Low-Loss EELS Investigations on Atomically Thin $Mo_xW_{(1-x)}S_2$ Nanoflakes for Delving into Their Optoelectronic Properties

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For more than a decade, the scientific community has developed a broadening interest in atomically thin 2D materials; due to their attractive mechanical, thermal and electronic properties [1]. Within this family of materials, transition metal dichalcogenides (TMD) have been on the peak of this research interest lately [2-6]. These materials present a TX_2 type where T is a transition metal of groups IV, V or VI, and X stands for a chalcogen (S, Se or Te) [7].

Focusing on their electronic properties, a point of great interest application-wise is band gap tuning. In bulk, materials, one of the major techniques used for this purpose consists on alloying materials with different band gaps [3, 4]. Up until now, the only atomically thin alloy types reported for TMDs have been of the $Mo_xW_{(1-x)}Se_2$ [3] or the $Mo_xW_{(1-X)}S_2$ [4] . For the second one, evidence of a band gap shift with the alloying degree in monolayers has been found. This evidence is supported both theoretically (by density functional theory (DFT)) and experimentally (via photoluminescence).

Electron energy-loss spectroscopy (EELS), when focused on low-losses (< 50 eV), can offer the possibility to analyze the optoelectronic properties of materials. When performed in a TEM, this technique has been proven to be an excellent optical absorption spectroscopy tool at the nanoscale [5,6,8,9]. This opens up the possibility not only to perform this kind of studies for different alloying degrees, but for different stacks of layers in the same material.

For this study, $Mo_xW_{(1-x)}S_2$ single crystals with various alloying degrees (x=0, 0.3, 0.5, 0.7, 1) have been grown by chemical vapor transport[4]. The crystals have been mechanically exfoliated and transferred onto TEM grids. The alloying degree of the samples has been characterized using STEM, by deducing the ratio of Mo and W by the different intensities in STEM of both elements [4].

Then, low-loss EELS has been performed in a FEI Titan Low-Base probe-corrected TEM equipped with a monochromator at 80 keV, providing an energy resolution of ~0.2 eV. For this, areas showing stacks of few layers were selected and identified using optical and low-magnification TEM images (see Figure 1.a). In these regions, the spectrum-line (SPLI) acquisition mode was used to take several EEL spectra over several stacks of layers. For each region showing the same number of layers (plateau/steps shown in figure 1.b.), spectra over spatial regions ranging between 5 and 30 nm were integrated. After zero loss peak removal [8,9] different features have been analyzed for the resulting spectra, which can be seen in Figure 1.c. For several stacks showing a different number of layers in each one of the alloying degrees, the band gap feature has been studied using a linear fit. In these alloys, this feature appears between 1.5 and 2 eV altogether with the A, B exciton peaks [3]. Furthermore, two other peaks, which have already been identified as features resulting from Van Hove singularities and another exciton (C) for MoS_2 [10] (α and β in figure 1.c), have been studied in the same areas.

The results for these analyses are shown in Figure 2. Regarding the band gap zone (figure 2.a), even though there is no unequivocal proof of a correspondence between the number of layers of each stack and its band gap behavior, there is a clear correlation between the average gap of each sample and its alloying degree, As for the features related to Van Hove singularities (Figure 2.b and 2.c), there is a measurable shift of the peaks when modifying the number of layers within the same alloying degree. However, the shift of these peaks with the alloying degree is not conclusive except for MoS_2.

To conclude, this study delves deeper into the optoelectronic properties of atomically thin 2D layer TMD alloys unveiling potential future applications for this kind of materials [11].

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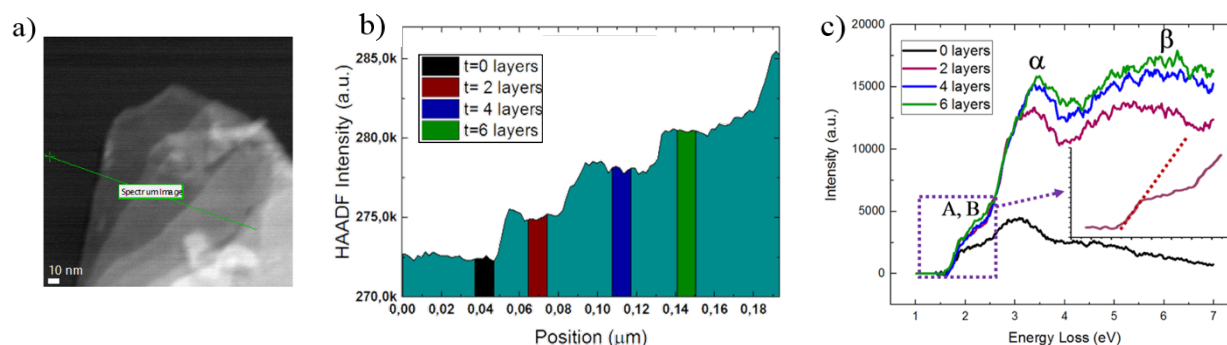
Figure 1.   a) HAADF-STEM micrograph of a $Mo_xW_{(1-x)}S_2$ sample flake showing a SPLI. b) Intensity profile obtained in Fig. 1a, highlighting the plateaus where the EEL spectra have been integrated. c) Integrated EEL spectra showing the band gap region (purple square) and the α and β Van Hove features.
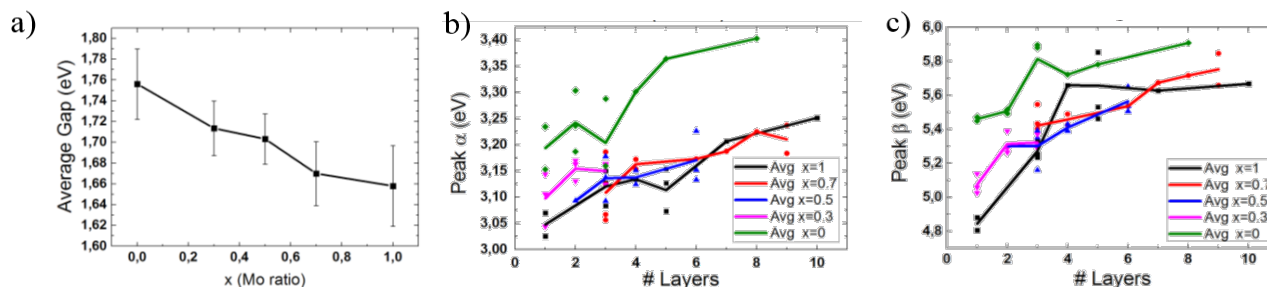

Figure 2.   a) Average gap measured for different alloying degrees. b) and c) Behavior of the α (and C exciton) and β peaks (respectively), related to Van Hove singularities, with the alloying degree and the number of layers.