

Spectroscopic properties of BN layers

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Hexagonal boron nitride (h-BN) is a wide band gap semiconductor (~ 6.5 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]. For instance electron mobility of graphene has been shown to be preserved when graphene is supported by a h-BN film. Until recently, properties of h-BN materials were poorly known due to both the scarcity of crystals and suitable investigation tools. This situation has changed thanks, first, to the development of dedicated photoluminescence (PL) and cathodoluminescence (CL) experiments running at 4K and adapted to the detection in the far UV range [2, 3, 4], and second to the availability of high quality single crystals [5]. Thanks to these tools, h-BN has been shown to display original optical properties, governed, in the energy range 5.5 – 6 eV, by strong excitonic effects [2, 3, 6], in agreement with the most reliable theoretical calculations [7, 8].

In this talk, we will examine the interplay between structure, defects and spectroscopic properties of BN layers and how these properties can be further exploited for the characterization of these nanostructures. We carry out optical and structural characterizations of this material by combining PL, CL measurements at 4K in the UV range (up to 7eV), HRTEM observations and Electron Energy Loss Spectroscopy (EELS) in TEM and STEM modes, using a Libra 200 equipped with an electrostatic monochromator operating at 80 kV. Thin layers have been obtained by mechanically exfoliating small crystallites. Exfoliated flakes were reported first on SiO₂ substrates for AFM thickness measurements and second on TEM grids.

We will show first, that, whatever the structure, bulk or nanoscale, excitonic luminescence consists of two series of lines called S and D. Thanks to the imaging capability of the CL, emission, related to D lines, is found to be localized on 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. D/S ratio can therefore be used as a qualification parameter of the defect densities present in the layers [9].

Second, we will show that EELS provides an alternative approach to the nature of electronic excitations by inspecting the low losses in the 0 – 20 eV range. Pioneering work performed on BN SWNT has shown the potentialities of this approach [10]. One can indeed access under controlled illumination conditions, to the onset of optical transitions. It is now possible to investigate the angular dependence of these transitions at a nm scale and with an energy resolution below 100 meV. To this aim we applied the technique developed in [11] and fully adapted to the Libra200. By operating in the reciprocal space, angular Resolved EELS has been performed on foils cut in a HPHT h-BN single crystal along definite crystallographic orientations. We will first show that the difference in the dispersion of the excitation to p* and s* states is dramatically revealed from a w-q mapping of the B-K edge recorded along the (001) q-direction. Second, we will show that by gathering spectra in the high symmetry directions, we can probe the whole Brillouin zone and represent the plasmon dispersion as a function of the q momentum transferred to the h-BN layers.

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