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# Luminescence properties of hexagonal boron nitride layers

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Hexagonal boron nitride (hBN) is a wide band gap semiconductor (6.4 eV), which can be synthesized, as graphite, its carbon analog, as bulk crystallites, nanotubes and layers. These structures meet a growing interest for deep UV LED and graphene engineering [1]. Knowing better the intrinsic properties of this material is therefore highly desirable. We attempt to have a better comprehension of the optical and electronic properties of thin BN layers, in correlation with their structural properties and to better know, how these properties can be further exploited for the characterization of these nanostructures and how electronic properties of graphene can be impacted by underlying BN layers.

To this aim, we combined TEM structural analyses performed in a monochromated Libra 200 TEM and cathodoluminescence experiments at 4K using a dedicated set-up implemented in a JEOL FEG-SEM and adapted to the detection in the far UV range [2, 3]. Data recording is available in a spectroscopic mode or in a hyperspectral imaging mode thanks to the imaging capability of the microscope.

In this work, we have first investigated the luminescence properties of different hBN sources (HPHT [4], PDCs [5] and commercial samples) in the near band edge energy range (5 - 6 eV). In this energy range, luminescence properties are governed by strong excitonic effects and consist of D and S lines [2, 3]. Emission related to D lines (5.3 – 5.5 eV) has been proved to be due to structural defects, such as grain boundaries, as identified by TEM [3]. In defect free areas, D lines completely vanish and S lines (5.75 – 5.9 eV) only are observed. As shown in Fig.1, S lines display similar features whatever the sample source. S emission consists of four main lines S1 – S4. Although the exact nature of these lines is still a debated issue, their constant observation in various kinds of samples let to identify them as the intrinsic luminescence of the bulk material [6].

In a second step, we studied luminescence in thin layers, obtained by mechanically exfoliating small crystallites. Exfoliated flakes were reported on SiO<sub>2</sub> substrates for AFM thickness measurements and luminescence experiments. We first have shown that the transfer procedure on the substrate can highly impact the luminescence. Indeed if reported flakes display folds or ripples, excitons get trapped on these defects. S line emission vanishes and emission is dominated by D lines and is highly localized at the defects [7]. We used this effect as a check of the structural quality of the flakes and in such a way we managed to prepare defect free flakes, that is with no D band in their emission spectrum, with various thicknesses from 100L to 6L from both an HPHT crystal and a commercial powder. As shown in Fig.2, their S-emission dramatically changes, when reducing the number of layers. The relative intensity of S3-4 lines progressively decreases whereas the one of S1-2 lines increases. This rise of the S1-2 line is accompanied by that of related phonon replica corresponding to the E2g mode [3] as outlined by the dashed lines in Fig.2. In the thinnest layers, emission is therefore restricted to the S1-2 line only, identified as a signature of the 2D confinement [6].

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[2] P. Jaffrennou et al., Phys. Rev. B **77** (2008) 235422

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[7] L. Schué et al in preparation (2016)

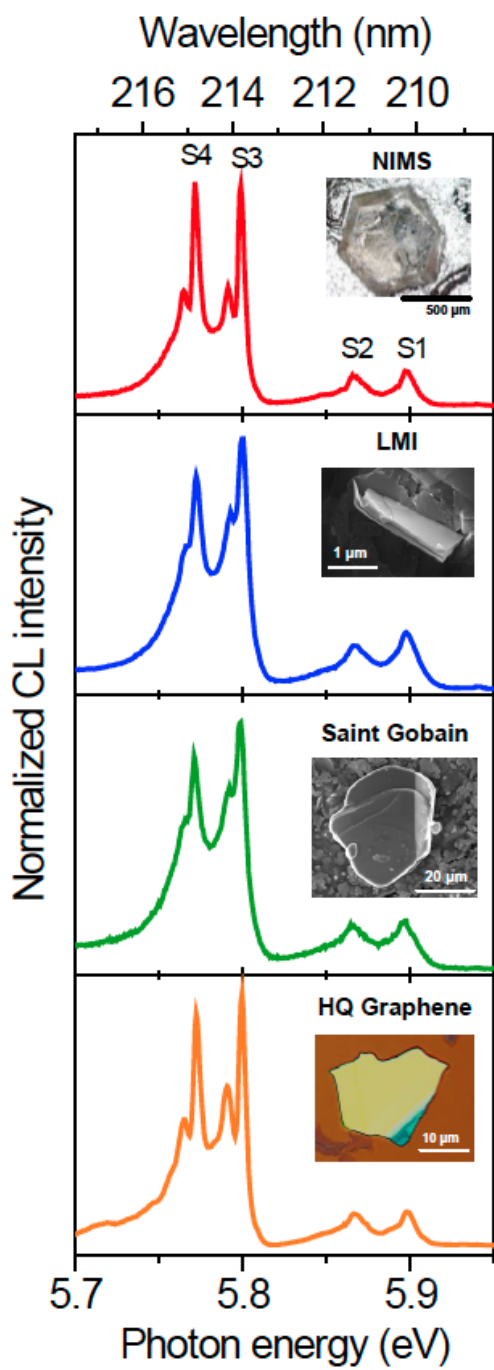


Fig 1 : CL spectra of hBN bulk samples from different synthesis techniques

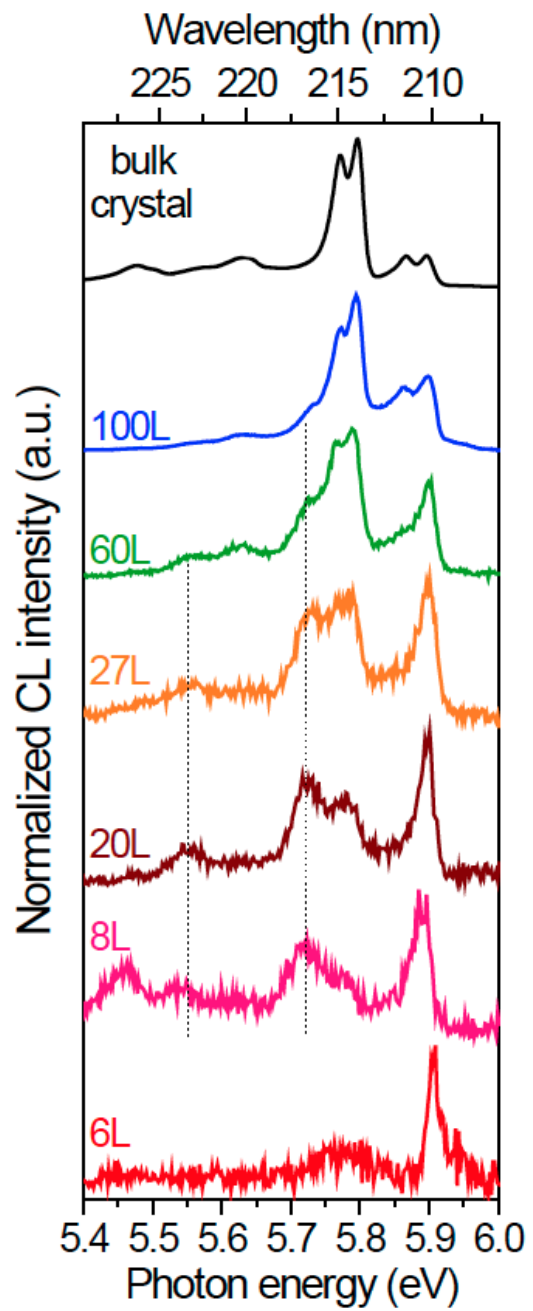


Fig2 : Evolution of CL spectra versus the thickness of exfoliated samples. The dashed lines indicate phonon replica of the S1-2 line.