Multi-modal analysis of 2D materials with the XPS-SEM CISA Workflow

2D materials

Single-layer 2-dimensional materials are actively being investigated across a wide range of fields due to the unique properties they exhibit compared to their bulk equivalents. Materials such as molybdenum disulfide (MoS_2) and graphene, for instance, are seeing potential uses in electronics, medicine, and composite materials. Notably, the properties of 2D materials can be tailored to specific applications through careful modification of their surface chemistry and structure. In order to fully understand these materials and monitor their chemistry, multi-modal observation is often necessary, pairing multiple imaging and analysis techniques to deconvolute molecular-scale changes.

In this application note, single-layer MoS_2, deposited on a silicon oxide surface, was analyzed using the Thermo Scientific Correlative Imaging and Surface Analysis (CISA) Workflow. CISA combines scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS) instrumentation into a single, correlated workflow that can not only provide imaging and surface analysis but can also incorporate complimentary techniques, such as Raman spectroscopy.

While SEM can easily visualize 2D materials, these layers are typically too thin to be easily characterized with energy-dispersive X-ray (EDX) analysis. XPS, meanwhile, cannot easily resolve surface structures, but can clearly detect what material is present and quantify any chemical changes that might occur to it. XPS instrumentation, like the Thermo Scientific™ Nexsa™ G2 Surface Analysis System, can also incorporate a Raman spectrometer that is coincident with the XPS analysis position. The addition of Raman spectroscopy can enhance the analysis of defects and provide a clear idea of the number of layers of a 2D material that are present.

By combining these complementary tools, CISA is capable of providing comprehensive information about the distribution and composition of 2D materials.

XPS-Raman analysis of MoS_2
Elemental quantification with small spot XPS

Two areas of a MoS_2 sample were investigated. The first, indicated by the red square in Figure 1, was imaged using the XPS SnapMap capability of the Nexsa G2 System. This rapidly acquires data across a defined area, with a corresponding spectrum collected at each pixel. Once the image is processed, the concentration of Mo can be seen across the region. The sample was expected to have a uniform, homogeneous layer of MoS_2 across the surface, indicated by a Mo 3d peak; however, from the image it appears to be patchy, with light areas representing a strong Mo signal and dark areas representing weak or no signal.

Analysis positions at light (P1) and dark (P2) areas were chosen; XPS survey spectra and elemental quantification for these positions is shown in Figure 1. These results indicated that MoS_2 is present at P1 and absent at P2. High-resolution scans were also acquired to determine which chemical states were present. The S2p data showed the expected metal sulfide while the Mo 3d data showed that there was MoS_2, but also MoO_3, present.
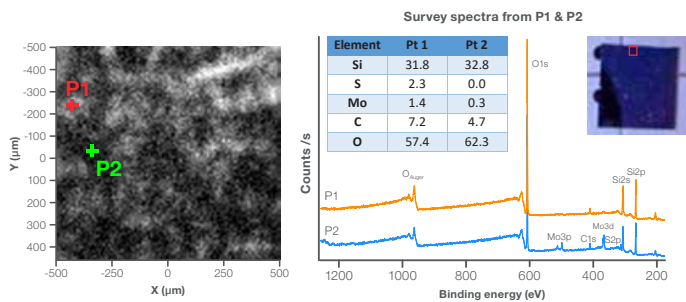
Figure 1. Left: XPS SnapMap of the MoS₂ surface recorded at the location indicated by the red box (inset, top right). Right: Elemental distribution and XPS spectra at P1 and P2, marked by crosses in the SnapMap image.
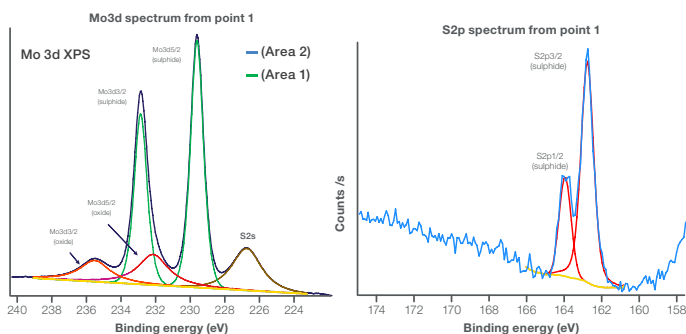

Figure 2. High-resolution XPS spectra for Mo3d and S2p recorded at P1 in the SnapMap image. Two bonding states of molybdenum were observed on the light-colored flake: sulfide and oxide (Mo^{6+}).

Mo$_{sulphide}$	Mo^{6+}	S
30.7%	10.6%	58.8%

Table 1. Chemical quantification of the MoS₂ sample

Analyzing layer thickness with Raman spectroscopy

Raman spectra were collected at P1 and P2 and then compared to a bulk reference of MoS₂. As with XPS, no signal for MoS₂ was seen at P2. A spectrum was recorded at P1, which showed different splitting of the two Raman peaks compared to the bulk material. This indicates that there is likely an ultra-thin sheet of MoS₂ present, potentially just a single atomic layer.
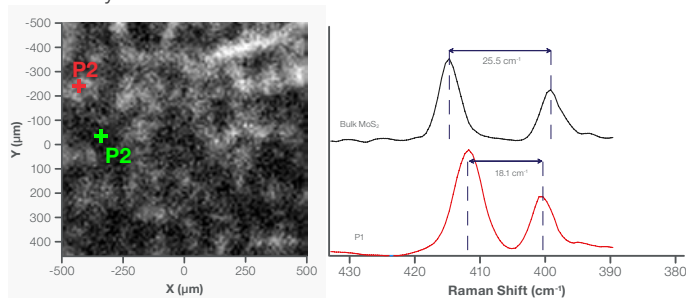

Figure 3. Left: XPS SnapMap of the MoS₂ surface recorded at the location indicated by the red box (inset, top right). Right: Raman spectra collected at P1 and MoS₂. The P1 splitting peaks were compared to a reference spectrum of bulk MoS₂; this suggests that the material is likely present in an ultra-thin layer.

The same analysis was performed on a second portion of the sample (Figure 4, Area 2). Here, there was a much more uniform appearance to the layer, as evidenced from the Mo$_{3d}$ XPS SnapMap image. The XPS spectra indicate that there is slightly more oxidation here as well, which is shown by the increase in the oxide peak in Figure 5 (left, arrow). The Raman data suggests that the number of layers is greater than in the first area, as the separation between the two peaks in the Raman spectrum is greater than in P1, although it is still not as wide as in the bulk material.
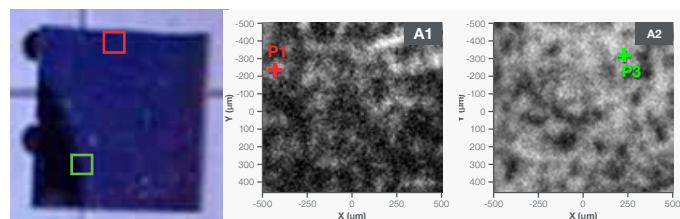

Figure 4. Left: Recording locations on the MoS₂ modified sample surface. Middle: XPS SnapMap recorded at the red square. Right: XPS SnapMap recorded at the green square.
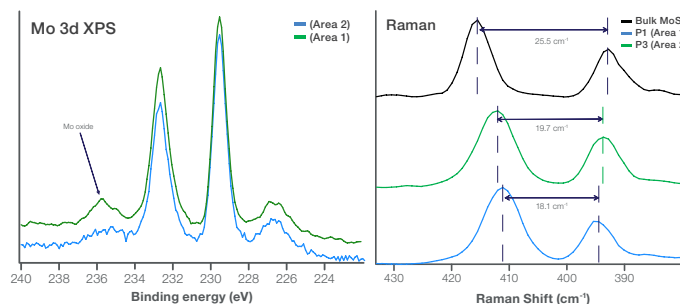

Figure 5. Left: Increased oxidation seen in Area 2 (P3) (arrow). Right: Increased separation between the two Raman peaks suggests an increase in the number of layers.

Correlation with SEM

Once spectroscopic analysis was completed, the sample could be transferred from the Nexsa G2 System into a Thermo Scientific™ Axia™ ChemiSEM. A 5 kV beam and a secondary electron detector allowed the structures on the sample surface to be easily visualized. Tile sets collected using Thermo Scientific Maps Software showed triangular features that match with the locations where MoS_2 was measured in the Nexsa G2 System. In A1, where the Mo signal was sparse, and the Raman data showed single layers, individual triangle features can be seen. In A2, where the film appeared more continuous and the Raman data showed a potentially thicker layer, overlapping triangular features can be seen.
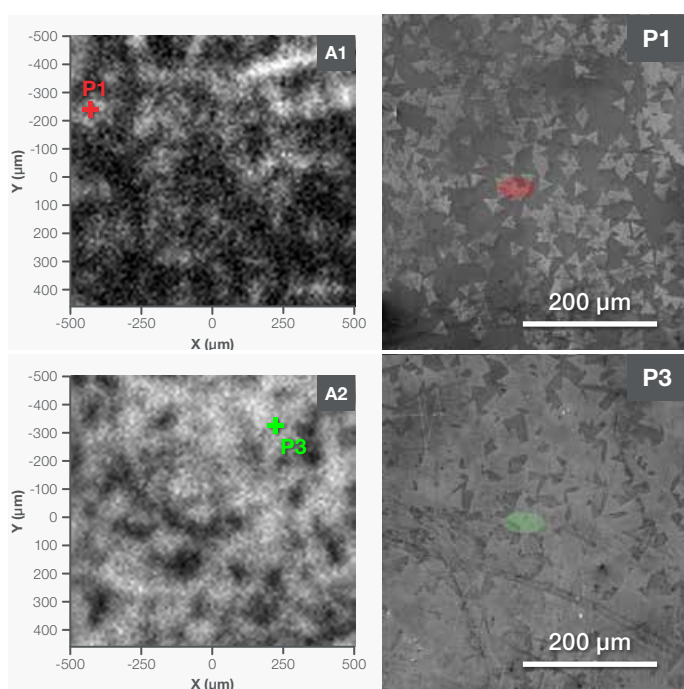
Conclusions

The combined application of XPS, Raman spectroscopy, and SEM in the CISA Workflow enables the high-quality visualization and chemical identification of 2D materials. CISA can also automatically align to the same exact position on the stage by coordinating with Thermo Scientific Maps Software, saving time and ensuring that multimodal data is seamlessly aligned without the need for identifying features. In this case study, both the chemistry and structure of MoS_2 deposited on a SiO_2 surface were clearly determined. It was also shown that both MoS_2 and MoO_3 were present, and that there is a variation in the number of layers at different regions of the surface. Layers consisted of triangular MoS_2 facets that could potentially overlap, depending on the local concentration of deposited MoS_2.

Figure 5. SEM shows a lower density of triangular structures in the area where single-layer MoS_2 was identified on the Nexsa G2 System.

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