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Raman spectroscopy can be used to characterize the composition of two-dimensional Mo$_{1-x}$W$_x$S$_2$ monolayer alloys ($0 \leq x \leq 1$).
Two-dimensional (2D) materials, such as graphene, BN, and MoS$_2$, have attracted extensive interest in recent years due to their unique structures, fundamental physical properties, and potential applications. Layered transition-metal dichalcogenides MX$_2$ (M=Mo, W, Nb, Ta; X=S, Se, Te), a class of materials with covalently bonded layers stacked together by weak van der Waals forces, are a rich source of 2D crystals. The direct band-gap nature and hence the emergence of strong photoluminescence (PL) in single layer transition-metal dichalcogenides have made them appealing materials for electronic and optoelectronic devices. Band gap engineering of 2D monolayers is important for those applications. To achieve band gap tuning in 2D monolayers, alloying transition-metal dichalcogenides has been proposed by theoretical calculations and demonstrated in experiments.

The key to band gap engineering in monolayer alloys is mixing the end compositions at atomic scale. Structure characterization of 2D alloys is challenging. Atomic-resolution scanning transmission electron microscopy (STEM) can directly image and discriminate individual atoms. Raman spectroscopy could also be a powerful tool to characterize structures of 2D alloys. For bulk semiconductors, frequency shift was used to determine alloy compositions and peak broadening was used to indicate alloy degree. For 2D materials, Raman spectroscopy has been widely used in characterizations of graphene, MoS$_2$, and WS$_2$. In this work, we performed a systematic Raman scattering investigation on a series of Mo$_{1-x}$W$_x$S$_2$ monolayers. The first-order Raman active $A_1$ and $E$ modes and several second-order Raman modes were observed. Polarization dependent Raman scattering measurements were performed to confirm the assignment of $A_1$, $E$ and second-order Raman modes in Mo$_{1-x}$W$_x$S$_2$ monolayers. In Mo$_{1-x}$W$_x$S$_2$ monolayers, the $A_1$ and $E$ modes showed one-mode and two-mode behaviors, respectively. The composition-dependent Raman frequency and full width at half maximum (FWHM) of the dominant Raman modes were discussed.
designated crystal and polarization directions in this work. In the polarized Raman measurements, for Z(XX)Z configuration, a polarization analyzer was placed right after the edge filter and the polarization direction was parallel to the polarization of incident laser beam. The Z(XY)Z configuration was conducted by placing a half-wave plate before the analyzer in Z(XX)Z configuration.

Results and Discussion

Mo$_{1-x}$W$_x$S$_2$ monolayer flakes were cleaved from the corresponding bulk single crystals onto SiO$_2$/Si substrates (oxide thickness of 300 nm). Optical imaging and AFM imaging (Figures 1a and 1b) were used to locate and identify Mo$_{1-x}$W$_x$S$_2$ monolayers as reported in our previous work. Further, compared with Mo$_{1-x}$W$_x$S$_2$ few-layered and bulks, Mo$_{1-x}$W$_x$S$_2$ monolayers showed smaller frequency difference between $A'$ and $E'$ and much stronger PL emission. Figure 1c shows composition-dependent unpolarized Raman spectra of Mo$_{1-x}$W$_x$S$_2$ monolayers with $W$ composition $x$ changing from 0 to 1. Taking Mo and W atom as the same and considering the very small lattice mismatch between two end component MoS$_2$ (3.15 Å)$^{51}$ and WS$_2$ (3.153 Å)$^{52}$ the space group of single layer Mo$_{1-x}$W$_x$S$_2$ is expected to be P6$_3$m2 (point group D$_{3h}$). There are totally 9 normal vibration modes at the Γ point in the Brillouin zone for MoS$_2$ and WS$_2$ monolayers,$^{47,53}$ in which two accessible first-order Raman active modes can be observed in backscattering experiment$^{44,54,55}$ in MoS$_2$ and WS$_2$ monolayers: $A'$ and $E'$. The atomic displacement of Raman modes $A'$ and $E'$ is shown in Figure 1d. The $A'$ mode is an out-of-plane vibration involving only the S atoms while the $E'$ mode associates to in-plane displacement of transition metal Mo or W and S atoms. Similar to that of Mo$_{1-x}$W$_x$S$_2$ bulk alloys,$^{48,49}$ $A'$ and $E'$ modes of Mo$_{1-x}$W$_x$S$_2$ monolayer alloys showed one-mode and two-mode behaviors, respectively. That is, $A'$ mode shifts continuously as the $W$ composition $x$. While two phonon branches associated to $E'$ modes of MoS$_2$ and WS$_2$ are observed in alloys. As the composition of $W$ increases, the relative intensity of WS$_2$-like $E'$ mode increases, while that of the MoS$_2$-like $E'$ mode decreases. The intensities of $A'$ and $E'$ modes of WS$_2$ monolayer is much stronger than that of other Mo$_{1-x}$W$_x$S$_2$ samples (Figure 1c) due to the resonance enhancement (B exciton energy of WS$_2$ centered at $-2.36$ eV$^{40}$).

In order to confirm the assignments of $A'$, $E'$ modes as well as the second-order Raman features in Mo$_{1-x}$W$_x$S$_2$ monolayer alloys, polarization-dependent backscattering experiments have been carried out. For D$_{3h}$ point group, the corresponding polarizability tensors of the above two first-order Raman modes $A'$ and $E'$ are:

$$\alpha (A') = \begin{bmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{bmatrix},$$

$$\alpha (E') = \begin{bmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & -d \end{bmatrix}$$

Based on polarizability tensor, $A'$ mode should be observed only under Z(XX)Z configurations, but not in Z(XY)Z configurations.

E' mode should be present under both Z(XX)Z and Z(XY)Z configurations. The Raman peak around 400-420 cm$^{-1}$ (Figure 2) presented only at Z(XX)Z configuration was confirmed to be $A'$.

The Raman peaks at $\sim380$ cm$^{-1}$ and 350 cm$^{-1}$ (Figure 2) presented both under Z(XX)Z and Z(XY)Z configurations were confirmed to be MoS$_2$-like and WS$_2$-like $E'$ modes, respectively. Note that, for WS$_2$ monolayer, the lower lying Raman band at $\sim350$ cm$^{-1}$ consists of two components (Z(XY)Z configuration in Figure 2f): one is assigned to $E'$ mode at $\sim355$ cm$^{-1}$, and the other is assigned to 2LA(M) at $\sim350$ cm$^{-1}$. In addition, the intensity of 2LA(M) mode in both unpolarized (Figure 1c for $x=1$) and Z(XX)Z (Figure 2f) configurations is the strongest one due to a double-resonant Raman process$^{44}$ and dramatically decreases in Z(XY)Z configuration (Figure 2f). The other second-order (SOR) modes (at 263, 295 and 323 cm$^{-1}$) can be attributed to the combinations of phonons at M point. The Raman peak at $\sim323$ cm$^{-1}$ is weaker in Z(XY)Z configuration than that in Z(XX)Z configuration, while the peaks at 263 and 295 cm$^{-1}$ disappear in Z(XY)Z configuration.

For Mo$_{1-x}$W$_x$S$_2$ monolayer alloys with $x=0, 0.20$ and 0.42 (Figures 2a-c), the asymmetric broad Raman peak at $\sim450$ cm$^{-1}$ can be assigned to the overlap of a longitudinal acoustic mode 2LA(M) and a normally Raman inactive $A_2$ optical mode.$^{43}$ In addition, the intensity of the Raman peak at $\sim450$ cm$^{-1}$ decreases obviously in the corresponding Z(XY)Z configuration. For Mo$_{1-x}$W$_x$S$_2$ monolayer alloys with $x=0.20$, 0.42, 0.61 and 0.77 (Figures 2b-c), detailed multi-peak curve fittings (as shown in the Figures 2b-e insets) are performed and the assignment of peaks can be carried out by comparing the locations and polarization dependence with that of the constituent end samples MoS$_2$ and WS$_2$.$^{43,44}$ The Raman peak at $\sim360$ cm$^{-1}$ appearing from $x=0.13$ to $x=0.77$ was assigned to an alloy disorder-related peak.$^{49,58}$

Figure 3a shows the composition-dependent Raman frequencies of the different Raman modes in Mo$_{1-x}$W$_x$S$_2$ monolayer alloys. With the increasing of $W$ composition, MoS$_2$-like $E'$ peak shifts to lower frequency, while WS$_2$-like $E'$ peak moves slowly towards higher frequency. The $A'$ modes upshift with increasing $W$ composition in monolayer alloys. These variation trends of Raman frequencies are similar to that of Mo$_{1-x}$W$_x$S$_2$ bulk alloys (Figure 4b).$^{49}$ The peak frequency of disorder-related mode at $\sim360$ cm$^{-1}$ is not sensitive to alloy composition. The peak frequency at $\sim346$ cm$^{-1}$ (2LA (M) of WS$_2$) overall shows a decrease trend with decreasing $W$ composition. Since the monolayer alloys have random distributions of Mo and W atoms without phase separation throughout all W contents,$^{51}$ Mo, W or S atoms should have several different nearest Mo and W coordination configurations in Mo$_{1-x}$W$_x$S$_2$ monolayer alloys. This can introduce reduced mass and force constant fluctuation$^{32}$ which is responsible for the asymmetric line shapes and peak broadening (see Figure 1c).

The variation of FWHM of the first-order Raman active modes are depicted in Figures 3b and 3c. The FWHM of $A'$ mode increases from $\sim6.2$ cm$^{-1}$ (at $x=0$) to $\sim12.9$ cm$^{-1}$ (at $x=0.61$) and then decreases to $\sim5.7$ cm$^{-1}$ at $x=1$ (Figure 3b). The maximum peak width at intermediate $W$ compositions may indicate disorder-induced broadening. For $E'$ modes (see Figure 3c), as the $W$ composition increases, the FWHM of WS$_2$-like $E'$ increases first from $\sim10.8$ cm$^{-1}$ (at $x=0.20$) to $\sim13.7$ cm$^{-1}$ (at $x=0.42$), then decreases to $\sim4.8$ cm$^{-1}$ at $x=1$. The
FWHM of MoS₂-like E' mode almost monotonically increases from ~4 cm⁻¹ (at x=0) to ~11.6 cm⁻¹ (at x=0.88), instead of reaching a maximum peak width at intermediate W composition. This needs further investigation.

MREI model has been successfully used to predict and fit lattice vibrational modes of mixed crystal structures, such as AB₁₂C₆ type⁵⁹ and ABₓCₓ type.⁶⁰ The MREI model is based on the assumptions of isotropism and randomness.⁶¹ i.e., (1) same kind of atoms vibrate in the same amplitude and phase and (2) all substituted atoms are randomly distributed. Previous STEM imaging revealed random distributions of Mo and W atoms, which verifies the ‘randomness’ assumption.⁶² Based on MREI model for Mo₁₋ₓWₓS₂ monolayer alloys (Figure 4a), ignoring the S-S interactions, we can write the motion equation for A₁ mode,

\[ m_s \ddot{\mu}_s = -(1-x)F_3 \dot{\mu}_s - xF_2 \dot{\mu}_s \]

where \( m_s \) and \( \mu_s \) are mass and displacement of the S atoms. The terms \( F_1 \) and \( F_2 \) are force constants representing interactions between S-Mo, S-W along vertical direction, respectively (Figure 4a). Linear changing of force constants on alloy composition is assumed,

\[ \frac{F_1}{F_{10}} = \frac{F_2}{F_{20}} = 1 - \theta_1 x \]

where \( F_{10} \) and \( F_{20} \) are the limiting values of force constants \( F_1 \) and \( F_2 \), respectively, as \( x \to 0 \). The parameter \( \theta_1 \) takes into account the variation of force constants.

\[ \omega^2 = \frac{1}{m_s}(1-\theta_1 x)F_{10} + x(1-\theta_1 x)F_{20} \]

This predicts one mode behavior for A₁ mode, consistent with experimental observation. For E' mode, the motion equations are

\[ m_s \ddot{\mu}_s = -(1-x)F_3 (\mu_s - \mu_Mo) - xF_4 (\mu_s - \mu_W) \]

\[ m_Mo \ddot{\mu}_Mo = -2F_3 (\mu_{Mo} - \mu_s) - xF_5 (\mu_{Mo} - \mu_W) \]

\[ m_W \ddot{\mu}_W = -2F_4 (\mu_W - \mu_s) - (1-x)F_5 (\mu_W - \mu_{Mo}) \]

where \( m_s \), \( m_{Mo} \) and \( m_W \) are the mass of S, Mo and W atoms, \( \mu_s \), \( \mu_{Mo} \) and \( \mu_W \) are the displacement of S, Mo and W atoms, respectively. \( F_3 \), \( F_4 \) and \( F_5 \) are force constants representing interactions between S-Mo, S-W and Mo-W along horizontal direction, respectively (see Figure 4a). Instead of linear changing of force constants on alloy composition which gives a poor fitting for experimental E' data (see Figure S1), quadratic changing of force constants is assumed.

\[ \frac{F_3}{F_{30}} = \frac{F_4}{F_{40}} = \frac{F_5}{F_{50}} = 1 - \theta_2 x - \theta_3 x^2 \]

where \( F_{30}, F_{40} \) and \( F_{50} \) are the limiting values of force constants \( F_3, F_4 \) and \( F_5 \), respectively, as \( x \to 0 \). The parameters \( \theta_2 \) and \( \theta_3 \) take into account the variation of force constants. Similarly, we can get two eigenvalues (details in supporting information). This predicts two-mode behavior for E' mode, also consistent with experimental observation. If ignoring weak inter-layer interactions in Mo₁₋ₓWₓS₂ bulk alloys, all formulas used in this model are the same for monolayer alloy and bulk alloy. The Raman active modes (A₁ and E' for monolayer, and A₁₈ and E₂₈ for bulk) frequency variation with composition is presented in Figure 4b. The Raman frequency shift is similar for monolayer and bulk alloys. Least square fitting was used to fit the experimental data using equation (4) and (9). The experimental data can be well fitted, giving similar force parameters for monolayer alloy and bulk alloy (Table 1). Substituting these parameters into equation (4), for monolayer samples, we can get

\[ \omega_{A_1} = 401.6(0.002x^2 + 0.080x + 1)^{1/2} \]

Meanwhile, substituting these parameters into equation (9), we can get relationship between frequency and alloy composition for MoS₂-like and WS₂-like E’ modes (see supporting information). The composition-dependent Raman shift can be used to determine the composition in mixed Mo₁₋ₓWₓS₂ monolayer alloys.

Conclusions

In summary, the Raman spectra of Mo₁₋ₓWₓS₂ monolayer alloys were studied with W composition x from 0 to 1. The dominant first-order Raman active A₁’, E’ and several second-order Raman modes have been observed in the range 100–480 cm⁻¹. A₁’ and E’ modes showed one-mode and two-mode behaviors in Mo₁₋ₓWₓS₂ monolayer alloys, respectively. The broadening of A₁’ and WS₂-like E’ modes in the alloys has been observed. The MREI-model was successfully used to predict mode behaviors and fit the composition-dependent Raman frequencies of A₁’ and E’ modes. The Raman frequencies of A₁’ and E’ modes can be used to quantify Mo/W compositions.

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Author Contributions
L.X. and Y.H. conceived and designed the experiments. D.D. and Y.H. synthesized Mo$_x$W$_2$S$_2$ single crystals. Y.C. N.M., Q. F. and M.Z. exfoliated Mo$_x$W$_2$S$_2$ samples and performed optical imaging, AFM, Raman characterizations. Y. Z., X. Z. and P. T. performed MREI calculations. Y.C. and L.X. co-wrote the manuscript. J. Z. revised the manuscript. All authors discussed the results and commented on the manuscript.

Notes and references
44. A. Berkdemir, H. R. Gutiérrez, A. R. Botello-Méndez, N. Perea-


Figure 1. (a) Optical micrograph of exfoliated Mo$_{0.47}$W$_{0.53}$S$_2$ flake deposited on the 300 nm SiO$_2$/Si substrate. Monolayer and bilayer regions are indicated by arrows and marked by “1L” and “2L”, respectively. (b) AFM image of the Mo$_{0.47}$W$_{0.53}$S$_2$ monolayer (1L) in panel (a). The inset shows the height profile along the blue dashed line. (c) Raman spectra of Mo$_{x}$W$_{1-x}$S$_2$ monolayers with different W composition $x$. The three solid (blue) lines guided by eyes show frequency shift of E’ and A’$_1$ peaks with W composition $x$. (d) The schematics of displacement of atoms for the Raman active E’ and A’$_1$ modes in Mo$_{0.47}$W$_{0.53}$S$_2$ monolayer.
Figure 2. Polarized Raman spectra of Mo$_{1-x}$W$_x$S$_2$ monolayer alloys in the range 250–480 cm$^{-1}$ in Z(XX)$_Z$ and Z(XY)$_Z$ configurations with different W composition $x$ (a) $x=0$; (b) $x=0.20$; (c) $x=0.42$; (d) $x=0.61$; (e) $x=0.77$ and (f) $x=1$. The first-order Raman peaks $E'$, $A'$, and several second-order modes are marked by arrows. The insets in (b)-(e) show the detailed line shape fits in the range marked by squares. The solid lines show the experimental curves, while the dashed lines show the fitting results. The arrows in the insets indicate the corresponding fitted peak positions.
Figure 3. (a) Composition-dependent Raman frequencies and full width at half maximum (FWHM) of $A_1'$ (b) and $E'$ (c) modes of Mo$_{1-x}$W$_x$S$_2$ monolayer alloys.
Figure 4. (a) The schematics of force constants used in MREI model. (b) Composition-dependent Raman frequencies of $E'$ and $A_1'$ ($E_{1g}$ and $A_{1g}$ for bulk) modes in Mo$_{1-x}$W$_x$S$_2$ alloys. The solid and dashed lines are the MREI fits of Mo$_{1-x}$W$_x$S$_2$ monolayers and bulks, respectively and the scattered square and triangle points are the experimental data of Mo$_{1-x}$W$_x$S$_2$ monolayers and bulks.
Table 1. MREI-model parameters for Mo_{1+x}W_{1-x}S_{2} monolayer and bulk alloys (Note: $F$ in $10^6$ amu cm$^{-2}$).

<table>
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<tr>
<th>Fitted Parameters</th>
<th>$A_1'(1L)$ or $A_{1B}$(bulk)</th>
<th>$E'(1L)$ or $E_2^1$(bulk)</th>
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<td>$F_{20}$</td>
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