

Ultrathin MoS₂ Membranes and Their Characterization Through HRTEM and Electron Diffraction Studies

J. Brivio¹, D.T.L. Alexander² and A. Kis¹

¹ Electrical Engineering Institute, EPFL, Lausanne 1005 CH

² Interdisciplinary Center for Electron Microscopy (CIME), EPFL, Lausanne 1005 CH

Molybdenum disulphide (MoS₂) is a layered material belonging to the metal dichalcogenide family which has been the subject of dislocations studies and polymorph identification by electron microscopy [1],[2]. MoS₂ has also been investigated for practical applications as a catalyst and as a lubricant. Due to the weak Van der Waals interactions between its layers, MoS₂ can be exfoliated into single layers in the same way as graphene. The important difference among graphene and MoS₂ is that, while the former in its pristine form is a semi-metal, the latter is a semiconductor. For this reason, recently the focus of our research has shifted to single layer MoS₂ (1L-MoS₂) which, with a direct band-gap of 1.8eV, is a candidate for future ultrathin electronic and optoelectronic devices [3].

The subject of the present study is 1L and few layers MoS₂ flakes. A key aspect of the work is the correlative optical, atomic and transmission electron microscopy characterization of the same MoS₂ flake. First, depositing MoS₂ flakes on a thick substrate allows their thickness determination by optical contrast and atomic force microscopy (AFM). Next, in order to achieve the electron transparency necessary for TEM studies, we developed a transfer technique that allows moving a selected flake onto a patterned 20 nm thick Si₃N₄ membrane on which electron diffraction and HRTEM experiments are performed. A holder compatible with our samples was designed and assembled for TEM observation in a commercially available microscope. Figure 1 shows a MoS₂ single layer flake before and after its transfer onto the electron transparent substrate. HRTEM and SAED observations allowed determination of the lattice parameters, which are found to be the same among the 1L and thicker flakes. However, we observe an important distinction between diffraction patterns acquired from single and multilayer MoS₂, which is due to symmetry breaking and can be used to identify single layers using only TEM. Diffraction spots belonging to the same {1100} family show systematically modulated intensities in the case of single-layer flakes, whereas in the case of 2L and multilayer MoS₂ the intensities are invariant. This difference arises from a symmetry-breaking effect of the 1L form of MoS₂, which loses the six-fold symmetry of the bulk crystal. Confirmed by simulation, this effect gives an easy method of identifying single layers using TEM [4]. As for graphene, we are also able to distinguish between 1L and thicker MoS₂ flakes observing how significantly diffraction spot intensities change while tilting the sample [5]. The flake thickness can be also determined without tilting the sample by HRTEM observation of the edges, as shown in Figure 2. Near the edges the flakes are often folded back on themselves, making it possible to obtain information about the vertical stacking. Not only it is possible to count the number of layers, but it is also possible to observe and measure the relative rotation or twisting between different layers at the fold. In the presentation we shall also discuss the possibility that using a high contrast (Cs = 2 mm) pole piece allows the observation of contrast associated with nm-scale height undulations (ripples) in lattice images of monolayer and bilayer MoS₂ flakes, that would not be apparent using Cs-corrected imaging.

Together with graphene, the isolation of single-layer MoS_2 will improve our knowledge of 2D systems and expand their field of applications [5]. Moreover, the fabrication of suspended MoS_2 membranes enables further electron microscopy studies of this material, currently being planned.

References

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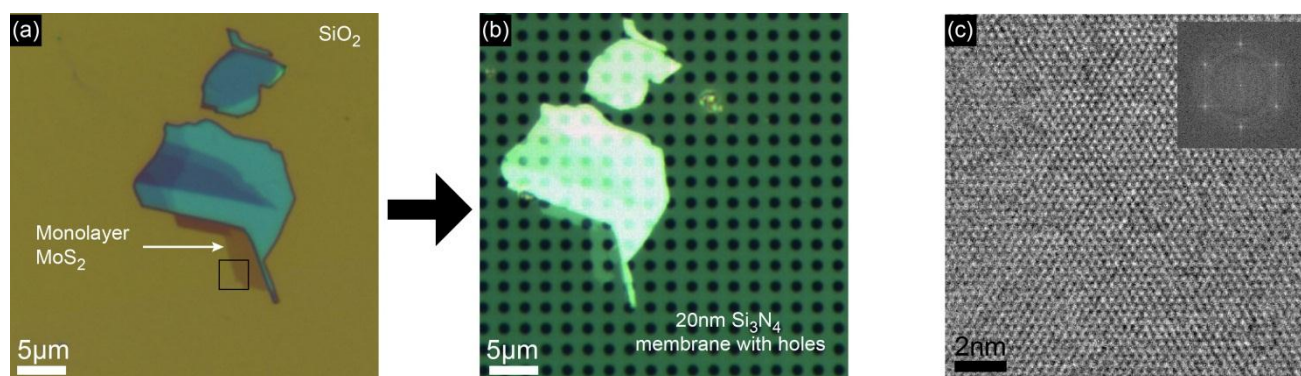


Figure 1. 1L- MoS_2 layers are exfoliated on SiO_2 substrates (a) and transferred on the Si_3N_4 membranes after optical and AFM thickness determination (b). (c) HRTEM image of the 1L region.

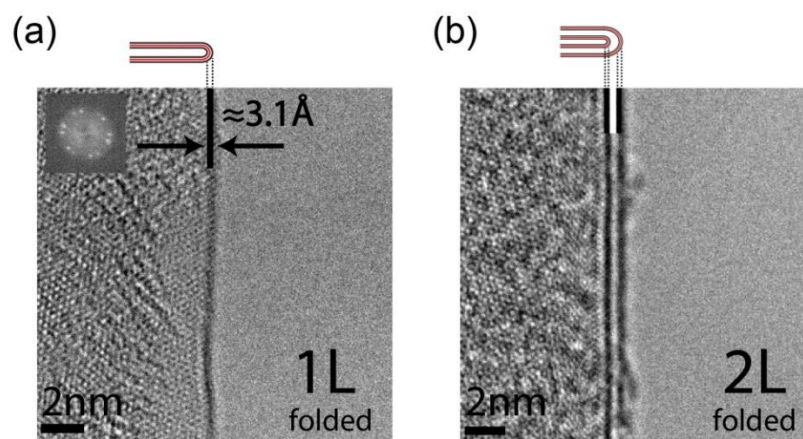


Figure 2. HRTEM images of flake edges. (a), 1L flake edge showing the characteristic folding which appears as a dark fringe. The inset shows the diffractogram of the folded region. The two crystals are rotated with respect to each other. (b) 2L folded edges showing a higher number of fringes.