Exfoliated Black Phosphorus: Raman Analysis and Degradation Process in Ambient Conditions

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Black Phosphorus (bP), a lamellar crystal of tetravalent P atoms stacked by weak van der Waals interactions, has attracted interest because two-dimensional confinement leading to high carrier mobility and tunable direct band gap has been observed in exfoliated thin layers. Studying the properties of exfoliated bP is, however, challenging because of a fast degradation upon exposure to ambient conditions. This talk presents experimental insights about the degradation process of bP and covers the various signatures in the Raman spectra of pristine and degraded samples. [1,2] In the first part, we take advantage of a procedure carried out in a glove box to acquire the Raman response of the layers in their pristine states. Raman spectra of mono-, bi- and multilayered bP (Figure 1) show important signatures of layer confinement that can be readily understood using symmetry and mode analyses. In the second part, we investigate the stability and degradation of the layers using TEM-EELS, LEEM, AFM and *in-situ* Raman spectroscopy. The experiments reveal that a combination of oxygen, light and moisture provides the essential ingredients leading to the oxidation of the layers. They also highlight a surprising thickness dependence of this photo-oxidation reaction, which behavior is consistent with an electron transfer model (redox reaction) that predict a kinetics influenced by quantum confinement. To gain further insights, we probe the influence of this degradation on the wetting properties of thin bP films in different humidity conditions. A statistical analysis of the formation of bubbles at the surface shows a decrease of the wettability of the surface with layer thickness. This behavior is ascribed to the accumulation of phosphoric acid in the bubbles due to degradation. From our analysis of the results and a simple rate equation model, it is found that: i) A threshold humidity is necessary for water condensation; ii) The photo-oxidation occurs on single bubble sites; iii) bP layers immersed in water slowly thickens and crumbles anisotropically due to degradation and water etching. Finally, we show that the level of degradation in ultrathin layers can be directly measured using the A_g^1/A_g^2 intensity ratio in the Raman spectra - higher the ratio (>0.2) indicates lower degradation level.

References

[1] A. Favron et al, Arxiv-1408.035v2 (2014)
[2] A. Favron et al., Nature Materials, **14**, 826-832 (2015).

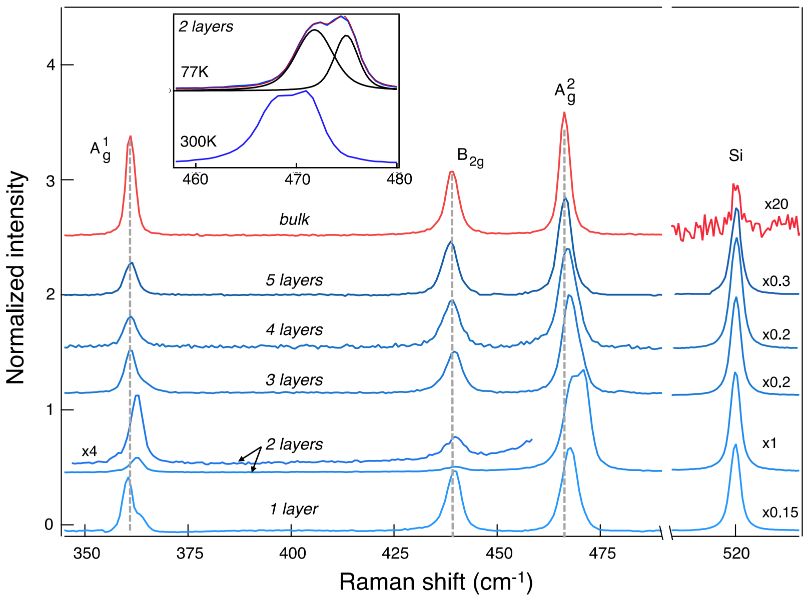

Figure 1 – Raman spectra of bP layers. Highlighted (inset) is the splitting of the A^2_g mode and the enhancement of the Raman intensity for the bilayer.