O 26 Particles and clusters I

Time: Tuesday 15:45–18:30 Room: WIL A317

O 26.1 Tue 15:45 WIL A317

Growth and in-situ oxidation of Rhodium nanoparticles on $\alpha - Al_2O_3(0001)$ — •Philipp Nolte, A. Stierle, N. Kasper, C. Ellinger, N.Y. Jin-Philipp, G. Richter, and H. Dosch — Max-Planck-Institute for Metals Research, Heisenbergstraße 3, 70569 Stuttgart

To understand the catalytic activity of 4d transition metal nanoparticles, it is important to study their oxidation behaviour. In general, due to their reduced dimensions and their interaction with the support, the oxidation will differ from the corresponding single crystal surfaces, for example in the ability to form surface oxide layers. We studied the growth and oxidation of Rh particles on the $\alpha - Al_2O_3(0001)$ surface.

Rh-nanoparticles on $\alpha - Al_2O_3(0001)$ can be grown by electron beam evaporation in UHV. As we deduce from x-ray diffraction, the particles grow (111)-oriented and epitaxially. The surface lattice can nearly be described by a $R(\sqrt{3} \times \sqrt{3})30°$-orientation on the substrate, but with a lattice mismatch of 2%. For an effective material deposition of 2 nm, the formation of flat particles with the shape of truncated hexagonal pyramids could be observed by transmission electron microscopy.

In an in-situ x-ray diffraction experiment at the MPI-MF beamline at ANKA, we studied changes of Crystal Truncation Rods of the Sapphire surface after evaporation of Rh to obtain information about the metal-support interface. The formation of Rh_2O_3 could be observed in an atmosphere of molecular oxygen with $p = 3 \cdot 10^{-2}$ mbar and a substrate Temperature $T_S = 400°$ C.

O 26.2 Tue 16:00 WIL A317

Deviations in exp. and calc. sputtering yields of Cu, Ag, and Au with keV noble gas ions — •Wolfgang Eckstein[1] and Rainer Behrisch[2] — [1]IPP, 85748 Garching ,MPI — [2]IPP, 85748 Garching, MPI

The sputtering yields of metals have been calculated for noble gas ions at different incident energies with the program TRIM.SP. The results in dependence on the incident energy have been approximated with an algebraic formula. In the plots representing the energy dependence of the sputtering yield, the sputtering yields which have been measured by different authors are introduced. For most solids the measured yields scatter within a factor of two around the calculated curves. However, for the noble metals Cu, Ag, and Au the measured yields are systematically about a factor of two higher than the calculated values. Possible reasons for this discrepancy are that the surface binding energy is lower than the heat of sublimation taken in the TRIM.SP calculations. This may be caused by surface roughening during ion bombardment. Surface atoms may be moved to places with a lower binding energy. Due to the roughening also atom clusters may be released, which is not included in TRIM.SP.program. Another reason could be deviations in the interaction potential used as input in the calculations.

O 26.3 Tue 16:15 WIL A317

Growth of supported gold nanoparticles: the influence of substrate material, temperature, and laser irradiation — •N. Borg, D. Blázquéz-Sánchez, C. Hendrich, H. Ouacha, F. Hubenthal, and F. Träger — Institut für Physik and Center for Interdisciplinary Nanostructure Science and Technology - CINSaT, Universität Kassel, Heinrich-Plett-Straße 40, D-34132 Kassel

In order to tailor the optical properties of metal nanoparticles (NPs) for different applications, a variety of parameters must be considered and can be changed. Here, the substrate material as well as its temperature during growth has been varied systematically to clarify the influence of these parameters. Gold nanoparticles (AuNPs) with radii ranging from 0.5 to 12 nm were prepared under ultrahigh vacuum conditions by deposition of gold atoms on quartz, sapphire and titanium dioxide substrates followed by Volmer-Weber-growth. As a consequence of this self-organised assembly we obtained NP ensembles with a broad size and shape distribution where the shape is strongly correlated to the size of the NP. We measured the influence of the substrate material, and the temperature on the shape of the particles. In addition, the method of laser assisted growth has been applied to further tailor the NPs. This technique was developed in our group and takes advantage of the optical properties of metal NPs to overcome the correlation between the shape and the size, the objective being to produce NPs with desired, well-defined shapes and variable sizes. Depending on the wavelength and the fluence of the laser light we can stabilise the mean axial ratio of the AuNPs at values ranging from 0.19 to 0.98 independent of size.

O 26.4 Tue 16:30 WIL A317

Oxidation of mass-selected Au_n clusters (n=2-9) on SiO_2/Si — •Rainer Dietsche, Dong Chan Lim, Moritz Bubek, Young Dok Kim, and Gerd Ganteför — Fachbereich Physik, Universität Konstanz, 78464 Konstanz

Mass-selected Au cluster anions consisting of less than 9 atoms were deposited on etched Si wafer surfaces covered with native oxide layers. Oxidation and reduction of the Au clusters were studied using X-ray Photoelectron Spectroscopy (XPS). For n=2,4,6,8 exposures of the clusters to atomic oxygen environments result in the appearance of additional peaks at the Au 4f level, which are characteristic for the Au-oxide formation.

For the odd numbered clusters, the Au-oxide formation is much less pronounced. In particular, it can be observed that there is no characteristic feature of the Au-oxide formation for Au_7. This result suggests that each additional atom can drastically change chemical proporties of the deposited clusters consisting of the less than 9 atoms. Moreover, the even-odd pattern indicate that chemistry of the clusters correlates with electronic structures rather than with specific adsorption/reaction sites.

O 26.5 Tue 16:45 WIL A317

Dynamic final state effect for the photoemission of gold clusters on graphite: comparison with scanning-tunneling spectroscopy — •Heinz Hövel and Ingo Barke — Universität Dortmund, Experimentelle Physik I, 44221 Dortmund, Germany

We present an experimental study for the electronic properties of metal clusters on surfaces. For the specific case of the confined Shockley surface state on the top (111) facets of gold clusters on graphite [1] we were able to detect the quantized electronic structure with two independent experimental techniques, scanning tunneling spectroscopy (STS) and ultraviolet photoelectron spectroscopy (UPS). Here we present new UPS data and their analysis which shows a quantitative agreement if we compare the density of states, extracted from the STS spectra by averaging over the cluster size distribution, with the UPS spectra using a deconvolution to compensate the dynamic final state effect [2] which leads to a systematic asymmetric broadening of all valance band UPS features [3].

[1] I. Barke, H. Hövel, Phys. Rev. Lett. **90**, 166801 (2003).
[2] H. Hövel, B. Grimm, M. Pollmann, B. Reihl, Phys. Rev. Lett. **81**, 4608 (1998).
[3] H. Hövel, I. Barke, Prog. Surf. Sci., submitted for publication.

O 26.6 Tue 17:00 WIL A317

Electronic and geometric structures of Au nanostructures on HOPG studied using XPS and STM — •Ignacio Lopez, Dong Chan Lim, Rainer Dietsche, and Young Dok Kim — Department of Physics, Universität Konstanz. D-78457, Germany

Au nanostructures grown on mildly sputtered Highly Ordered Pyrolytic Graphite (HOPG) surfaces were studied using Scanning Tunneling Microscopy (STM) and X-ray Photoelectron Spectroscopy (XPS), and the results were compared with those of Ag on the same substrate. By varying defect densities of HOPG and Au coverages, one can create Au nanoparticles with various sizes. At high Au coverages, it is observed that Au structures significantly desviate from the ideal truncated octahedral structure: the existence of many steps between different Au planes can be observed, most likely due to high activation barriers for the Au atoms on the topmost plane of the Au structures jumping over the step edges down to the next plane. This result implies that the particle growth at room temperature is strongly limited by kinetic factors. Using XPS, much less positive core level shifts of the Au 4f level with decreasing particle size was found, compared to the core level shifts of the Ag 3d level in the similar particle size range on HOPG. Together with our results of the Auger analysis of the Ag data, we suggest that the metal/substrate charge transfer is an important factor to determine the core level shifts of the metal nanoparticles on HOPG, i.e. Ag is (partially) positively charged, whereas Au negatively on HOPG. It is demonstrated that XPS can be a useful tool to study metal-support interactions, which can play an important role for e.g. heterogeneous catalysis.

O 26.7 Tue 17:15 WIL A317

Spectroscopic properties of molecules in small gold-nanoparticle aggregates — •M. Ringler, S. Funk, M. Borowski, T. Soller, A. Susha, G. Raschke, T. A. Klar, and J. Feldmann — Photonics and Optoelectronics Group, Physics Department and CeNS, Ludwig-Maximilians-Universität München, Germany

Plasmonic properties of metallic nanostructures alter the spectroscopic properties of their nano-environment. Understanding and controlling this phenomenon is of utmost interest both from a fundamental point of view and with regard to sensing applications. Fluorophores attached to single gold-nanoparticles are quenched by energy transfer [1] and radiative rate suppression [2], on nano-structured metal films, enhanced fluorescence is observed [3]. We will discuss the intermediate regime of small aggregates of a few nanoparticles. We will present experimental results of their joint influence on the properties of attached or enclosed molecules.

[1] Dulkeith et al., Phys. Rev. Lett. 89, 203002 (2002)
[2] Dulkeith, Ringler et al., Nano Lett. 5, 585 (2005)
[3] Lakowicz, Anal. Biochem. 337, 171 (2005)

O 26.8 Tue 17:30 WIL A317

Dynamics of gold nanoparticles on the surface of thin polymer films — •Simone Streit[1], Henning Sternemann[1], Christian Gutt[2], Virginie Chamard[3], Aymeric Robert[4], and Metin Tolan[1] — [1]Exp. Physik I, Universität Dortmund, 44221 Dortmund, Germany — [2]DESY (HASYLAB), Notkestr. 85, 22607 Hamburg, Germany — [3]LTPCM, 1130 rue de la piscine, 38402 St Martin d'Hères, France — [4]ESRF, BP 220, 38043 Grenoble Cedex, France

Surface x-ray photon correlation spectroscopy (XPCS) is used to measure the dynamic structure factor $S(q,\tau)$ of nanometer sized gold particles moving on the surface of thin polymer films. Above the glass transition of the polymer the dynamic structure factor is found to follow the peculiar form $S(q,\tau) \sim \exp[-(t/\tau)^{\alpha}]$. For the exponent a value $\alpha = 1.5$ is observed, representing a faster than exponential decay of the correlation function. A dispersion relation from $q = 0.01$ to 0.06 Å^{-1} is obtained, corresponding to lengthscales of several hundred Å. The relaxation time τ scales as q^{-1} in contrast to the q^{-2} behavior of simple Brownian diffusive motion. This type of correlation function corresponds to a power law distribution of particle velocities which has also been observed e.g. in aging bulk soft matter systems. The special form of the dynamic structure factor characterizes the hyperdiffusive motion of the gold nanoparticles.

O 26.9 Tue 17:45 WIL A317

Negative differential resistance and nonclassical capacitive behavior in networks of metal clusters — •Huijing Zhang, Dirk Mautes, and Uwe Hartmann — Institute of Experimental Physics, University of Saarbrücken, P. O. Box 151150, D-66041 Saarbrücken

Monolayers of small metal clusters of type Au55[P(C6H5)3]12Cl6 were investigated with a low-temperature ultrahigh vacuum scanning tunneling microscope. Apart from the usual charge-quantization phenomena, such as Coulomb blockade and staircase, negative differential resistance was observed by performing measurements at distinct locations on the cluster layers. The latter phenomenon can be understood from a "gate" effect caused by neighboring clusters and involving a nonclassical behavior of the capacitances generated by the nanoscale metal particles.

O 26.10 Tue 18:00 WIL A317

Measurement of the size of embedded metal clusters by mass spectrometry, transmission electron microscopy and small angle X-ray scattering — •C. Hendrich[1], L. Favre[1], D. N. Ievlev[1], A. N. Dobrynin[1], P. Lievens[1], K. Temst[1], W. Bras[2], U. Hörmann[3], E. Piscopiello[3], and G. Van Tendeloo[3] — [1]Laboratorium voor Vaste-Stoffysica en Magnetisme, K.U.Leuven, Leuven, Belgium — [2]DUBBLE@ESRF, Netherlands Organisation for Scientific Research (NWO), Grenoble, France — [3]Elektonenmicroscopie voor Materiaalonderzoek, Universiteit Antwerpen, Antwerp, Belgium

We investigated ensembles of nanometer sized Au, Co, Er and FePt clusters which were embedded in MgO grown simultaneously on mica substrates. The particles were produced by a laser vaporization source and characterized by time-of-flight mass spectrometry before embedding them into the matrix. The size distribution of the clusters before sample preparation was compared to that obtained by transmission electron microscopy after preparation. These well characterized samples were used for investigations by small angle X-ray scattering (SAXS). By using the Guinier analysis to evaluate the scattering data we could extract the average radii of the embedded clusters. We found a good agreement of this data with the cluster sizes obtained from the mass spectra and with the dimensions determined from the transmission electron micrographs. Furthermore, we also investigated samples which were produced at an elevated substrate temperature and found an increased average cluster radius in the SAXS measurements which we attribute to diffusion and coalescence emerging at higher sample temperatures.

O 26.11 Tue 18:15 WIL A317

Tailoring the dimensions of colloidal gold nanoparticles by laser irradiation — •F. Vogel, C. Hendrich, F. Hubenthal, and F. Träger — Instiut für Physik and Center for Interdisciplinary Nanostructure Science and Technology - CINSaT, Universität Kassel, Heinrich-Plett-Straße 40, D-34132 Kassel

Colloidal gold nanoparticles (AuNPs) are used in many different fields and, especially for industrial applications, are often needed in large quantities. However, a substantial drawback of most production methods is that the prepared AuNPs exhibit broad size and shape distributions. In this contribution, we present our recent experiments with the objective of tailoring the size of AuNPs in solution with laser light in order to overcome the drawback mentioned above. In our experiments colloidal AuNPs were prepared by wet chemical reduction of $HAuCl_4$. Post-synthesis irradiation with laser light permits tailoring of the dimensions of the nanoparticles by diffusion of surface atoms and, especially at high fluences, removal of atoms. Thus, it is possible to eliminate all particles of undesired sizes and shapes by choosing appropriate photon energies and light intensities.

First experiments on colloidal AuNPs with a mean radius of $< r >= (7.5 \pm 1.5)$ nm show a pronounced reduction of the HWHM (half width at half maximum) of the surface plasmon resonance (SPR) from 0.37 eV to 0.21 eV and an increased absorption at higher photon energies by the modified AuNPs. The increase and shift of the SPR to higher photon energies can be attributed to a narrowed shape distribution. Consequences of the laser treatment for the size distribution are under examination.