

# Coarsening of mass-selected Au clusters on amorphous carbon at room temperature

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## Motivation

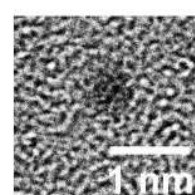
- Deposition of metallic clusters and their rearrangement on substrates
    - fundamental issues in surface science in context with
      - strong dependence of physical and chemical properties of clusters on the cluster size
      - controlled use of growth kinetics can offer an important tool for the fabrication of nano-structures of various shape, size and lateral distribution
  - Systems of Au nano-clusters deposited on different substrates → important as industrial catalysts:
    - small Au clusters (2-3 nm) exhibit exceptional catalytic activity in CO-oxidation reactions
  - Possible technological applications of deposited Au clusters are hampered by
    - the lack of methods providing cluster pinning on desired surface sites
    - the required high long-term stability of the cluster-size distribution
  - The time evolution of deposited clusters proceeds
    - by the mass transport via surface diffusion of whole clusters or their atomic constituents.
  - In both cases the mass transport depends on the substrate topography
    - governs the mobility of all deposited species:
      - on a perfect HOPG surface giant rates for sliding and diffusion of whole clusters (L. Bardotti et al., Phys. Rev. Lett. **74**, 4694 (1995))
      - surface defects and step edges represent pinning centres for migrating clusters and lead to their immobilization (S. Gibilisco et al., J. Chem. Phys. **125**, 084704 (2006))
  - Some information is available on the coarsening of non-mass-selected Au clusters on amorphous carbon (a-C) substrate (M. Wanner et al., Phys. Rev. B. **72**, 045426, (2005))
  - No information on the behaviour of rigorously mass-selected clusters:
    - high diffusivity of mass-selected metal clusters on a smooth single-crystal surface like HOPG quickly leads to the rapid formation of large two-dimensional (2D) cluster aggregates whereby mass selection is lost
  - This motivated the study of the cluster coarsening and the mass transport processes for
    - mass-selected Au<sub>n</sub> clusters, n = 4, 6, 13 and 20
    - finite distribution of mass-selected Au<sub>m</sub> clusters (10 ≤ m ≤ 20) immobilized on a-C substrates
      - ambient conditions (relative air humidity between 30% and 55%)
      - at room temperature (between 22° and 28° C)
- characteristic for any (industrial) application

## Theory of the surface Ostwald Ripening (OR)

- To describe the coarsening of metal clusters on surfaces we consider
    - the general case of a system comprising discrete three-dimensional (3D) isolated clusters randomly distributed on the substrate
  - The system is typically metastable
    - the cluster ensemble tends to lower its total free energy by redistributing the ensemble material into fewer clusters
      - the cluster ensemble coarsens:
        - the average cluster size increases and
        - the total number of clusters decreases with time.
  - If the surface-diffusion fields around clusters (i.e. areas around clusters defined by the diffusion length) overlap the coarsening proceeds via surface OR (W. Ostwald, Z. Phys. Chem. (Leipzig) **34**, 495 (1900)):
    - smaller clusters shrink or even disappear in favour of the larger ones, which grow as a direct consequence of the Gibbs-Thomson effect
  - The classical theory of OR adapted and applied to clusters on surfaces (B. K. Chakraverty, J. Phys. Chem. Solids **28**, 2401(1967))
    - describes the mechanism of cluster coarsening in case of a 3D cluster distribution with spherical cap shapes and different radii R
    - such distribution can be characterized by
      - its average cluster radius  $\bar{R}(t)$
      - its density of clusters on the substrate  $n_c(t)$
  - The kinetics of the OR is usually discussed in terms of two different limiting cases:
    - A. Diffusion-limited kinetics if ad-atom diffusion is rate-determining
    - B. Reaction- or attachment-limited kinetics if the attachment/detachment of ad-atoms at the cluster surface is the limiting process.
  - Theory suggests simple power laws for  $\bar{R}(t)$  in case of the mass transport performed through the contact perimeter between cluster and substrate:
    - Case A.  $\bar{R}^4(t) = \bar{R}^4(0) + K_d t$
    - Case B.  $\bar{R}^3(t) = \bar{R}^3(0) + K_r t$
- where  $K_d$  and  $K_r$  are constants with time.

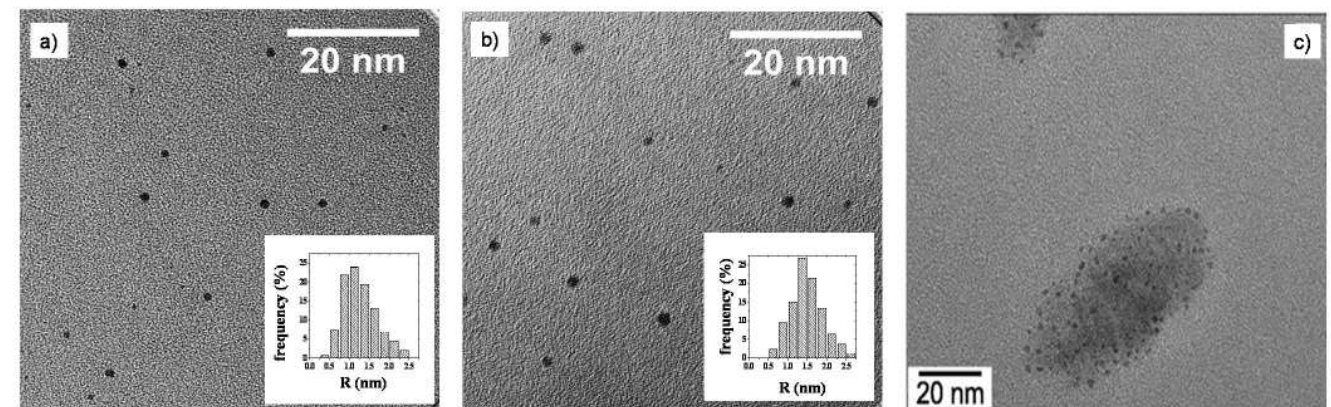
## Experimental details

- Samples prepared by low-energy beam cluster deposition of
  - Au<sub>n</sub> clusters n = 4, 6, 13 and 20 with  $n_c = 2.12 \cdot 10^{17} \text{ m}^{-2}$
  - Au<sub>20</sub> clusters with  $n_c = 1.06 \cdot 10^{17} \text{ m}^{-2}$
  - finite distribution of Au<sub>m</sub> clusters (10 ≤ m ≤ 20) with  $n_c = 2.65 \cdot 10^{17} \text{ m}^{-2}$  on 10 nm thin commercial amorphous carbon (a-C) substrate.
- Samples stored after deposition at room temperature in a container under ambient conditions
- TEM experiments carried out using a Philips CM200 FEG/ST electron microscope at 200 keV electron energy
- TEM micrographs recorded using a 2048×2048 pixel charge coupled device (CCD) camera
- Exposure time of 0.5 s
- The experimental resolution limit corresponds to Au clusters with R=0.3 nm (see the TEM image)



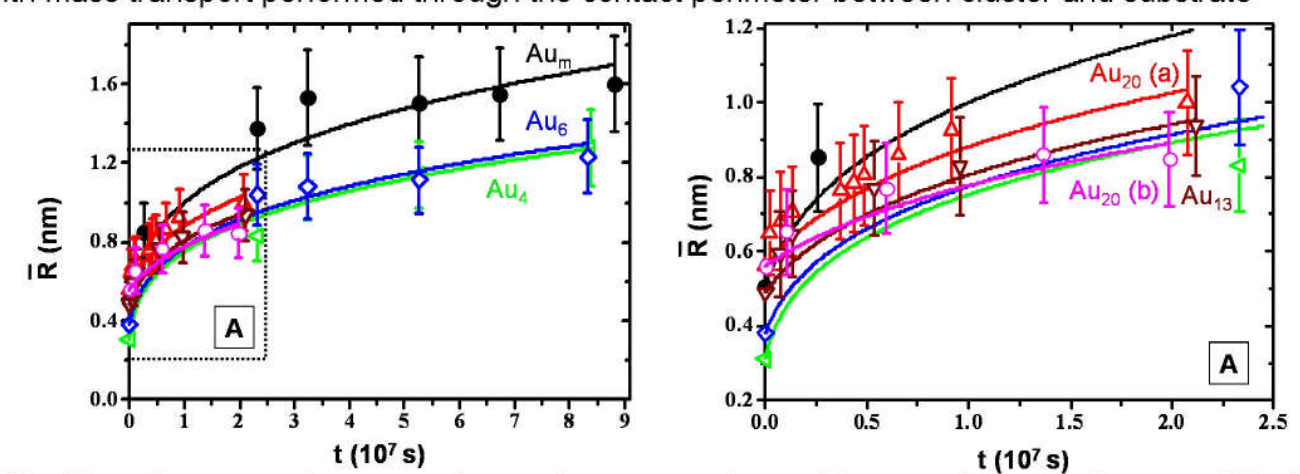
## Growth kinetics of Au clusters

- TEM images for the sample prepared by deposition of mass-selected Au<sub>m</sub> clusters (10 ≤ m ≤ 20) on a-C:
  - 9 months and b) 32 months after deposition
  - for comparison, TEM image for sample deposited with non-mass-selected Au clusters on a-C, 4 months after deposition (M. Wanner et al., Phys. Rev. B. **72**, 045426, (2005))
- The inserts in a) and b) show the corresponding histograms of cluster radii.



Different growth kinetics of the non-mass-selected distribution of Au clusters as compared to that of the mass-selected Au clusters

- Average Au clusters radius  $\bar{R}(t)$  as a function of time for mass-selected Au clusters:
  - symbols: experimental data
  - lines: fits of the data for diffusion-limited kinetics of surface OR under steady-state conditions with mass transport performed through the contact perimeter between cluster and substrate



Significant increase of average cluster size even under ambient conditions by Au-atom diffusion described by the power law for the diffusion-limited case of the surface OR (case A)

- Possible influence of cluster coalescence due to their Brownian motion is excluded:
  - high density of surface defects on a-C surface which represent pinning centres for migrating clusters
  - quantitatively: estimation by the ratio  $\tau_s/\tau_b$  of the times within the average cluster sizes double by surface OR and by coalescence due to Brownian motion (A. Imre et al., Surf. Sci. **441**, 133 (1999))

$$\frac{\tau_s}{\tau_b} < 1350 \frac{\ln(L) \varphi(\theta) k_B T \xi}{R^2(0) \gamma} < 2 \cdot 10^{-5}$$

L = 2.5 the constant screening distance;  $\xi$  - the relative surface coverage of the a-C film by Au clusters;  $\gamma = 1.5 \text{ Jm}^{-2}$ : the Au-surface energy;  $k_B$  the Boltzmann constant; T = 298 K: the absolute temperature;  $\varphi(0) = 0.45$  for Au clusters with Marks-decahedral structure (R. Popescu et al., Phys. Rev. B **76**, 235411, (2007))

Value of  $\tau_s/\tau_b \ll 1$  → cluster coalescence due to the Brownian motion negligible

- The  $K_d$  values obtained from the fit curves
  - the calculation of the surface mass-transport diffusion coefficient  $D_s$

$$D_s = \frac{45 \ln(L) \varphi(\theta) k_B T}{8 \omega^2 \gamma n_0} K_d$$

$\omega = 1.7 \cdot 10^{-29} \text{ m}^3$ : the Au atomic volume;

$n_0 = 10.8 \cdot 10^{18} \text{ m}^{-2}$  the number of sites on M-Dh Au cluster surface

$$D_s = (1.1 \pm 0.1) \div (3.8 \pm 0.4) \cdot 10^{25} \text{ m}^2 \text{ s}^{-1} \text{ at room temperature}$$

## Conclusions

- The deposition of mass-selected Au<sub>n</sub> (n = 4, 6, 13, 20) clusters on a-C does not prevent the coarsening
- TEM experiments show a significant increase of average cluster size even under ambient conditions at room temperature
- Au cluster coarsening with time
  - due to the lateral diffusion of individual Au atoms as the dominant mass transport mechanism
  - negligible cluster coalescence due to their Brownian motion
- The best fit of the experimental and calculated  $\bar{R}(t)$ 
  - coarsening kinetics described by diffusion-limited surface OR with the mass transport performed through the contact perimeter between cluster and substrate
- Derived values of the surface mass-transport diffusion coefficient:
  - $D_s = (1.1 \pm 0.1) \div (3.8 \pm 0.4) \cdot 10^{25} \text{ m}^2 \text{ s}^{-1}$
- The coarsening kinetics of mass-selected Au clusters on a-C substrate:
  - comparable for the smaller Au<sub>n</sub> clusters with n = 4, 6 and 13
  - accelerated for Au<sub>20</sub> clusters
- Coarsening is most pronounced for the sample with finite distribution of Au<sub>m</sub> clusters (10 ≤ m ≤ 20)
  - due to the presence of an initial distribution of different cluster sizes already directly after deposition
- Different effects during ripening for non-mass-selected Au clusters (from very small up to 3.5 nm) deposited on a-C as compared to that of mass-selected Au clusters on the same substrate

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