Formation of nano-size clusters and deposition on surfaces
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Outline

- Introduction
  - Difference between radiofrequency (e.g., CH₄) and magnetron plasmas
- Deposition of nano-particles
- Properties of deposited nano-particles
- Thermal annealing of nano-particle films
Particle formation:
(a) Hydrocarbon (e.g., CH$_4$) plasmas

(i) Radical formation by electron impact

\[ e^- + CH_4 \Rightarrow e^- + CH_2 + H_2 \]

(ii) Radical-molecule reaction, e.g.,

\[ CH_2 + CH_4 \Rightarrow C_2H_4 + H_2 \]
and

\[ CH_2 + C_n H_m \Rightarrow C_{n+1} H_{m+2} \]

SEM picture of carbon particles grown in Ar/C$_2$H$_2$ rf plasma (HT. Do, Ph.D.- thesis)
Mass spectra of positive ions: 
**Ar/CH\textsubscript{4} vs. Ar/C\textsubscript{2}H\textsubscript{2}**

\[
\text{CH}_3 + C_nH_m \rightarrow C_{n+1}H_{m+2} + H
\]

\[
\text{C}_2H + C_{2n}H_2 \rightarrow C_{2n+2}H_2 + H \\
\rightarrow \text{nano-particles (hydrogen-poor)}
\]

(b) Particle formation in Magnetron plasmas:

**Nucleation and Formation of primary clusters**

Typical evolution:
Starting point:
Slow sputtered atoms A

Nucleation (3-body reaction):
A + A + X → A₂ + X

**Cluster growth by atom adsorption**

Cluster growth (atom adsorption):
Aₙ + A → Aₙ₊₁

**Particle growth**

Coagulation:
Aₙ + Aₘ → Aₙ₊ₘ

C. Hollenstein (Ecole Polytechnique Lausanne, Switzerland)
Ion energy distribution of Ti$^+$ ions vs. pressure

High-energy tail of sputtered metal atoms

Increased „cooling“ at larger pressures:
(i) Increase of thermal ions
(ii) Decrease of energetic ions
Nano-size particle formation

Nano-size particle growth from sputtered atoms in the aggregation region of a magnetron discharge
Mass separation in quadrupole mass filter
Deposition of nano-size particles on surfaces
Nano-size Ag particles on Si(100)

Size distribution of deposited Ag clusters with and without mass filter.
Melting of deposited nano-size Ag clusters

X-ray diffraction pattern of deposited Ag nano-clusters

\[ \Delta T = \frac{4\sigma M T_{\text{bulk}}}{\Delta H_m r \rho} \]
Cluster size dependence vs. time

After 30 s, a second layer starts growing - before the first layer is completed

N/µm² - 280 to 390
14 to 24 nm
Deposition time 8 mins and 15 mins

Mean size: 50 nm

Clusters continue to grow on surfaces at prolonged deposition times
Deposited films from 5 nm Ag clusters

Average size ~ 34.5 nm

Cluster size (nm)

Number of particles

Energy (keV)

SiKα

AgLα

Intensity (arb. unit)
Rapid thermal annealing
(473 K – 1073 K)

T=293 K → 873 K:
Melting of irregularly shaped clusters and formation of spherical clusters with reduced surface energy.

T=1073 K ?
Rapid thermal annealing: 873 K and 1073 K

**873 K**
- Mean size: 70 nm
- Average size ~ 70 nm

**1073 K**
- Two-sizes: 25 nm and 60 nm
- Average size ~ 36 nm
Fragmentation of nano-size clusters

Proposed physical mechanism: thermal oscillations
P.V. Kashtanov, R. Hippler, B.M. Smirnov, S.R. Bhattacharyya
EPL, 90 (2010) 16001
Not fully understood yet!
Thanks

Prof. C.A. Helm + group
Prof. B.M. Smirnov
Prof. S.R. Bhattacharyya
Dr. Zdenek Hubicka
Dr. H. Wulff
Dr. V. Stranak
Dr. I. Shyjumon
M. Ganeva
S. Drache

P.V. Kashtanov
Prof. M. Tichy
Dr. M. Quaas
Dr. A. Majumdar
Dr. H.T. Do
V. Sushkov
Thank you