Appendix of CSC 2024 PhD proposal

More detailed document

Synthesis and characterization of h-BN for future applications

Keywords:

Synthesis processes, crystal growth, Hexagonal Boron Nitride, crystal, TEM, SEM, AFM, 2D-nanomaterial, microstructural, chemical, electroluminescent, characterizations

Abstract:

2D-nanomaterials present a remarkable potential to be used for electronic and optoelectronic applications and they have been intensively investigated in the past few years. Graphene is indeed the next potential superstar material for the electronics industry, with a thinner, stronger and much faster electron conductor than silicon. However, without any natural energy band-gap, graphene's conductance cannot be switched off. To overcome this issue, a promising technique is the integration of ultrathin layers of graphene and boron nitride into two-dimensional heterostructures. In this context, availability of well-crystallized h-BN graphene-like nanosheets with high purity and lateral size over 30 μm is a key point in the development of advanced convenient electronic devices. Another innovative solution consists in integrating C sp^2 domains into the hexagonal BN (h-BN) sheet, in order to modulate the electronic properties of the material.

For several years now, we became more deeply invested in the preparation of such h-BN based 2D nanomaterials and we recently succeeded in synthesizing self-standing h-BN few- and mono-layers by exfoliation of h-BN single crystals synthesized by combining the Polymer Derived Ceramics route with a Spark Plasma Sintering (SPS) and further addition of crystallization promoter (see ref. 1-3). Advantage of this dual process is that we may control the two-step synthesis: the chemical preparation of precursor on the one hand, the crystal growth stage of the resulting powder on the other hand. However,the current BN size remains still insufficient to allow stamping graphene onto BN and some impurities are still detected. In order to increase both the size and purity of product, a new high-pressure crystal growth process is being adapted, which turns out really very efficient to deliver much more larger Boron Nitride Nanosheets (BNNs). However, degrees of freedom of the process are important (purity of reactants, amount of additive agents, yield product, growth temperature-time-ramp-pressure and atmosphere…) and need to be well understood to get well crystallized nanosheets of a few hundred microns. Furthermore, synthesis/processing mechanisms (reactivity between the preceramic precursor and dopants, control and understanding of crystal growth, significance of nucleation sites number and distribution…) have to be better understood and mastered in order to control and improve the h-BN synthesis.

To manage these stages, a fine characterization of each step of the process is proposed during the PhD, in order to highlight critical steps and to define the key-parameters involved in the synthesis,and better explain their influence on the resulting products (crystallinity, purity, microstructure, properties…).

The PhD candidate will be in charge of the synthesis of precursors, high temperature-high pressure crystal growth from the resulting powder, and characterization of the products. The global investigation (XRD, Raman and IR spectroscopies, cathodoluminescence…) will be completed by a more local complementary approach (SEM, TEM, AFM…). Complementary physical characterization will be implemented thanks to collaborations with other French laboratories. The key-parameters governing the quality of BN-based will be then identified, and modified so that to obtain large, pure and defect free BNNs with highly improved physical properties.

PhD Supervision

The PhD's program can be structured into three different parts: first, synthesis of preliminary precursors, second, the crystals growth, and third their characterization. Therefore, the PhD will be conducted in two laboratories of Lyon city (France):

- Laboratoire des Multimatériaux et Interface (LMI, Université Claude Bernard Lyon1, UMR CNRS 5615),
- Laboratoire MATEriaux Ingénierie et Science (Mateis, INSA de Lyon, UMR CNRS 5510).

Supervision of the Ph-D student will be ensured by one professor of each laboratory: Bérangère TOURY, from LMI, will be more involved in the chemical synthesis aspects, while Philippe STEYER, from the MATEIS lab, will be more concerned by the deep characterization of the resulting materials. Taking into account the high multi-disciplinary character of the study, supervision will also be shared with two other colleagues of both laboratories, specialists in C-based nanomaterials (Pr. Catherine JOURNET-GAUTIER) and in growth process (Dr. Vincent GARNIER).

Some of their relevant papers appear below:

1. S. Yuan, S. Linas, C. Journet, P. Steyer, V. Garnier, G. Bonnefont, A. Brioude, B. Toury**, Pure & crystallized 2D BN sheets synthesized via a novel process coupling both PDCs and SPS methods,** *Scientific reports*, *Volume 6*, *2016, Page 20388.*
2. S. Yuan, B. Toury, C. Journet, A. Brioude, **Synthesis of hexagonal boron nitride graphene-like few layers,** *Nanoscale, 2014, 6, 7838-7841*
3. S. Yuan, C. Journet, S. Linas, V. Garnier, P. Steyer, S. Benayoun, A. Brioude, B. Toury, **How to Increase the h-BN Crystallinity of Microfilms and Self-Standing Nanosheets: A Review of the Different Strategies Using the PDCs Route,** *Crystals, 6, 2016, Page 55.*
4. Y. Li, V. Garnier, P. Steyer, C. Journet, B. Toury, **Millimeter-Scale Hexagonal Boron Nitride Single Crystals for Nanosheet Generation,** ACS Applied Nano Materials 2020, 3, 2, 1508–1515
5. Camille Maestre, Bérangère Toury, Philippe Steyer, Vincent Garnier and Catherine Journet, **Hexagonal boron nitride: a review on selfstanding crystals synthesis towards 2D nanosheets**, Journal of Physics: Materials, Vol. 4, N° 4 (2021) 044018C.
6. C. Maestre, Y. Li, V. Garnier, P. Steyer, S. Roux, A. Plaud, A. Loiseau, J. Barjon, L. Ren, C. Robert, B. Han, X. Marie, C. Journet, B. Toury, **From the synthesis of hBN crystals to their use as nanosheets in van der Waals heterostructures**, 2D Materials 9 (2022) 035008
7. A. Schmitt, D. Mele, M. Rosticher, T. Taniguchi, K. Watanabe, C. Maestre, C. Journet, V. Garnier, G. Fève, J. M. Berroir, C. Voisin, B. Plaçais, and E. Baudin, **High-field 1/f noise in hBN-encapsulated graphene transistors**", Phys. Rev. B 107, L161104
8. Sébastien Roux, Christophe Arnold, Fulvio Paleari, Lorenzo Sponza, Eli Janzen, James H. Edgar, Bérangère Toury, Catherine Journet, Vincent Garnier, Philippe Steyer, Takashi Taniguchi, Kenji Watanabe, François Ducastelle, Annick Loiseau, and Julien Barjon, **Radiative lifetime of free excitons in hexagonal boron nitride**, Physical Review B 104 (2021) L161203

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