Preparation of Large-area Vertical 2D Crystal Hetero-structures Through the Sulfurization of Transition Metal Films for Device Fabrication

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Abstract

We have demonstrated that through the sulfurization of transition metal films such as molybdenum (Mo) and tungsten (W), large-area and uniform transition metal dichalcogenides (TMDs) MoS_2 and WS_2 can be prepared on sapphire substrates. By controlling the metal film thicknesses, good layer number controllability, down to a single layer of TMDs, can be obtained using this growth technique. Based on the results obtained from the Mo film sulfurized under the sulfur deficient condition, there are two mechanisms of (a) planar MoS_2 growth and (b) Mo oxide segregation observed during the sulfurization procedure. When the background sulfur is sufficient, planar TMD growth is the dominant growth mechanism, which will result in a uniform MoS_2 film after the sulfurization procedure. If the background sulfur is deficient, Mo oxide segregation will be the dominant growth mechanism at the initial stage of the sulfurization procedure. In this case, the sample with Mo oxide clusters covered with few-layer MoS_2 will be obtained. After sequential Mo deposition/sulfurization and W deposition/sulfurization procedures, vertical WS_2/MoS_2 hetero-structures are established using this growth technique. Raman peaks corresponding to WS_2 and MoS_2, respectively, and the identical layer number of the hetero-structure with the summation of individual 2D materials have confirmed the successful establishment of the vertical 2D crystal hetero-structure. After transferring the WS_2/MoS_2 film onto a SiO_2/Si substrate with pre-patterned source/drain electrodes, a bottom-gate transistor is fabricated. Compared with the transistor with only MoS_2 channels, the higher drain currents of the device with the WS_2/MoS_2 hetero-structure have exhibited that with the introduction of 2D crystal hetero-structures, superior device performance can be obtained. The results have revealed the potential of this growth technique for the practical application of 2D crystals.

Video Link

The video component of this article can be found at https://www.jove.com/video/56494/

Introduction

One of the most common approaches to obtain 2D crystal films is using mechanical exfoliation from bulk materials[1,2,3,4,5]. Although 2D crystal films with high crystalline quality can be easily obtained using this method, scalable 2D crystal films are not available through this approach, which is disadvantageous for practical applications. It has been demonstrated in previous publications that using chemical vapor deposition (CVD), large-area and uniform 2D crystal films can be prepared[6,7,8,9]. Direct growth of graphene on sapphire substrates and layer-number-controllable MoS_2 films prepared by repeating the same growth cycle are also demonstrated using the CVD growth technique[10,11]. In one recent publication, in-plane WSe_2/MoS_2 hetero-structure flakes are also fabricated using the CVD growth technique[12]. Although the CVD growth technique is promising in providing scalable 2D crystal films, the major disadvantage of this growth technique is that different precursors have to be located for different 2D crystals. The growth conditions also vary between different 2D crystals. In this case, the growth procedures will become more complicated when demand grows for 2D crystal hetero-structures.

Compared with the CVD growth technique, the sulfurization of pre-deposited transition metal films has provided a similar but much simpler growth approach for TMDs[13,14]. Since the growth procedure involves only metal deposition and the following sulfurization procedure, it is possible to grow different TMDs through the same growth procedures. On the other hand, the layer number controllability of the 2D crystals may also be achieved by changing the pre-deposited transition metal thicknesses. In this case, growth optimization and layer number control down to a single layer are required for different TMDs. Understanding growth mechanisms is also very important for the establishment of complicated TMD hetero-structures using this method.

In this paper, MoS_2 and WS_2 films are prepared under similar growth procedures of the metal deposition followed by the sulfurization procedure. With the results obtained from the sulfurization of Mo films under sulfur sufficient and deficient conditions, two growth mechanisms are observed during the sulfurization procedure[15]. Under the sulfur sufficient condition, a uniform and layer-number-controllable MoS_2 film can be obtained after the sulfurization procedure. When the sample is sulfurized under the sulfur deficient condition, the background sulfur is not sufficient to form a complete MoS_2 film such that the Mo oxide segregation and coalescence will be the dominant mechanism at the early

growth stage. A sample with Mo oxide clusters covered by few layers of MoS_2 will be obtained after the sulfurization procedure[15]. Through sequential metal deposition and following sulfurization procedures, WS_2/MoS_2 vertical hetero-structures with layer number controllability down to a single layer can be prepared[15,16]. Using this technique, a sample is obtained on a single sapphire substrate with four regions: (I) blank sapphire substrate, (II) standalone MoS_2, (III) WS_2/MoS_2 hetero-structure, and (IV) standalone WS_2[17]. The results demonstrate that the growth technique is advantageous for the establishment of vertical 2D crystal hetero-structure and is capable of selective growth. The enhanced device performances of 2D crystal hetero-structures will mark the first step toward practical applications for 2D crystals.

Protocol

1. Growth of Individual 2D material (MoS_2 and WS_2)

1. **Transition metal deposition using an RF sputtering system**
   1. A clean 2 x 2 cm^2 sapphire substrate is placed on the sample holder with the polished side toward the targets of the sputtering system for the transition metal deposition. Sapphire substrates are chosen due to sapphire's chemical stability at high temperatures and atomic-flat surfaces.
   2. Pump down the sputtering chamber to 3 x 10^{-6} torr sequentially using a mechanical pump followed by a diffusion pump.
   3. Inject the Ar gas into the sputtering system and keep the gas flow at 40 mL/min using a mass flow controller (MFC).
   4. Keep the chamber pressure at 5 x 10^{-2} torr using a manual pressure control valve and ignite the Ar plasma. Keep the output power at 40 W.
   5. Decrease the chamber pressure to 5 x 10^{-3} torr using a manual wheel Angle poppet valve.
   6. Manually open the shutter between the sapphire substrate and the 2-inch metal target and start the metal deposition. During the deposition procedure, keep the sputtering power at 40 W for both Mo and W. The background pressure is kept at 5 × 10^{-3} torr with 40 mL/min Ar gas flow.
   7. Control the sputtering time to deposit transition metal films with different thicknesses. Due to the thin metal thickness, sputtering times will provide better control over the film thickness than the readings from the quartz crystal resonator.
   NOTE: The layer numbers of MoS_2 and WS_2 grown using the method discussed in the current manuscript are proportional to the sputtering times of the pre-deposited Mo and W films. The determination of sputtering times to obtain MoS_2 and WS_2 with required layer numbers is based on the cross-sectional high-resolution transmission electron microscopy (HRTEM) images for samples with different sputtering times. However, if the pre-deposited Mo and W films are too thick, Mo and W oxide segregation will become the dominant growth mechanism, instead of planar MoS_2 and WS_2 film growth. Therefore, the proportionality of layer numbers with the sputtering times is limited to few-layer TMDs. With the growth condition of MoS_2 in the current manuscript, the layer numbers will be proportional to the sputtering times when the MoS_2 film is fewer than 10 layers. The sputtering time is 30 s for the growth of 5-layer MoS_2.

2. **The sulfurization of the transition metal film**
   1. Place the sapphire substrates with pre-deposited transition metal films in the center of a hot furnace for sulfurization.
   2. Place the sulfur (S) powder upstream of the gas flow, 2 cm away from the heating zone of the furnace. In this position, the evaporation temperature for the S powder will be 120 °C when the substrate temperature increases to 800 °C. Precisely control the S powder weight for different transition metals for sulfurization. In the work, the S powder weight is 1.5 g for Mo and 1.0 g for W.
   NOTE: We determine sulfur powder amounts for the preparation of MoS_2 and WS_2 films based on the results obtained for each material prepared using different amounts of sulfur powder.
   3. Keep the furnace pressure at 0.7 torr. During the sulfurization procedure, 130 mL/min Ar gas was used as carrier gas.
   4. Ramp the temperature of the furnace from room temperature to 800 °C in 40 min with a temperature ramping rate of 20 °C/min. Keep the temperature at 800 °C until the sulfur powder is fully evaporated. After that, the heater power is switched off to lower the furnace temperature. It takes about 30 to 40 min for the furnace to reach room temperature from 800 °C.

3. Perform Raman spectrum measurements using a 488 nm laser[15,16,17]. Obtain the cross-sectional HRTEM images to verify the layer numbers of the 2D crystals[15,16,17].

2. The Growth of the WS_2/MoS_2 Vertical Single Hetero-structure

NOTE: This section is used to create a single hetero-structure consisting of a sapphire layer with 5 layers of MoS_2 and 4 layers of WS_2.

1. Follow the same procedure as step 1.1. Deposit the Mo film on the sapphire substrate using the RF sputtering system with a 30 s sputtering time.
2. Sulfurize the Mo film following the same sulfurization procedures as step 1.2 for the growth of MoS_2. Five layers of MoS_2 will be obtained after the sulfurization procedure.
3. Follow the same procedures as step 1.1. Deposit the W film on the MoS_2/sapphire substrate using the RF sputtering system with a 30 s sputtering time.
4. Sulfurize the W film following the same sulfurization procedure of step 1.2 for the growth of WS_2. Four layers of WS_2 will be obtained on top of the MoS_2 after the sulfurization procedure.
   NOTE: The metal deposition and sulfurization procedure is the same as the individual material. The sputtering times of the Mo and W films are determined depending on the required layer numbers of MoS_2 and WS_2 layers. Double- or multi-hetero-structures can be established by repeating the same growth procedure. The sequence of the TMDs in the vertical hetero-structures can also be changed depending on the sample structure.

3. The Film Transferring and Device Fabrication Procedures

1. **The film transferring procedure of the 2D crystal films**
   1. Spin coat three drops of poly(methyl methacrylate) (PMMA) on the TMD film to cover the whole film at room temperature. The two-stage rotation speeds of the spinner are 500 rpm for 10 s and 800 rpm for 10 s. After curing at 120 °C for 5 min, the PMMA thickness is around 3 µm.
   2. Place the PMMA/TMD/Sapphire sample in a Petri dish which is filled with deionized (DI) water.
   3. Peel off one corner of the PMMA/TMD film from the sapphire substrate using tweezers in DI water.
   4. Heat 250 mL of 1 M KOH aqueous solution (14 g KOH pellets mixed with 250 mL water) in a beaker to 100 °C. Move the sample in the heated KOH aqueous solution and continue peeling the PMMA/TMD film until the film is completely peeled off from the substrate. Peeling requires about 1 min to complete.
   5. Use a separate sapphire substrate to scoop up the PMMA/TMD film from the KOH solution. Move the film to a 250 mL beaker filled with DI water to wash off residue KOH on the film. At this stage, the adhesion between the PMMA/TMD film and the sapphire substrate to scoop the film is weak. Therefore, the film will de-attach from the sapphire substrate after immersion into the DI water.
   6. Repeat steps 3.1.4 - 3.1.5 three times using new DI water to make sure that most of the residue KOH is removed from the film.
      NOTE: The adhesion between each TMD layer is much stronger than TMDs with the sapphire substrate. Therefore, the same transferring procedure can be applied to either individual MoS_2/WS_2 materials or their hetero-structures. The 2D crystal films will be completely peeled off from the substrate, which is similar to the peeling of the MoS_2/graphene hetero-structure discussed in a previous publication[18]. Depending on the purpose of transferring the film, the substrate mentioned in this step can either be a sapphire substrate or a SiO_2/Si substrate with pre-deposited electrodes, as described in step 3.2. Other substrates can also be used for this purpose.

2. **The fabrication of 2D crystal transistors.**
   1. Use standard photolithography to define electrode patterns on SiO_2/Si substrates[15,16,17]. Source and drain electrodes made of 10 nm titanium (Ti) or 100 nm gold (Au) are fabricated on a 300 nm SiO_2/p-type Si substrate.
   2. Immerse the SiO_2/Si substrate with pre-patterned source/drain electrodes into the beaker filled with DI water and attach to the TMD side of the PMMA/TMD film as prepared in step 3.1.
   3. Bake the sample at 100 °C for 3 min, after the film is attached to the SiO_2/Si substrate, to remove water residue.
   4. Drip three drops of PMMA on the sample with the PMMA/TMD film to cover the whole surface and make the film more firmly attached to the substrate.
   5. Place the sample in an electronic dry cabinet for at least 8 h before moving to the next step.
   6. Fill two different 250 mL beakers with acetone. Immerse the sample attached with the PMMA/TMD film sequentially into the two different beakers filled with acetone for 50 and 10 min, respectively, to remove the top PMMA layer.
   7. Define the transistor channel using standard photo-lithography and reactive-ion etching[15,16,17]. Back-gate MoS_2 and WS_2/MoS_2 hetero-structure transistors are fabricated[15,16,17]. The channel length and width of the devices are 5 and 150 µm, respectively.
   8. Use a dual-channel system sourcemeter instrument to measure the current-voltage characteristics of the transistors[15,16,17].

Representative Results

The Raman spectrum and the cross-sectional HRTEM images of individual MoS_2 and WS_2 fabricated using the sulfurization of pre-deposited transition metals are shown in **Figure 1a-b**[17], respectively. Two characteristic Raman peaks are observed for both MoS_2 and WS_2, which correspond to in-plane E^1_{2g} and out-of-plane A_{1g} phonon vibration modes in the 2D crystals. The frequency difference Δk of two Raman peaks for the MoS_2 sample is 24.1 cm^{-1}, which suggests that 4 - 5 layers of MoS_2 was obtained[19]. However, it is difficult to determine the possible layer number directly from the large Δk value 63.4 cm^{-1} of WS_2[17]. The cross-sectional HRTEM images of the two samples, shown in **Figure 1c-d**, have revealed that 5- and 4-layer MoS_2 and WS_2 are obtained for the two samples, respectively. The results have demonstrated that through sulfurizing the transition metals, large-area and uniform MoS_2 and WS_2 films can be obtained.
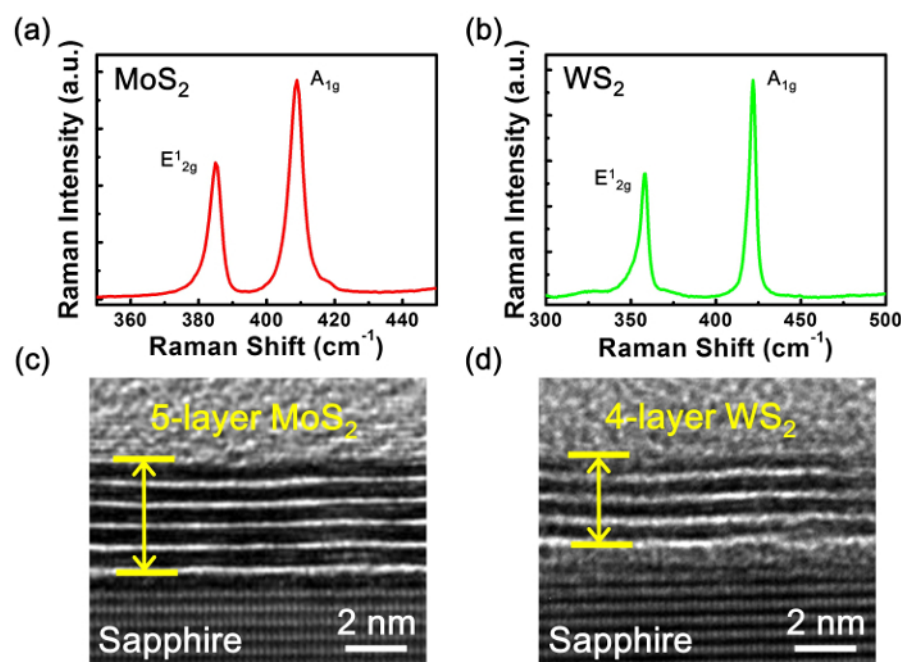
The cross-sectional HRTEM image of the 1.0 nm Mo film sulfurized under the sulfur deficient condition is shown in **Figure 2a**, wherein clusters covered with few-layer 2D crystals were observed. These results indicated that two growth mechanisms were observed during the sulfurization procedure[15]. Under the sulfur sufficient condition, sulfur-for-oxygen reactions took place quickly such that planar MoS_2 covered the whole sample in a short time. This planar MoS_2 film on the sample surface could prevent further material migration such that a uniform and layer-number-controllable MoS_2 film could be obtained after the sulfurization procedure. However, when the sample was sulfurized under the sulfur deficient condition, the background sulfur was not sufficient to form a complete MoS_2 film such that the Mo oxide segregation and coalescence was the dominant mechanism at the early growth stage. In this case, a sample with Mo oxide clusters covered by few-layer MoS_2 would be obtained after the sulfurization procedure[15]. The schematic diagram describing the model of the transition metal sulfurization is shown in **Figure 2b**[15]. Since two growth mechanisms were observed during the sulfurization procedure, there was an upper limit for the MoS_2 layer number with one-time growth.

Using sequential metal deposition with sulfurization procedures discussed above, a WS_2/MoS_2 single hetero-structure was prepared after two procedures of transition metal deposition/sulfurization. The Raman spectra and the cross-sectional HRTEM image of the sample are shown in **Figure 3a-b**[17]. Besides the characteristic Raman peaks corresponding to MoS_2 and WS_2, respectively, the identical layer number 9 with the summation of the individual 5- and 4- layer MoS_2 and WS_2 suggests that the sample was a WS_2/MoS_2 single hetero-structure. Following similar growth procedures, a WS_2/MoS_2/WS_2 double hetero-structure was prepared after three procedures of transition metal deposition/sulfurization. The Raman spectra and the cross-sectional HRTEM image of the sample are shown in **Figure 3c-d**. With a similar observation of MoS_2 and WS_2 characteristic Raman peaks discussed above, only three layers of 2D crystals were observed for this sample. These results have revealed that (a) good layer number controllability down to a single layer was obtained for this growth technique and (b) a vertical 2D crystal double hetero-structure can be established in three atomic layer thickness[16].

Another sample with half-covering transition metal deposition was prepared to show the possibility of selective growth using the growth technique discussed in this report. By shielding half of the sapphire substrate during the 1.0 nm Mo deposition, half of the substrate could be covered with MoS$_2$ after sulfurization. After that, the sample was rotated 90° to deposit W to cover half of the sapphire substrate. The same sulfurization procedure was conducted again. In this case, four regions with (a) blank sapphire substrate, (b) standalone MoS$_2$, (c) WS$_2$/MoS$_2$ hetero-structure, and (d) standalone WS$_2$ were obtained within a single sapphire substrate[17]. The picture and the Raman spectra of the four different regions on the sample are shown in **Figure 4**. As shown in the figure, large-area and uniform WS$_2$ and MoS$_2$ films and their vertical hetero-structures were selectively grown on the same sapphire substrate. These results have indicated that besides the establishment of vertical hetero-structures, the growth method of transition metal sulfurization selectively grew 2D crystals on substrates. This flexibility may give more room to practical device fabrications based on 2D materials and their hetero-structures.

To compare the device performance of the transistors with the MoS$_2$ and the WS$_2$/MoS$_2$ vertical hetero-structure as device channels, two transistors were fabricated following the fabrication procedure described in step 3 of the protocol. The schematic diagram showing the fabrication procedure is also shown in **Figure 5a**. The I$_D$-V$_{GS}$ curves of the devices at V$_{DS}$ = 10 V are shown in **Figure 5b**. Compared with the MoS$_2$ transistor, a substantial drain current increase was observed for the hetero-structure device. The field-effect mobility values of the two devices with MoS$_2$ and WS$_2$/MoS$_2$ hetero-structure as the channels extracted from the curves are 0.27 and 0.69 cm^2/V·s, respectively. Our previous prediction of electron injection from WS$_2$ to MoS$_2$ and from higher electron concentration channels under thermal equilibrium could be responsible for this phenomenon.

After the thin Mo film deposition, the sample was moved out of the sputtering chamber and exposed to air. Since the Mo film is very thin, it was oxidized and formed Mo oxides quickly under ambient conditions. The XPS curve (X-ray photoelectron spectroscopy) of the sample before the sulfurization procedure is shown in **Figure 6a**. As shown in the figure, the film was composed of MoO$_2$ and MoO$_3$ before the sulfurization procedure. These results suggest that the Mo film was oxidized during the transferring procedure from the sputtering chamber to the hot furnace. The other supporting evidence for the formation of the 2D crystal hetero-structure may have come from the equivalent selective etching of the 2D crystal hetero-structure. For this purpose, we have demonstrated that atomic etching can be achieved for both MoS$_2$ and WS$_2$ using low-power oxygen plasma treatment[20]. We can achieve equivalent selective etching to the vertical hetero-structure by repeating the atomic layer etching procedure. The Raman spectrum of the etched and un-etched 4-layer WS$_2$/3-layer MoS$_2$ vertical hetero-structure are shown in **Figure 6b**. The atomic layer etching times were consistent with the layer number of WS$_2$ (4 times). The observations of both MoS$_2$ and WS$_2$ Raman peaks on the un-etched region, and MoS$_2$ signals only on the etched region, suggest that a vertical hetero-structure was established using the growth technique discussed in this paper.


Figure 1: Individual 2D crystals of MoS$_2$ and WS$_2$. (a, b) The Raman spectra and (**c, d**) the cross-sectional HRTEM images of standalone MoS$_2$ and WS$_2$, respectively[17]. The samples are obtained by sulfurizing 1.0 nm Mo and W films prepared by a sputtering system. As shown in the Raman spectra, two characteristic Raman peaks were observed for both MoS$_2$ and WS$_2$, which corresponded to in-plane E_{2g}^1 and out-of-plane A_{1g} phonon vibration modes in the 2D crystals. The layer number numbers of MoS$_2$ and WS$_2$ grown using the method discussed in the current manuscript were proportional to the sputtering times of the pre-deposited Mo and W films. The determination of sputtering times to obtain MoS$_2$ and WS$_2$ with required layer numbers is based on the cross-sectional HRTEM images for samples with different sputtering times. However, if the pre-deposited Mo and W films are too thick, Mo and W oxide segregation will become the dominant growth mechanism instead of the planar MoS$_2$ and WS$_2$ film growth. Therefore, the proportionality of layer numbers with the sputtering times was limited to few-layer TMDs. With the growth conditions of MoS$_2$ in the current manuscript, the layer numbers will be proportional to the sputtering times when the MoS$_2$ film is fewer than 10 layers. The sputtering time is 30 s for the growth of 5-layer MoS$_2$. This figure has been modified from Wu et al.[17] Please click here to view a larger version of this figure.
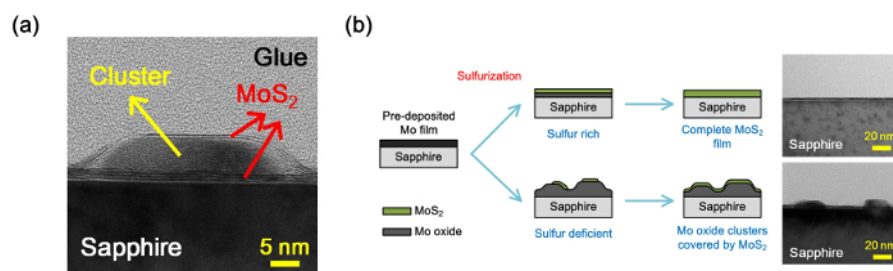
Figure 2: The growth model of transition metal sulfurization. (**a**) The cross-sectional HRTEM image of the 1.0 nm Mo film sulfurized under the sulfur deficient condition and (**b**) The schematic diagram describing the model for the transition metal sulfurization[15]. The growth conditions of the sample prepared with no sulfur powder placed in the furnace is referred to as the sulfur deficient condition. Since there is always residue sulfur accumulation near the downstream of the growth chamber after repeating growth cycles, it is expected that a small amount of sulfur will still diffuse to the sample surface and result in MoS_2 growth. However, under such sulfur deficient conditions, not all the pre-deposited Mo will be transformed into MoS_2. This figure has been modified from Wu et al[15]. Please click here to view a larger version of this figure.
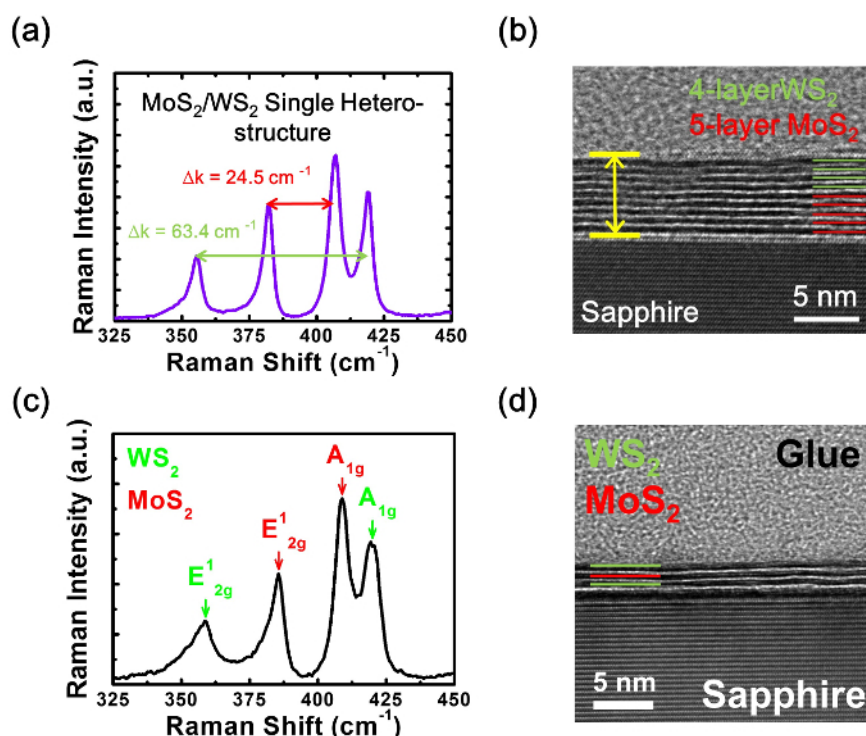

Figure 3: MoS$_2$/WS$_2$ single- and double-hetero-structures. The Raman spectra and the cross-sectional HRTEM images of WS$_2$/MoS$_2$ (**a, b**) single- and (**c, d**) hetero-structures[16,17]. As shown in the Raman spectrum, the in-plane E_{2g}^1 and out-of-plane A_{1g} phonon vibration modes of both MoS$_2$ and WS$_2$ are observed for the 2D crystal hetero-structures. The panels have been modified from Chen et al. and Wu et al.[16,17] Please click here to view a larger version of this figure.
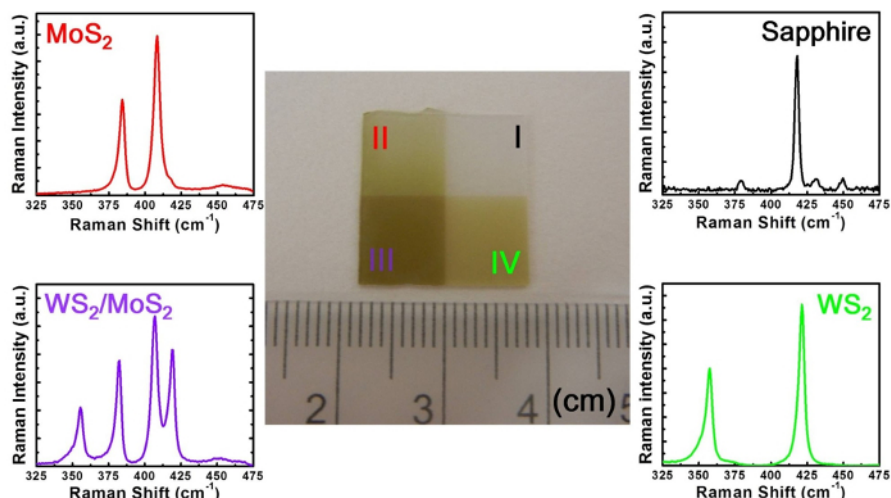
Figure 4: Selective growth of 2D crystals. The picture and the Raman spectra of four regions of the sample prepared with half-covering transition metal depositions on a single sapphire substrate[17]. Raman spectra in the (**a**) blank sapphire substrate, (**b**) standalone MoS_2, (**c**) WS_2/MoS_2 hetero-structure and (**d**) standalone WS_2 regions of the sample revealed characteristic Raman peaks. This figure has been modified from Wu *et al.*[17] Please click here to view a larger version of this figure.
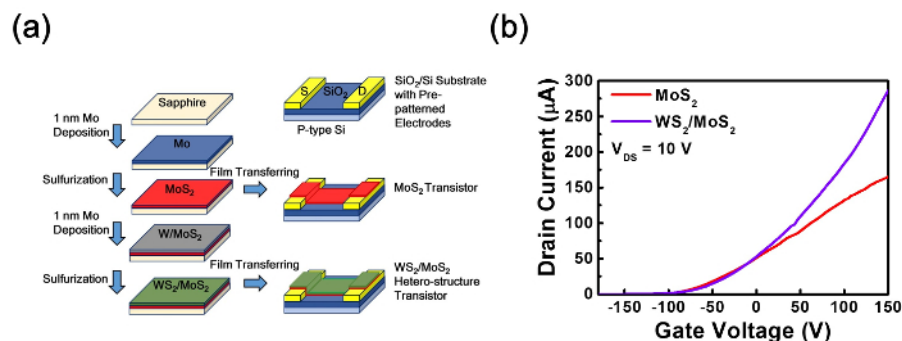
Figure 5: The device performance of MoS2 and WS_2/MoS_2 vertical hetero-structure transistors. (**a**) The fabrication procedure of the transistors with the MoS_2 and the WS_2/MoS_2 vertical hetero-structure as the channels and (**b**) the I_D-V_{GS} curves of the two devices at V_{DS} = 10 V[17]. The thicknesses of 1.0 nm for Mo and W films were obtained from the readings of the quartz crystal resonator. The sputtering times were 30 s for both materials. This figure has been modified from Wu *et al.*[17] Please click here to view a larger version of this figure.
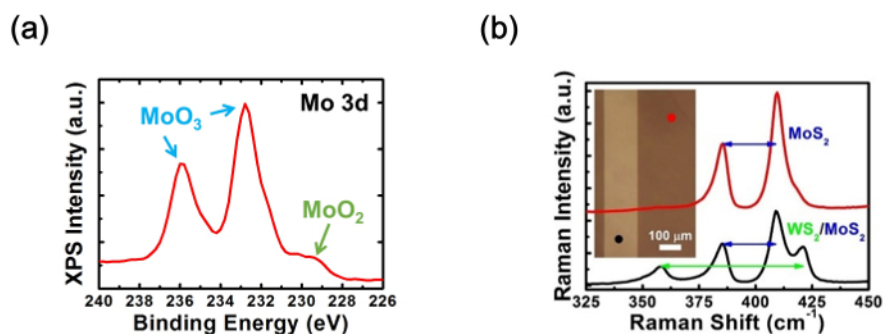
Figure 6: The oxidation of pre-deposited Mo films and the equivalent selective etching of WS_2/MoS_2 vertical hetero-structures. (**a**) The XPS curve of the sample with the pre-deposited Mo film before the sulfurization procedure. The film is composed of MoO_2 and MoO_3 before the sulfurization procedure. These results suggest that the Mo film was oxidized during the transferring procedure from the sputtering chamber to the hot furnace. (**b**) The Raman spectra of the etched and un-etched 4-layer WS_2/3-layer MoS_2 vertical hetero-structure. After four times of atomic layer etchings, only MoS_2 peaks were observed on the etched region; Panel B has been modified from Chen *et al.*[20] Please click here to view a larger version of this figure.

Discussion

Compared with conventional semiconductor materials such as Si and GaAs, the advantage of 2D materials for device applications lies in the possibility of device fabrication with very thin bodies down to several atomic layers. When the Si industry advances into the <10 nm technology

node, the high aspect ratio of Si fin FET will make the device architecture unsuitable for practical applications. Thus, 2D materials have emerged due to their potential to replace Si for electronic device applications.

Although the most studied 2D material, graphene, is expected to exhibit high mobility values, its zero bandgap nature has led to no OFF state for the graphene transistors. In this case, other 2D materials such as TMDs with visible bandgap values have come into consideration. Nowadays, the most common approach to obtain large-area TMDs is to use the CVD technique. Although this growth technique does provide large-area and uniform TMD films, the choice of appropriate precursors and different growth temperatures for different TMDs is disadvantageous for the development of complicated structures such as 2D material hetero-structures. In this case, the sulfurization of transition metals as discussed in this paper has become a promising approach for the establishment of TMD hetero-structures. It is possible to sulfurize different TMDs under similar sulfurization conditions.

One important issue for the growth of 2D materials is the layer number controllability. The layer number controllability of the MoS_2 film prepared by sulfurizing transition metals as discussed in this paper was achieved by controlling the pre-deposited Mo film thicknesses. The thickness of the Mo film was controlled by the sputtering time. In the case of 30 s sputtering time, the Mo film thickness was estimated to be ~1 nm. After the sulfurization procedure, five layers of MoS_2 should be obtained[17]. In the case of 10 s sputtering time, a mono-layer MoS_2 should be obtained[16].

The major limitation of this growth method lies in the maximum layer numbers with one-time sulfurization. As discussed in the previous section, after the thin Mo film deposition, the sample was moved out of the sputtering chamber and exposed to the air. Since the Mo film was very thin, it was oxidized and formed Mo oxides quickly under the ambient condition. Therefore, if the pre-deposited Mo film is too thick, the planar MoS_2 will not be sufficient to prevent Mo oxide segregation during the sulfurization procedure, and a sample with clusters of multi-layer MoS_2 covering Mo oxides will be obtained. With the growth conditions adopted in this paper, the highest MoS_2 layer number was around 10 with a one-time growth cycle.

To overcome this disadvantage, if a MoS_2 film with a layer number larger than 10 is required, it is possible to repeat the same growth procedure of metal deposition and sulfurization to obtain the film with the required number of layers[11]. The sulfurization of pre-deposited transition metals has provided the possibility of scalable TMD film growth with good layer number controllability. Using this approach, the establishment of vertical hetero-structures and selective growth on sapphire substrates has also been demonstrated. The growth technique discussed in this paper will mark an important step toward the practical application of 2D crystals. With the enhanced device performance of 2D crystal hetero-structures, 2D materials can be a possible candidate for the development of nm-sized electronic devices. In future work, stacking 2D materials to establish various hetero-structures to obtain different optical and electrical properties with individual material will be an important issue for practical applications.

Disclosures

The authors have nothing to disclose.

Acknowledgements

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