

O 20: Nanostructures at Surfaces II

Time: Monday 16:00–19:15

Location: WIL B321

O 20.1 Mon 16:00 WIL B321

3d nanoparticle deposition on a W(110) surface — ●HENDRIK BETTERMANN, MATTHIAS WERNER, and MATHIAS GETZLAFF — Institute of Applied Physics, University of Duesseldorf

Nanoparticles and clusters are interesting objects both from a fundamental perspective and for technological applications due to their unique electronic and magnetic behavior. These properties are significantly influenced by size and structure of the particles. Our contribution is focused on FeNi alloy nanoparticles deposited on a W(110) surface, additionally in comparison with other magnetic 3d nanoparticles. The particles are generated by a UHV compatible continuously working Arc Cluster Ion Source (ACIS) and subsequently mass selected in a static electric field. Scanning Tunneling Microscopy (STM) is our main method to study these objects. We will report on size and structural properties of FeNi nanoparticles with diameters between 4 and 15 nm which satisfy softlanding conditions at kinetic energies well below 0.1 eV per atom.

O 20.2 Mon 16:15 WIL B321

FeRh on Cu(100): Cluster substrate interaction in terms of band structure — ●IVAN BAEV¹, TORBEN BEECK¹, KARI JÄNKÄLÄ², MICHAEL MARTINS¹, and WILFRIED WURTH¹ — ¹Institut für Experimentalphysik, Universität Hamburg — ²University of Oulu

Very small clusters are an important subject for a detailed understanding of emerging physical properties such as catalytic behavior or magnetic moments. Theoretical models are often limited to small scales because of their complexity. But band structure calculations of metallic crystals have already been performed since the 1960's and are by now well understood. This forms an ideal reference for experimental measurements.

We will present measurements of the Cu(100) band structure along the ΓX direction measured by photoelectron spectroscopy and the influence of small FeRh clusters deposited via soft landing on the copper surface. Changes to the band structure are very strong and depend on the size and the type of clusters atoms involved.

The hybridization of the clusters with the substrate is distinct and affects the copper band in a symmetry adapted way. We will show how it is able to change the substrate band structure atom by atom. Ideally this will enable the tailoring of perfect systems for each given application by tailoring atomic orbitals: e.g. for magnetism a high density of states at the Fermi edge with high spin polarization is desirable while for catalytic materials a matching of molecular orbitals with the surface electronic states is more favorable.

This work is supported by the collaborative research center SFB 668.

O 20.3 Mon 16:30 WIL B321

Fabrication of nanoscaled Fe deposits by focused electron beam processes as catalyst for C-nanostructures growth — ●ESTHER CARRASCO, FAN TU, MARTIN DROST, FLORIAN VOLLNHALS, HANS-PETER STEINRÜCK, and HUBERTUS MARBACH — Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058, Erlangen, Germany

The fabrication of clean iron nanostructures under UHV conditions is feasible via the technique of electron beam induced deposition (EBID) [1]. Fe is also successfully employed as a catalyst for the growth of carbon nanotubes (CNTs) by chemical vapor deposition (CVD) [2]. Control of the structure and location of individual CNTs with lithographic precision over large substrates is desired for their applications in electronic devices. By using EBID, we are able to design an arbitrary distribution of metal nanostructures, which can be used as a template for the fabrication of secondary C-nanostructures by CVD. The objective is twofold: i) a controlled fabrication of novel carbon nanostructures via catalytic growth from the structured EBID deposits. ii) the fabrication of single wall carbon nanotubes (SWCNTs) with specific characteristics from localized iron dots with diameters below 8 nm. Latest results will be presented and discussed. This work was supported by the DFG via grant MA 4246/1-2, MA 4246/2-1, Funcos FOR 1878 and the Cluster of Excellence Engineering of Advanced Materials of the FAU Erlangen-Nürnberg.

[1] T. Lukaszcyk et al., Small 4 (2008) 841

[2] C. Mattevi et al., J Phys. Chem. C 112 (2008) 12207

O 20.4 Mon 16:45 WIL B321

STXM and NEXAFS study of the autocatalytic growth of EBID precursors — ●FLORIAN VOLLNHALS, FAN TU, MARTIN DROST, ESTHER CARRASCO, ANDREAS SPÄTH, HANS-PETER STEINRÜCK, and HUBERTUS MARBACH — Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058, Erlangen, Germany

Electron beam induced deposition (EBID) is a technique for the direct fabrication of nanostructures on surfaces with full lithographic control.^[1] In EBID, a metal-organic precursor is adsorbed on a surface and locally decomposed by a highly focused electron beam. Non-volatile fragments form a deposit while volatile ones are pumped off.

The generally low purity of the deposits is a major challenge. In the case of Fe(CO)₅, the high attainable purity of 95+ %at. is linked to autocatalytic decomposition and subsequent growth of the Fe seeds at RT.^[2] To study this behavior, which is also expected for other precursors, we prepared EBI deposits from Fe(CO)₅ and Co(CO)₃NO on Si₃N₄ membranes in UHV and used STXM and NEXAFS to find that Fe(CO)₅ gives rise to linear growth of nearly pure Fe, while the behavior of Co(CO)₃NO is complex and yields oxygen rich CoC_xN_yO_z.

Supported by the DFG via grant MA 4246/1-2, MA 4246/2-1, the excellence cluster Engineering of Advanced Materials of the FAU Erlangen-Nürnberg and two granted beamtimes at the PoLLux STXM at the Swiss Light Source.

[1] W. van Dorp et al., J. Appl. Phys. 104 (2008), 0801301.

[2] M.-M. Walz et al., Angew. Chem. Int. Ed. 49 (2010), 4669.

O 20.5 Mon 17:00 WIL B321

Electron Quantization Effects in Pristine and Isophorone-Modified Gold Nano-Islands on MgO Thin Films — ●CHRISTIAN STIEHLER, WOLF-DIETER SCHNEIDER, NIKLAS NILIUS, and HANS-JOACHIM FREUND — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

Electron quantization is a fundamental phenomenon that accompanies the transition from bulk metals to nanoclusters. The associated opening of a gap at the Fermi level crucially affects various properties of the nanostructures, e.g. its electrical and optical behavior and its performance in catalytic reactions [1]. By using low-temperature STM and related spectroscopy, we have investigated the electronic structure of 2D Au islands on MgO/Ag(001) thin films, containing between 50-200 atoms [2]. The bare islands exhibit characteristic quantum well states (QWS), arising from the spatial confinement of the Au-6p-orbitals. To explore the impact of molecular adsorption on this quantized structure, we have attached small quantities of isophorone (C₉H₁₄O) onto the Au islands. For ultra-small aggregates, we find a formation of Au-isophorone hybrid structures with clear fingerprints for the formation of covalent bonds between the two species. For larger islands, preferential adsorption of the molecules along the cluster perimeter is observed as well as a rigid downshift of the Au QWS that can be understood in terms of electron donation to the isophorone.

[1] M. Valden, X. Lai, D. W. Goodman, Science 281, 1647 (1998)

[2] C. Stiehler, Y. Pan, W.-D. Schneider, P. Koskinen, H. Häkkinen, N. Nilus, H.-J. Freund, PRB 88, 115415

O 20.6 Mon 17:15 WIL B321

From insulator to conductor: infrared reflectivity of inverted fishnet designs — ●STEFANO DE ZUANI¹, MARCUS ROMMEL², HELGA KUMRIC¹, AUDREY BERRIER¹, JÜRGEN WEIS², BRUNO GOMPF¹, and MARTIN DRESSEL¹ — ¹Physikalisches Institut und Research Center SCoPE, Universität Stuttgart, Pfaffenwaldring 57, 70550 Stuttgart, Germany — ²Max Planck Institute for solid state research, Heisenbergstrasse 1, 70569 Stuttgart, Germany

Metallo-dielectric nanocomposites at the insulator-to-metal transition show a discontinuity in their static conductivity and real permittivity in the infrared region that can in principle be described by percolation theories, assuming a random distribution of the metallic inclusions inside the insulating matrix. But what happens in ordered structures when random percolation is suppressed? We perform a systematic study on nearly closed, 20 nm thick gold films made of periodically arranged gold squares of size a separated by 10 nm gaps on a dielectric substrate. We perform reflectivity and spectroscopic ellipsometry investigations from the visible to the infrared range, increasing the

gold filling factor f by changing the size of the squares a from 100 to 3600 nm. Our measurements reveal that square arrays with f around 0.9 exhibit a strongly decreasing reflectivity in the near-infrared range when a is decreasing. Solving Maxwell's equations under the full 3D boundary conditions leads to a reasonable agreement between theory and experiment. Regions of very large near-field enhancement in the gaps can be seen over a large frequency range and are responsible for the trapping of the incident light in the patterned structure.

O 20.7 Mon 17:30 WIL B321

Field effect and charging in layered 2D materials — ●THOMAS BRUMME, MATTEO CALANDRA, and FRANCESCO MAURI — Institut de minéralogie et de physique des milieux condensés, Université Pierre & Marie Curie, Paris, France

In recent years, materials with reduced dimensionality such as graphene, dichalcogenides or chloronitrides have attracted a lot of attention because of their interesting physical properties. Particularly challenging is the possibility of doping these systems by using a field-effect transistor (FET). In an ion-liquid based FET configuration the charging of the nanolayers is substantial and thus allows for the investigation of the transition from a band insulator, to a metal and, eventually, to a superconductor [1]. Despite the extensive use of such FETs, many questions remain open. It is, *e.g.*, unclear what changes are induced in the nanolayer by the large electric field. Furthermore the distribution of the induced charge is usually obtained from simple Thomas-Fermi models, that can be inappropriate. In this work [2], we develop a first-principles framework to describe nanolayers in FET configuration. We include the external electric field and the charging in the calculations of the geometric and electronic structure of different nanolayer systems. In the case of ZrNCl we show that the charge doping profile in the nanolayer is very different from what has been proposed in previous analysis based on simple screening models.

[1] Nat Mater **9**, 125 (2010). Science **338**, 1193 (2012).

[2] T. Brumme, M. Calandra, and F. Mauri, in preparation.

O 20.8 Mon 17:45 WIL B321

STM-induced Doping on Si(553)-Au — ●INGO BARKE¹, STEFAN POLEI¹, PAUL C. SNIJDERS², STEVEN C. ERWIN³, FRANZ J. HIMPEL⁴, and KARL-HEINZ MEIWES-BROER¹ — ¹University of Rostock, Institute of Physics, 18051 Rostock, Germany — ²Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA and Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996, USA — ³Center for Computational Materials Science, Naval Research Laboratory, Washington, DC 20375, USA — ⁴Department of Physics, University of Wisconsin-Madison, Madison, Wisconsin 53706, USA

One-dimensional systems are notoriously difficult to dope because the dopant atoms interrupt the continuity of the quantum wires. Here we propose an alternative route based on transient doping, where charge injection from the tip of a scanning tunneling microscope drives the quasi one-dimensional system Si(553)-Au into an excited structural phase [1]. Time-dependent measurements enable access to the system's dynamics revealing rapid fluctuations due to a competition between excitation and decay. The current-dependent lifetimes hint at a barrierless decay of the excited (*i.e.* doped) state, letting the system behave like an optically excited molecule in close analogy to an excimer.

[1] Polei et al., PRL **111**, 156801 (2013).

O 20.9 Mon 18:00 WIL B321

Do you believe in thermodynamics? Towards a predictive modeling of adsorbed clusters. — ●CHIARA PANOSSETTI, DENNIS PALAGIN, and KARSTEN REUTER — Technische Universität München, Germany

Materials applications generally require the stabilization of engineered atomic clusters at solid surfaces. For metal-doped $M@Si_n$ cages this can be achieved either via controlled deposition of preformed clusters or direct silicide formation at Si surfaces. Particularly for the latter, technologically appealing approach quantitative theory could effectively aid experimental design by predicting deposition conditions at which desired cluster structures form spontaneously at the surface. We propose to approach this problem by suitably combining configurational sampling within an *ab initio* thermodynamics framework. Hereby, the stability of globally optimized geometries of different stoichiometry can be compared through evaluation of thermodynamic functions. Our results demonstrate the possibility of a qualitative prediction of experimental mass-spectra abundances of isolated $M@Si_n$ clusters, suggesting ther-

modynamics to primarily rule cluster formation in the cluster source. The possibility of extending this equilibrium picture towards cluster formation at extended surfaces will be critically evaluated.

O 20.10 Mon 18:15 WIL B321

Cluster Nucleation and Growth from a Highly Supersaturated 2D Phase: Ag/Fe₃O₄(001) — ●ROLAND BLIEM¹, LUKAS PERNECZKY¹, ZBYNEK NOVOTNY¹, DAVID FOBES², ZHIQIANG MAO², MICHAEL SCHMID¹, ULRIKE DIEBOLD¹, and GARETH PARKINSON¹ — ¹Vienna University of Technology, Vienna, Austria — ²Tulane University, New Orleans, Louisiana, USA

The nucleation and growth of Ag clusters at the $(\sqrt{2} \times \sqrt{2})R45^\circ$ -Fe₃O₄(001) surface was studied using scanning tunneling microscopy (STM). This surface functions as a robust adsorption template, stabilizing a complete array of Ag adatoms with a nearest-neighbor distance of 0.84 nm to temperatures as high as 670 K. As the coverage exceeds 1 ML, the number of Ag adatoms exceeds the number of available adsorption sites and the system enters a supersaturated state. Cluster nucleation occurs spontaneously at room temperature and, with mild annealing, the nuclei grow at the expense of the surrounding material. This behavior cannot be reconciled with any of the established growth modes. From an analysis of the denuded zones, or “vacancy trails”, associated with each cluster, three distinct growth processes are discerned. Cluster nuclei are mobile and diffuse to step edges, capturing otherwise stable Ag adatoms encountered along their path. With the clusters immobilized, adatom diffusion and capture takes over as the dominant process. Above 720 K, the $(\sqrt{2} \times \sqrt{2})R45^\circ$ reconstruction is lifted, and the system evolves rapidly to large (>10 nm) nanoparticles, consistent with the thermodynamic preference for 3D crystallites.

O 20.11 Mon 18:30 WIL B321

Unraveling structural and catalytic properties of Au-Pt nanoalloys — ●LINN LEPPERT¹, RODRIGO Q. ALBUQUERQUE², ADAM S. FOSTER³, and STEPHAN KÜMMEL¹ — ¹Theoretical Physics IV, University of Bayreuth, Germany — ²Institute of Chemistry of Sao Carlos, University of Sao Paulo, Sao Carlos, Brazil — ³COMP/Department of Applied Physics, Aalto University School of Science, Aalto, Finland

The high catalytic activity of Au nanoparticles (NPs) is a prime example for the special properties of metal clusters. By alloying, *e.g.* with Pt, the properties of Au NPs can further be significantly improved. However, the fundamental question of why alloying improves the NP properties is still poorly understood. Moreover, there is an ongoing debate on the mixing patterns of these systems. While theory predicts core-shell NPs, homogeneously mixed NPs are observed in experiment. In this contribution we address structural and electronic properties of Au-Pt NPs using density functional theory and semi-empirical molecular dynamics simulations. We show that the discrepancy between theory and experiment might have its reason in a misinterpretation of x-ray diffraction patterns. Furthermore, we discuss that special catalytic properties of Au-Pt NPs are expected based on general considerations, *i.e.*, inherent properties of the Au and Pt component, respectively.

O 20.12 Mon 18:45 WIL B321

Nanooxidation - Oxidation kinetics of small Rh nanoparticles — ●PATRICK MÜLLER^{1,2}, HESHMAT NOEI^{1,2}, THOMAS F. KELLER¹, BJÖRN ARNDT^{1,2}, PETER WOCHNER³, ROBERTO FELICI⁴, and ANDREAS STIERLE^{1,2} — ¹Deutsches Elektronen-Synchrotron, 22603 Hamburg, Germany — ²Fachbereich Physik, Universität Hamburg, 20355 Hamburg, Germany — ³Max-Planck-Institut für Festkörperforschung, 70569 Stuttgart, Germany — ⁴European Synchrotron Radiation Facility, 38043 Grenoble, France

Metal nanoparticles (NPs) are used in many technical fields such as heterogeneous catalysis and biosensors. Although the oxidation behaviour of transition metal surfaces was studied in depth in the past, the oxidation kinetics of small NPs is poorly understood. The traditional oxidation theory proposes different growth laws for single crystal surfaces, but does not take into account the properties of NPs like their shape. In recent studies the oxidation theories were modified to also comprise geometrical aspects as the curvature of the NP by using a spherical model [1,2]. Our experiments focused on the systematic study of the size dependence of the oxidation kinetics of half spherical Rh NPs with particles sizes from 2 to 12 nm on sapphire at 573 K and 10^{-3} mbar oxygen pressure. The experiments were carried out at the MPI beamline at ANKA and beamline ID03 at the ESRF. We employed x-ray reflectivity and grazing incidence small angle x-ray scattering. Our results demonstrate a dramatic change in the oxidation kinetics

for the smallest NPs. [1] A. Ermoline, E. L. Dreizin, Chem. Phys. Lett. 505, 47 (2011);[2] A. T. Fromhold Jr., J. Phys. Chem. Solids 49, 10 (1988)

O 20.13 Mon 19:00 WIL B321

Structural Changes of Cobalt Nanoparticles during Chemical Reactions: A RHEED Study — ●STEPHAN BARTLING, INGO BARKE, HANNES HARTMANN, STEVE JÄGER, and KARL-HEINZ MEIWES-BROER — University of Rostock, Institute of Physics, 18051 Rostock, Germany

Size-selected cobalt oxide clusters deposited on amorphous alumina

films can act as selective and efficient nanocatalysts for the dehydrogenation of cyclohexane [1]. In this contribution we present a new setup for reflection high energy electron diffraction (RHEED) under reactive conditions up to a pressure of 10^{-3} mbar. Soft-landed Co clusters of sizes in the nm range are exposed to oxygen and heated during the experiment. The evolution of RHEED patterns shows that the particles significantly change their structure at a critical temperature. The contributing phases are discussed in view of expected cobalt oxide stoichiometries and morphologies.

[1] E.C. Tyo et al., ACS Catalysis **2** (11), 2409 (2012)