Probing spectroscopic properties of BN and black phosphorous layers

L.Schué[1,2], E. Gaufrès[1,3], A. Favron[3], F. Fossard[1], A. Pierret[1,], J. Barjon[2], F. Ducastelle[1], R. Martel[3] and A. Loiseau[1],

[1]LEM, ONERA-CNRS, Châtillon, France
[2]GEMAC, Université Versailles St Quentin – CNRS, Versailles , France
RQMP and Département de chimie, Université de Montréal, Montréal, France

In this talk, we examine the interplay between structure and spectroscopic properties of both BN and Black Phosphorous (P(black)) mechanically exfoliated layers and how these properties can be further exploited in 2D layered heterostructures, beyond graphene. Spectroscopic properties were studied using cathodoluminescence (CL) at 4K, Raman spectroscopy, HRTEM and Electron Energy Loss Spectroscopy (EELS) using a monochromated Libra 200 TEM-STEM at 80 kV.

Hexagonal boron nitride (h-BN) is a wide band gap semiconductor (~ 6.5 eV), with sp^2 hybridation, which meets a growing interest for deep UV LED and graphene and 2D materials engineering [1]. Knowing better the intrinsic properties of this material therefore highly desirable. H-BN displays original optical properties governed, in the energy range 5.5 – 6 eV, by strong excitonic effects, consisting of D and S lines [2]. Thanks to the imaging capability of the CL, emission, related to D lines, is proved to be due to structural defects identified by TEM as grain boundaries or folds. In defect free areas of thin layers, D lines completely vanish and S lines only are observed. S lines are therefore identified as the intrinsic luminescence of the material [2]. We will show how exfoliated layers could be prepared with no D band and that their S-emission dramatically changes when reducing the number of layers, providing with a signature of the 2D confinement [3]. Low-loss-EELS is an alternative approach to the nature of electronic excitations. One can indeed access to the onset of optical transitions and investigate their angular dependence. We will show that we can probe the whole Brillouin zone of BN layers appropriately cut in a HPHT h-BN single crystal along definite crystallographic orientations and represent the plasmon dispersion as a function of the q momentum [4].

P(black) thin layers have recently raised interest for their original semi-conducting properties, such as tunable direct bandgap and high carrier mobilities. Their study is however very challenging due to its fast degradation under ambient conditions. Thanks to Raman and core-loss EELS spectroscopy, we have investigated the chemistry of degradation and shown that this phenomenon is due to a thickness dependant photo-assisted oxidation reaction with absorbed oxygen in water. This oxidation is consistent with electron transfer model based on quantum confinement. On this basis we carried out appropriate manipulation procedures opening a route to first Raman TEM and Low-loss EELS measurements on pristine mono-, bi- and multi layers, which will be discussed [5].

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