Spectroscopy of monolayer and multilayer tungsten disulfide under high pressure

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ABSTRACT

Recently exfoliated monolayer and multilayered transition metal dichalcogenide (TMDs) have gathered significant interest based on their tunable bandgap and extremely high carrier mobility. We have investigated the Raman and photoluminescence spectra of monolayer and multilayer WS2 as a function of pressure. The Raman-inactive mode B1u, which is activated by structural disorder, was revealed at 6.7 GPa in monolayers, at 8.0 GPa in bilayers, and at 13.7 GPa in multilayers, respectively. With the enhancement of pressure-induced interlayer interaction, the crystal phase transition due to layer sliding like 2Hc to 2Ha occurs at 14.8 and 18.7 GPa in bilayers and multilayers, as evidenced by the split of E12g and B1u. The electronic phase transition of the monolayer is supposed to be a direct K-K bandgap changing to an indirect K-bandgap at 2.6 GPa. These observations contribute to a better understanding of the impact of interlayer interactions on the modulation of WS2 energy bands and structure, as well as fundamental studies of two-dimensional layered materials, which can inform the development of device applications.

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Two-dimensional (2D) materials possess a wide range of tuning properties, including semiconductors, metallization, and superconducting states, that are determined by their structures. Among them, 2D transition metal dichalcogenide (TMDs) are one of the most promising candidates for future scale-up transistors due to their tunable bandgap. Interestingly, they adopt a unique electronic band structure that can be transformed from indirect bandgap to direct bandgap in monolayer TMDs. The successful preparation of two-dimensional monolayer and multilayer TMDs have revealed many excellent properties. For example, 2D TMDs with desirable bandgaps and high carrier mobility can be used to make new photodiodes in the future and have a wide range of applications in the field of integrated electronic devices.

Similar to graphite, WS2 has a layered structure with interlayer interactions through van der Waals forces, which makes the physical properties of WS2 layer dependent. For example, bulk WS2 with an indirect bandgap transforms into a direct bandgap semiconductor when reduced to monolayer thickness accompanied by a significant improvement in the photoluminescence (PL) intensity. Furthermore, compared to multilayer and bulk material WS2, monolayer WS2 has no interlayer coupling effect. By studying monolayer WS2 and comparing it with other layers, there is potential to deepen our understanding of the WS2 electronic band structure. Additionally, WS2 single molecule film has the highest quantum yield and the largest fluorescence excitation energy compared to other TMDs, making it a promising material for optoelectronic devices.

Applying pressure using diamond anvil cell (DAC) is an effective method to modulate and probe the crystal and electronic structure of semiconductors and has been widely used in a variety of TMDs. High pressure, as a pure and clean method that does not introduce impurities, can significantly change the interlayer distances and interactions, as well as the lattice constant of WS2 and the angle between W–S bonds.

To date, the structural evolution of bulk, multilayer, or powder WS2 under high pressure has been intensively studied, and the 2Hc to 2Hα crystal phase transition and the semiconductor–metal transition
transition under high pressure have been revealed. However, there is a lack of high pressure studies of the electronic band structure of different number of layers (crystal phase transitions, electronic phase transitions, etc.) In our paper, we reveal the changes in the crystal structure as well as the electronic band structure of different number of layers of WS2 (monolayer, bilayer, and multilayer) under high pressure, which is crucial for understanding the external modulation of thin-layer TMDs and has not been mentioned in previous studies. Specifically, previous studies have shown that both multilayer and monolayer WS2 has a strong dependence on the state of stress. For multilayer WS2, whether it undergoes phase transition depends on pressure transmission medium (PTM). On different substrates, the high pressure structural changes undergoes phase transition depends on pressure transmission medium. For WS2, there are normally four Raman modes, namely A1g, E1g, E2g, and B1u (Raman-inactive) are observed [the schematic diagrams of these three Raman modes are shown in Fig. 1(a)]. Among them, the principle of the N peak located near 310 cm$^{-1}$ is not clear, and since it disappears in the monolayer, it may be related to the low wave number mode E2g. As the layer number decreases, the E2g mode blueshifted and the A1g mode redshifted. The E2g mode shifts from 356.6 cm$^{-1}$ in the monolayer to 357.6 cm$^{-1}$ in the multilayer, and the A1g mode shifts from 420.7 cm$^{-1}$ to 418.5 cm$^{-1}$. The increase in frequency of the E2g mode is due to the weakening of the dielectric screening with decreasing layers, which strengthens the long-range Coulomb interaction between the effective charges and thus increases the restoring force on the atoms. The redshift of the A1g mode is due to the weakening of the binding force resulting from the weak interactions between the layers with decreasing layers.

The PL spectra of WS2 multilayer, trilayer, bilayer, and monolayer at ambient pressure are shown in Fig. 1(c). The stronger PL peak at about 2 eV is a direct K-K bandgap [K-valley of conduction band (CB) and the K-hill of valence band (VB)], and an exciton peak at lower energy is indirect A-Γ bandgap. As the layer reduces to a monolayer thickness, the indirect exciton peak disappears and the direct exciton peak increases significantly in intensity. In addition, the A-Γ bandgap increases with decreasing number of layers because the Γ point has a strong interlayer coupling, which results in a cross between the indirect gap and the direct gap. The competition between the K-K and A-Γ transition leads to an increase in the intensity of the direct exciton peak. Additionally, as shown in the inset figure of Fig. 1(c), a weaker peak on the left shoulder of the A peak is from negative trion (A$^{-}\cdot\cdot\cdot$).

In this work, we measured the high pressure Raman spectra of different number of layers of WS2 as well as the PL spectra. High pressure Raman fitting examples of the characteristic peaks of the (a) multilayer, (c) bilayer, and (e) monolayer at selected representative pressures are shown in Fig. 2. Figures S1 and S2 in the supplementary material show the variation of all Raman modes with pressure. For different number of layers, all Raman vibrational modes are blueshifted with pressure. The pressure decreases the distance between two molecular layers, causing an enhancement of the interlayer van der Waals interaction, and the enhanced interlayer interaction leads to an increase in the effective repulsive force on the atoms, resulting in an increase in the effective repulsive force on the atoms, resulting in an increase in the effective repulsive force on the atoms, resulting in an increase in the effective repulsive force on the atoms, resulting in an increase in the effective repulsive force on the atoms.
FIG. 2. Raman spectra and fitted plots of (a) multilayer, (c) bilayer, and (e) monolayer WS$_2$ at different pressures; Raman shift evolution with pressure for Raman vibration modes A$_{1g}$, B$_{1u}$, and E$_{1g}$ in the (b) multilayer, (d) bilayer, and (f) monolayer. The shift rate of each mode is labeled.
increase in the vibrational frequency. This effect causes both in-plane and out-of-plane vibrational mode to be blueshifted under pressure. By comparing our own data with Duwal and Nayak’s, we found a basic match, as shown in Fig. S3.7,8 Interestingly, B1u, the Raman-inactive vibrational mode appears in multilayers, bilayers, and monolayers at 13.7, 8.0, and 6.7 GPa, respectively, which is activated by structural disorder.6 It is not difficult to find that as the layer number increases, the B1u modes are activated at higher pressures, as shown in Table I, which suggest that an increase in the number of layers will allow the pressure exerted on the sample to be shared by more. This makes it more stable and less likely to induce the disorder.

The splitting phenomenon is quite common in other TMDs and its cause has been attributed to changes in stacking faults due to layer sliding between layers similar to the crystal phase transition from 2Hc to 2Hl.11-13 The schematics of 2Hc and 2Hl structures are shown in Fig. S4. In our report, E'2g and B1u split at 18.7 and 14.8 GPa in the multilayer and bilayer, indicative of a crystal phase transition due to stacking changes from 2Hc to 2Hl led by the layer sliding through compression. This structural transition comes from the layer sliding between adjacent layers in the WS2 material, and the layer sliding affects the E'2g in-plane vibrational mode and B1u out-of-plane vibrational mode, leading to the emergence of the split of E'2g and B1u.

There is no layer sliding in the monolayer and naturally no peak splitting. Furthermore, in order to investigate whether structural distortion and phase transition are reversible, the Raman spectra after decompression to ambient pressure are shown in Fig. S5.

Table I shows the pressure required for split phenomenon, which further shows that as the layer number increases, greater pressure is required to activate the E'2g and B1u mode split, with the difference primarily dependent on the number of layers.

Nayak et al. discovered that multilayer WS2 also showed a variation in the slope of the E and A modes, as a function of pressure. Moreover, the metallization of multilayer WS2 was found by Duwal et al. at 37 GPa,1 accompanied by a slip-induced crystal phase transition of 2Hc to 2Hl. It is worth mentioning that in Duwal’s experiments, he explored both the cases of no PTM and He as PTM, demonstrated that the presence of He atoms limited the slip motion of the layers and suppressed the shear-induced crystal phase transition, like inhibiting the appearance of B1u peaks. The reason for helium resisting the shear stress is due to low compressive strength under pressure.2 Compared to He, the higher compressive strength of Ar under pressure introduced additional shear stress and triggered the activation of the B1u mode, but at higher pressure than the case of no PTM. In addition, we discussed all the factors that could be affected by the pressure conditions, as shown in the supplementary material.

Specifically, for the multilayer sample, Duwal et al. found a knee point of blueshift rate of E'2g mode at ~5 GPa both on the case of no PTM and on He as PTM. In our work, there is a similar knee point of E'2g mode at ~5 GPa on multilayer WS2 for Ar as PTM. It may be due to local structural distortion, especially interlayer distortion, caused by compression. It is worth noting that this distortion is not related to the pressure conditions since it all happens at 5 GPa.

Notably, with higher pressure, it is found that multiple pressure coefficients also manifested for E'2g and A1g in monolayer, bilayer, and...
multilayer WS$_2$ as shown in Fig. 2. We attribute the discontinuity of the fitting slopes in frequency of A$_{1g}$ and E$_{2g}$ modes of the monolayer, bilayer, and multilayer WS$_2$ with pressure to be structural disorder and crystal phase transition since it corresponds to the emergence pressure of the B$_{1u}$ mode and the splitting of the E$_{2g}$ and B$_{1u}$ modes, which is a perfect verification of structural disorder and 2H$_c$ to 2H$_a$ phase transition at these pressures.

Table II shows the blueshift rate of the typical Raman mode at the pressure points corresponding to the structural disorder and crystal phase transition; combined with Fig. 2, we can see that the corresponding slope changes are accompanied by slight jumps or changes in slope at the corresponding pressure points. We notice that as pressure increases, the A$_{1g}$ mode shifts much faster than the E$_{2g}$ mode, which can be ascribed to the distinct vibrational feature of A$_{1g}$ and E$_{2g}$ vibration modes. Pressure influences A$_{1g}$ most because it corresponds to out-of-plane S-S vibrations, which are bound by weak van der Waals interactions, while the E$_{2g}$ mode is related to W-S vibrations that are linked through strong covalent bonds.

Table S1 compares the blueshift rate tables for E$_{2g}$ and A$_{1g}$ modes on different substrates for different number of layers of WS$_2$. It reveals that the blueshift rates of A$_{1g}$ mode on the monolayer are nearly identical on the diamond (approximately 3 cm$^{-1}$/GPa) and significantly lower than on other substrates (PMMA and SiO$_2$/Si). These results suggest that the response of monolayer samples to pressure will enhance under a substrate that is more prone to deformation due to external stress.

The PL spectra of the monolayer under high pressure and the bandgap of the monolayer, bilayer, and trilayer with pressure are shown in Fig. 3. In addition, the schematic diagram of the inferred evolution of band structure are shown in the insets of Figs. 3(c)–3(e). It is noteworthy that the bandgap of the monolayer WS$_2$ increases as pressure rises up until 2.6 GPa, after which the bandgap decreases. The PL

![Figure 3](image-url)
peak changes from blueshift to redshift. The blueshift before 2.6 GPa is due to the compression, which causes the VB and CB to move away from the Fermi surface, resulting in the increase in the bandgap. The states at the CB-A point and the VB-K point make a pair of bonding and antibonding states with mainly $d_{x^2-y^2}$ and $d_{xy}$ of W, while the states at the CB-K point mainly originate from $d_z^2$ of W. As the applied pressure increases, the bond angle of S–W–S increases, the coupling of the CB-A and the VB-K weakens, thus the band of A-K decrease. As shown in Fig. 3, as the pressure continues to increase, the energy difference between K-K bands increases and A-K decreases. Therefore, a crossover of A-K happened at 2.6 GPa. Similarly, the pressure-induced direct to indirect A-K transition happens in other monolayer TMDs, such as MoS$_2$ at $\sim$1.9 GPa, WTe$_2$ at $\sim$3.5 GPa, and MoSe$_2$ at $\sim$3.7 GPa. It can be proved that strain engineering of layered materials can modulate the band structure.

In addition to studying the PL spectra of the monolayer, we also analyzed the PL spectra of the bilayer and trilayer and compared them with those of the monolayer. The results showed that the direct exciton peak of the bilayer and trilayer undergoes a blueshift followed by a redshift phenomenon, which is consistent with the behavior observed in the monolayer. However, the indirect exciton peak consistently undergoes a redshift, which suggests that indirect A-G bandgap decreases as pressure increases as shown in Figs. 3(d) and 3(e). While the K-K gap increases and A-K decreases, which is similar to the evolution of the band structure of bilayer and trilayer MoS$_2$. This reduces the probability of K-K transition and increases the probability of A-K transition. So the A-K transition replaced the K-K transition. All in all, no electronic phase transition happened in the bilayer and trilayer.

In this work, we have investigated Raman spectra of monolayers, bilayers, and multilayers as well as PL spectra of monolayers, bilayers, and trilayers under high pressure. Crystal phase transitions due to layer sliding appear in bilayers and multilayers, and the pressure required for the layer sliding increased with the number of layers, as evidenced by the split of $E_{2g}$ and $B_{1u}$. In contrast, crystal phase transitions were not detected in monolayers. For all samples, blueshifts occur in both $E_{2g}$ and $A_{1g}$ as the pressure increases. The monolayer is considered as K-K direct bandgap to A-K indirect bandgap transitions at 2.6 GPa. For bilayers and trilayers, there are no electronic phase transitions. The different properties under pressure induction of monolayers and multilayers are available to help us better understand the effects of interlayer interactions on the WS$_2$ structure and energy bands and other fundamental studies of 2D materials. The unique optical behavior of different number of layers may be important for practical applications, such as the development of a variety of novel devices involving strong coupling of mechanical, electrical, and optical properties of layered nanomaterials.

See the supplementary material for specific experimental details.

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### DATA AVAILABILITY

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

### REFERENCES