Raman Spectroscopy Study of Ultrathin Tungsten Nitride (W_5N_6)

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Introduction

- The field of 2D materials has shown remarkable potential for applications in a plethora of fields from electronics to pharmaceuticals.
- Transition Metal Nitrides (TMNs) are a new group of non-Van der Waals, covalently bonded 2D materials with unique properties.
- In particular, the novel material W_5N_6 exhibits extraordinary hardness and electrical conductivity.

Objective

- This study aims to shed light on the structure and properties of W_5N_6.

Methods

Sample Preparation

- Thin flakes of the precursor WSe_2 were mechanically exfoliated using scotch tape and were deposited onto a Si substrate.
- Flakes were nitridized in a quartz tube furnace at 800°C for 45 minutes using NH_4OH as a nitrogen source and Ar as a carrier gas. The reaction is isoelectronic with the one displayed in Figure 2.

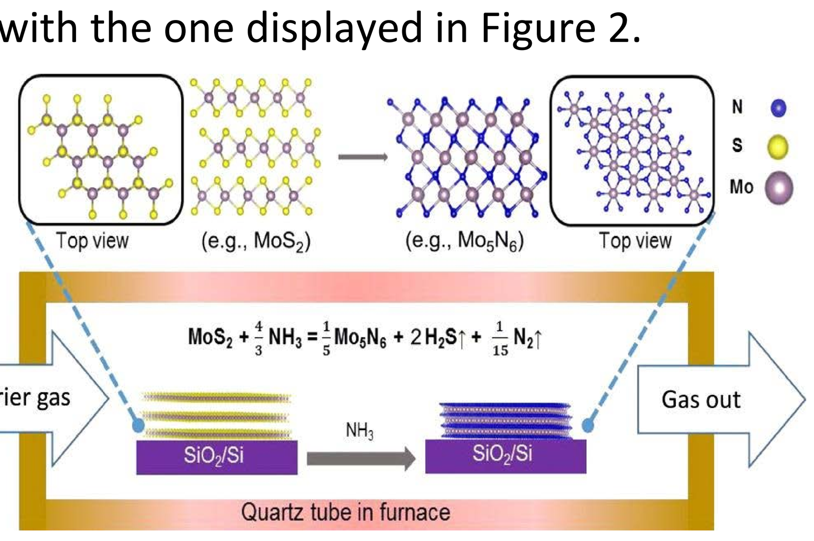

Figure 1. Schematic Image of Nitridation from MoS_2 to Mo_5N_6[1]

Raman Spectroscopy

- Raman spectroscopy is a non-destructive, inelastic scattering technique used to probe the vibrational modes of a crystal.
- It can be used to "fingerprint" a substance.
- Raman spectroscopy was performed on samples of varying thickness and at various angles. A 532 nm wavelength was used.
- The peak at ~256 cm^{-1} was fit using an asymmetric Fano lineshape.
- Equation 1 was used to fit polar plots of intensity against angle.

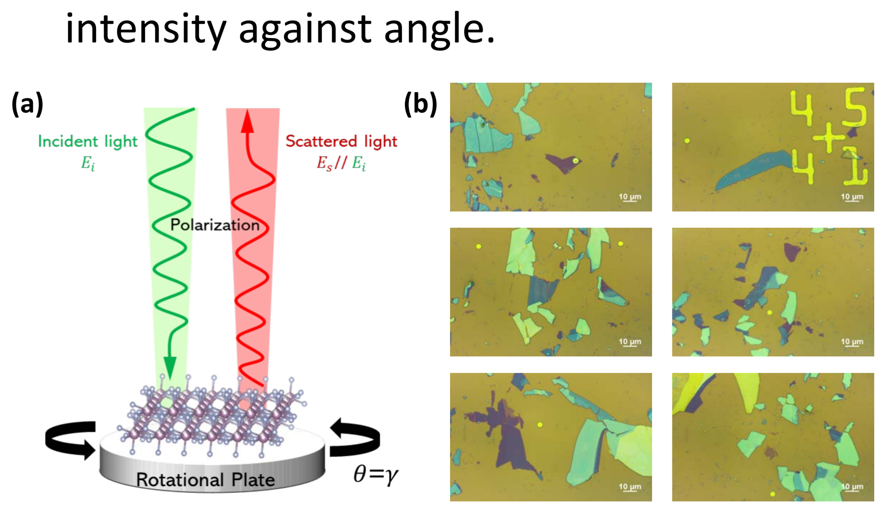

Figure 2. Experimental Setup and Samples. (a) Schematic of the angular dependent Raman setup. (b) Optical microscope images of W_5N_6 samples of varying thickness.

Results

Thickness Dependence Raman

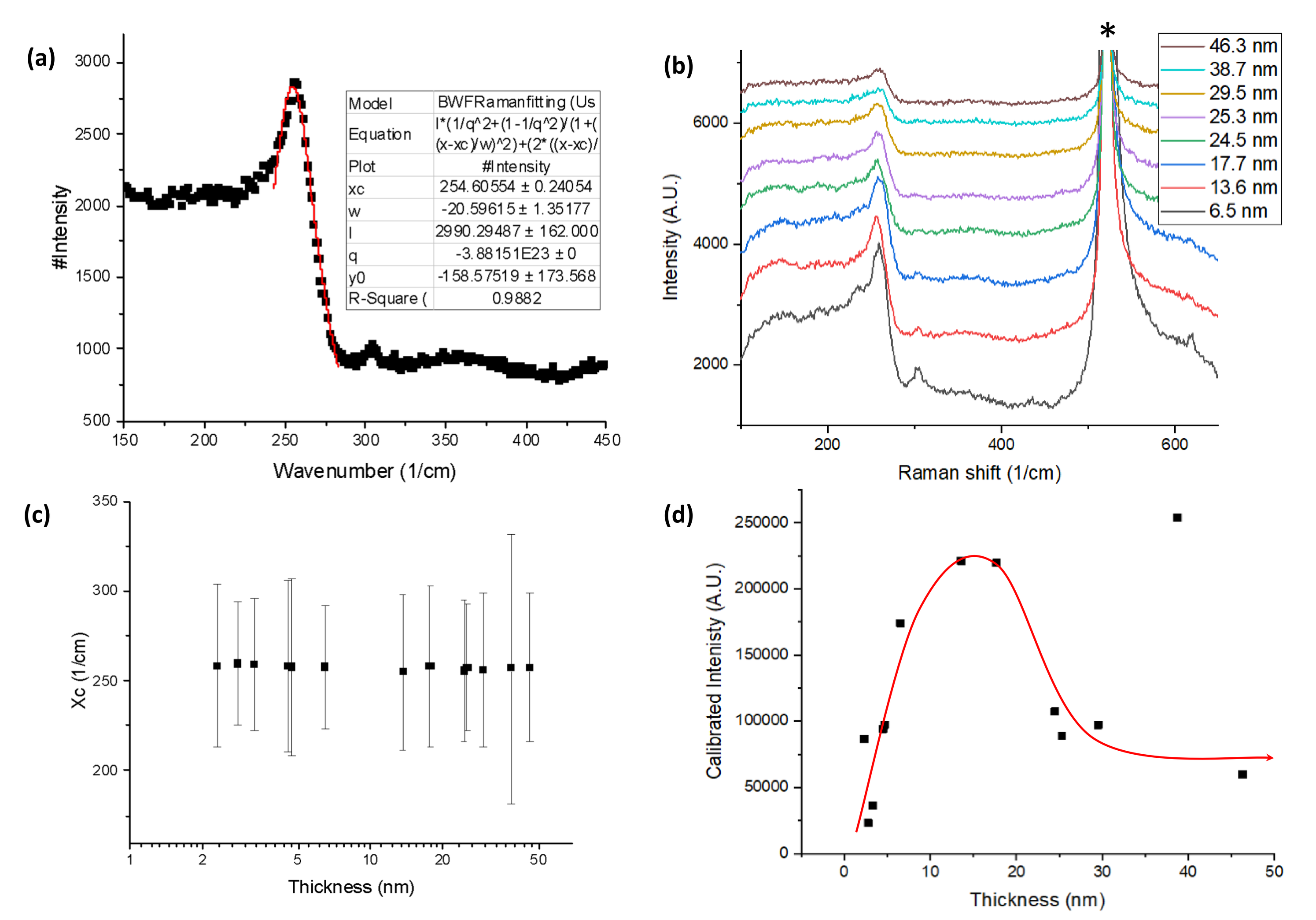

Figure 4. Investigation of the thickness dependence of the Raman spectra of W_5N_6 (a) Typical Raman peak fitting at ~256 cm^{-1} for W_5N_6 . (b) Raman spectra from 6 samples of varying thickness. The peak marked with "*" is from the Si substrate. (c) Raman Shift plotted against thickness in 13 different samples. The error bars represent the full-width half-maximum of the peak. (d) Calibrated intensity plotted against thickness in 13 different samples. The red line indicates the observed trend.

Angle Dependence Raman

$$I = \hat{e}_i^T \cdot R \cdot \hat{e}_s = [cos\theta \quad sin\theta \quad 0]^T \cdot \begin{bmatrix} d & 0 & 0 \\ 0 & -d & 0 \\ 0 & 0 & 0 \end{bmatrix} \cdot [cos\theta \quad sin\theta \quad 0] = d \cdot cos^2\theta - d \cdot sin^2\theta = d \cdot \cos(2\theta)$$

Equation 1. Derivation of the equation used to fit Figures 5c and 5d. $\hat{e}_i^T$ is the polarization vector representing incident light while $\hat{e}_i$ is the polarization vector representing scattered light. R is the Raman tensor for the E_{2g} mode.

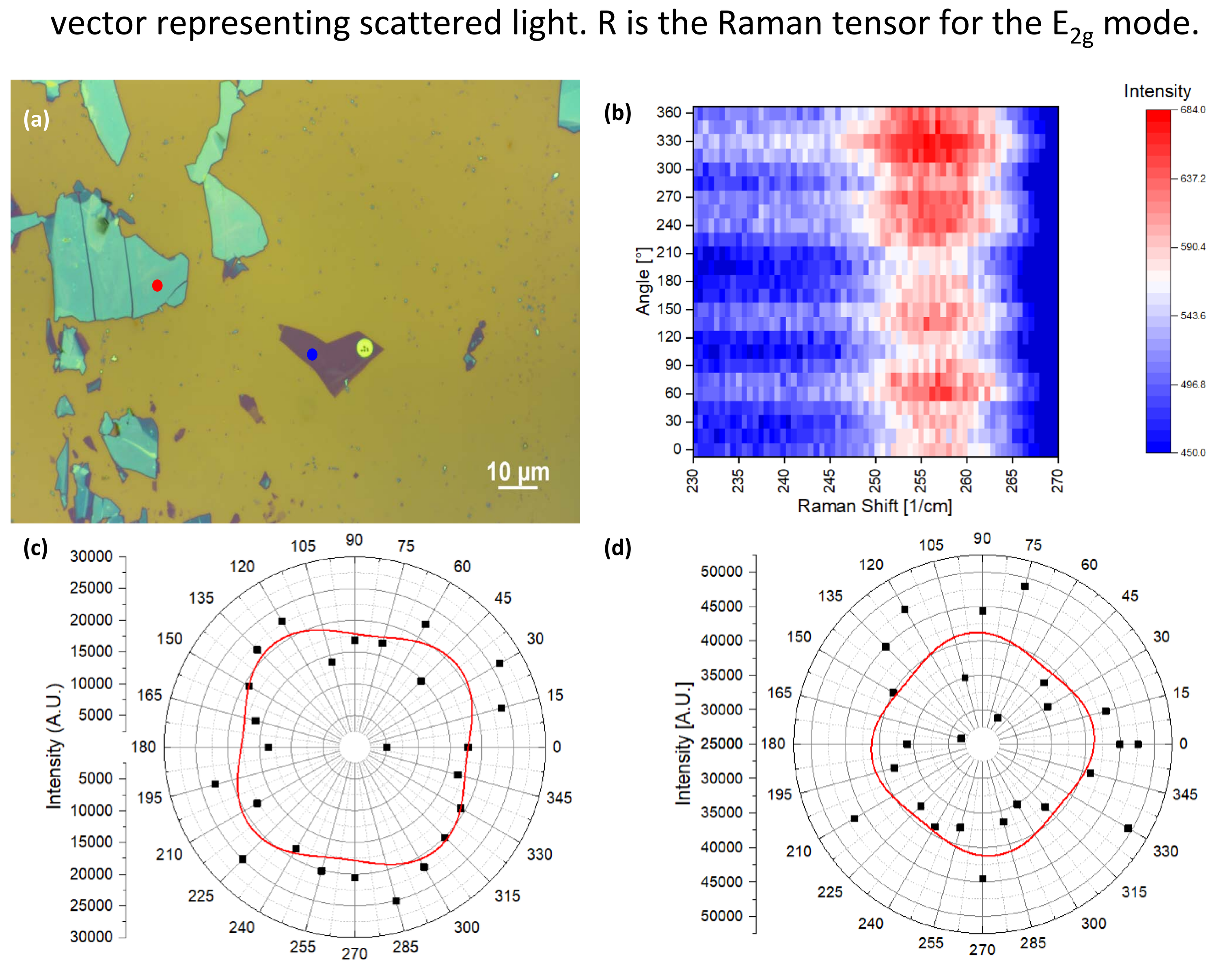

Figure 5. Investigation of the angular dependence of the Raman spectra of W_5N_6 (a) Optical microscope image of the W_5N_6 flakes measured. Measurements were taken at the red (24.5 nm) and blue dots (6.5 nm). (b) Heatmap of Raman intensity with respect to angle and Raman shift. (c) Polar plot of E_{2g} mode in the thicker (24.5 nm) sample. (d) Polar plot of E_{2g} mode in the thinner (6.5 nm) sample.

Discussion

- The Raman peak at ~256 cm^{-1} aligns with previous measurements of W_5N_6.
- W_5N_6 has a peak at ~570 cm^{-1}, but this peak was not observable given its overlap with silicon's peak at ~520 cm^{-1}.
- The Raman spectra is consistent with phonon dispersion calculations[3]. The plateau left of the peak at ~256 cm^{-1} coincides with phonon modes lower in frequency than ~256 cm^{-1} (~7.67 THz).

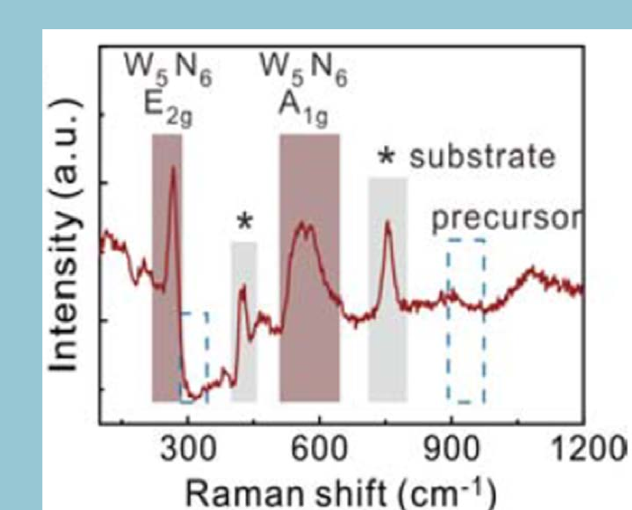

Figure 6. Raman spectra of W_5N_6 on sapphire substrate.

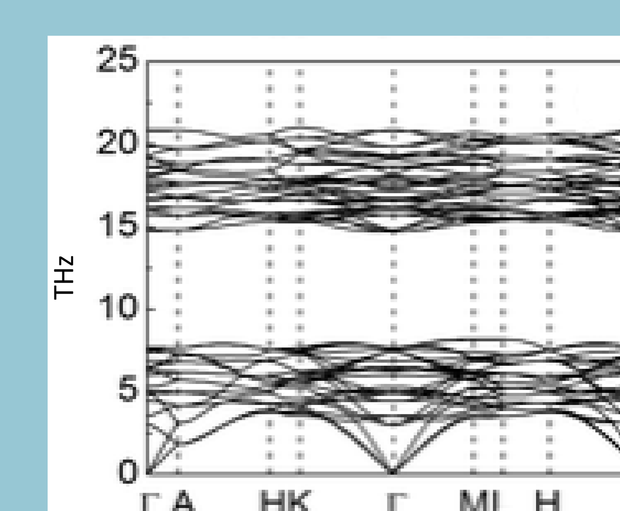

Figure 7. W_5N_6 Phonon dispersion calculations[2].

Thickness Dependence Raman Analysis

- Figure 3c shows that Raman Shift has a negligible relationship with thickness.
- This behavior is consistent with the expected behavior of E_{2g} mode, which vibrates in the basal plane and should not have thickness dependence.
- In Figures 3b and 3d, the intensity first increased with and then decreased with thickness, barring one outlier.
- The initial increase is due to photons being more likely to scatter with an increasing amount of material while the decrease is due to the destructive interference of the incident light reflected by the substrate[3].

Angular Dependence Raman Analysis

- As demonstrated by Figure 5, W_5N_6 exhibits 4-fold symmetry.
- This is consistent with theoretical predictions. The peak at ~256 cm^{-1} is ascribed to an E_{2g} mode, which has 4-fold symmetry in the D6h point group.

Acknowledgements

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