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<td>Author(s)</td>
<td>Zheng, Shoujun; Sun, Linfeng; Yin, Tingting; Dubrovkin, Alexander M.; Liu, Fucai; Liu, Zheng; Shen, Ze Xiang; Fan, Hong Jin</td>
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Monolayers of $W_xMo_1-xS_2$ alloy heterostructure with in-plane composition variations

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We report the fabrication of single-crystal monolayer $W_xMo_1-xS_2$ alloy triangles using chemical vapor deposition method. Raman and photoluminescence property are investigated in correlation to the composition. In the monolayer triangles, the photoluminescence peak shifts continuously from 687.4 nm at the triangle center to 633.6 nm at the edge, corresponding to a switch from MoS$_2$ to WS$_2$ across the heterojunction. This composition-graded alloy may have interesting functions in broadband photodetection and multi-color light emission.

Since the discovery of graphene, two-dimensional (2-D) materials have attracted increasing attentions in recent years due to their unique electrical and optical properties and functions. Compared to graphene (near zero bandgap), 2-D transitional metal dichalcogenides (TMDs), such as MoS$_2$, WSe$_2$, transit from indirect band gap in bulk form to direct band gap in monolayers. Monolayer MoS$_2$ is a flexible and strong material with a high Young’s modulus, comparable to stainless steel. Due to inversion symmetry breaking in monolayer MoS$_2$, transitions at K and K’ momentum space can be selectively excited by left circularly polarized and right circularly polarized light which has potential applications in valleytronics. Single crystal 2-D TMDs have been synthesized by chemical vapor deposition (CVD) method, which is so far the major method to obtain large-scale monolayers of various types of TMDs.

Band gap engineering of TMDs monolayer for their potential optical applications such as photodetectors can be realized by applying strain, stacking of dissimilar TMDs, and doping. Forming heterojunctions of TMDs is another route to tuning the optical and electrical properties. Theories have predicted some interesting physical properties of vertically stacked 2-D heterostructures with respect to individual monolayers. For example, vertical stacked graphene/WS$_2$/graphene trilayers have shown enhanced photon absorption and electron-hole creation, making them promising in efficient flexible photovoltaic devices. Graphene/h-BN heterostructures have been fabricated on lithographically patterned h-BN atomic layers. Recently, in-plane heterostructure TMDs such as MoS$_2$–WS$_2$, WS$_2$–WSe$_2$, MoSe$_2$–WSe$_2$, and Mo$_1-x$W$_x$Se$_2$ have been synthesized in one step by CVD method. Position dependent photoluminescence (PL) of monolayer WS$_2$ has been reported, which may be caused by impurity. As for 2-D TMDs alloy materials, they are theoretically predicted stable under ambient conditions. Selenium-doped MoS$_2$ monolayer and MoS$_2$Se$_{2(1-x)}$ alloy were directly grown by CVD method to tune the monolayer band gap. Mechanical exfoliated Mo$_1-x$W$_x$S$_2$ and Mo$_1-x$W$_x$Se$_2$ monolayer alloys have also been obtained with a continuous tuning of their band gaps. However, $W_xMo_1-xS_2$ alloy with variable band gap in monolayer by CVD method has not been reported. Here, we demonstrate our one-step CVD growth of a $W_xMo_1-xS_2$ monolayer alloy with position-dependent composition. Both PL and Raman mapping results show that our samples are in-plane composition-graded alloy across the MoS$_2$–WS$_2$ heterostructure that changes gradually from MoS$_2$–dominated phase in the center region to WS$_2$–dominated phase near the edge. Such heterostructures with alloyed interface differ from the recently reported MoS$_2$–WS$_2$ heterojunction which have has a distinct interface between the two phases. Realization of such single-crystal monolayers with inhomogeneous bandgaps could be important to the application in wideband photodetection and multi-color light emissions.

Our sample was grown by CVD method (see setup in Fig. 1(a)) similar to previously reported procedure. MoO$_3$ and WO$_3$ powder were dispersed into ethanol, and then dropped onto different places of Si/SiO$_2$ substrates. The Si/SiO$_2$ substrates were put into a one-end-sealed...
small quartz tube, and the small tube was then pushed into the center of a 25 mm-diameter quartz tube. 0.2 g sulfur was put at the edge of quartz tube. First, the tube was flushed by Ar gas flow at 200 sccm for 15 min in order to eliminate air, then maintained at an atmospheric pressure with continuous Ar flow at 10 sccm. The furnace was then ramped to 550 °C in 10 min, then to 850 °C at a rate of 5 °C /min, and finally maintained at 850 °C for 10 min. After the growth, the furnace was switched off and cooled to room temperature naturally. WxMo1-SxS2 samples were found near to the WO3 source.

SEM characterization was conducted using field emission scanning electron microscope with energy dispersive x-ray analysis (JEOL JSM-6700F). Atomic force microscopy (AFM) and scanning near-field optical microscope (SNOM) were measured by a scattering-type system (Neaspec) at an excitation wavelength of 11.2 μm. Photoluminescence (PL) mapping at excitation wavelength of 532 nm and 457 nm was obtained from a WITEC CRM200 Raman system with 150 line mm−1 grating. Raman mapping at excitation wavelength of 457 nm was measured on a WITEC CRM200 Raman system with 1800 line mm−1 grating. Raman spectrum at excitation wavelength of 532 nm was obtained from a Renishaw Invia Raman microscope.

As the melting point of WO3 (1473 °C) is much higher than that of MoO3 (800 °C), MoS2 is expected to grow first followed by WS2 during the increase of furnace temperature. A typical SEM image of the as-synthesized sample is shown in Fig. 1(b), in which we can find numerous triangle-shaped crystals. Microscopic optical image of one typical monolayer triangle shows homogeneous contrast (Fig. 2(a)). However, in SEM image taken from the same triangle (Fig. 2(b)), a contrast between the center and edge part can be inspected and a small triangle at the center is spotted. This contrast indicates that the big triangle contains two kinds of materials. From AFM measurement, the height of this triangle is determined to be about 0.7 nm, which is uniform from the edge to the center (Fig. 2(b)). Figure 2(c) is the AFM image of one triangle. There is only a very slight difference between the center and the edge part. Therefore, we may conclude that this triangle is a single layer. In other words, the heterostructure is formed in a lateral direction. Figure 2(d) is a SNOM phase image of the same triangle in Fig. 2(c) recorded using an incident laser of 11.2 μm. The signal of scattering-type SNOM is related to dielectric constant of materials. The contrast of two colors in one triangle is another evidence of the heterostructure, in addition to the SEM image. More SNOM data of two triangles are presented in supplementary material. Note that the intensity of SNOM signal of some triangles is continuous from center to edge, rather than a shape contrast, which is consistent with a mixed composition from the center to edge.

It is further realized that this monolayer is not a MoS2–WS2 two-phase heterojunction, but with a WxMo1–SxS2 alloy interface with varying composition. The first evidence can be provided by Raman result. Figure 3(a) is the optical image of one triangle alloy taken by the Raman spectrum.
CCD, and Fig. 3(b) shows the Raman spectra recorded from six points marked in Fig. 3(a). We can clearly see that the $E_{2g}$ mode and $A_{1g}$ mode shift from point 1 (at the edge) to point 6 (at the center). Figs. 3(c) and 3(d) show Raman intensity mappings of the peak centered at 356 cm$^{-1}$ ($E_{2g}$ mode of WS$_2$) and at 384 cm$^{-1}$ ($E_{2g}$ mode of MoS$_2$), respectively. The mappings by the $A_{1g}$ mode in Figs. 3(e) and 3(f) show similar results. Based on these Raman intensity mapping images, one may conclude that our sample is composed of MoS$_2$–WS$_2$ two-phase heterojunction with a sharp interface. In fact, it has been reported that the Raman spectra of W$_x$Mo$_{1-x}$S$_2$ alloy by exfoliation still look similar to that of MoS$_2$ even when the $x$ value reaches 0.42. It is important to note that the Raman spectrum at each point in Fig. 3(b) is different from each other. At point 1, the Raman shift of $E_{2g}$ mode is 356.1 cm$^{-1}$ and the $A_{1g}$ mode is 418.2 cm$^{-1}$. From point 1 to point 3, the intensity of $A_{1g}$ mode is unchanged, but $E_{2g}$ mode decreases. At the center region (point 6), The $E_{2g}$ mode of MoS$_2$ locates at 384.5 cm$^{-1}$ and the $A_{1g}$ at 404.0 cm$^{-1}$. The difference between the two modes is 19.5 cm$^{-1}$ which is consistent with the monolayer MoS$_2$. At point 5, the difference (23.1 cm$^{-1}$) becomes larger. At point 4, which is the transition region between WS$_2$ and MoS$_2$, the Raman spectrum shows three peaks which are mixed with vibration modes of WS$_2$ and MoS$_2$. Our Raman spectra of six points at Fig. 3(b) correspond very well to that of W$_x$Mo$_{1-x}$S$_2$ alloy obtained by mechanical exfoliation. Therefore, it can be inferred that our sample is an alloy heterostructure, rather than a distinction heterojunction. To further confirm the alloy composition, Raman spectra were also measured using the excitation wavelength of 532 nm. Point 1 and point 2 show WS$_2$ like Raman spectra. However, compared to pure WS$_2$, two additional peaks are present between the $E_{2g}$ and $A_{1g}$ modes of WS$_2$. We propose that Mo doping is responsible for two additional peaks. Raman spectrum of Point 3 is composed of peaks from both MoS$_2$ and WS$_2$, but the later becomes very weak. At the central region, Point 4 shows MoS$_2$ like Raman spectrum but the $A_{1g}$ mode is broader than that of pure MoS$_2$. These data further corroborate that our sample is composed of W$_x$Mo$_{1-x}$S$_2$ alloy heterostructure with different composition from center to the edge of the triangle.

We now present and discuss the PL results. Due to the transition from indirect band gap of bulk materials to direct band gap of monolayer, both MoS$_2$ and WS$_2$ have strong PL emissions in monolayers but with different PL peak positions (band gap of MoS$_2$~1.85 eV and WS$_2$~1.98 eV). Figure 4(a) is one selected triangle used for PL characterization at an excitation wavelength of 532 nm. As the PL intensity of WS$_2$ monolayer is approximately two orders of magnitude that of MoS$_2$ in our samples, the center of the triangle appears dark (Fig. 4(b)). The difference in PL intensity in our sample could result from the different defect concentrations between the center region and edge part. In general, the PL emission intensity of monolayer WS$_2$ is drastically higher than that of monolayer MoS$_2$. And, this has been attributed to higher concentration of defects or unintentional doping in the monolayer MoS$_2$ compared to WS$_2$. By mapping selectively the fitted PL intensity of the MoS$_2$ spectra (Fig. 4(c)), we can clearly see that center region of the triangle is close to MoS$_2$. As for the mapping of the fitted peak intensity of WS$_2$, the image becomes indistinguishable from Fig. 4(b), which is unsurprising since the PL intensity of WS$_2$ is much stronger than that of MoS$_2$. Figure 4(d) shows the PL spectra selected from the six points, which present the position-dependent peak position and intensity. Consistent to the mapping, the PL intensity drops dramatically from point 1 to point 6, and the peak position simultaneously shifts from 633.6 to 687.4 nm. At point 5 and point 6, the PL spectra are characteristics of MoS$_2$ (see the two peaks in inset of Fig. 4(d)); however, peak A red shifts compared to the pure MoS$_2$ monolayer that we will discuss later. To show the shift more clearly, the normalized spectra were presented in supplementary material. It has been shown that the PL peak position of TMDs alloy can shift continuously by tuning the composition of different elements. Therefore, it is

![FIG. 4. Photoluminescence characterization.](image-url)
reasonable that the PL shift of our sample results from the composition inhomogeneity at different positions of individual triangle. Similar PL spectra obtained by excitation with a shorter-wavelength (457 nm) laser line show another peak (peak B) that also shifts with location in the same trend with peak A.  

Position dependent PL of pure WS 2 monolayer has been reported previously, 23,24 in which the blue shift was observed only near the edge and the shift was due to variation of the W to S atomic ratio. 23 The PL redshift in our study originates from composition inhomogeneity from the edge region to the center; possible reason for this composition inhomogeneity is that WS 2 and MoS 2 are doped into each other during the growth. Peak A and peak B of MoS 2 and WS 2 are the direct excitonic transitions at the Brillouin zone K point from conduction band to valence band, 5,34 due to spin-orbit coupling in valence band. The position of peak A of pure MoS 2 in our sample is 675.4 nm, and 625.0 nm to spin-orbit coupling in valence band. We can see that the composition of the alloy has been calculated. "MoxW1" 13

The monolayer heterostructure possesses position-dependent band gap from center to edge, based on which the composition of the alloy has been calculated. Mo,W S alloy with different band gap may have interesting applications as photodetectors and multi-color light emitters.

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30. See supplementary material at http://dx.doi.org/10.1063/1.4908256 for more SNOM, Raman, and PL data of our samples.