Dynamic AFM/STM Investigations of Au_{55} Monolayers

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Motivation

Investigation of monolayers of Au_{55} deposited on Au (111) by dynamic AFM/STM:

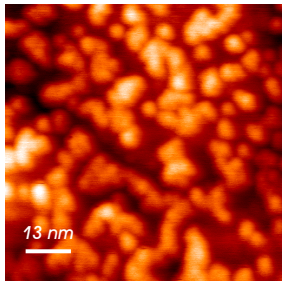
- *Non-contact atomic force microscopy (NC-AFM):*
  - *powerful imaging technique*
  - *high-resolution measurements of the conservative and non-conservative tip sample interaction possible*
- *Au_{55} clusters – exhibit interesting size-effect-dominated chemical and physical properties*

Our interest

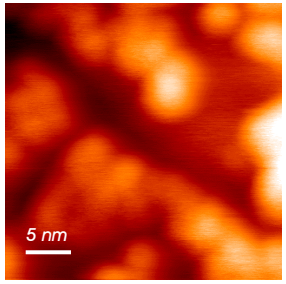
- *The dominating interaction between probe and clusters ⇒ contrast mechanisms for the imaging of Au_{55} clusters*
- *The electronic properties of the cluster-substrat arrangement: i. e. charge transfer between clusters and substrate*
- *Mechanisms of the dissipative interaction between clusters and the microscope probe*

NC-AFM images

Surface topography: locally ordered cluster monolayer islands



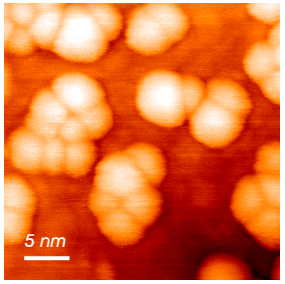
Oscillation amplitude A = 8.2 nm
Sample bias U = -0.3 V



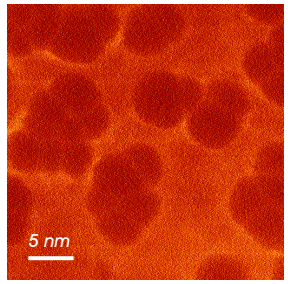
Oscillation amplitude A = 8.2 nm
Sample bias U = -0.5 V

Dynamic STM images

Frequency shift



Damping



Oscillation amplitude A = 5.8 nm
Mean tunneling current I = 0.06 nA
Sample bias U = 2V

Experiment

Sample preparation:

- *Deposition of 50 nm thick Au film on HOPG under vacuum conditions*
- *Subsequent annealing in UHV results in atomically flat (111) teraces*
- *Dissolving Au_{55} cluster powder in CH_2Cl_2*
- *Depositing the clusters from Au_{55}/CH_2Cl_2 solution on the Au substrate by spin coating*

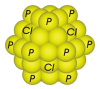
Caracterization:

Dynamic AFM/STM:

- *UHV conditions*
- *Silicon cantilevers that have a diamond-like high aspect ratio extratip at the apex [1]; typical curvature radius ~ 1nm; spring constant k = 40 N/m; resonant frequency f_0 = 290 kHz*

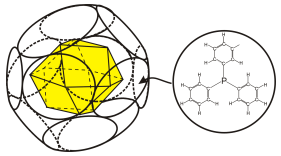
Au_{55} structure

Stoichiometry: $Au_{55}[(C_6H_5)_3P]_{12}Cl_6$



1.4 nm

(a)

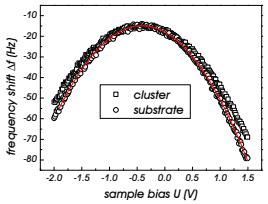


(b) 2.1 nm

(a) „Undressed" Au_{55} cluster:
- *Two-shell closed-packed arrangement: 1 + 12 + 42*
- *Surface gold atoms: 12 linked with the ligand molecules $P(C_6H_5)_3$; 6 linked with Cl*

(b) „Dressed" Au_{55} cluster:
- *Thermally induced rotation of the phenyl groups C_6H_5 around the Au-P axis gives a time averaged circular shape similar to an umbrella*
- *Ligand exchange even at room temperature is present*

Contact potential measurements

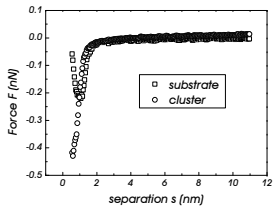


Frequency shift versus bias voltage curves Δf(U) recorded by NC-AFM.

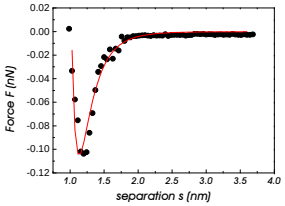
- *The Δf(U) curves are characterized by the relation $\Delta f \sim (U\text{-}U_{CPD})^2$ where U_{CPD} is the contact potential between tip and surface.*
- *No difference could be observed between the contact potential measured on the substrate and above individual clusters.*
- *The measured contact potential has a value of U_{CPD} = 0.4 ± 0.01 V. The contact potential between diamond and Au (111) is U ≈ 0.05 V.*

References:
[1] MikroMasch, DP15/Hi´RES/AlBS.
*[2] H. Hölscher et al., Phys. Rev. B **64**, 0754021-6 (2001).*
*[3] B. C. Stipe et al., Phys. Rev. Lett. **87**, 0968011-4 (2001).*
*[4] H. Hölscher et al., Phys. Rev. B **61**, 12678-81 (2000).*

Conservative interactions



Force versus distance curves F(s) recorded by NC-AFM.

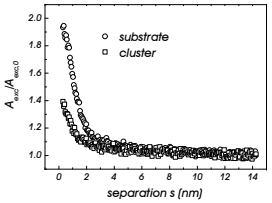


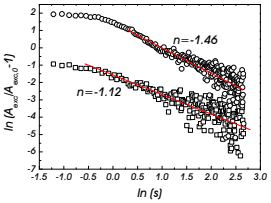
The short-range interaction is obtained by subtracting the F(s) curve on the substrate from the one above an individual cluster.

- *The short-range interaction can be described by a short-range force derived from a simple Lenard-Jones pair potential [4]. The fit parameter was the binding energy E_0.*

A value of E_0 = 230 meV was deduced.

Non-conservative interactions





- *The damping of the cantilever oscillation due to the surface is directly related to dissipative forces [2]. The excitation amplitude A_{exc} as a function of the separation s between tip and sample was recorded in dynamic STM. An increase in dissipation is observed as the tip approaches individual clusters as well as the bare substrate.*
- *The dissipation curves can be fit with a inverse power law s^n. An exponent n = -1.12 is obtained for the curves recorded on individual clusters and n = -1.46 for the ones recorded on the bare substrate. These values are in good agreement with n = -1.3 obtained by Stripe et al. [3] corresponding to electric-field-mediated Joule dissipation.*

Summary

- *Locally ordered Au_{55} monolayer islands deposited on Au(111) were imaged with high resolution by dynamic AFM/STM.*
- *Conservative and dissipative interactions between tip and individual clusters as well as the bare substrate were investigated.*