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Excitation energy dependence of Raman spectra of few-layer WS_2

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ABSTRACT

Raman spectra of few-layer WS_2 have been measured with up to seven excitation energies, and peculiar resonance effects are observed. The two-phonon acoustic phonon scattering signal close to the main $E_{2g}{}^1$ peak is stronger than the main peaks for excitations near the A or B exciton states. The low-frequency Raman spectra show a series of shear and layer-breathing modes that are useful for determining the number of layers. In addition, *hitherto* unidentified peaks (X_1 and X_2), which do not seem to depend on the layer thickness, are observed near resonances with exciton states. The polarization dependences of the two peaks are different: X_1 vanishes in cross polarization, but X_2 does not. At the resonance with the A exciton state, the Raman-forbidden, lowest-frequency shear mode for odd number of layers appears as strong as that for the allowed case of even number of layers. This mode also exhibits a strong Breit-Wigner-Fano line shape and an anomalous polarization behavior at this resonance.

Introduction

Two-dimensional semiconductors, including transition metal dichalcogenides (TMDs) such as MoS_2, $MoSe_2$, and WS_2 are attracting much interest owing to unique 2-dimensional physical phenomena and superior opto-electronic properties that are advantageous for future devices. Spin-valley coupling [1–4] and strong electron-hole interaction due to reduced dielectric screening [5–7] lead to several novel phenomena such as the valley Hall effect and observation of exciton-polaritons [8–10]. High electrical mobility and a large on/off ratio as well as large oscillator strength for optical transitions make them suitable for transistors [11,12], photodetectors [13,14], solar cells [15], biosensors [16] and light-emitting-devices [17,18] compatible with flexible electronics. Because of the strong electron-hole interaction, excitonic features play important roles in determining the optical properties of these materials. For example, in the absorption spectrum, the excitonic features are most prominent: the A exciton state associated with the bottom of the conduction band and the top of the valence band at the K and K′ points of the Brillouin zone and the B exciton state that is associated with the spin-orbit-split valence band are commonly observed [5,19,20]. In addition, the C exciton state associated with a higher energy band gap is observed [21–23]. The energetic separation between the A and B exciton states is determined by the spin-orbit interaction and is about 0.15–0.45 eV.

Raman spectroscopy is widely used to determine the number of layers and other important properties of layered 2-dimensional materials [24–29]. For TMD's, care should be taken because many of the commonly used excitation lasers are in resonance with one of the exciton states. For example, the 632.8 nm line of a He-Ne laser is closer to the resonance with the A and B excitons of MoS_2 [20,21,30], and many anomalous behaviors are observed when this laser line is used as the excitation source [28,31,32]. The resonance Raman effects, therefore, have become an important issue, and the correlation of anomalous resonance effects with different excitonic states is very interesting [23,33–35]. However, the contributions of A and B exciton states tend to be mixed in MoS_2 and $MoSe_2$ since the spin-orbit splitting is not large enough. WS_2 is a particularly useful because of a large spin-orbit splitting (~0.4 eV), which makes it relatively easy to probe the exciton-related phenomena for A and B excitons separately [5]. The conduction band also shows a small spin-orbit splitting. In the case of MoS_2, the higher valence band and the lower conduction band have the same spin, and so the exciton associated with the lowest energy transition is optically active (bright exciton). However, in the case of WS_2, because the spin-orbit splitting in the conduction band has an opposite sign, the lowest-energy exciton is not optically active (dark exciton) [36]. Therefore, the presence of the dark exciton state which has a slightly different energy than the bright exciton state should be taken into account in interpreting optical effects in this energy range. In this work, we measured the Raman spectra of mono- and few-layer WS_2 using up to seven excitation energies, some of which are in resonance with the A, B, or C exciton. Resonance effects are most pronounced in the low-frequency

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region in which the rigid shear and layer-breathing modes appear. Several new features are found and identified in the low-frequency Raman spectra of few-layer WS_2.

Methods

Few-layer WS_2 samples were prepared by mechanical exfoliation from WS_2 flakes (HQ Graphene) on Si substrates with a 285 nm SiO_2 layer. We identified the number of layers by comparing the optical contrast, PL, and Raman measurements [29,37–39]. The Raman measurements were performed in ambient conditions with seven excitation sources: the 325 and 441.6 nm (3.82 and 2.81 eV) lines of a He-Cd laser; the 457.9, 488, 514.5 nm (2.71, 2.54 and 2.41 eV) lines of an Ar ion laser; the 532 nm (2.33 eV) line of a diode-pumped-solid-state laser; and the 632.8 nm (1.96 eV) line of a He-Ne laser. A 50× objective lens (0.8 N.A.) was used to focus the laser beam onto the sample. The scattered light was collected by the same objective lens (backscattering geometry) and dispersed with a Horiba iHR550 spectrometer (2400 grooves/mm). We used reflective volume holographic filters (Ondax and OptiGrate) to prevent the laser line from entering the spectrometer. To avoid local heating, the laser power was kept at 50 μW for all measurements. The Raman intensities are normalized by the silicon Raman intensity including the resonance effect [40] for each excitation energy to correct for the efficiency of the detection system. The multiple interference effect from the substrate is accounted for [41] by using the dielectric functions and refractive indices of monolayer and bulk WS_2 from the literature [19,42]. Reflectance contrast spectra were obtained by measuring the reflectance spectra of the sample and the bare substrate using a supercontinuum laser (Fianium sc-400) and calculating $[R(\text{sample}) - R(\text{substrate})]/[R(\text{sample}) + R(\text{substrate})]$. The spectral resolution ranged between 0.3 cm^{-1} (1.96 eV) and 1.5 cm^{-1} (3.82 eV).

Results

Monolayer WS_2 consists of a tungsten layer sandwiched between two sulfur layers, forming a so-called tri-layer (TL) as shown in Fig. 1a. The point group corresponds to D_{6h} for bulk, D_{3h} for odd number of layers, and D_{3d} for even number of layers

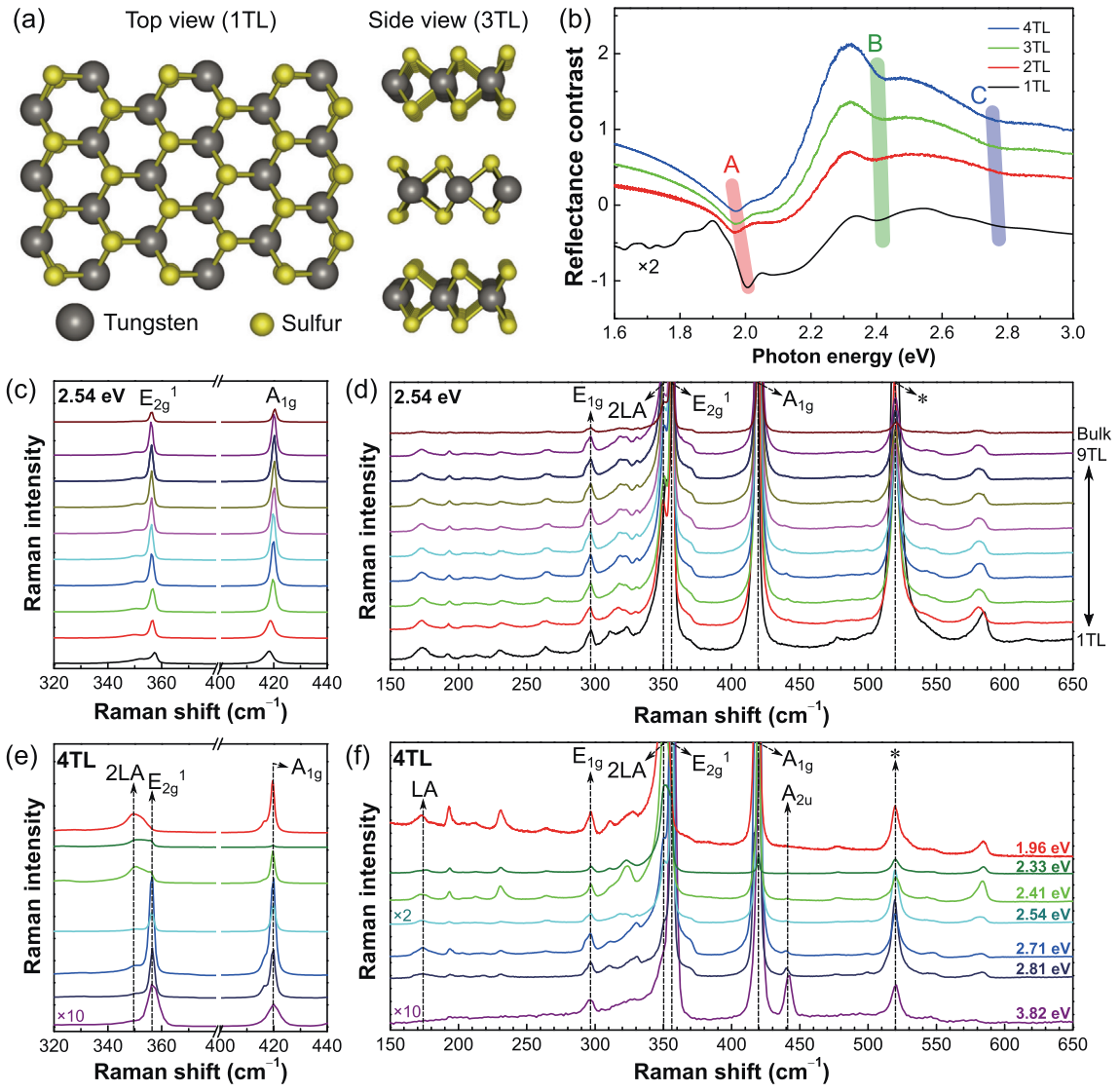

Fig. 1. (a) Crystal structure of monolayer (top view) and 3TL (side view) WS_2. (b) Reflectance contrast spectra of 1TL to 4TL. Thickness dependence of Raman spectrum of (c) main peaks (E_{2g}^1 and A_{1g}) and (d) weaker peaks measured with 2.54 eV excitation. Excitation energy dependence of Raman spectrum of 4TL WS_2 for (e) main peaks and (f) weaker peaks. The silicon signal at 520 cm^{-1} is marked by *.

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