Towards large-scale hexagonal boron nitride 2D layers: a chemical approach

Catherine Journet
Bérangère Toury
Yangdi Li
Vincent Garnier
Philippe Steyer

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http://lmi.cnrs.fr

from molecule ... ... to material

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BN fibers
new precursors

micro- and meso-porous BN
by template or direct synthesis

BN nanotubes

$h$-BN coatings

Laboratoire des Multimatéraux et Interfaces

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**General context**

*h-BN* also called white graphite

- **Graphite**

- **B**
- **N**

- 0.34 nm

- **Electron insulator** ~ 6.0 eV
- **Refactory behavior**
- **Hexagonal structure**
- **Chemical stability** > 900°C under air
- **High thermal conductivity**

- **Great potential for electronics and optics**

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Zhongwei Zhang et al 2017 Nanotechnology 28 225704

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Towards layered hBN

Several needs of h-BN samples:

- Thick layers to be used as substrate for graphene
- Encapsulating layers of graphene and other 2D materials
- Dielectric layers in heterostructures

Need of both monolayers and thick layers (> 10 – 50 nm)
Our approach

High quality h-BN source

Polymer Derived Ceramics (PDCs)
- Tailored molecular precursor
- Non-oxide system for high purity
- Liquid precursors easy to handle
- Possibility for various shaping methods for specific ceramic shape

Spark Plasma Sintering (SPS)
- Rapid and efficient processing method for densification on both lab scale and industrial level
- Softer condition compared with HPHT method (2100°C, 5.5GPa, 80h)

S. Yuan, et al. Nanoscale. 2014, 6, 7838-7841

Polymer Derived Ceramics (PDCs) route

- **Synthesis**: \((\text{NH}_4)_2\text{SO}_4 + \text{NaBH}_4 \text{ in tetraglyme}\)
- **Polyborization**: Pressure vessel 50°C / 7 days
- **Li}_3\text{N**: Cristallisation promoter additivation
- **Pyrolysis**: Ceramisation 1000-1800°C / N

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Combination PDCs + SPS


Spark Plasma Sintering (SPS)

90 MPa
770 A
1800°C
1h

stabilized 600°C, 1h

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polycrystalline sample made of single crystal flakes


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Characterization of the bulk material

① Before abrasion:
- ratio $B/N = 0.97$ (close to 1)
- $< 0.5\%$at. for O1s and $1.3\%$at. for C1s

② After abrasion (1µm):
- elimination of C and O (just contaminants)
- preferential sputtering of nitrogen atoms
Influence of the crystallization promoter

<table>
<thead>
<tr>
<th>No.</th>
<th>Pre-ceramic Composition</th>
<th>Li$_3$N wt. %</th>
<th>Temperature °C</th>
<th>Pressure MPa</th>
<th>Dwelling time hour</th>
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<tbody>
<tr>
<td>1</td>
<td>PBN</td>
<td>0</td>
<td>1800</td>
<td>90</td>
<td>1</td>
</tr>
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<td>2</td>
<td>PBN+Li$_3$N</td>
<td>5</td>
<td>1800</td>
<td>90</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>PBN+Li$_3$N</td>
<td>10</td>
<td>1800</td>
<td>90</td>
<td>1</td>
</tr>
</tbody>
</table>
Influence of the crystallization promoter

- Li$_3$N addition necessary for obtaining well-crystalized h-BN flakes
- No significant structural difference between 5% and 10 wt.%
- Ceramic yield decreases when increasing Li$_3$N amount
Influence of the sintering T

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<tbody>
<tr>
<td>1</td>
<td>PBN+Li$_3$N</td>
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<td>1200</td>
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<tr>
<td>2</td>
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<tr>
<td>3</td>
<td>PBN+Li$_3$N</td>
<td>5</td>
<td>1800</td>
<td>90</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>PBN+Li$_3$N</td>
<td>5</td>
<td>1950</td>
<td>90</td>
<td>1</td>
</tr>
</tbody>
</table>
Flakes size with $T$ to reach a maximum area of 276 $\mu m^2$ at 1800°C and decrease at 1950°C when sintering. Flakes are significantly larger above 1500°C.

- pellets show similar features
- composed of defined BN domains stacked into flakes and growing in different orientations

Best compromise between 1500 and 1800°C.
Influence of the sintering $T$

**Raman**

- **1200°C**
  - Frequency Shift (cm$^{-1}$): 1366.2 cm$^{-1}$
  - FWHM: 8.61 cm$^{-1}$

- **1500°C**
  - Frequency Shift (cm$^{-1}$): 1366.1 cm$^{-1}$
  - FWHM: 8.07 cm$^{-1}$

- **1800°C**
  - Frequency Shift (cm$^{-1}$): 1366.0 cm$^{-1}$
  - FWHM: 7.81 cm$^{-1}$

- **1950°C**
  - Frequency Shift (cm$^{-1}$): 1365.8 cm$^{-1}$
  - FWHM: 8.31 cm$^{-1}$

**XRD**

- **1200°C**
  - Intensity (a.u.)
  - Peaks (100), (002), (004), (100), (102), (006)

- **1500°C**
  - Intensity (a.u.)
  - Peaks (100), (002), (004), (100), (102), (006)

- **1800°C**
  - Intensity (a.u.)
  - Peaks (100), (002), (004), (100), (102), (006)

- **1950°C**
  - Intensity (a.u.)
  - Peaks (100), (002), (004), (100), (102), (006)

**Very good Raman signature with a FWHM $\approx 8$ cm$^{-1}$**

**Good crystalline structure of h-BN**
Influence of the crystallization promoter and sintering T

- Investigation of optical and excitonic properties
- Identification of different classes of defects and their impact on optical properties

Collab. GEMAC & ONERA (A. Plaud, L. Schue, J. Barjon, A. Loiseau)

A tool of interest

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Influence of the crystallization promoter and sintering T

Indication of the overall material quality, accounting for both purity and crystallinity

- Observation of intrinsic exciton emission (S-lines)
- Absence of defect-related emissions (D-lines)
- Presence of impurities when increasing the sintering temperature: contamination?

Collab. GEMAC & ONERA (L. Schue, J. Barjon, A. Loiseau)
From h-BN pellets ... towards flakes

well-crystallized h-BN bulk sample (pellet)

flake (single crystal)
Characterization of the flakes

Perfect large flakes with a perfect layers stacking

Large single crystal convenient for exfoliation

Semiconductor
Characterization of the flakes

Different intensities in relation to different flakes thicknesses

1366 cm⁻¹

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From h-BN pellets ... towards flakes

- well-crystallized h-BN bulk sample (pellet)
- mechanical exfoliation using the tape method
  - « chemical » exfoliation in a solvent under sonication
- flake (single crystal)
- BNNSs

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Characterization of the BNNSs

BNNS rolled onto itself

hexagonal lattice characteristic from the in-plane arrangement

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Characterization of the BNNSs
BNNS as ideal candidate for graphene substrate / encapsulating layer / 2D layers stacking

Increase of the crystallinity by adding Li$_3$N
- Higher crystallinity at lower temperature

Interest in combining the PDCs route & the SPS to get h-BN large single crystals

After exfoliation, large (tens of µm) and defect-free BNNSs obtained

S. Yuan et al. Crystals, 6, 55 (2016)
Thank you for your attention!