Structural analysis of two-dimensional semiconductors through polarized Raman

Authors

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Industry/application

Semiconductor, Material Science

Product used

Thermo Scientific™ DXR3xi Raman Imaging Microscope

Goal

Study the polarized Raman response of 2D semiconductors.

Key benefits

Detailed structural understanding of semiconductor crystal lattice and orientation.

Introduction

Promising prospects for improving electronics rely on novel materials and designs, especially those involving two-dimensional (2D) semiconductors. Unlike bulk semiconducting materials, there are unique conductive and structural properties that only appear in few-layer crystals, making 2D semiconductors a rich field of study.[1] The thinness of these materials means it is very important to be able to study the specific crystalline lattice structure in detail. Each monolayer is only three atoms thick so any structural defects in the crystal lattice can have significant impact on the material properties. Any analytical technique that can reveal this type of structural information becomes extremely important in researching the next generation of semiconductors. Molybdenum disulfide, MoS_2, belongs to a particular class of 2D semiconductors with many interesting conductive properties.[2] By studying the structure of 2D MoS_2 under polarized Raman microscopy, more specific details of the crystalline structure can be determined.[3]

A monolayer sheet of MoS_2 consists of a single plane of molybdenum atoms sandwiched between two planes of sulfur atoms. This creates a relatively simple crystalline lattice with few vibrational modes, making MoS_2 a perfect system to showcase the structural information derived from polarized Raman spectroscopy. MoS_2 has two main Raman peaks, an in-plane vibration from the lateral oscillation of sulfur atoms in the lattice labelled as E^1_{2g} at 381 cm^{-1}, and an out-of-plane vibration known as A_{1g} at 408 cm^{-1}.[4]

Polarized Raman spectroscopy involves a laser source that must be linearly polarized when incident upon the sample. The resulting Raman scattering passes through a second polarizer, called the analyzer polarizer, before reaching the detector. The analyzer polarizer can be finely tuned to any angle relative to the sample orientation. Polarization measurements are used to determine the isotropic nature of a material (how sensitive the Raman spectra is to sample orientation), as well as the symmetry of specific vibrational modes (by a calculated depolarization ratio).[3,5]

Results

Manually exfoliated MoS_2 samples were tested on the Thermo Scientific DXR3xi Raman imaging microscope with a 532 nm excitation laser. By investigating the depolarization ratio of the two MoS_2 peaks, we can gain significant information about the material structure of specific vibrations. Figure 1 and Table 1 show the Raman peaks and their intensities, respectively, for the four distinct polarization conditions used to find the depolarization ratio.

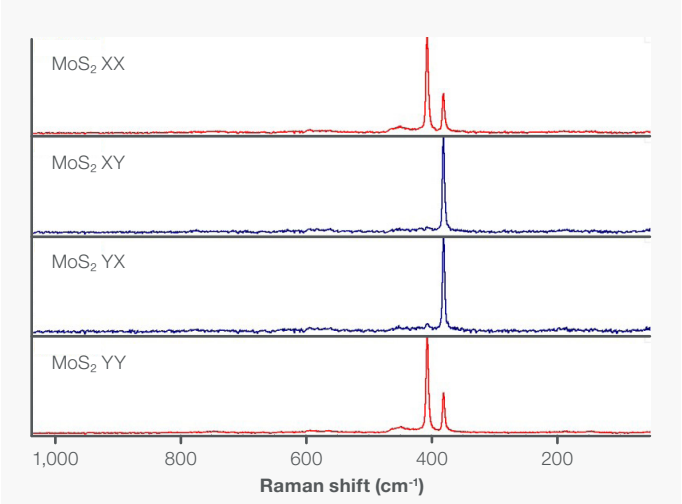

Figure 1. Spectra taken from few layer MoS_2 crystals under four distinct polarization conditions.

Polarization state	In-plane peak intensity (arb. unit)	Out-of-plane peak intensity (arb. unit)
I_XX	403.8	770.5
I_XY	409.8	11
I_YX	403.4	15.6
I_YY	416.4	754

Table 1. The Raman peak intensities for the in-plane E^1_{2g} and out-of-plane A_{1g} vibrations.

The values in Table 1 can be used to calculate the depolarization ratios (ρ) for the in-plane and out-of-plane MoS_2 peaks with the following formula where I represents the Raman intensity of either the perpendicularly or parallelly polarized conditions:[5]

$$\rho = \frac{(I_{\perp})}{(I_{\parallel})}$$

For the in-plane peak, under both horizontally (X) and vertically (Y) polarized laser excitation the depolarization ratios are 1.015 and 0.969 respectively. Meanwhile, for the out-of-plane peak the ratios are 0.014 and 0.021. In depolarization analyses, polarized vibrations have ratio values less than 0.75 while depolarized vibrations have ratio values greater than or equal to 0.75.[5] From this, we can make several statements about the structure of MoS_2. It is an isotropic crystal where the in-plane vibration is an asymmetric, depolarized band and the out-of-plane vibration is a symmetric, polarized band.

This is a great example of a simple polarized Raman experiment. However, this study can be taken further by varying the analyzer polarizer in 5° increments (from 0 to 180°). This reveals more detailed structural information about the MoS_2 crystals, as seen in some selected spectra in Figure 2 and a radar plot of the Raman intensity as a function of analyzer angle in Figure 3.

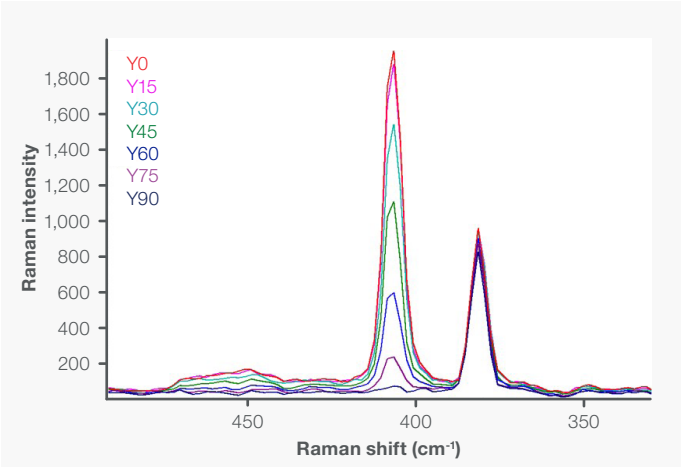

Figure 2. Spectra (for a vertically polarized laser) shown on a common y-axis scale where the analyzer is stepped in 15° increments. The Y0 spectrum represents a parallel laser / analyzer polarizer configuration while the Y90 is a perpendicular configuration.

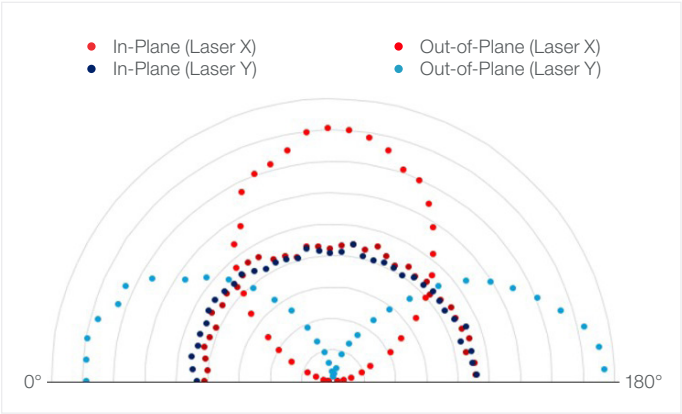

Figure 3. The plot shows data taken with the analyzer polarization set in 5° increments from 0 to 180° (clockwise around the circle). The concentric arcs represent Raman intensity in increments of 100 (arb. unit). The colored points represent the two MoS_2 peaks (in-plane E^1_{2g} and out-of-plane A_{1g}) under two laser polarization states.

Although by standard polarization analysis with four distinct polarization conditions MoS_2 appears to be isotropic, the polarization response for the out-of-plane A_{1g} peak shown in Figure 3 shows some deeper complexity in its response. The radar plot in Figure 3 allows for a simple visual depiction of peak intensity under various polarization angles, making it very easy to visualize aberrations in the expected response. It is anticipated that an isotropic material would have a consistent and uniform trend in its peak intensity, shown as a smooth curve in the lobe shape of the radar plot. The in-plane peaks show a consistent peak intensity, forming a circular shape on the plot as expected for an asymmetric peak. However, the out-of-plane peak intensities in the plot show a small, consistent shoulder feature where the Raman intensity unexpectedly drops when the analyzer angle is 20° from the parallel state. The asymmetric shape in the detailed polarization plot above implies a slight anisotropic nature to the out-of-plane crystalline structure that is not revealed in the standard four condition XX / XY / YX / YY analysis and only becomes evident with very small steps in the analyzer polarization angle. The nuances of this response merit further study, but the additional information provided by polarized Raman spectroscopy is very promising for the study of 2D semiconductors like MoS_2.

Conclusion

Polarized Raman spectroscopy allows for a more in-depth understanding of the structural elements of 2D semiconductors and provides excellent analytical capabilities for determining the symmetries and orientations of molecular vibrations in their crystalline lattices. Determining if specific vibrations are polarized or depolarized can be used to confirm theoretical lattice structures and aid in identifying in-plane vs out-of-plane vibrations for new materials. Furthermore, since polarized Raman spectroscopy is very sensitive to crystallographic orientation, it can reveal additional information about localized strain or defects that alter the lattice structure.

References

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