

Structural and low-loss characterization of synthetic 2D-TMDs

Nalin Mehta, A.^{1,2}, Groven, B.^{1,3}, Chiappe, D.¹, Favia, P.¹, Bender, H.¹, Delabie, A.^{1,3}, Caymax, M.¹ and Vandervorst, W.^{1,2}

¹ Imec, Kapeldreef 75, 3001 Leuven, Belgium, ² Department of Physics and Astronomy, KU Leuven, 3001 Leuven, Belgium, ³ Department of Chemistry, KU Leuven, 3001 Leuven, Belgium

Two-dimensional transition metal dichalcogenides (2D-TMDs) have attracted significant attention in recent years due to unique optical and electronic properties arising from their low-dimensionality. Among them, MoS₂ and WS₂ are the most investigated 2D-TMDs and have been demonstrated to be good candidates for opto- and nano-electronic applications. The material properties depend strongly on the atomic structure of the material and vary significantly with increasing number of layers and their stacking w.r.t. each other. While aberration correction in a scanning transmission electron microscope (STEM) allows for atomic resolution imaging of these two-dimensional materials, recent advances in monochromators in modern TEMs has enabled an energy resolution of under 150meV for EELS (electron energy loss spectroscopy). This improved energy resolution in EELS helps reduce the zero-loss tail and aids in resolving the interband transitions, band-gap onset, surface and bulk plasmons. EELS in an aberration corrected STEM is therefore the only spectroscopic technique with the potential to provide insight into the chemical and electronic structures with atomic-resolution whereas optical spectroscopy techniques are constrained by the diffraction limit.

In this work, we investigate two synthetic 2D-TMDs, namely MoS₂ and WS₂ which are deposited using wafer-scale chemical vapor deposition (CVD) techniques. The MoS₂ is grown using Mo(CO)₆ at high-temperatures (> 700C), whereas WS₂ is grown using WF₆ at relatively low-temperatures (450C) where H₂S is the sulfur source in both cases. The material is transferred onto TEM grids and investigated in a double-corrected Titan G2 equipped with a monochromator, operated at 60kV to avoid beam damage. High-resolution STEM is used to characterize the crystal structure, local stacking and various crystal defects present in the material. Fig. 1 a. shows the HAADF-STEM image of CVD-WS₂ grown on amorphous Al₂O₃ which has a full monolayer coverage with some triangular islands which are 2-3 layers thick. The atomic resolution STEM image (Fig. 1b) on one of the islands shows the variation in thickness and stacking in a CVD-WS₂ layer. Low-loss spectra shown in Fig. 2 are acquired in spectrum-imaging mode and several spectra are integrated from regions with varying number of layers (1 to 3) which are distinguished based on HAADF intensities. A blue shift in the energy-loss is evident as the number of layer increases where the shift in $\pi+\sigma$ plasmon peak is much more pronounced than the π plasmon peak. Moreover, the ratio between the peak intensities of the π and $\pi+\sigma$ plasmon decreases with increasing number of layers. This is in good agreement with previous theoretical studies [1], [2]. These results will be discussed in depth to gain insight into the opto-electronic properties of synthetic 2D-TMDs and how they vary with local crystal structure.

[1] P. Johari and V. B. Shenoy, "Tunable dielectric properties of transition metal dichalcogenides," in *ACS Nano*, 5, 5903 - 5908 (2011).

[2] A. Kumar and P. K. Ahluwalia, "Tunable dielectric response of transition metals dichalcogenides MX₂ (M=Mo, W; X=S, Se, Te): Effect of quantum confinement," *Phys. B Condens. Matter*, 407, 4627 - 4634 (2012).

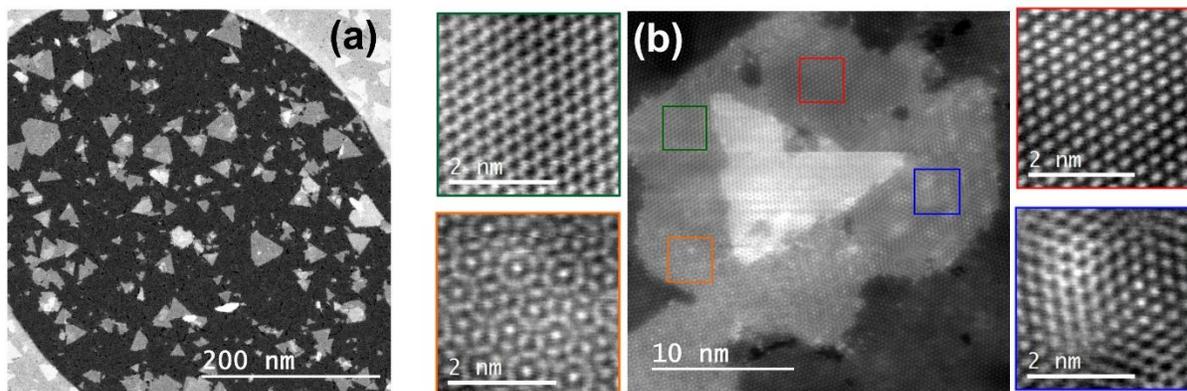


Figure 1: (a) HAADF-STEM image of monolayer CVD-WS₂ with 2-3 layers thick islands grown over the first layer. (b) Atomic resolution HAADF-STEM image of one of the islands showing the variation in thickness and stacking.

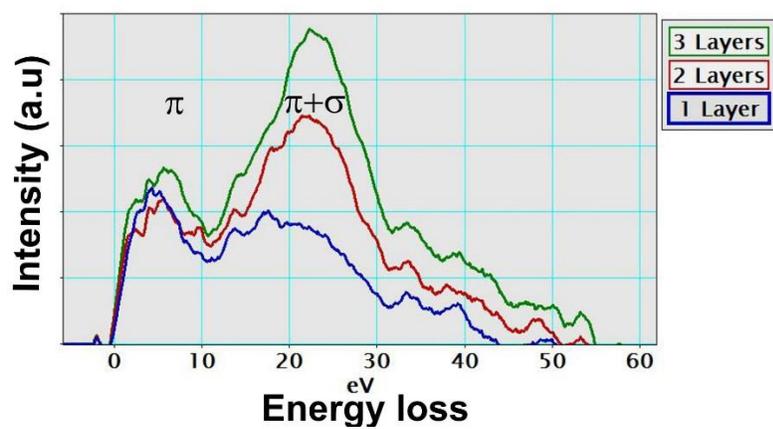


Figure 2: Low-loss EELS spectra of CVD-WS₂ showing evolution of the π and $\pi + \sigma$ plasmon peaks as a function of layer thickness.