate of TiOx nanoparticles was achieved. The effect of HiPIMS parameters on nanoparticles deposition rate, their size and chemical composition was investigated. It was shown that size can be controlled in range 5-25 nm.

O 82.10 Thu 12:45 MA 043

Patterned deposition of nanoparticles on arbitrary substrates using hydrogel nanomembranes — NIKOLAUS MEYERBRÖKER and ●MICHAEL ZHARNIKOV — Angewandte Physikalische Chemie, Universität Heidelberg, 69120 Heidelberg, Germany

Patterns of nanoparticles (NPs) on solid supports are usually restricted to a particular substrate or a class of substrates. Here we present a procedure which decouples the patterning step from the target substrate, enabling the fabrication of custom designed NP assemblies on nearly any solid support, including non-flat ones. The procedure relies on a hydrogel template prepared on the primary, conductive substrate and transferred to the target support as a sacrificial nanomembrane. The template is structured by electron beam lithography (EBL) which seals predefined areas of poly(ethylene glycol) based hydrogel film, making them inert to NP deposition in contrast to pristine areas that adsorb NPs in high densities. The deposition of NPs, occurring from an aqueous solution into the transferred membrane, follows EBL generated structure, delivering the desired NP pattern on the target support after removal of the organic matrix. Efficiency and flexibility of the procedure is illustrated by creating a variety of representative sub-micrometer patterns of densely packed gold and silver NPs on glass, including a useful pattern of a miniaturized quick-response code. The arrangement of NPs in these patterns corresponds to the negative image of EBL generated template, which is especially useful for designs where large areas covered with NPs are separated by thin, NP-free stripes.

O 82.11 Thu 13:00 MA 043

Single-island formation on prepatterned surfaces: a simulation approach — ●OLEG BULLER¹, WENCHONG WANG², LIFENG CHI², and ANDREAS HEUER¹ — ¹Institut für Physikalische Chemie, WWU, Münster — ²Physikalisches Institut, WWU, Münster

Interesting structures are observed in vapor deposition experiments with organic semiconducting molecules on surfaces which are prepatterned with gold on a silicon oxide substrate. The gold is forming a regular grid. The interaction of the deposited molecules is much higher with the gold rather than with the substrate. In dependence on the experimental parameters flux, substrate temperature, and lattice size different structures are observed, reaching from the absence of molecular clusters to the limit of multi-island formation per square.

We use a simple discrete stochastic model to reproduce the observed structures and the scaling of the formations with substrate temperature, flux and lattice size. Among others we check to which degree the experimentally relevant scenario of just a single cluster per square can be understood from a theoretical perspective.

O 82.12 Thu 13:15 MA 043

Optical Printing of Hybrid Plasmonic Nanostructures — ●ALEXEJ KLUSHYN^{1,2}, ANDREAS GRAW^{1,2}, ANASTASIA BABYNINA^{1,2}, PAUL KÜHLER^{1,2}, SPAS NEDEV^{1,2}, THEOBALD LOHMÜLLER^{1,2}, and JOCHEN FELDMANN^{1,2} — ¹Photonics and Optoelectronics Group, Ludwig Maximilian University of Munich, Munich, Germany — ²Nanosystems Initiative Munich (NIM), Munich, Germany

Hybrid assemblies of nanoparticles made from different materials are intriguing systems for the reason that the combined properties of a hybrid structure can often outperform the properties of its individual components. However, the exact positioning of the individual particles in a dimer configuration right next to each other is challenging and usually requires high-end nanofabrication methods such as scanning probe or eBeam lithography.

Here, we introduce an all-optical approach for the precise patterning of dimer structures of both plasmonic and non-metallic nanoparticles. First, we will demonstrate how individual gold particles can be optically printed on glass by optical force [1] and illustrate strategies to apply this method for the fabrication of plasmonic nanoantennas. Second, we will show how both, metallic and non-metallic nanoparticles, can be patterned in a dimer configuration with a precision of a few nanometers by taking advantage of plasmonic heating and near-field effects.

[1]A.S. Urban, A.A. Lutich, F.D. Stefani, and J. Feldmann; Nano Lett. 2010, 10(12), 4794-4798