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2D materials and their heterostructures appear very promising for numerous applications. Whether it is used as a substrate or as an active layer, high quality 2D hexagonal boron nitride presents high hopes. Compared with conventional SiO<sub>2</sub> substrate, lattice matching and absence of dangling bonds make boron nitride nanosheets (BNNSs) and graphene excellent pairing materials and give incentive to develop various Van der Waals heterostructures.

Vapor-phase processes like Chemical Vapor Deposition can achieve large scale coverage, but selfstanding hexagonal boron nitride crystals provide exfoliated nanosheets of unrivaled purity and crystal quality which are still preferred for demanding applications.

In order to achieve high quality and large BNNSs, we propose a synthesis way by the Polymer Derived Ceramics (PDCs) route involving polyborazylene as precursor, combined with sintering techniques [1]. Our hBN already demonstrated a very high crystalline quality attested by the FWHM value, 7.6cm<sup>-1</sup>, as one of the best reported in literature. [2]

Here, we explore the growth mechanisms of hBN crystals. SEM and X-ray tomography observations (Figure 1) provide insights on secondary structures on the crystal surface. Nucleation and growth orientation are addressed. Process parameters are explored and enable process improvement assessed by optical characterizations.

## References

- [1] Y. Li, V. Garnier, C. Journet, J. Barjon, A. Loiseau, I. Stenger, A. Plaud, B. Toury, P. Steyer, Nanotechnology, 30 (2019) 035604
- [2] Y. Li, V. Garnier, P. Steyer, C. Journet, B. Toury, ACS Applied Nano Materials, 2 (2020) 1508

## Figures



**Figure 1:** (left) Optical microscope view of hBN crystal; (middle) SEM view of an hBN crystal edge; (right) 3D extracted view of entangled crystals inside the as-obtained ingot from X-ray tomography.