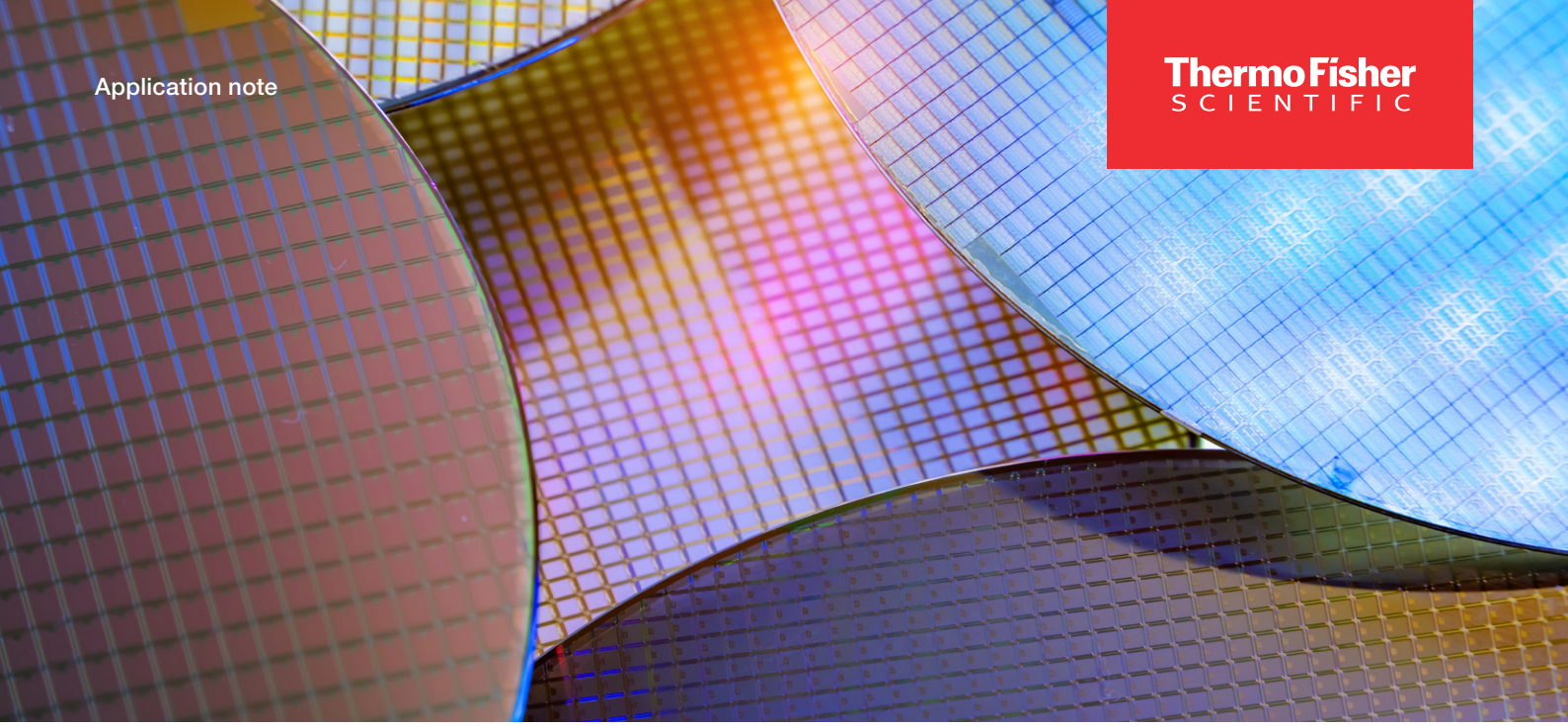

Application note

Identifying subtle structural differences in 2D semiconductors using Raman microscopy

Author

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Industry/application

Semiconductor/material science

Product used

Thermo Scientific™ DXR3xi Raman Imaging Microscope

Goal

To demonstrate the significant differences in Raman spectra even between very similar semiconducting materials.

Key benefits

Excellent discrimination between minor structural differences.

Introduction

Two-dimensional (2D) semiconductors, apart from their fascinating electrical and mechanical properties, are known for their very simple crystalline structure, often made up of only one or two elements. The materials' specific crystalline lattices and structures make them very well-suited for analysis by Raman microscopy. Raman microscopy can monitor (through the phonon modes of the crystalline lattice) fine structural differences in these materials, such as the effects of elemental substitution within an otherwise similar structure. The clear spectral fingerprints found with Raman microscopy make the technique particularly well-suited for investigating closely related materials.

A common class of 2D semiconductors are the family of Transition Metal Dichalcogenides (TMDCs). They form simple monolayer and few-layer structures of the form MX_2 where M is a transition metal atom and X represents a chalcogen atom.[1] Two common examples, which are the materials of interest here, are molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2). Both materials share the same structure of a heavy transition metal atom sandwiched between layers of sulfur atoms. Each respective transition metal forms a trigonal prismatic structure bonded with six sulfur atoms (Figure 1).[2,3]

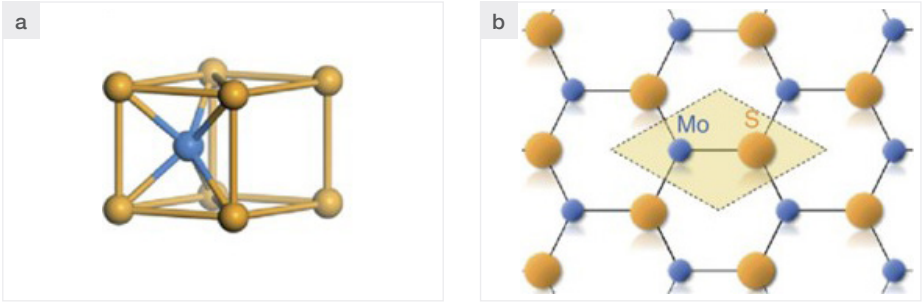

Figure 1. a) A side view of the MoS_2 unit cell; b) a top-down view of a monolayer MoS_2 crystal (reproduced from Cao, T., Wang, G., Han, W. *et al*).[GM1.1][3]

However, these materials differ significantly in the atomic mass of the transition metals (the atomic mass of Mo is 95.95 amu while the atomic mass of W is 183.84 amu), and vary slightly in the size of the crystalline unit cell, where the MoS_2 unit cell has dimensions a/b = 0.3150 nm and c = 1.2300 nm while WS_2 has dimensions a/b = 0.3153 nm and c = 1.2323 nm.[2]

At a simple level, Raman spectroscopy is measuring the energies of lattice or bond vibrations, so bond length and molecular weight will affect the vibrational energy, and thus the Raman shift of the spectral peaks. With the established differences in atomic mass (and very slight differences in unit cell dimensions—0.095% difference in a/b and 0.187% difference in c) of MoS_2 and WS_2, comparing the Raman spectra of these two materials can readily show the structural sensitivity of Raman spectroscopy in semiconducting materials.

Experimental conditions

Data was collected on the DXR3xi Raman Imaging Microscope using a 455 nm excitation laser and 10x magnification objective. Few-layer WS_2 was acquired after it was grown directly on a gold substrate, and bulk MoS_2 was mechanically exfoliated to reduce a sample to a few-layer thickness. The standard Raman collection parameters were a total acquisition time of 0.5 s (0.005 s exposure repeated 100 times) at 4 mW for WS_2 and 6 mW for MoS_2. The data was collected with a 50 µm pinhole aperture and 5 cm^{-1} spectral resolution. Polarized Raman measurements were conducted with the laser horizontally polarized and the analyzer polarizer set both parallel and perpendicular to the laser polarization state.

Results

The standard 2D crystal forms of MoS_2 and WS_2 show distinctive Raman spectra (Figure 2). The peaks for each semiconductor can be labelled for the specific vibrational modes, with both an in-plane (labeled as E^1_{2g}) and out-of-plane (designated as A_{1g}) component in each material.[4,5]

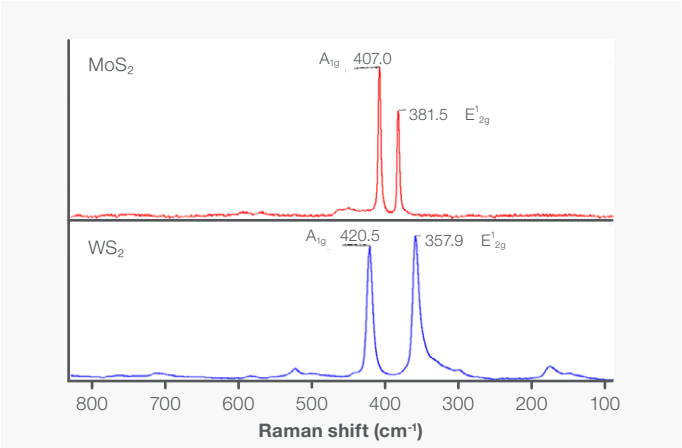

Figure 2. The dominant Raman peaks of 2D MoS_2 and WS_2 with the peak positions and structural notations labeled.

In Raman spectroscopy, replacing an atom with a heavier isotope or element typically results in a spectral shift to lower vibrational frequencies (due to the increased mass of the heavier atom affecting the vibrational mode). Indeed, the heavier metal atom of tungsten instead of molybdenum demonstrates this behavior in the in-plane, E^1_{2g} vibration where the Raman response is due to the lateral motion of sulfur and metal atoms relative to one another. However, the out-of-plane, A^1_g vibration, which is dominated by sulfur atom motion (while the metal atoms are only weakly involved) shows an opposite shift in the Raman spectra due to the substitution of heavier W atoms. This occurs because the out-of-plane mode is controlled by the effective restoring force (sometimes referred to as cohesive pressure) acting on the sulfur atoms, not an interaction between the sulfur and metal atoms. This can be especially evident in few-layer samples where the respective interlayer van der Waals forces make the cohesive pressure even greater in WS_2 than in MoS_2, increasing the restoring force on the sulfur atoms and shifting the out-of-plane peak to higher frequency.[6] By substituting in a heavier tungsten atom, it alters the out-of-plane force constants, leading to a greater restoring force and corresponding Raman peak shift.

Taking the Raman analysis a step further, one can confirm the structural similarities (of the trigonal prismatic lattice structures) of both MoS_2 and WS_2 with polarized Raman measurements, which reveal the structural symmetries of the vibrational modes (Figure 3).[7]

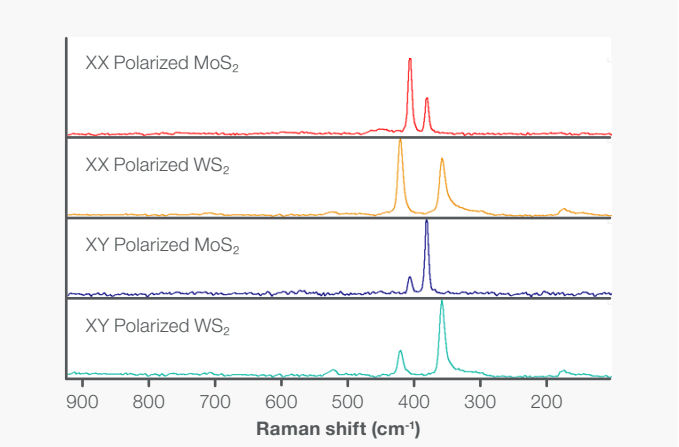

Figure 3. Parallel (XX) and perpendicular (XY) polarized Raman spectra for both MoS_2 and WS_2. Y axis values (arb. units) are shown here in full-scale rather than common scale and are recorded in Table 1.

Material	Polarization	In-plane peak intensity (arb. unit)	ρ (IP)	Out-of-plane peak intensity (arb. unit)	ρ (OOP)
MoS_2	$I_{\parallel}$	120.2	1.06	264.3	0.11
	$I_{\perp}$	126.9		28.9	
WS_2	$I_{\parallel}$	176.1	0.76	241.7	0.19
	$I_{\perp}$	133.7		45.5	

Table 1. Peak intensities and depolarization ratios (ρ) for both MoS_2 and WS_2 under polarized Raman analysis. ρ values greater than 0.75 are considered depolarized while values less than 0.75 are polarized.[8]

Both MoS_2 and WS_2 exhibit similar polarized Raman responses where the parallel polarization measurement has a strong out-of-plane A^1_g peak that drops significantly in the perpendicularly polarized measurement. By calculating the depolarization ratios ($\rho = I_{\perp}/I_{\parallel}$) for both MoS_2 and WS_2 one can conclude that both MoS_2 and WS_2 are isotropic crystals with asymmetric, depolarized in-plane E^1_{2g} vibrations and symmetric, polarized out-of-plane A^1_g vibrations (see Table 1).

Conclusions

Although this study focused on two specific materials with uniform crystalline structures, the principles seen here can be used in a Raman spectral analysis of many other semiconducting materials. Understanding the effect of atomic mass on a Raman spectrum can be especially useful in studying the defects of 2D semiconductors, where any atomic substitution or doping will yield changing Raman signals, much like those shown in this work. This allows researchers to leverage the structural specificity of Raman spectroscopy to easily analyze novel semiconducting materials.

The ability to distinguish subtle structural and mass-dependent differences using Raman spectroscopy highlights the value of the DXR3xi Raman Imaging Microscope for advanced semiconductor materials research.

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