Synthesis of Bismuth-Based Nanoparticles into an Imidazolium Ionic Liquid by Reactive Magnetron Sputtering

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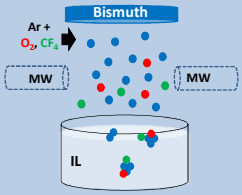
Introduction

Nanoparticules (NPs) have attracted significant attention from the materials science community due to their unique physical properties. In this field, the synthesis by sputtering on low vapor pressure liquids presents the interest to lead to NPs with high purity and sharp size distribution. However, up to now, this process was only used for metallic NPs synthesis. Our objectives is to investigate the formation of various Bi-based compound NPs thanks to the reactive sputtering of a Bi target in controlled atmosphere of $Ar/O_2/CF_4$ gas mixture on [BMIM][TFSI] ionic liquid (IL).

The reactive sputtering process

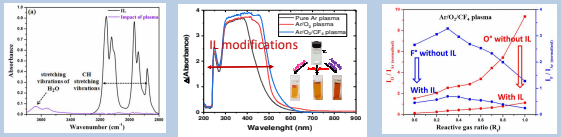
Radiofrequency reactive magnetron sputtering:
Target / IL distance = 8 cm
RF power = 50 W
Gas mixture: Ar/ O_2 / CF_4 – Φ_{total} = 30 sccm – Pr = 2 Pa

Modification of IL by MW plasma:
MW source / IL distance = 7 cm
MW power = 90 W per probe
Gas mixture: Ar/ O_2 / CF_4 – Φ_{total} = 30 sccm – Pr = 2 Pa



IL modification only by MW plasma

FTIR **UV-visible absorption** **OES**

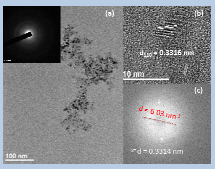


When IL is placed into the reactor, ↘ F and O radical density → Higher radicals consumption by IL

After 1h of MW plasmas, low chemical modification (FTIR): less than 1% of IL is modified.
The high change in color and UV-visible absorption is most probably due small degradation around the aromatic cation.

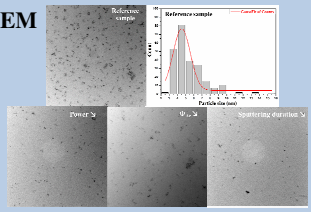
NPs formation by rf sputtering in Ar

HR-TEM



- NPs size distribution centered on ≈ 4-5 nm. Not influenced by power, flow rate or time.
- When rf power, flow rate or time ↘, NPs density seems to ↘.

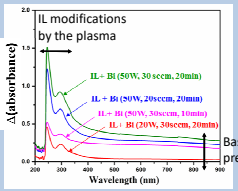
TEM



RF sputtering of Bi target in pure Ar plasma → well crystalized metallic Bi° NPs

Conditions for reference sample: *Power = 50W* Φ_{total} *= 30 sccm* *Duration = 20 min*

UV-visible absorption

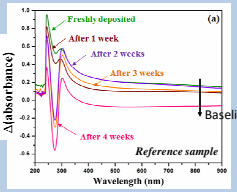


Baseline linked to presence of Bi° NPs

Baseline in 600-900 nm range indicates the presence of absorbing metallic NPs.

Dispersion ageing

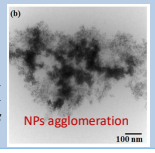
UV-visible absorption



With time, metallic NPs agglomerate and sediment. → Will ease the NPs isolation from the IL for further applications.

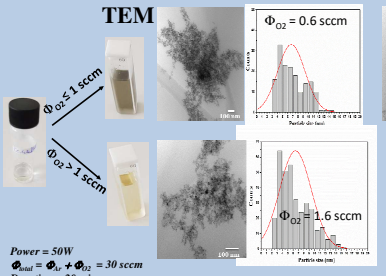
Baseline ↘ → NPs sedimentation

TEM
After 4 weeks



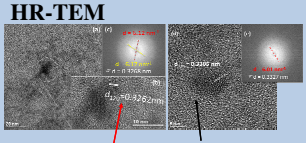
NPs formation by rf sputtering in Ar/O_2

TEM



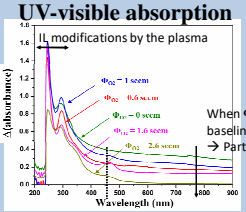
Power = 50W
$\Phi_{total} = \Phi_{Ar} + \Phi_{O2}$ *= 30 sccm*
Duration = 20 min

HR-TEM



Bi_2O_3 NP Bi° NP

UV-visible absorption



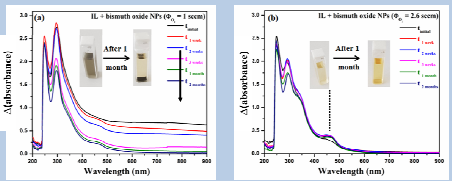
When Φ_{O2} ↗, baseline ↘ → Part of Bi NPs ↘

New peak link to Bi_2O_3 NPs presence

NPs synthesized for all Φ_{O2} but more agglomerated.
For high Φ_{O2}, well-crystallized Bi_2O_3 NPs are observed, but no core-shell.
Depending on Φ_{O2}, part of Bi_2O_3 to Bi NPs is controlled (as for thin films deposition).

Dispersion ageing

UV-visible absorption

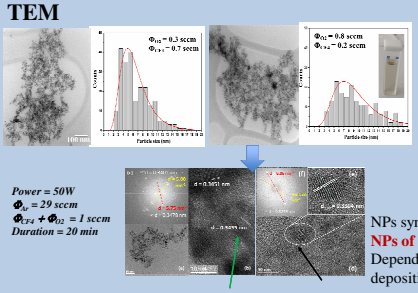


With time, baseline ↘ → sedimentation of Bi NPs

After 1 week, peak at 450 nm ↗ then stable → Peak link to Bi_2O_3 NPs agglomeration ?

NPs formation by rf sputtering in Ar / O_2 / CF_4

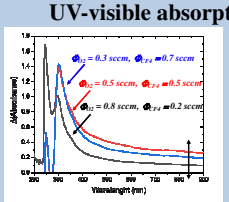
TEM



Power = 50W
Φ_{Ar} *= 29 sccm*
$\Phi_{CF4} + \Phi_{O2}$ *= 1 sccm*
Duration = 20 min

$Bi_xO_yF_z$ or Bi_xF_y NP Bi° NP

UV-visible absorption

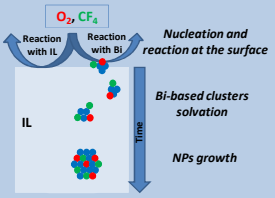


No peak around 450 nm link to agglomerated Bi_2O_3 NPs

Baseline variation → Variation of Bi NPs part. Also observed for thin film deposition.

NPs synthesized for all Ar/O_2/CF_4 mixtures.
NPs of Bi- fluoride or oxyfluoride are observed, but no core-shell.
Depending on Φ_{O2}, part of $Bi_xO_yF_z$ to Bi NPs change (as for thin film deposition)

Proposed mechanism



- All NPs are spherical → growth into IL volume.
- Calculations show O_2 solvation is low as used pressure and temperature → low reaction of gas into IL → Bi-O and Bi-F bonds formed from radicals reaction.
- O and F radicals are very reactive species → very low diffusion length into IL → Bi-O and Bi-F bonds formed from radicals reactions at IL top surface.
- Even for high Φ_{O2} and Φ_{CF4}, metallic NPs observed (different from thin film deposition) → NP "protected" from radicals reaction by rapid solvation OR lower radicals density available due to their reaction with IL itself.

Conclusions and perspectives

- We succeed obtaining NPs of Bi-based compounds by rf sputtering on IL for all Ar/ O_2 / CF_4 mixtures. Depending on the gas mixture, Bi, Bi_2O_3 or BiO_xF_y NPs are formed.
- We propose a mechanism based on radicals interaction with sputtered Bi atoms at the top IL surface and then a NP growth into the IL volume.

→ Further experiments will be conducted to understand reactive gas / growing NPs interaction.

Plathinium 2021
September 13th- 17th, 2021
Virtual meeting