

Correlation of structural, nanomechanical and electrostatic properties of single and few-layers MoS₂

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Abstract

Layered transition metal dichalcogenides have attracted significant attention due to their potential applications in electronic and optical devices [1]. Molybdenum disulphide (MoS₂) is one of the most stable layered materials of this class. In the bulk form this semiconductor material has an indirect band gap of 1.3 eV and is used in a broad range of diverse applications, e.g. as a photocatalyst and dry lubricant, as well as for photovoltaic power generation and photo-electrochemical hydrogen and Li ion batteries production. Monolayer MoS₂ has a 1.8 eV direct band gap and prominent electro- and photoluminescent properties, making it a likely candidate for applications in photodetectors and light-emitting devices operating in the visible range [2]. Additionally, single layer MoS₂-based field-effect transistors demonstrated very promising electronic characteristics, such as a large current on/off ratio and sub-threshold swing [3].

As electronic and optical properties of MoS₂ are strongly thickness dependent, it is essential to precisely ascribe the measured parameters to individual layers. Raman spectroscopy has been widely used to determine the number of layers and examine the relevant changes in material properties, as the vibrational spectrum is sensitive to the sample thickness. On the other hand, surface potential of layered materials is also strongly dependent on the number of layers [4] and the nanomechanical properties of those layers, arising from both intrinsic structure and defects as well as from the sample-substrate interface. Here, we perform mapping of mechanically exfoliated MoS₂ flakes with the aim to precisely correlate their structural, nanomechanical and electrostatic properties on the nanoscale.

The MoS₂ layers were formed by a standard mechanical exfoliation process. Single- and few-layer MoS₂ flakes were deposited from bulk crystals onto Au substrates. The properties of the samples were investigated using Scanning Kelvin Probe Microscopy (SKPM), Ultrasonic Force Microscopy (UFM) and Raman spectroscopy mapping. The surface potential (V_{CPD}) measurements have been performed by SKPM, which also provided information on sample morphology, as well as a quantitative determination of the local thickness of MoS₂. The results are directly linked to Raman spectroscopy.

Thickness of individual flakes was defined using AFM, where the 1st layer on the substrate has a thickness of ~1 nm. Consequent layers thicknesses have been estimated considering an interlayer separation of 0.7 nm, and correspond to 1, 5, 8 layers and bulk, respectively for the flake presented here (Figure 1a). Typical Raman spectra obtained for the same flake are shown in Figure 1f. Two prominent peaks are attributed to E_{2g}¹ (opposite vibration of two S atoms with respect to Mo) and A_{1g} (out of plane vibration of S atoms in opposite directions), respectively. As the number of layers increases, E_{2g}¹ vibration softens, while the A_{1g} vibration stiffens, i.e. the Raman shift between E_{2g}¹ and A_{1g} modes becomes generally larger in good agreement with previous results [5]. Figures 1d and 1e show the Raman mapping images of E_{2g}¹ and A_{1g} intensities, respectively, using 532 nm laser line. The maps clearly indicate the same thickness-dependent trends as observed in the individual spectra, allowing us to use such maps for a clear indication of the layer thickness. Moreover, the intensities of both modes, while being generally homogeneous within each individual flake, show a clear change of the contrast at the flake border, i.e. increasing/decreasing for E_{2g}¹ and A_{1g} modes, respectively. This behaviour reflects the defective nature and possible inhomogeneity of the chemical composition of the thick flake boundaries. Overall, Raman spectroscopy results suggest a role for stacking-induced changes in intralayer bonding and a combination of van der Waals and Coulomb interlayer interactions [5].

Nanomechanical mapping was performed using UFM with a sample vibration of low amplitude (5-10 Å) and very high frequency (~4 MHz), which makes the cantilever dynamically extremely rigid at the ultrasonic frequency and allows the probing of very stiff materials (k in range up to 10,000 N/m). We observe nanomechanical variations across the MoS₂ flakes, which appear linked to the thickness-dependent sample-substrate interface. For example, significantly larger variations, including the presence of small delaminated or freestanding areas, are observed in the 1L region compared to the thicker areas of material (Figure 1c where the brighter contrast corresponds to mechanically stiffer areas).

Surface potential mapping of the same flake is presented in Figure 1b. For the entire MoS₂ crystal, the contact potential difference value, V_{CPD} is significantly lower than that of the gold substrate, where V_{CPD} of 1L is being notably the lowest. The absolute V_{CPD} value increases with the layer thickness, though the bulk value is compromised by decoration of the surface by environmental adsorbates, leading to a modification of the surface potential. With this exception, distribution of the surface potential within each layer is homogeneous. Additionally, relatively larger V_{CPD} value has been measured at the thick flake boundaries, which can be attributed to the presence of chemically active sides similar to the graphene case.

In conclusion, we have performed a comprehensive study of structural, nanomechanical and electrostatic properties of MoS₂ in dependence on the layer thickness. These results and a detailed understanding of the layer properties are essential for potential optoelectronic applications.

References

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Figures

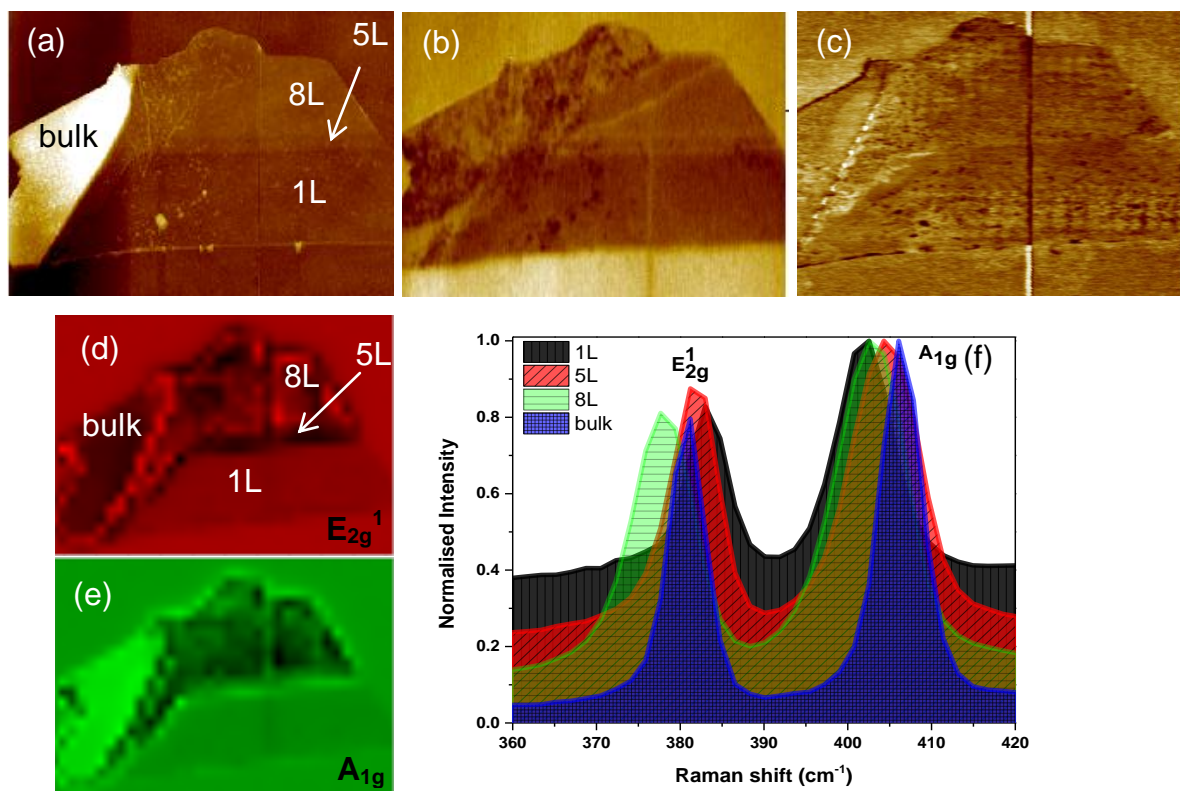


Figure 1. Topography (a) and surface potential (b) images of MoS₂ flake acquired using SKPM, indicating the number of constituent layers and the corresponding UFM nanomechanical response (c). Scan size is (10x7) μm^2 . Raman intensity maps based on E_{2g}¹ (d) and A_{1g} (e) intensities for the same flake and representative Raman spectra for different thicknesses of the MoS₂ flake (f).