Mean Inner Coulomb Potential of Au Clusters Analyzed by Transmission Electron Holography

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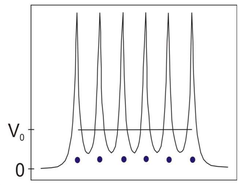
Mean Inner Coulomb Potential (MIP)

The MIP V_0 is the volume-averaged electrostatic part of the crystal potential [*H.A. Bethe, Ann. Phys. (Leipzip) 87, 55 (1928)*]:

$$V_0 = \frac{h^2}{2\pi m e \Omega} \sum_i n_i f_i^{el}(0)$$

h: Planck constant
m: electron mass
e: electron charge
Ω: unit cell volume
n_i: occupation number for the atomic species i within the unit cell
$f_i^{el}(0)$: atomic scattering factor in forward direction



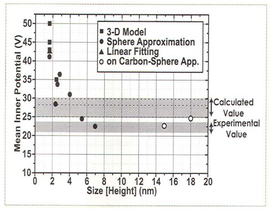
Correlation of the MIP with the amplitude of the electron wave scattered in forward direction

Determination of the MIP by off-axis electron holography under kinematical diffraction conditions according to:

$$\Delta\varphi = C_E V_0 t$$

C_E: interaction constant
Δφ: phase shift between the electron wave passing through a sample with a known thickness *t* and a vacuum reference wave.

MIP values of bulk Au ⟶ experimental values between 16.8 and 30.2 V
theoretical values between 25.0 and 35.9 V



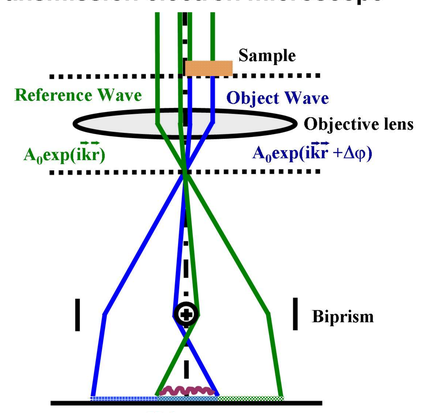
S. Ichikawa et al., JEOL News 38, 6 (2003)

Results of recent electron holography experiments:

- Strong increase of the MIP of nano-scaled Au clusters supported on TiO_2 up to 50 V (see diagram on left-hand side)
- Increasing of the *effective* MIP of C for ultra-thin amorphous carbon films up to V_0 = 65 V as compared to V_0 = 9 V for the bulk carbon
  [*M. Wanner et al., Ultramicroscopy 2006*]

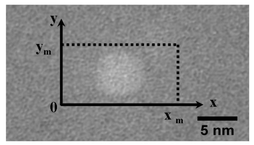
MIP increase for nano-scaled objects as a general phenomenon ?

Off-axis electron holography (EH) in a transmission electron microscope



Electron holography on Au nano-clusters

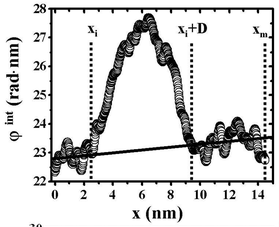
Samples were prepared by low-energy-beam cluster deposition of Au_n clusters with 10≤n≤20 atoms on amorphous carbon substrates



Gray-scale coded reconstructed phase shift for a gold cluster with D=6.9 nm

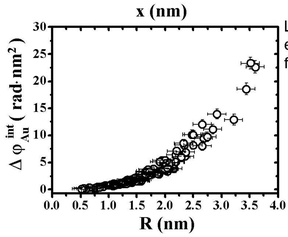
256 gray levels between

black → Δφ = 2π rad
white → Δφ = 2π rad



Left: phase profile of the cluster displayed above after integration along y before background subtraction:

$$\varphi^{int}(x) = \int_0^{y_m} \varphi(x,y)\,dy$$



Left: integrated phase shifts for a cluster ensemble (123 Au clusters) plotted as a function of the cluster radius:

$$\Delta\varphi_{Au}^{int} = \int_{x_i}^{x_i+D} \left[\varphi^{int}(x) - \varphi_{sub}^{int}(x)\right] dx$$

Large phase shifts of small clusters compared to the values expected from V_0 of bulk gold

Description of the MIP of Au clusters

Atoms in a cluster are compressed due to surface tension. If the strain is confined entirely to the cluster surface [*A. Tamura et al., J. Phys. C 15, 4975 (1982), P. Kluth et al., Appl. Phys.Lett. 85, 3561 (2004)*], *surface* atoms are under uniform compressive strain ε whereas *core* atoms are unstrained.

Since $V_0 \sim 1/\Omega_{at}$ (Ω_{at} atomic volume of *core* Au atoms, which is identical to the bulk ones) a distinction between the *surface* and *core* atoms with different atomic volumes is necessary.

Expression for the MIP of Au in Au clusters:

$$V_0^{cl} = \left[\underbrace{\left(1-\frac{N_S}{N_T}\right)V_0}_{\text{Contribution of } core \text{ atoms}} + \underbrace{\frac{N_S}{N_T}\frac{V_0}{(1+\varepsilon)^3}}_{\text{Contribution of compressed } surface \text{ atoms}}\right]$$

N_S : number of Au *surface* atoms
N_T : total number of Au atoms
V_0 : MIP of *core* Au atoms = MIP of bulk Au
ε : uniform strain of surface atoms
$(1+\varepsilon)^3\,\Omega_{at}$: volume of compressed *surface* atoms

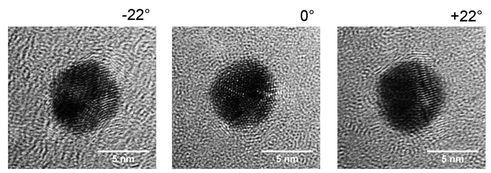
Calculation of the integrated phase shift of clusters:

$$\Delta\varphi_{Au}^{int} = C_E V_0^{cl} \iint_{\Sigma} t(x,y) = C_E \left[\left(1-\frac{N_S}{N_T}\right)V_0 + \frac{N_S}{N_T}\frac{V_0}{(1+\varepsilon)^3}\right]\Omega_{cl}$$

Ω_{cl}: geometrical cluster volume

Structure and shape of Au clusters

Determination of the Au-cluster shape:
High-resolution TEM images of Au clusters were performed under normal illumination (0°) and after tilting the sample by ± 22°.

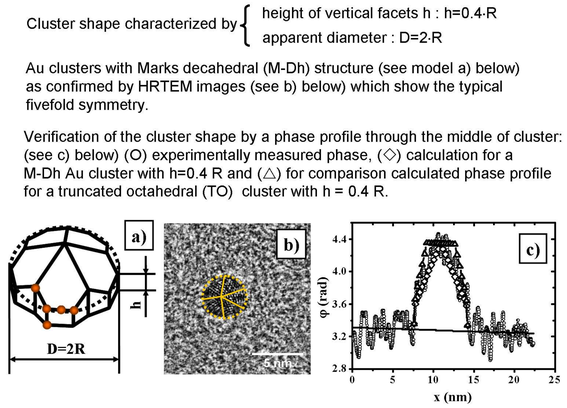


Projected cluster area increases by about 5% in the tilted positions

Cluster shape characterized by { height of vertical facets h : h=0.4·R ; apparent diameter : D=2·R

Au clusters with Marks decahedral (M-Dh) structure (see model a) below) as confirmed by HRTEM images (see b) below) which show the typical fivefold symmetry.

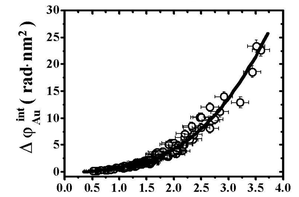
Verification of the cluster shape by a phase profile through the middle of cluster: (see c) below) (○) experimentally measured phase, (◇) calculation for a M-Dh Au cluster with h=0.4 R and (△) for comparison calculated phase profile for a truncated octahedral (TO) cluster with h = 0.4 R.



The mean inner potential of *core* Au atoms

The MIP value of *core* Au atoms, which corresponds to the MIP of bulk Au, is calculated by least-square fit of the experimental $\Delta\varphi_{Au}^{int}(R)$ using

$$\Delta\varphi_{Au}^{int} = C_E V_0^{cl} \iint_{\Sigma} t(x,y) = C_E \left[\left(1-\frac{N_S}{N_T}\right)V_0 + \frac{N_S}{N_T}\frac{V_0}{(1+\varepsilon)^3}\right]\Omega_{cl}$$

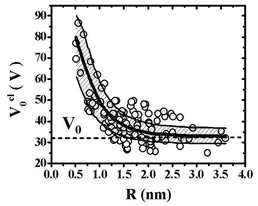


with V_0 as the only fit parameter

⇨ **V_0 = (32.2 ± 3.6) V**

in good agreement with the MIP of bulk Au

Mean inner potential of Au clusters



Strong increase of the MIP in small clusters

experimental MIP of Au (○)

$V_0^{cl,\,e}(R) = \Delta\varphi_{Au}^{int}(R) / (C_E\,\Omega_{cl}(R))$

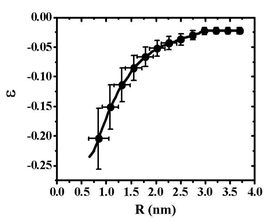
$\Delta\varphi_{Au}^{int}(R)$: measured phase shifts
$\Omega_{cl}(R)$: cluster volume

calculated MIP of Au (solid line)

$$V_0^{cl} = \left(1-\frac{N_S}{N_T}\right)V_0 + \frac{N_S}{N_T}\frac{V_0}{(1+\varepsilon)^3}$$

with : V_0 = 32.2 V and
ε(R), N_T(R) and N_S(R) (see table bottom left)

Uniform compressive strain of *surface* atoms ε(R) and number of atoms in clusters



ε(R) estimation based on the atom density of Au clusters

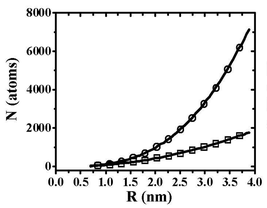
$\rho(R) = N_T / \Omega_{cl}(R)$

as the average values between

⇨ { upper limit $\rho(R) = \rho_{bulk}$=59 atoms/nm³ ; lower limit $\rho(R) = \rho_{cl}$

ρ_{bulk}: atom density in bulk *fcc* Au

ρ_{cl} : atom density of Au clusters considering a minimum density of 48 atoms/nm³ for a cluster with two closed-shells by density functional theory calculations



Left: (○) total number of atoms N_T(R) and (□) number of surface atoms N_S(R) for M-Dh clusters according to [*C.L. Cleveland et al., Phys. Rev. Lett 79, 1873 (1997)*]

Cluster radii R calculated for closed atomic shells clusters taking into account e(R)

Conclusions

- Strong increase of the MIP values in Au clusters due to uniform compressive strain of *surface* atoms and corresponding increase of the electron density
- General description of the MIP in clusters by distinguishing between { *surface* atoms / *core* atoms } with different atomic volumes
- Determination MIP of *core* Au atoms (corresponding to the MIP of bulk Au)

  V_0 = 32.2 ± 3.6 V

  in good agreement with the MIP of bulk Au calculated by density functional theory (M. Schowalter et al., Appl. Phys. Lett. 88, 232108 (2006))
- Increase of the MIP ⟶ increase of the amplitude of scattered electron wave in forward direction $f_{Au}^{el}(0)$

⇩

Modified scattering factors should be considered for the evaluation of images and diffraction patterns of nano-scaled objects.

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