Variable Temperature Raman and Photoluminescence Micro-Spectroscopy

Transition Metal Dichalcogenides: 2D MoS$_2$ and WSe$_2$

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BACKGROUND

Atomically thin two-dimensional materials, such as graphene, have attracted significant research interests because of their extraordinary physical properties. [3, 6-10] Two-dimensional transition metal dichalcogenides TMDC (MX$_2$ where M= transition metal and X= S, Se or Te) typically have a finite band gap below 3 eV. As a semiconducting alternative to graphene, the remarkable properties of TMDCs have promising applications in photonics, optoelectronics, field effect transistors, and energy storage devices. [1-6] Many interesting phenomena emerge at cryogenic temperatures, and often, additional or new information about a sample can be obtained with temperature dependent measurements. Temperature dependent Raman measurements can be used to understand the electron-phonon interaction and their effect on transport and electronic device performance. Here, we report on the variable temperature Raman micro-spectroscopy analysis of MoS$_2$ and WSe$_2$.

Variable temperature Raman analysis of two-dimensional quantum materials is complicated by the limited luminescence (low signal-to-noise ratio) due to their low absorption rate, low conversion efficiency, and often a low laser input power (to avoid heating), especially in low temperature environments. At cryogenic temperatures, acquiring a signal from the material requires either long integration times or complicated optical setups aimed at improving the collection efficiency. Moreover, complicated high numerical aperture setups have a short depth of focus (<1 µm) and are highly susceptible to temperature fluctuations in the laboratory environment that cause expansion/contraction of the optical components, resulting in the sample drifting out of the excitation spot.

The MicroReveal Raman solution uses an in-vacuum, temperature-controlled, high NA objective in conjunction with a low-thermal mass sample holder to quickly ramp temperature with high thermal stability and minimal thermal expansion. The result is a low-drift, variable temperature Raman spectroscopy setup that can rapidly measure samples across a wide temperature range (4K - 350K). For additional details on the MicroReveal Raman instrument, see the Technical Guide.
EXPERIMENTAL SETUP

The measurements were performed with a Raman setup that consists of a sample environment with temperature control from 4K to 350K. A low thermal mass sample holder with built-in heater and thermometer were used to set the sample temperature. A laser source was focused onto the sample with a vacuum compatible 100x, 0.75NA objective lens. The signal was collected in reflection geometry and directed to a spectrometer using pre-aligned, filtering optical cubes.

The pre-aligned optical cubes are used to quickly couple the sample environment to the spectrometer. An enclosure surrounds the cubes to prevent light leak. The filtering cubes were configured for the excitation source with simultaneous white light imaging to aid in sample feature location. The specific sample feature of interest was located using internal nanopositioners and kept in focus through the full temperature range using a low drift sample holder (<30 µm over the full temperature range).

Sample

Among the TMDC materials, MoS$_2$ is one of the most stable layered materials. In bulk it is an indirect band gap semiconductor with a band gap of approximately 1.3 eV. Its band gap increases when the number of layers is decreased, ultimately reaching a direct band gap of 1.8 eV for monolayer MoS$_2$. [7-8] Similar to graphene, MoS$_2$ has strong Raman scattering intensity. [9-10] The Raman peak positions depend upon the number of layers; therefore, it is possible to determine the number of layers from the Raman spectra. [11] The temperature dependent Raman of MoS$_2$ provides information about electron-phonon interactions and transport properties that have a large impact on electronic device performance. The MoS$_2$ sample used in this study was on a sapphire substrate and was acquired directly from 2D Layer, Inc.

Monolayer tungsten diselenide, WSe$_2$, is a representative material of atomically thin transition metal dichalcogenides (TMDC), with high photoluminescence (PL) quantum yield and large spin-orbit coupling induced spin splitting. Even though they are only a few atoms thick, the WSe$_2$ structures have remarkable chemical and mechanical stability and they can be used as a platform to study quantum confinement effects in a quasi 2D system. Decreasing the number of layers enhances the confinement effects which result in a larger band gap and ultimately causes a transition from an indirect band gap to a direct band gap. Therefore, confined WSe$_2$ is a promising candidate for nanoscale field-effect transistors and solar cell applications. Temperature dependent Raman and PL are used to explore the rich excitonic physics in monolayer WSe$_2$ for both optoelectronics [12] and valleytronics applications. The WSe$_2$ sample used in this study was on a sapphire substrate and was acquired directly from 2D Layer, Inc.
RESULTS & DISCUSSION

**MoS₂ Raman Results**

A white light image (T = 5K) of the MoS₂ on sapphire sample is shown in Figure 1a, and a mixture of single, double, and multilayer MoS₂ triangular flakes can be seen. At base temperature, a monolayer flake was located and moved into the laser spot for the collection of temperature dependent Raman spectra.

Raman spectra of MoS₂ depict two prominent modes, E₁²g which appears at approximately 384 cm⁻¹ due to an in-plane vibration and an A₁𝑔 mode which appears at approximately 406 cm⁻¹ due to an out of plane vibration mode. In single-layer MoS₂, the E₁²g and A₁𝑔 modes are separated by approximately 18 cm⁻¹. Raman spectra were collected from 5K to 300K, see Figure 2. In general, both the E₁²g and A₁𝑔 peaks sharpen and shift to higher energy as the temperature decreases from 300K to 5K. [9-10]

![Figure 2: MoS₂ temperature dependent Raman spectra with IsoPlane spectrometer](image)

**WSe₂ Raman and Photoluminescence Results**

A white light optical image (T = 5K) of the WSe₂ on sapphire sample is shown in Figure 1b, and a mixture of single, double, and multilayer WSe₂ triangular flakes can be seen. At base temperature, a monolayer flake was located and moved into the laser spot for the collection of temperature dependent Raman spectra (Figure 3).

Previous experiments with WSe₂ have uncovered several peaks that are not present in the corresponding bulk spectra. While modes that are Raman active in the bulk are also Raman active in the thin films, the reverse is not always true due to the reduced symmetry in thin films. Bulk WSe₂ has peaks at 178, 250, and 253 cm⁻¹, corresponding to the Raman-active E₁𝑔, E₁²g, and A₁𝑔 modes respectively. Raman spectra for few layer WSe₂ reveal a peak near 250 cm⁻¹ (E₁²g and A₁𝑔 modes) and a broad shoulder near 260 cm⁻¹ as well as an additional small Raman peak near 310 cm⁻¹ (A₂' mode). [8, 11-12]

Temperature-dependent steady-state photoluminescence (PL) was studied on the same WSe₂ flake as the Raman experiments. WSe₂ on sapphire has three states: localized exciton, free exciton, and trion, that contribute to the observed PL. A laser power of 31 µW at 532 nm was used for the excitation source to allow discrimination of the excitonic states. At temperatures below 100K, the localized exciton is the primary contributor to the observed PL. However, between 105 and 130K, the free exciton is the primary contributors to the observed PL, see Figure 4. Above 130K both the free exciton and trion contribute to the measured PL. [8, 11-12]

![Figure 3: WSe₂ temperature dependent Raman spectra with FERGIE spectrometer](image)

![Figure 4: Temperature dependent photoluminescence spectra of WSe₂ with 532nm excitation, 5s collection time.](image)
CONCLUSIONS

Temperature-dependent measurements play an important role in the development and characterization of new materials. As the dimensionality is reduced from bulk (3D) to monolayers (2D), phase transitions, molecular thermal activities, and symmetry changes in crystal structure necessitate precise control over the sample temperature and the measurement environment.

For non-destructive spectroscopic studies, the added complexity associated with thermo-mechanical drift and stability become more important when systematically varying temperature throughout an experiment. For the MoS$_2$ sample, the E$_{1}$ and A$_{1}$ peaks broaden and shift to lower energy as the temperature is increased 5K to 300K, see Figure 2. These results agree with expectations and previously reported results. Raman spectra of WSe$_2$ thin films, shown in Figure 3, are particularly interesting because of the overlap of the E$_{1}$ and A$_{1}$ modes across the temperature range and a mode at approximately 260 cm$^{-1}$ which has been proposed in the literature as a substrate mediated uniaxial strain induced mode. WSe$_2$ also has a substrate mediated temperature dependent steady-state photoluminescence. On sapphire the ratios of the 3 emitting states for WSe$_2$ change at temperatures below 100K, see Figure 4.

Together with recent advances in closed-cycle cryogenic systems, incorporating a rapidly equilibrating low thermal mass sample stage and an in-vacuum, high numerical aperture objective lens coupled to the Fergie or IsoPlane spectrometers with pre-aligned cubes, yielded a variable temperature Cryo-Optic platform with aberration-free Raman spectroscopy and photoluminescence studies. Researchers now have access to cryogenic systems with integrated Raman spectroscopy and imaging capabilities. The MicroReveal Raman solution significantly reduces consumable costs and the time required to setup a variable temperature Raman experiment. Researchers can quickly achieve their ideal experimental environment and focus efforts on developing and characterizing new materials.

To learn how the MicroReveal Raman solution can be used to enhance your research, consider submitting your sample to our Applications Lab for a free preliminary analysis.

CLICK HERE TO SUBMIT YOUR SAMPLE TO THE APPLICATIONS LAB CHARACTERIZATION QUEUE!

REFERENCES

2. Lu, J.; Liu, H.; Tok, E. S.; Sow, C. Interactions between lasers and two-dimensional transition metal dichalcogenides *Chem. Soc. Rev.* 2016, 45, 2494

Acknowledgments

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