Synthèse de nanoparticules par ablation laser : principes – exemples – applications

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Introduction to nanoparticles
Properties versus scales

- Different properties at different scales

- Discrete electronic level vs Electronic band structure

**Metal. NPs**

**Surface Plasmon Resonance (SPR)**

Absorption peak: SPR

Resonant oscillation of conduction e- stimulated by E


**Oxide NPs**

Superparamagnetism

Some numbers

Hyp: spherical NP constituted by \( n \) atoms
\( r_s \) Wigner-Seitz atomic radius

\[
R = r_s \cdot n^{(1/3)}
\]

Diameters
- \( 1 \text{ nm} \approx 45 \text{ atoms} \)
- \( 3 \text{ nm} \approx 1272 \text{ atoms} \)
- \( 5 \text{ nm} \approx 5844 \text{ atoms} \)
- \( 10 \text{ nm} \approx 43249 \text{ atoms} \)

Ratio \( R = \frac{\text{Surface atoms}}{\text{Number of atoms in cluster}} \)

(\(*) G. Schmid, Endeavour, Cluster and Colloids – Bridges Between Molecular and Condensed Material, 14 (1990)

\[\begin{array}{cccccc}
& 13 & 55 & 147 & 309 & 561 \\
\text{Atoms number} & \rightarrow & \\
\text{Number of shells} & 1 & 2 & 3 & 4 & 5 \\
\text{Number of atoms in cluster} & M_{13} & M_{55} & M_{147} & M_{309} & M_{561} \\
\text{Percentage surface atoms} & 92\% & 76\% & 63\% & 52\% & 45\%
\end{array}\]
Homogeneous nucleation; vapor phase

Thermodynamic Approach

Free energy change
\[ \Delta G(r) = 4 \cdot \pi \cdot r^2 \cdot \gamma + \frac{4}{3} \cdot \pi \cdot r^3 \cdot \Delta G_v \]

Surface free energy vs Volume free energy
\[ \Delta G_s = \frac{k \cdot T}{V_c} \cdot \ln \frac{P}{P_s} \]

- \( S > 1 \): Saturated vapor; Spontaneous nucleation possible
- \( S < 1 \): just vaporisation

\[ \Delta G(n) = \delta \cdot n^{2/3} - k \cdot T \cdot \ln S \cdot n \]

\[ \delta = (36 \cdot \pi \cdot V_e^{1/3}) \gamma \]

\( k \): Boltzmann Constante
\( T \): nucleation Temperature
\( S \): sursaturation rate

Sursaturation needed
\( S = P / P_s \)
- \( P \): vapor partial pressure, \( P_s \): saturated vapor pressure @ \( T_s \)
- \( T_s \): interface Temperature

adiabatique expansion

Sursaturation conditions \( \rightarrow \) gas under high pressure (He, thermal conductivity)

surpersonic beam
specific process
Laser vaporisation sources: principle
History – Smalley source


NP composed of 60 Carbon Atoms (C$_{60}$ fullerene – Bucky Ball)
Ag Dense NP composed of 55 Silver Atoms
Cluster: Magic number

Molecular dynamics simulation, growth process of isolated Co clusters in gas phase

Expected structures for 13, 55 and 147 atoms.

Unexpected structure for 38 atoms. Decahedra structures for 75 and 146 atoms.

**Principle:**

Cluster Beam Generator (CBG); Laser Vaporisation Sources (LVS); Free Cluster Generator (FCG)

**Principle:**
- Target vaporization with laser
- Gas injected by a pulsed valve
- Nucleation room from the design of Milani-De Heer³
- Clusters growth control

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**synthesis of NPs in the vapor**

**cluster (NPs) Beam Generation**

NP Beam Generator (home made)

Combined matrix & NPs properties / NPs scale effect

Gaudin, Constantinescu, Champeaux, Dumas-Bouchiat « A dual pulsed laser set-up for the synthesis of nano-sized clusters », submitted
Limoges laser vaporisation source
Smalley’s childs

Kaya, Tokyo, Japan

Perez, Melinon, Dupuis, Broyer, PL

Fielicke, Nieuwegein, The Netherlands

Kreibig, Aachen, Germany

Lievens, Leuven, Belgium
Low Energy Cluster Beam Deposition (LECBD)

Modelling from Haberland et al. Mo NPs stacks on Mo substrate¹

- **Cluster @ 0.1 eV/at:**  
  keep their flying characteristics  
  Highly porous stacks of NPs (~50%)²  
  Weak adherence  
  - Probability of NP fragmentation is weak

- **Cluster @ 1 eV/at:**

- **Clusters @ 10 eV/at:**

Dense « epitaxial » (Mo on Mo-substrate)


Approximation, overestimated cluster velocity:
NP velocity $V_{\text{max}} \approx$ gas velocity $V_{\text{échappement}}$ (sound velocity $v_\infty$)

\[ v_\infty = \frac{2k}{m_{H_e}} \left( \frac{\gamma}{\gamma - 1} \right) = 1700 \text{m/s (He)} \]

Cobalt NP:
Kinetic-E $\approx$ 0.7 eV/at
Cohesion-E (bulk) $\approx$ 4.5 eV/at  

\[ E_{\text{cinétique}} \ll E_{\text{cohésion}} \]

NP keep their flying shape (shape memory)

**NP growth: homogeneous nucleation theory**

Kinetic equations for NP-NP reactions:

\[
\frac{dn_{k}^{*}}{d\tau(t)} = \sum_{i+j=k} C_{ij} \cdot n_{i}^{*} \cdot n_{j}^{*} - \sum_{i} C_{ik} \cdot n_{i}^{*} \cdot n_{k}^{*}
\]

- \( C_{ij} \): coalescence probability between a \( i \)-NP and a \( j \)-NP
- \( n_{i}^{*} = \frac{N_{i}}{N} \): reduced variable
- \( n_{j}^{*} \): number of \( j \)-sized NPs
- \( n_{k}^{*} \): number of \( k \)-sized NPs

Formation rate of \( k \)-sized NP resulting from the coalescence of a \( i \)-NP and a \( j \)-NP

Number of events where \( k \)-sized NPs form bigger NPs

\[
\tau = \int_{0}^{t} 16\pi R_{1}^{2} \left( \frac{kT(t')}{\pi m_{i}} \right)^{\frac{1}{2}} \cdot \frac{N}{V(t')} \, dt'
\]

NP size distribution fct of a single parameter: condensation rate \( \tau \)

Silver nanoparticles

HR-TEM image of Silver NPs embedded in amorphous C-matrix

NPs well crystallised in fcc structure at RT

Isolated Ag NP

FFT

Five fold symmetry

Cuboctahedral  Icosahedral  Decahedral

Narrow size distribution

Surface Plasmon Resonance of silver at $\lambda = 379$ nm

NPs keep their metallic nature
NP growth: homogeneous nucleation theory

Kinetic equations for NP-NP reactions:

\[
\frac{dn_k^*}{d\tau(t)} = \sum_{i,j,k \leq j} C_{ij}^* n_i^* n_j^* - \sum_i C_{ik}^* n_i^* n_k^*
\]

Formation rate of k-sized NP resulting from the coalescence of a i-NP and a j-NP

Number of events where k-sized NPs form bigger NPs

\[ n_i^* = \frac{N_i}{N} \]

\[ n_j^* \text{ number of i-sized NPs} \]

\[ n_j^* \text{ number of j-sized NPs} \]

NP size distribution fct of a single parameter: condensation rate \( \tau \)

\[
\tau = \int_{0}^{t} 16\pi R_i^2 \left( \frac{kT(t')}{\pi m_1} \right)^{\frac{3}{2}} \frac{N}{V(t')} dt'
\]

Theoretical

Experimental (data collected from TEM images)

Ag, Co, Cu- NPs in PLD-Al2O3 matrix

Optical properties

Electrical properties*

MIM structure

\[ Z_l = \frac{R}{1 + R^2 C^2 \omega^2} - j \frac{R^2 C \omega}{1 + R^2 C^2 \omega^2} \]

\[ C = \varepsilon_r \varepsilon_0 \frac{S}{d} \]

Vanadium NPs

- Crystallised ~3 nm metallic NPs at RT, sharp size distribution
- High deposition rate (50 nm of V-NPs per 15 min)
- Flexible choice of materials:
  - Isolated NPs embedded in different matrix
  - Stacks of NPs (porosity properties)

NPs well crystallised in cc structure at RT
Vanadium dioxide (VO2) thermochromic mat.

Reversible first order Insulator to Metal Transition at ~68°C (close to RT)

VO₂ properties

- Semi conductor at Low Temperature
- Metallic at High Temperature \((T > 68°C)\)

Extracted from ref 1

1 J.F. Morin, Physical Review Letters, 1959

❖ Abrupt changes in electrical resistivity and optical properties (IR range)
Nanosized VO₂ NPs vs VO₂ PLD thin films

**V NPs**

post annealing @ **300°C**, \( P_{O_2}: 3.3 \times 10^{-2} \text{ mbar} \), Al₂O₃, MgO or Glass substrate

**VO₂ NPs**

- well crystallized
- mono-oriented

**PLD VO₂ thin film**

- deposited at **700°C**, \( P_{O_2}: 2.2 \times 10^{-2} \text{ mbar} \), Al₂O₃ substrate

- ~150-200 nm sized grains

**Only substrate peaks**

No peak of VO₂, no long range order
Nanosized VO$_2$ NPs vs VO$_2$ PLD thin films

<table>
<thead>
<tr>
<th>Measurement</th>
<th>$T_c$(°C)</th>
<th>$\Delta T$(°C)</th>
<th>$\Delta \lambda$</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO$_2$ NPs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transmittance</td>
<td>54</td>
<td>12</td>
<td>8</td>
</tr>
<tr>
<td>Resistivity</td>
<td>58</td>
<td>12</td>
<td>4.10$^2$</td>
</tr>
<tr>
<td>VO$_2$ PLD</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transmittance</td>
<td>68</td>
<td>3</td>
<td>5.5</td>
</tr>
<tr>
<td>Resistivity</td>
<td>72</td>
<td>5</td>
<td>1.10$^5$</td>
</tr>
</tbody>
</table>

NPs vs dense films:
- **Increase** of hysteresis width
- **Decrease** of $T_{\text{MIT}}$

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1ANR Project MUFRED 2017-2019: VO$_2$ integration in microsystems:
SPCTS, Xlim Limoges, LMGP Grenoble, IETR Rennes, Thales Paris, Lab-STICC Brest

Gaudin, Champeaux, Dumas-Bouchiat «From metallic vanadium nanoparticle assemblies to thermochromic VO$_2$ behaviour», submitted
Combine VO₂ NPs & VO₂ PLD thin films

\( T_{\text{max}} = 0.57, \ T_{\text{min}} = 0.15, \ T_{\text{transition}} = 68^\circ \text{C}, \) hysteresis width: 2°C

\( T_{\text{max}} = 0.80, \ T_{\text{min}} = 0.20, \ T_{\text{transition}} = 60^\circ \text{C}, \) hysteresis width: 10°C
Nanocomposite: VO$_2$ NPs/Thin films

Coalescence and NPs growth observed with annealing time

- NP size: <10 nm, 60-80 nm, 120-150 nm

- $T_{\text{reached}} = 370^\circ\text{C}$, 10 min
- $T_{\text{reached}} = 450^\circ\text{C}$, 35 min
- $T_{\text{reached}} = 510^\circ\text{C}$, 60 min

- $\Delta T \sim 11^\circ\text{C}$
- $\Delta T \sim 6^\circ\text{C}$
- $\Delta T \sim 3^\circ\text{C}$
Cobalt NPs: stacking

- Contraction of the crystal lattice$^1$
- Exhibition of a $\sqrt{t}$ dependence$^2$
- Chudnovsky model: magnetic entity 9nm$^3$

Applications, playing with magnetic NPs ...
Hard magnetic film
Grenoble/institut Neel/ N.M. Dempsey

\( \mu_0 M_r \leq 1.35 \, \text{T} \)

\( \mu_0 H_c \leq 2.6 \, \text{T} \)

(006)

\( (BH)_{\text{max}} = 400 \, \text{kJ/m}^3 \)
Focus on Thermo-Magnetic Patterning: TMP


IEEE Front Cover, sept 2016

IEEE TRANSACTIONS ON MAGNETICS
A PUBLICATION OF THE IEEE MAGNETICS SOCIETY
SEPTEMBER 2016 VOLUME 52 NUMBER 9 IEMGAQ (ISSN 0018-9464)

(a) Calculated map of the vertical component of the stray field at a height of 100 nm above the patterned SmCo film. (b) Phase shift map measured with a flexible cantilever soft coating probe. (c) and (d) Phase shift maps measured with a stiff cantilever hard coating probe. From the paper, “Some Aspects of Magnetic Force Microscopy of Hard Magnetic Films,” by G. Ciuta et al., Art. no. 6500408.

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Step 1
Magnetic film oop magnetized in one direction

Step 2
Nanosecond pulsed laser irradiation under reverse external magnetic field

Step 3
Heat diffusion through the

Step 4
Local reversal of magnetization
Array of μ-magnets

Laser fluence adapted not to damage the film
Magnetisation reversed on 1.5 μm

Magnetic stray fields & forces

Z-component of the magnetic stray field @ 10 μm above the magnet array

Superparamagnetic NPs ø 3 μm
20 % wt Fe₃O₄ 80 % wt Polystyrene

Magnetic field → tens of mT
Magnetic trapping force → hundreds of pN

\[
\frac{\partial B}{\partial z} = 10^6 \text{T/m} @ 2 \text{ nm}
\]

@ 10 μm above

Fₘₗ = 10^{-10} \text{N}
Microfluidic potential: NPs sorting

$F_d = \frac{4}{3} \pi r_{\text{bead}}^3 (\rho_{\text{bead}} - \rho_{\text{medium}}) g$

$F_d = 6 \pi \eta r_{\text{bead}} (u_{\text{fluid}} - u_{\text{bead}})$

$F_m = \mu_0 V_{\text{mag}} M \nabla H$

$\mu$-fluidic channel in PDMS, width = 500 $\mu$m, $t_{\text{PDMS}}$ on film $\approx$ 10 $\mu$m

NPs sorting by guiding: Dynamic mode

NPs sorting by trapping

No external magnetic field
No power source
Stray fields restrict to the region of interest
Adapted to space restricted (microscopy)

High gradient magnetic separation-HGMS

B0: initial composition
- 65.6% PS NPs
- 34.4% Magnetic NPs

After a first pass through the channel
B1: selected solution
- 99.9% PS NPs

High fluid flow to clean the channel
B2: solution with magnetic beads
- 99.5% Magnetic NPs

Flow cytometry analysis
- Non-trapped beads: Initial concentration
- Trapped beads: Final concentration

Highly efficient for NPs
Highly efficient for tag Cells (Jurkat & HEK) 95% / 5%

μ-magnetic imprinting MMI, N.M. Dempsey

0 - TMP structure
1 - Hard magnetic beads sprinkled onto master structure and concentrated at the interfaces of micro-magnets
2 - polymer binder poured over the hard magnetic beads
3 - Solid composite peeled off the master structure

-Magnéquench® NdFeB powders GA50

Scanning μ-Hall probe

- Cheap
- Flexible
- Transparent
- Biologically compatible
- One Master for thousands prototypes

Extract the $B_z$ magnitude

Other Free NP sources
Vanessa Orozco Montes, Cedric Jaoul, Pascal Tristant

Limoges Free NP source based on magnetron sputtering

Poster:
Optical Emission Spectroscopy

Orozco Montes, Free Ag & Cu NPs based on magnetron sputtering, Best Poster Award E-MRS (2016)
Orozco Montes, Electrical behavior of Al2O3 films doped with Ag NPs, Best Poster Award Electroceramics XV (2016)
Many thanks to students and especially:

2009-2012
Luiz Fernando Zanini

2013-2016
Michael Gaudin

2014- ...
Maileth Vanessa Orozco Montes
Thank you for your attention