Magnetron sputtering of copper, silver, and gold onto oils for nanoparticle synthesis.

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Advantages of sputtering onto liquids for NP synthesis

1. Flexibility
   Large variety of elements can be sputtered

2. Reproducibility
   “Automatized” process + controlled environment

3. Purity
   Chemical reactants and by-products are avoided

**Classic colloidal synthesis**
- Solvent
- Metal salt
- Reducer
- Capping agent
- Nanoparticles
- Other reaction products
- Excess of reagents

\[ + O_2 / N_2 / \ldots \]
1. Working parameters
- Nature of sputtered material
- Nature of the liquid
- Sputter power
- Target – substrate distance
- Pressure
- Kind of sputtering process, ...

2. Plasma properties
- Particle fluxes
- Kinetic energies

3. Plasma-liquid interaction
- Deposition rates
- Heating of the liquid
- Liquid chemistry

4. Growth of nanoparticles

5. Applications of NPs

Our goal
- Collaborations with other research groups

- How do the NP grow?
- Can we control the size, shape, elemental composition?
- Are NP solutions stable?

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- How do the NP grow?
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- Are NP solutions stable?
Experimental set-up

Deposition chamber

- Magnetron

- Gas exhaust
- Turbo Pump + Primary pump
- Throttle valve

Load-lock chamber
(Outgassing the host liquid)

- Liquid Sample 4 ml
- Gate valve
- Valve
- Turbo Pump + Primary pump

Massflow Controller (Ar, O\textsubscript{2}, N\textsubscript{2})

Transfer arm

Gas exhaust
Castor oil as a host liquid

Castor oil = mixture of triglycerides
- ricinoleate ~ 90%
- oleate ~ 7%
- linoleate ~ 3%

Ricinus communis
Castor beans

Generic Triglyceride

- Withstand vacuum
- Low toxicity
- Low cost

Ricinoleate

Ricinoleic acid

Glycerol

Ricinus communis

Castor beans
Influence of the working parameters on the NP properties

Varying parameters are:
1. Deposition time
2. Sputter power
3. Kind of sputtering discharge: DCMS vs. HiPIMS
4. Viscosity of the host liquid
5. Sputtered metal (Au, Ag, Cu)

Methods of NP characterization:
1. UV-vis spectroscopy: optical properties, colloidal stability, and ageing of NP solutions
2. TEM: size and size distribution of NPs
1. Sputtering Gold on Castor oil
DC-MS of gold onto castor oil, a first look

\( p_{Ar} = 0.5 \text{ mTorr}, \text{ WD} = 20 \text{ cm}, t_s =5 \text{ min}, P = 80 \text{ W} \rightarrow \text{ Flux of metal atoms } : \Phi = (2.5 \pm 0.5) \times 10^{-7} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{min}^{-1} \)

- NP continue to grow for a few days after sputtering
- NP solutions are stable for a very long time
- Good reproducibility

\[ A_{\text{max}} (\text{a.u.}) \]

Stable for 1.5 year

\[ \text{Absorbance (a.u.)} \]

Wavelength (nm)

0 15 min
1 day
27 days

SPR band appears with time

\[ \text{Absorbance (a.u.)} \]

Wavelength (nm)

0 1 day

Sample 35
Sample 41

15 min

1 day
Effect of sputter time

\[ p_{Ar} = 0.5 \text{ mTorr}, \ WD = 20 \text{ cm}, \ P = 80 \text{ W}, \rightarrow \text{ Flux of metal atoms} : \Phi = (2.5 \pm 0.5) \cdot 10^{-7} \text{ mol} \cdot \text{cm}^{-2} \cdot \text{min}^{-1} \]
Different deposition times: ageing of the NP solutions
Effect of sputter power

$p_{Ar} = 0.5\, \text{mTorr}, \ WD = 20\, \text{cm}, \ t_s = 10\, \text{min}$
Different sputter powers: ageing of the NP solutions
DC-MS vs. (unipolar) HiPIMS

$p_{\text{Ar}} = 5 \text{ mTorr}, 80 \text{ W}, 10 \text{ min}$

DC-MS:
$\Phi = (1.8 \pm 0.2) \cdot 10^{-7} \text{ moles/cm}^2 \cdot \text{min}$

HiPIMS:
$T_{\text{on}} = 20 \mu\text{s}, I_{pk} = 0.3 \text{ A/cm}^2, f = 800 \text{ Hz},$
$\Phi = (0.9 \pm 0.1) \cdot 10^{-7} \text{ moles/cm}^2 \cdot \text{min}$
Ageing of the NP solutions
Effect of the liquid viscosity

0.5 mTorr, 20 cm, 80 W, 10 min, Liquid: polymerized* rapeseed oil
* Plasma treatment prior sputtering

<table>
<thead>
<tr>
<th>Viscosity (cP)</th>
<th>60</th>
<th>200</th>
<th>440</th>
<th>630</th>
<th>1000</th>
<th>1400</th>
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<tbody>
<tr>
<td>Surface tension</td>
<td>~ 32.7 mJ · m⁻²</td>
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Viscosities (cP)
- Castor oil = 700 cP (35.1 mJ m⁻²)
- Water = 0.9 cP
- Honey ~ 2000 – 10 000 cP

Film is obtained like on a solid surface
Effect of the liquid viscosity

Migration of NPs in solution

5 months

Absorbance (a.u.)

Wavelength (nm)

- 60 cP
- 200 cP
- 440 cP
- 630 cP
- 1000 cP
- 1400 cP
Effect of the host liquid viscosity

No TEM data for high viscosity liquids: impossible to remove the liquid from the TEM grid

XRD data for Au films

\[ d_{\text{Au}} (1000 \text{ cP}) = (10 \pm 1) \text{ nm} \]
\[ d_{\text{Au}} (1400 \text{ cP}) = (13 \pm 2) \text{ nm} \]
2. What if we sputter silver onto castor oil?
DC-MS of silver target onto castor oil

0.5 mTorr, 20 cm, 80 W, 3 min
\[ \Phi = (0.6 \pm 0.1) \cdot 10^{-7} \text{ moles/cm}^2 \cdot \text{min} \]
Ageing of the Ag-NP solutions

8.1 nm ± 5.0 nm.
TEM image 8 months after preparation.
Stability of nanoparticles in castor oil: Interaction energy calculations

\[ E_{\text{int}} = E_{\text{surf/CO}} - [E_{\text{CO}} + E_{\text{surf}}] \]

**GOLD**

\[ E_{\text{int}} = -0.14 \ \text{eV} \]

1/3 of triglyceride of ricinoleic acid

**SILVER**

\[ E_{\text{int}} = +0.16 \ \text{eV} \]
DC-MS vs. Unipolar & Bipolar HiPIMS

\[ P_{Ar} = 5 \text{ mTorr, } 80 \text{ W, } 10 \text{ min} \]
Flux DC-MS: \((1.8 \pm 0.2) \cdot 10^{-7} \text{ moles/cm}^2 \text{ min}\)

Flux HiPIMS: \((0.9 \pm 0.1) \cdot 10^{-7} \text{ moles/cm}^2 \text{ min}\)
\[ f = 800 \text{ Hz, } T_{ON, -} = 20 \mu\text{s, } I_{pk} = 0.3 \text{ A/cm}^2 \]

Flux B-HiPIMS: \((0.2 \pm 0.1) \cdot 10^{-7} \text{ moles/cm}^2 \text{ min}\)
\[ f = 800 \text{ Hz, } T_{ON, -} = 20 \mu\text{s, } I_{pk} = 0.3 \text{ A/cm}^2 \]
\[ V_+ = +300\text{V, } T_{ON, +} = 250 \mu\text{s, } T_{+/-} = 10\mu\text{s} \]

Number of particles larger than 20 nm
- 0.1\% for DC-MS,
- 1.3 \% for HiPIMS (B-HiPIMS_0)
- 4.2 \% for bipolar HiPIMS (BHHiPIMS_300)
3. What if we sputter copper onto castor oil?
Oxidation of Cu-NPs in castor oil

Sample was placed in the cell without stirring.

Copper (II) oleate $\rightarrow \text{Cu}_2\text{O}$ NPs


Sputtering onto Liquids: mechanism of NP formation

- Secondary growth of NPs
- Oxidation due to reaction with host medium and/or the atmosphere
- Coagulation in case of low colloidal stability

Possible post-sputtering processes

- Ar ions
- Atoms
- Primary clusters
- NPs