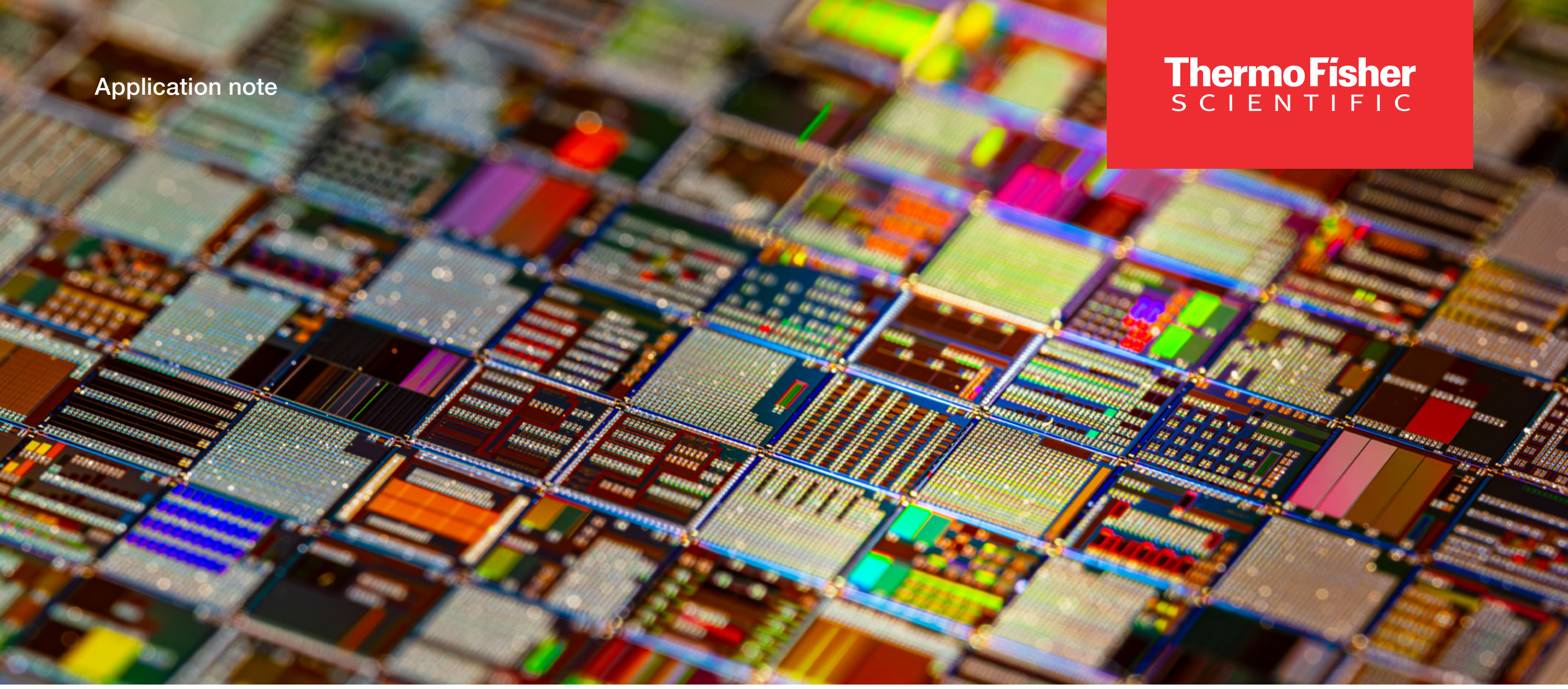

Raman Spectroscopy: Deciphering the Structural Dynamics of 2D Semiconductors

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Industry/Application:
Semiconductor, Material Science

Product Used:
Thermo Scientific DXR3xi Raman Imaging Microscope

Goal:
Study the peak structure of low-dimensional semiconductors

Introduction

Semiconductors form the foundation of all modern electronics. As industries constantly seek to make their technological devices even smaller and more efficient, and manufacturers continue to strive for more compact device architectures, the key to future develops may prove to be new, thin film materials. Thin film or two-dimensional (2D) semiconductors have unique properties and perform robustly even at monolayer thicknesses, allowing for complex electronic device performance at extremely small scale.[1] For example, the current silicon “2 nm” transistors used in the semiconductor industry have channel lengths of 10+ nm. Studies on 2D semiconductor transistors, especially MoS_2, show promising scalability to physical channel lengths below a 5 nm threshold—less than half the size of current transistors.[1] These materials have very well-defined crystal structures which make them excellent candidates for characterization through Raman spectroscopy. A common class of these materials is the transition metal dichalcogenide (TMDC) family such as molybdenum disulfide (MoS_2).[2,3] 2D semiconductors, like TDMCs, are characterized by two major structural elements: the in-plane lattice bonds and out-of-plane van der Waals (vdW) forces that bind the stacked layers of crystalline monolayers.[2]

Crystal Structure and Raman Signal

A naturally formed sample of MoS_2 is studied here using the Thermo Scientific DXR3xi Raman Imaging Microscope with a 455 nm excitation laser. The MoS_2 is manually exfoliated to thin the crystals from bulk form down to a two-dimensional, thin film layer.[3] This creates a very simple crystalline structure with simple vibrational modes. Indeed, MoS_2 has only two dominant Raman peaks, the E^1_{2g}, in-plane vibration at 381 cm^{-1}, driven by the lateral oscillation of S atoms, and the A_{1g}, out-of-plane mode at 408 cm^{-1}.[4] In thin / 2D samples, the A_{1g} peak (linked to the out-of-plane S vibrations) is significantly weaker than it is in the bulk crystal due to many fewer vdW forces between the layers (Figure 1). This out-of-plane peak also displays a redshift (to lower wavenumber values) in the thinner samples (Figure 2).[4] By taking a single crystal and repeatedly thinning it we can see the clear trend in these spectral changes produced by manual exfoliation (Table 1).

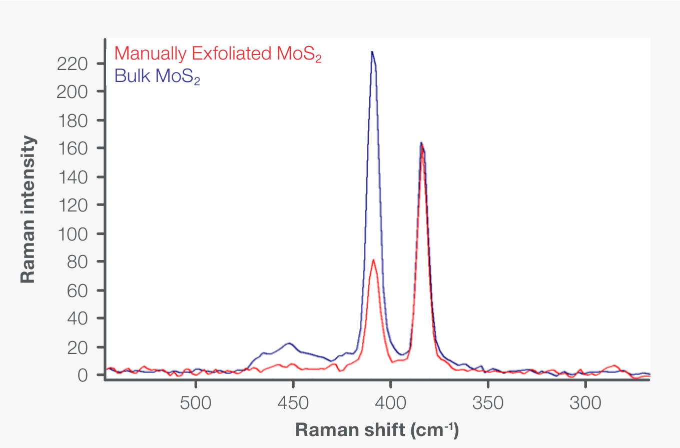

Figure 1. A comparison of bulk and manually exfoliated, 2D MoS_2 shown in common-scale. The in-plane E^1_{2g} peak shows the same intensity in both crystals while the out-of-plane A_{1g} peak decreases by a factor of 2.8 in the 2D crystal.

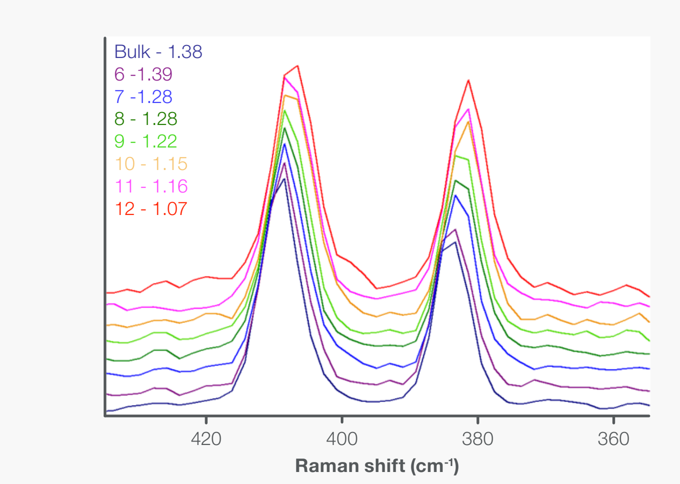

Figure 2. A series of numbered manual exfoliations of the same crystal. (Up through the 6th iteration there is no change in Raman response and those results are omitted for clarity.) Decreasing thickness of the crystals produces a decrease in the A_{1g} to E^1_{2g} peak ratio and a redshift of the out-of-plane peaks.

Number of Exfoliations	A_{1g} / E^1_{2g} Peak Ratio	A_{1g} Peak Position (Shift)**
None (Bulk Crystal)	1.38	409.09 (0.00) cm^{-1}
6*	1.39	408.66 (-0.43) cm^{-1}
7	1.28	408.30 (-0.79) cm^{-1}
8	1.28	408.12 (-0.97) cm^{-1}
9	1.22	407.84 (-1.25) cm^{-1}
10	1.15	407.29 (-1.80) cm^{-1}
11	1.16	407.47 (-1.62) cm^{-1}
12	1.07	407.06 (-2.03) cm^{-1}

* All exfoliation steps up to 6 are bulk MoS_2 with no variation in the A_{1g} / E^1_{2g} peak ratio.
** Peaks were fitted with a Gaussian profile to find the peak position.

Table 1. Raman spectral analysis was performed on increasingly thin layers below the bulk/2D threshold, showing the decreasing out-of-plane A_{1g} peak intensity (relative to the in-plane E^1_{2g} peak), alongside the redshift of the A_{1g} peak.

Tracking Crystal Thickness

Within crystals, especially in naturally formed crystals, a single region may fragment during repeated exfoliations and result in non-uniform layer thickness. In such situations, optical image analysis is insufficient to determine anything about layer thickness. This makes the Raman spectra an invaluable tool in analyzing the thickness and structure of layers. Figure 3 shows a single 2D crystal region, with various areas marked to highlight the spots analyzed.

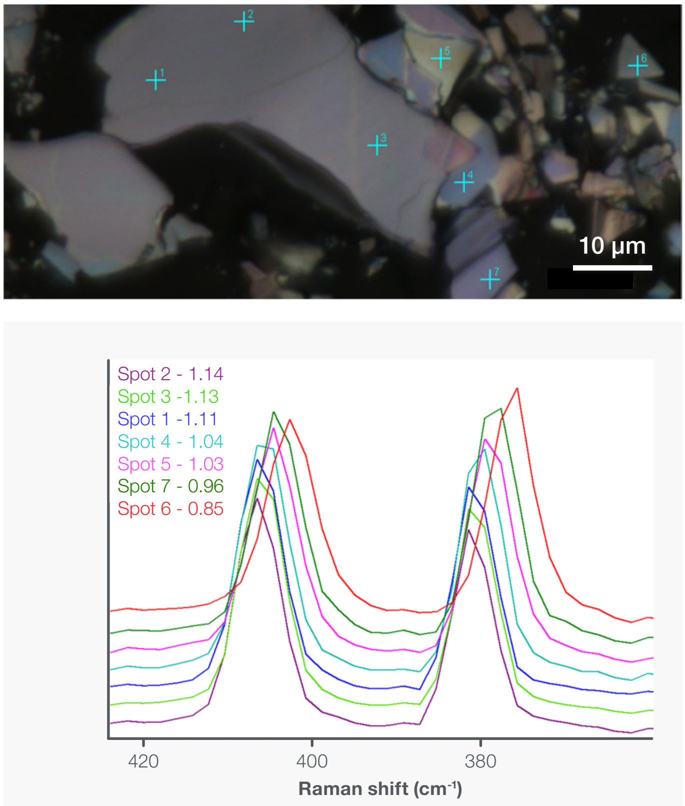

Figure 3. This MoS_2 crystal cluster was manually exfoliated 20 times, with multiple crystal faces of varying thicknesses. Although the entire surface is subjected to repeated thinning, there are still differences in crystal thickness as evidenced by the point spectra, with varying ratios of in- and out-of-plane peak intensities as well as peak positions. As a rule of thumb, the smaller crystals are thinner with a stronger relative in-plane peak.

Tracking Structural Variations

The Raman peaks of MoS_2 can reveal much more information than simply layer thickness. The shifting ratio of the out-of-plane A_{1g} peak to the in-plane E^1_{2g} peak can be used to study interlayer physics in these 2D crystal structures. For example, a Raman peak ratio analysis can reveal interfacial boundary conditions (Figure 4). In this sample, there is a stronger out-of-plane component to the lattice vibration along the crystal face boundaries. Given that there are no obvious peak shifts from differing layer thicknesses, the increased vdW forces at the boundaries may be due to another phenomena, such as a localized electronic charge accumulation in the boundary region.

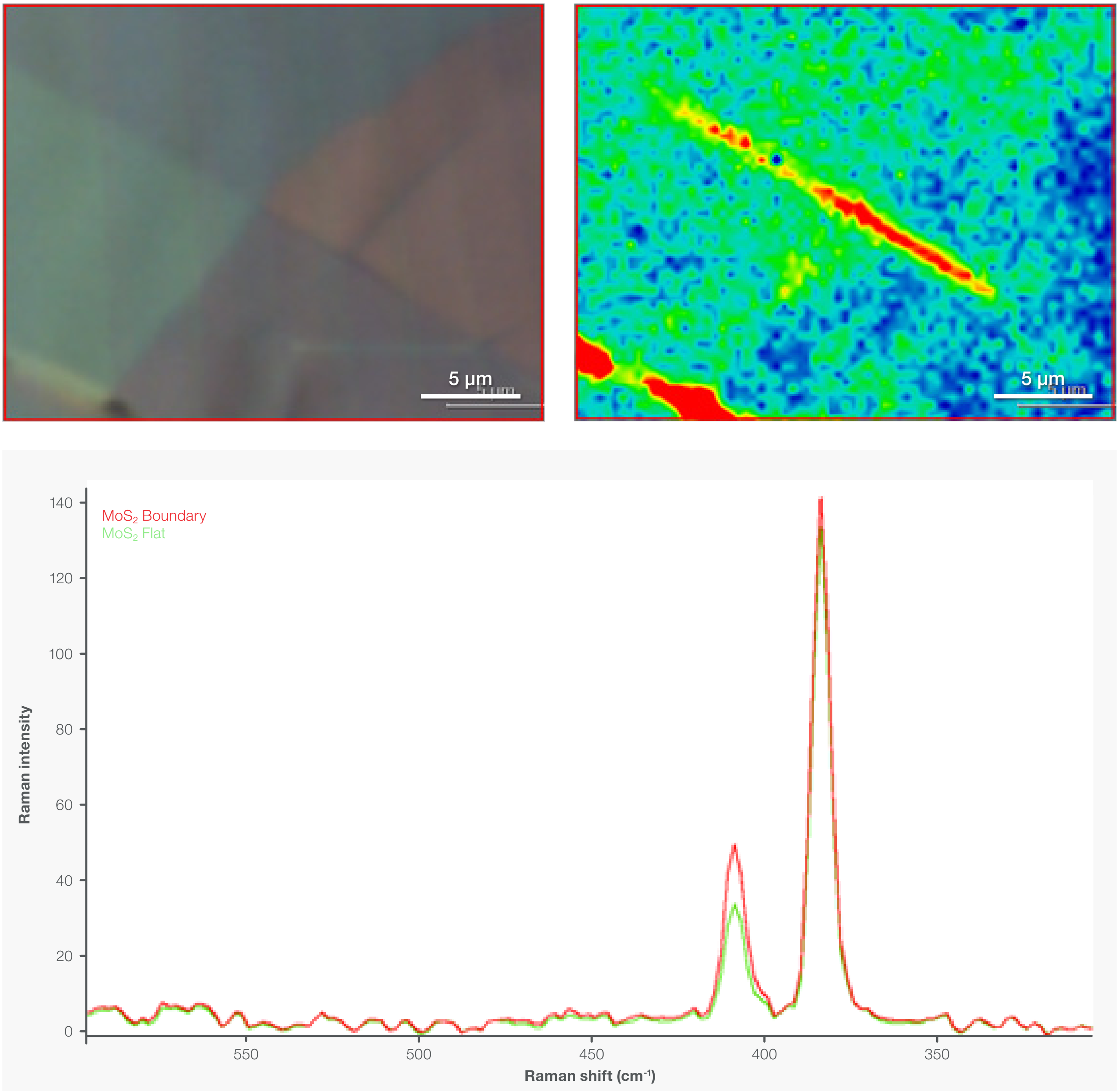

Figure 4. Optical (top left) and chemical (top right) images of the MoS_2 surface across a region of various crystal faces, with associated spectra (bottom) taken from the smooth surface and boundary regions respectively.

Studying Mechanical Strain

When working with 2D materials, it is important to note that peak shifts are dependent not only on multilayer thickness. Mechanical strain can have a significant impact on the Raman signal. This strain can be specifically applied by depositing 2D crystals over rough surfaces, or it can occur accidentally during device fabrication. Shown below is a layer that was wrinkled during exfoliation; this wrinkle is visible in the optical image on the left-hand side (Figure 5). The wrinkled region is across a single crystal plane with a uniform out-of-plane to in-plane ratio. Although the region of interest has uniform thickness, there is still a peak shift occurring across the stressed folds visible in the Raman chemical map.

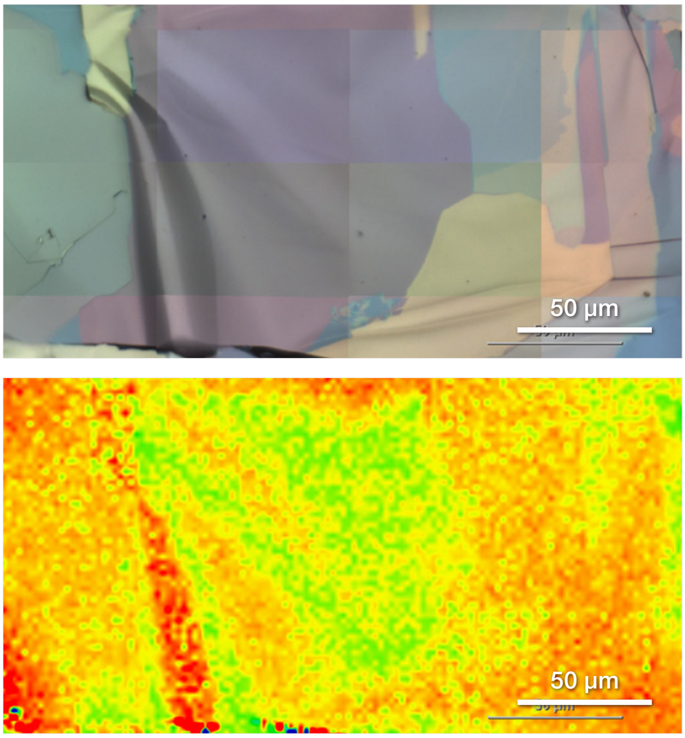

Figure 5. The optical (top) and chemical (bottom) images show a 2D exfoliated layer with a wrinkled surface contributing to mechanical stress and strain. The chemical image shows a peak shift of the in-plane E^1_{2g} mode between 380 (blue) and 385 (red).

Conclusion

Even with a seemingly simple molecular structure such as MoS_2 there is a huge wealth of information that can be gleaned from Raman spectroscopic analysis. Layer thicknesses, interlayer forces, and in-plane strain can all be quickly analyzed based on the two MoS_2 peaks. Monitoring changes in these in-plane and out-of-plane vibrations for this 2D semiconductor allows a researcher to characterize numerous properties with a rapid, non-destructive analysis.

References:

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