Effect of Polarization on the Raman Scattering of the 2D Material -Tungsten Disulphide

S. Bhattacharya[a)], A. V. Veluthandath[a)], C. C. Huang[b)], G. S. Murugan[b)], P. B. Bisht[a)*]
a)Department of Physics, Indian Institute of Technology, Madras, Chennai India – 600036
b)Optoeletronics Research Centre, University of Southampton, UK
** Email: bisht@iitm.ac.in*

Abstract: Raman-spectra of a few-layer tungsten disulphide (WS_2) on fused-silica substrate have been recorded with varying polarization of the excitation-laser. The polarization dependence of one of the Raman modes has been explained using the Raman cross-section. © 2019 The Author(s)
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1. Introduction

Layered transition metal dichalcogenides (TMDCs) are compounds of the form MX_2 having a lamellar structure consisting of stacks of 2D unit layers. Here a transition metal (M = Mo, W, Nb) is sandwiched between two chalcogen layers (X= S, Se). Each of the unit layer is bound together by strong ionic or covalent bond while the weak van der Waals force is responsible for binding the unit layers. The light matter interaction of these atomically thin TMDCs depend on the number of layers and are generally limited by their low absorption cross section and low photoluminescence quantum yield. Various studies have been performed to increase the light matter interaction including resonance enhancements using microcavities. Raman spectroscopy is a powerful technique for determining the number of layers in graphene and other TMDCs, stacking sequences, strain effects and the crystallographic orientation. In this work we study the dependence of the Raman spectra of tungsten disulphide (WS_2) on the layer thickness and polarization of the excitation laser source. It has been found that the Raman cross-section of one of the modes makes it polarization sensitive.

2. Experimental

Van der Waals Epitaxy (vdWE) has been used to synthesize WS_2 on fused silica substrate by using tungsten hexachloride (WCl_6) as the precursor to react with hydrogen sulphide (H_2S) gas [1]. Raman spectra have been recorded using a micro Raman spectrometer (Jobin Yvon, Labram HR 800) with a resolution of < 1 cm^{-1} at the excitation wavelength of 488 nm. Polarization dependent measurements have been carried out by using a polarizer (a half wave plate) at the excitation side and an analyzer at the detector side. To cancel out the errors due to polarization effects of the grating and the detector a scrambler is placed after the analyzer.

3. Results and Discussion

3.1 Determining the Number of Layers

The first order optical modes of WS_2 are denoted by E^1_{2g} and A_{1g}. A_{1g} modes indicate the out-of-plane displacement of S atoms (OC modes) while E^1_{2g} modes indicate in-plane relative motion of W and S atoms (IMC modes). Raman spectra of different layered samples of WS_2 on fused silica substrates were recorded as shown in Figure 1. According to the theoretical calculations of Liang and Meunier [2], the frequency difference between the A_{1g} and E^1_{2g} peaks for monolayer, bi-layer, tri-layer and four layers of WS_2 are 60.31, 62.18, 63.13 and 63.50 cm^{-1}, respectively. Our experimentally measured values as given in Table 1 are in agreement with those calculated in [2].

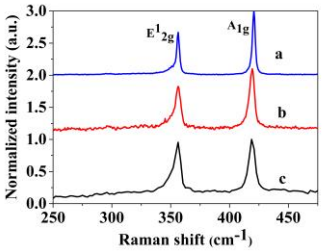

Fig 1. Raman spectra for WS_2 on silica substrate for different number of layers. a, b and c denotes the Raman spectra of multi-layered, bi-layer and tri-layer WS_2, respectively.

Table 1. Summary of the frequencies, frequency difference (Δω) for the main Raman modes and their intensity ratios with λ_{ex} = 488 nm.

Phonon modes	Raman shift (cm^{-1})	Δω ±0.01 (cm^{-1})	Intensity ratio (I_{A1g}/I_{E12g})	No. of layers
A_{1g} (cm^{-1}) E^1_{2g} (cm^{-1})	418.88 353.87	65.01	0.45	Multi-layered
A_{1g} (cm^{-1}) E^1_{2g} (cm^{-1})	418.87 355.6	63.27	0.73	3
A_{1g} (cm^{-1}) E^1_{2g} (cm^{-1})	417.83 355.58	62.25	0.95	2

3.2 Polarization Dependence of Raman Spectra

The Raman spectra for a typical multilayered sample are shown in Figure 2. It is found that when the polarization angle is changed gradually the ratio between the intensity of the two modes shows sinusoidal pattern. The intensity of the E^1_{2g} and A_{1g} modes at 0° polarization angle has been denoted by I_{E12g0} and I_{A1g0}, respectively. It was observed that though the E^1_{2g} mode intensity ratio is almost constant (curve b), the A_{1g} mode ratio has an oscillating feature (curve a). The ratio between A_{1g} mode and E^1_{2g} mode as a function of the polarization angle is shown by the curve c. This can be explained in terms of Raman cross-section by calculating the term $\langle \varepsilon_0 | R_j | \varepsilon_i \rangle$ which is finite for OC modes and zero for IMC modes. Here ε_i and ε_0 respectively, denote the incoming and outgoing light polarizations and R_j denotes the appropriate Raman tensor [3]. The incoming and outgoing light in this case have been assumed to have the same helicity.

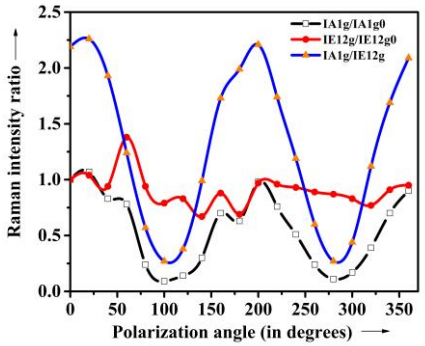

Fig. 2. The intensity ratio of A_{1g} (a), and E^1_{2g} (b) with respect to the intensity at 0° at various polarization angles. Curve c shows the intensity ratio between the A_{1g} and E^1_{2g} modes at various polarization angles.

4. Conclusion

In summary, the layer dependent Raman spectra of WS_2 deposited on fused silica have been studied here. The dependence of Raman scattering of multi layered WS_2 on the polarization of the excitation laser source reveals that only one of the Raman mode (A_{1g}) is sensitive to the polarization of the excitation laser.

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5. References

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