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Monolayers of $W_xMo_{1-x}S_2$ alloy heterostructure with in-plane composition variations

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We report the fabrication of single-crystal monolayer $W_xMo_{1-x}S_2$ 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. © 2015 AIP Publishing LLC.

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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.^{1–3} Compared to graphene (near zero bandgap), 2-D transitional metal dichalcogenides (TMDs), such as MoS_2 ,^{4,5} and WS_2 ,⁶ 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.³ 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.^{7–9} Single crystal 2-D TMDs have been synthesized by chemical vapor deposition (CVD) method,^{10–12} 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,¹³ stacking of dissimilar TMDs,¹⁴ and doping. Forming heterojunctions of TMDs is another route to tuning the optical and electrical properties. Theories have predicted some interesting physical properties of vertical stacked 2-D heterostructures with respect to individual monolayers.^{14–17} 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.¹⁸ Graphene/h-BN heterostructures have been fabricated on lithographically patterned h-BN atomic layers.¹⁹ Recently, in-plane heterostructure TMDs such as MoS_2 – WS_2 ,²⁰ WS_2 – WSe_2 ,²¹ and $MoSe_2$ – WSe_2 ²² have been synthesized in one step by CVD method. Position dependent photoluminescence (PL) of monolayer WS_2 has been reported^{23,24} which may be caused by impurity. As for 2-DTMDs alloy materials, they are theoretically predicted stable under ambient conditions.²⁵ Selenium-doped MoS_2 monolayer²⁶ and $MoS_{2x}Se_{2(1-x)}$ alloy²⁷ were directly grown by CVD method to tune the monolayer band gap. Mechanical exfoliated $Mo_{1-x}W_xS_2$ ²⁸ and $Mo_{1-x}W_xSe_2$ ²⁹ monolayer alloys have also been obtained

with a continuous tuning of their band gaps. However, $W_xMo_{1-x}S_2$ alloy with variable band gap in monolayer by CVD method has not been reported. Here, we demonstrate our one-step CVD growth of a $W_xMo_{1-x}S_2$ 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.²⁰ 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.²³ MoO_3 and WO_3 powder were dispersed into ethanol, and then dropped onto different places of Si/SiO₂ (285 nm SiO₂) surfaces. The Si/SiO₂ substrates were put into a one-end-sealed

FIG. 1. (a) CVD setup for the growth of $Mo_xW_{1-x}S_2$ alloy monolayers. (b) SEM image of a general view of the obtained sample.

FIG. 2. (a) Microscopic optical image of one $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ triangle and (b) the corresponding SEM image. A small triangle in the center region is visible. AFM height signal following the dashed line confirms the monolayer. (c) AFM image of one triangle, and (d) the corresponding SNOM phase image. The different contrast between the center and the edge indicates the composition difference.

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 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. $\text{W}_x\text{Mo}_{1-x}\text{S}_2$ samples were found near to the WO_3 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 WO_3 (1473 °C) is much higher than that of MoO_3 (800 °C), MoS_2 is expected to grow first followed by WS_2 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.²⁹ 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.³⁰ 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 MoS_2 – WS_2 two-phase heterojunction, but with a $\text{W}_x\text{Mo}_{1-x}\text{S}_2$ 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

FIG. 3. Raman characterization with the excitation wavelength of 457 nm. (a) Optical image of one triangle. (b) Raman spectra collected from 6 points in (a). Raman intensity mappings of the E_{2g}^1 mode of (c) WS_2 and (d) MoS_2 . Raman intensity mapping of the corresponding A_{1g} mode of (e) WS_2 and of (f) MoS_2 .

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}^1 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}^1 mode of WS_2) and at 384 cm^{-1} (E_{2g}^1 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 $\text{W}_x\text{Mo}_{1-x}\text{S}_2$ alloy by exfoliation still look similar to that of MoS_2 even when the x value reaches 0.42.²⁸ 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}^1 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}^1 mode decreases. At the center region (point 6), the E_{2g}^1 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 .³¹ 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 $\text{W}_x\text{Mo}_{1-x}\text{S}_2$ alloy obtained by mechanical exfoliation.²⁸ 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 .³⁰ 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}^1 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 $\text{W}_x\text{Mo}_{1-x}\text{S}_2$ 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 $\text{MoS}_2 \sim 1.85\text{ eV}$ and $\text{WS}_2 \sim 1.98\text{ eV}$).^{4,6} 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 .^{6,32,33} 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 ,³⁰ the image becomes undistinguishable 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.³⁰ It has been shown that the PL peak position of TMDs alloy can shift continuously by tuning the composition of different elements.^{27,29} Therefore, it is

FIG. 4. Photoluminescence characterization. (a) Optical image of one $\text{W}_x\text{Mo}_{1-x}\text{S}_2$ triangle. (b) Panchromatic PL image showing the intensity distribution. (c) PL intensity mapping of MoS_2 fitting from (b). (d) PL spectra collected from six points indicated in (a). Inset shows the PL spectra at point 5 and point 6 with peak fitting. (e) PL peak position as a function of the position, together with data of pure WS_2 and pure MoS_2 . The calculated x value of the $\text{Mo}_x\text{W}_{1-x}\text{S}_2$ monolayer alloy is also plotted.

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.³⁰

Position dependent PL of pure WS₂ 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 WS₂ and MoS₂ are doped into each other during the growth. Peak A and peak B of MoS₂ and WS₂ 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 MoS₂ in our sample is 675.4 nm, and 625.0 nm for pure WS₂ at the excitation wavelength of 532 nm. The peak A position from the six points all deviate from that of pure MoS₂ or WS₂, corresponding to different ratios of Mo to W in the W_xMo_{1-x}S₂ alloy region. The redshift at point 6 with respect to the pure MoS₂ can be explained by the Bowling effect in the monolayer W_xMo_{1-x}S₂ alloy.²⁸ Empirically, the PL peak position can be correlated to the composition according to equation²⁸

$$E_{W_xMo_{1-x}S_2} = xE_{WS_2} + (1-x)E_{MoS_2} - bx(1-x).$$

The bowling factor b makes the equation nonlinear, which is what we see in our results (Fig. 4(e)). In order to estimate the composition of the alloy, a reasonable value of b is needed. We assume the bowling factor to be 0.34 by setting the highest value of the above quadratic equation equal to our observed value of 687.4 nm (at point 6). Then, the composition at all six points are calculated and plotted in Fig. 4(e). Point 0 and point 7 represent the pure WS₂ and pure MoS₂. We can see that x decreases gradually from the edge region to the center. It is proposed that the composition variation stems from a change in the precursor concentration during the growth temperature rises up. Because of its lower melting point, MoO₃ sublimates first and give rise to the initial growth of MoS₂-dominating composition near the center region. Subsequently, further increasing temperature induces the growth of WS₂-dominating composition near the edge region. Hence, Mo_xW_{1-x}S₂ alloy monolayer with inhomogeneous PL is obtained after the whole growth.

In conclusion, we have realized Mo_xW_{1-x}S₂ monolayer alloy heterostructure with in-plane inhomogeneous composition using the conventional CVD method. It is proposed that MoS₂ grows first at the center followed by growth of Mo_xW_{1-x}S₂ along the edge of MoS₂. PL results show that the monolayer heterostructure possesses position-dependent band gap from center to edge, based on which the composition of the alloy has been calculated. Mo_xW_{1-x}S₂ alloy with different band gap may have interesting applications as photodetectors and multi-color light emitters.

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