

THz-Raman® Characterization of Graphene and Two-Dimensional Nanomaterials

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ABSTRACT

Two dimensional (2D) materials have attracted a lot of attention due to their optimal optoelectronic properties which are not found in the domain of silicon based electronic materials [1]. The identification and characterization of 2D materials, especially differentiation of few-layer from the bulk phase, is crucial for progress in materials research and manufacturing process development. Raman spectroscopy, and more specifically low-frequency/THz-Raman® analysis, has been recently introduced as a highly sensitive, real-time and non-destructive analytical tool for these novel materials [2]. The low-wavenumber region which can aid the quantification of layers is usually not accessible with conventional Raman spectroscopy systems. Using volume holographic grating (VHG) based filter technology, we have developed a THz-Raman® system that enables access to the low-frequency region with a single stage spectrometer.

Keywords: low-frequency Raman spectroscopy, terahertz spectroscopy, graphene, 2D materials, transition metal dichalcogenides

1 INTRODUCTION

Two dimensional materials, also referred to as layered materials, are materials consisting of a limited number of crystalline layers with atomic thickness that is in the range of few tens of Angstroms to a few nanometers. The electronic and optical properties of 2D materials are dramatically different from their bulk phase. The unusual characteristics of these materials arise from the fact that the electrons are free to move within a single layer, but restricted across layers. Therefore, studying the interlayer interactions is critical to understand the electrical, mechanical and optical properties of few layer systems. There do exist some methods in electron microscopy to study layer interaction [3], but Raman spectroscopy is a fast optical characterization technique that offers many advantages over electron microscopy.

2 METHOD

While conventional Raman spectroscopy has become a standard characterization tool in the past two decades, its true potential has not been realized due to the limitations of the thin film filter technology that is generally used to fabricate edge and notch filters. Interlayer interactions in

2D materials manifest themselves as vibrational modes in the 0.3-2 THz frequency range. These modes can be observed in the Raman spectra, but as Figure 1 highlights, these vibrational modes lie very close to the excitation laser line, and are hard to detect using conventional Raman spectrometers. In a THz-Raman® system, using VHG filters, the interlayer interactions can be easily detected as low-frequency phonon modes in the Raman spectrum.

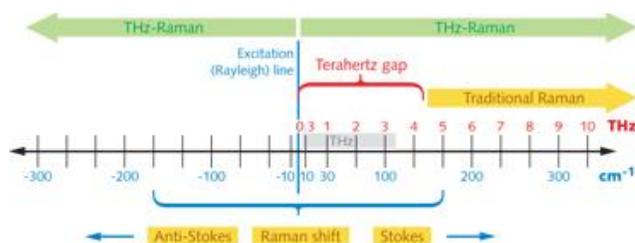


Figure 1: The THz gap with limited accessibility using conventional Raman spectrometers

The operating range of a THz-Raman® system is greater than a conventional Raman system and extends into the terahertz spectroscopy regime as shown in Figure 1. Since the THz-Raman® system provides access to the full chemical fingerprint region and simultaneous capture of both Stokes and anti-Stokes Raman shifts, it has been used extensively for the determination of polymorphism and crystallinity studies [4]–[6].

3 RESULTS AND DISCUSSION

The Raman spectroscopy data presented here were collected with excitation at 532 nm using an Ondax XLF-Micro-532 THz-Raman® system which was connected to an Andor SR500i single-stage spectrometer using a 50 micron fiber. The sample was mounted on an upright Leica microscope and illuminated using a 100x Olympus objective. For optical imaging a 455 nm LED was used as the illumination source.

3.1 Graphene

Graphene was the first 2D material to be discovered and possesses exceptional mechanical and electrical properties. The unusual properties of layered graphene materials are attributed to the interlayer interactions. The

frequencies of interlayer vibrations in these few layer graphene materials occur in the THz frequency regime and manifest themselves as low frequency Raman peaks close to the laser Rayleigh line. Tan and co-workers have shown the low energy phonons in Few-Layer Graphene are caused by interlayer coupling and are termed ‘C-band’, analogous to the well known G-peak that is universally present in the Raman spectra of all carbon allotropes [7]. This C band is essentially a low energy mode around 42 cm^{-1} in bulk graphite that involves the relative motions of atoms in adjacent planes. As the number of graphene layers in the sample decrease from the bulk phase down to single layer graphene (SLG), the C band shifts to lower energy i.e from 42 cm^{-1} to 24 cm^{-1} . While the peak intensity ratio of the G and 2D bands of layered Graphene can be used for determining the number of layers, the peak position of the high frequency G band itself does not change[8]. Thus the low-frequency C band is a more direct method to estimate the number of layers.

Cong and Yu have recently shown that not only is the C band sensitive to the number of layers in few-layer graphene, but is also indicative of the fold and twist in these layers. THz-Raman[®] peaks have been used to characterize both the number of layers and also their stacking configurations [9].

3.2 Transition metal dichalcogenides

The fact that graphene is a conductor sets some limitations on its potential applications. Alternate classes of materials to graphene, which have found greater traction in recent years, are collectively labeled Transition Metal Dichalcogenides (TMD or TMDC). While graphene lacks a band gap, TMDCs like MoSe₂ and MoS₂ have a direct band gap that can be chemically tuned to have a wide variety of electronic properties [3]. These materials can potentially be used in FET transistors, spin- and valleytronics, among other applications [10].

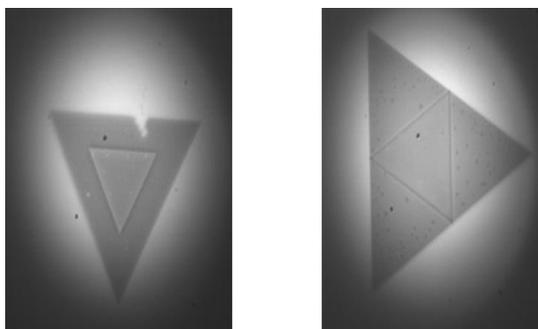


Figure 2: 100x magnified optical images of two-layer MoSe₂ flakes with 0° (left) and 60° rotation (right) between the layers.

Optical micrographs of two MoSe₂ samples are shown in Figure 2. The two configurations shown are both two-layered MoSe₂ structures, but are different in the relative orientation of the two layers. In the image on the left the two layers are indexed without any rotation around the common axis (going into the plane of the image) or alternatively, a 0° rotation. The image on the right shows a structure with a 60° rotation along the same axis.

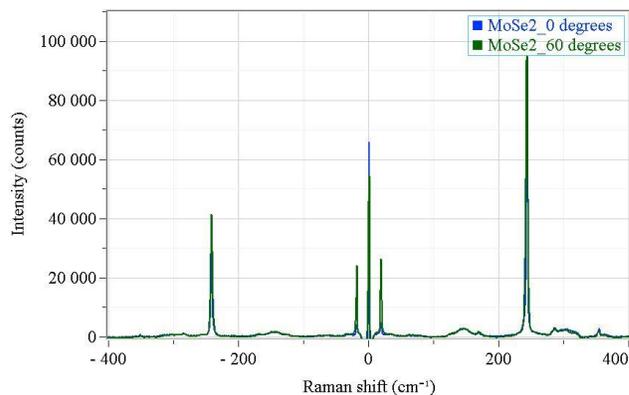


Figure 3: Normalized THz-Raman[®] spectra of two-layer MoSe₂ materials from Figure 2, showing a corresponding shift and change in magnitude and position of the 18 cm^{-1} peak with layer orientation.

Normalized THz-Raman[®] spectra of the two orientations of MoSe₂ configurations shown in Figure 3. The Raman spectra illustrate that regardless of orientation, both the two-layer MoSe₂ materials show an out-of-plane bulk mode as a peak at 242 cm^{-1} in the Raman spectrum. Akin to the case of graphene, the interlayer shear modes of MoSe₂ can be clearly seen in the low-frequency spectrum. The peaks corresponding to interlayer modes are located at approximately 18 cm^{-1} and can be easily verified by the fact that they are present in both the stokes and anti-stokes regions. These signals are indicative of both the number of layers and their orientation as shown in Figures 2 and 3. Other important structural attributes such as folds and twists can also be analyzed with this technique [3].

While the the intensity of the 18 cm^{-1} peak is very different for the two configurations, it would be prudent to verify the different configurations by the peak position too. A Voigtian (Gaussian-Lorentzian) band fitting procedure was performed on the 18 cm^{-1} peak seen in figure 3. Figure 4 shows the corresponding shifts due to orientation changes in the 18 cm^{-1} peak. The 60° oriented two-layer MoSe₂ has a peak at 18.9 cm^{-1} , but when the MoSe₂ layers are oriented at 0°, the peak has a bathochromic shift to 18.4 cm^{-1} , in addition to a large change in the intensity of the peak.

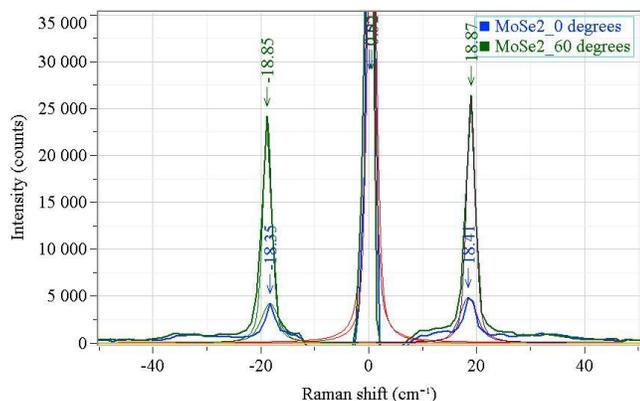


Figure 4: Gaussian-Lorentzian fits to the data in Figure 3, indicating a peak shift of 0.5 cm^{-1} between the 0° and 60° rotated MoSe_2 flakes.

4 CONCLUSION

The ability of THz-Raman[®] to interrogate low frequency modes has previously been used in polymorph discrimination and crystallinity studies. We have demonstrated that low-frequency Raman spectroscopy (THz-Raman[®]) provides direct information about the number and orientation of the layers in two dimensional materials. In addition, the THz-Raman[®] method is a non-destructive, real time and highly sensitive analytical tool for these novel materials. Specifically, we were able to show the correlation of interlayer orientation to the Raman frequency shift in the low-frequency region.

5 ACKNOWLEDGEMENT

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