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Toward epitaxially grown two-dimensional crystal hetero-structures: Single and double MoS_2/graphene hetero-structures by chemical vapor depositions

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Uniform large-size MoS_2/graphene hetero-structures fabricated directly on sapphire substrates are demonstrated with layer-number controllability by chemical vapor deposition (CVD). The cross-sectional high-resolution transmission electron microscopy (HRTEM) images provide the direct evidences of layer numbers of MoS_2/graphene hetero-structures. Photo-excited electron induced Fermi level shift of the graphene channel are observed on the single MoS_2/graphene hetero-structure transistors. Furthermore, double hetero-structures of graphene/MoS_2/graphene are achieved by CVD fabrication of graphene layers on top of the MoS_2, as confirmed by the cross-sectional HRTEM. These results have paved the possibility of epitaxially grown multi-hetero-structures for practical applications. © *2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4893448]

Compared with the half-century development of Si and compound semiconductors, the study of two-dimensional crystal graphene with its first discovery at 2004 is still at a very early stage. Nevertheless, the theoretically predicted high mobility of graphene has already emerged its possible application in high-speed electronics.[1,2] Owing to its wide absorption wavelengths and short carrier lifetime, graphene also has strong potential for optical devices.[3–5] Recently, graphene researchers start to turn their focus to the hetero-structures formed by stacking different 2-D materials after 10 yr of fundamental researches.[6] Besides graphene, the other promising 2-D material for building hetero-structures is molybdenum disulfide (MoS_2).[7–9] Different from the zero-bandgap graphene, monolayer MoS_2 exhibits a direct bandgap of 1.8 eV.[10] With such semiconductor characteristics, MoS_2 photodetectors have revealed responsivities around 7.5–100 mA/W, which is much higher than the graphene-based device (~1 mA/W).[5,11] By stacking exfoliated MoS_2 with exfoliated graphene, ultra-high responsivity ~0.22 A/W has been reported.[12] In the device architecture, the MoS_2 layer serves as a photo-excited electron provider due to its high absorption efficiency, whereas the graphene transports the photo-current due to its high carrier mobility.

In most recent publications, each layer of the 2-D material in the hetero-structures is formed by either mechanical exfoliation from bulk material or chemical vapor deposition (CVD) method.[11,12] The hetero-structure is established by sequentially reattach the films onto each other on a given substrate such as SiO_2/Si substrates. Although this method has been proved to be an easy and functional approach, the possible chemical contamination between layers and undefined film area would limit the practical applications of the hetero-structures. Furthermore, the voids and wrinkles introduced during the transferring procedure might also influence the device performance. Therefore, epitaxially grown 2-D material onto other 2-D material layers has strong potential for fabricating such hetero-structures. It has been proposed elsewhere that MoS_2 can be grown on graphene/Cu via CVD methods.[13] However, only small MoS_2 flakes were observed due to the un-avoidable chemical reactions between the precursors and the metal substrates. In order to maximize the film size of the hetero-structure, a non-reactive substrate, crystalline sapphire, is selected here to avoid the possible chemical reactions. The graphene/sapphire substrate is a promising candidate for further fabrication toward multi-compositions 2-D material hetero-structures.

In this work, MoS_2/graphene hetero-structures are formed by depositing MoS_2 films via CVD method onto the CVD-grown graphene/sapphire substrates. The uniform distribution of Raman frequency difference between E^1_{2g} and A_{1g} peaks across the film suggests that layer-number-controllable MoS_2 films can be grown on the graphene/sapphire substrates. The cross-sectional high-resolution transmission electron microscopy (HRTEM) image reveals the formation of MoS_2/graphene hetero-structure. From the X-ray photoelectron spectroscopy (XPS) spectra, not any chemical bonding could be observed between the MoS_2 and the underlying graphene. Moreover, photo-excited electron induced Fermi level shift of the graphene channel is observed on the MoS_2/graphene transistors device. These results suggest that MoS_2/graphene hetero-structures with good crystalline quality and wafer-size are obtained by our approach. By sequential CVD growing of one more layer of graphene onto the MoS_2/graphene, double hetero-structure of graphene/MoS_2/graphene is achieved, as confirmed by the cross-sectional HRTEM.

The graphene film is prepared by a CVD system equipped with a magnetic rod. The detailed growth procedure is discussed elsewhere.[14] The MoS_2 film was grown on

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the graphene/sapphire substrate by using the other 1-in. quartz tube furnace system. During the growth, 7 mg of $MoCl_5$ and 1 g of sulfur powders are placed at the center and the upstream of the furnace, respectively. The desired grown substrate was placed downstream 1.5 cm away from the center of the furnace. The furnace was then ramping up to 870 °C for 45 min under the Ar environment. The pressure of the system was kept at 2 Torr. The growth duration was set to 5 min after the furnace reaching 870 °C. After growth, the furnace was cooled to room temperature by switching off the heater. The Raman spectrums and PL measurements are performed by using HORIBA Jobin Yvon HR800UV Raman spectroscopy system equipped with 532 nm laser. The cross-sectional HRTEM images are obtained by using a FEI Tecnai G2 F20 transmission electron microscopy (TEM) system operated at 200 kV. The chemical bonds and structures of the samples are studied by using the PHI VersaProbe II Scanning XPS Microprobe.

In our previous publication, it has been demonstrated that few-layer graphene can be grown directly on sapphire substrates without metal catalyst.[14] Hetero-structures with different 2-D materials such as MoS_2 can be established by using the graphene/sapphire samples as new substrates. The pictures of the samples before and after MoS_2 growth are shown in Fig. 1(a). Before MoS_2 growth, a graphene film has been grown directly on the sapphire substrate.[14] As shown in the figure, full coverage of MoS_2/graphene single hetero-structure over the substrate is observed. However, a significant color difference is observed on the sample after the MoS_2 growth. The cross-sectional HRTEM image shown in Fig. 1(b) reveals clear bi-layer MoS_2/single-layer graphene hetero-structures. The layer thickness for MoS_2 and graphene are 0.67 and 0.4 nm, respectively, which are similar to the thickness of individual materials.[15,16] The Raman spectrum of this hetero-structure exhibits both Raman peaks of MoS_2 and graphene (Fig. 1(c)), which is consistent with the observation of the HRTEM image. One interesting phenomenon observed in the Raman spectrum is that the energy difference, ΔK, of MoS_2 is reduced to 20.8 cm^{-1}, which is lower than the ΔK value ~23.3 cm^{-1} of the bi-layer MoS_2 grown on sapphire substrates.[17] Such ΔK value reduction for the bi-layer MoS_2 on graphene suggests strong interaction at their interface so that the in-plane vibration (A_{1g}) is enhanced, while out-of-plane vibration (E^1_{2g}) is depressed.[18]

One important issue in fabricating the 2-D material hetero-structures is the controllability of layer number of MoS_2 on the graphene/sapphire substrate. By reducing the precursor $MoCl_5$ amount from 7 to 4 mg and keeping other growth conditions unchanged, we could prepare a different MoS_2/graphene hetero-structure with only single layer of MoS_2. The cross-sectional HRTEM image in Fig. 2(a) shows that the MoS_2 layer number is reduced to 1. The results suggest that layer number of MoS_2 in the hetero-structure can be tuned controllably by our CVD procedures. While layer number of MoS_2 can be controlled, the last issue to be investigated would be whether if chemical bonds are formed at the MoS_2/graphene interface. For examining the possible C-S bonding, XPS measurements are performed on the single-layer MoS_2/graphene hetero-structure (Figs. 2(b)–2(d)). Two peaks are observed in the S 2p curve at 162.2 and 163.4 eV,

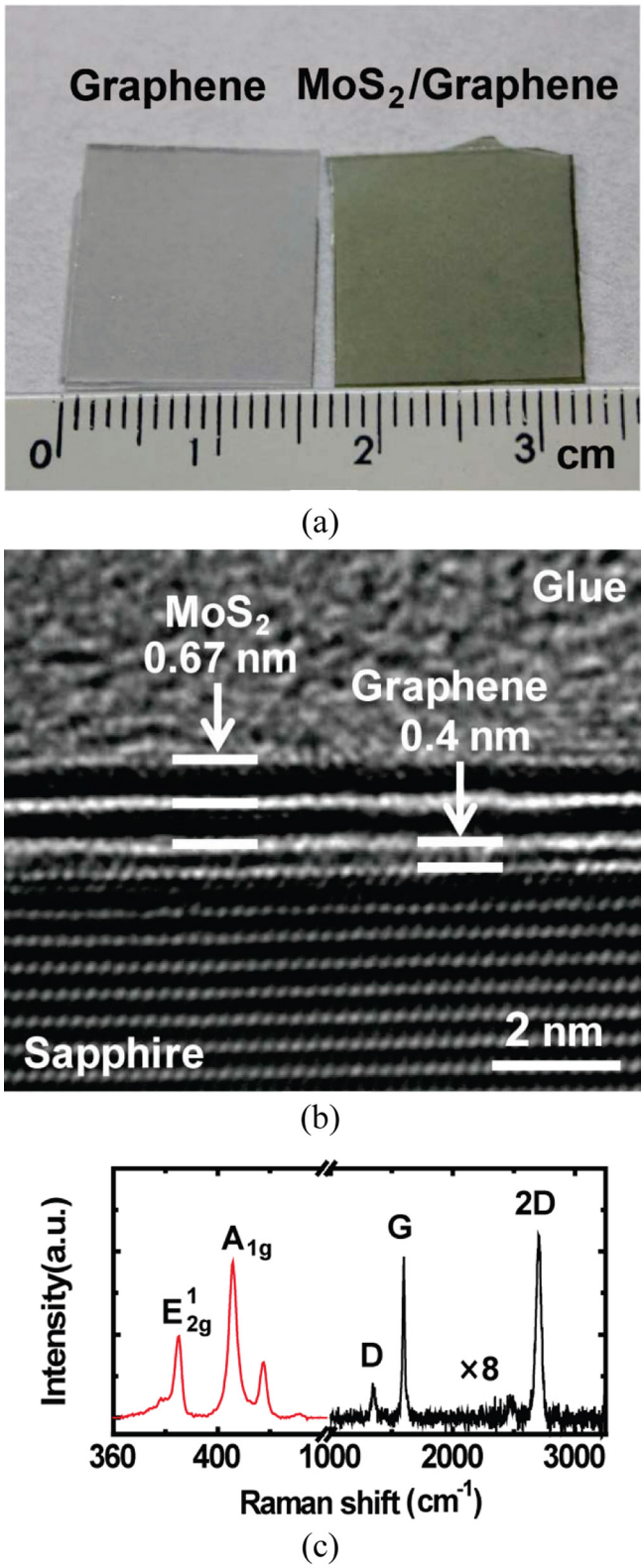


FIG. 1. (a) The pictures of the samples before and after MoS_2 growth. (b) The cross-sectional HRTEM image and (c) the Raman spectrum of the sample with bi-layer MoS_2/single-layer graphene hetero-structure.

which correspond to the S $2p_{1/2}$ and S $2p_{3/2}$ orbital of divalent sulfide ions (Fig. 2(b)). The Mo 3d curve shows two separated peaks at 229.4 and 232.4 eV, which correspond to the doublet Mo $3d_{5/2}$ and Mo $3d_{3/2}$, respectively (Fig. 2(c)). The lower-energy peak located at ~226 eV represents the S 2s signal, which is also observed in MoS_2 films.[19] The XPS

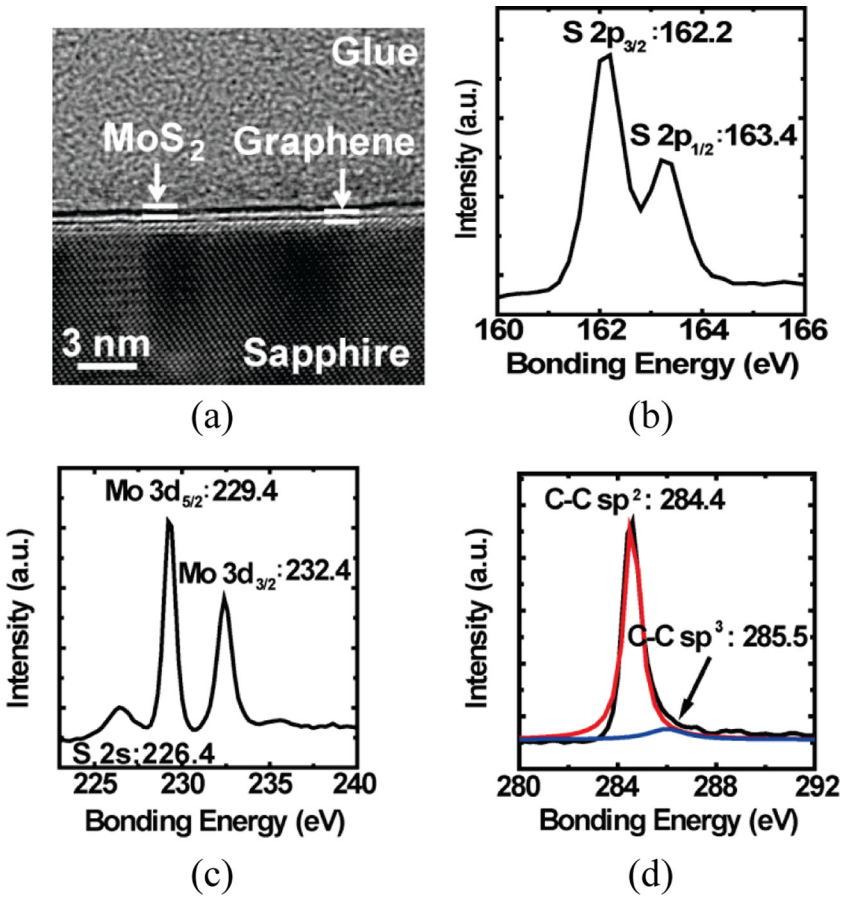
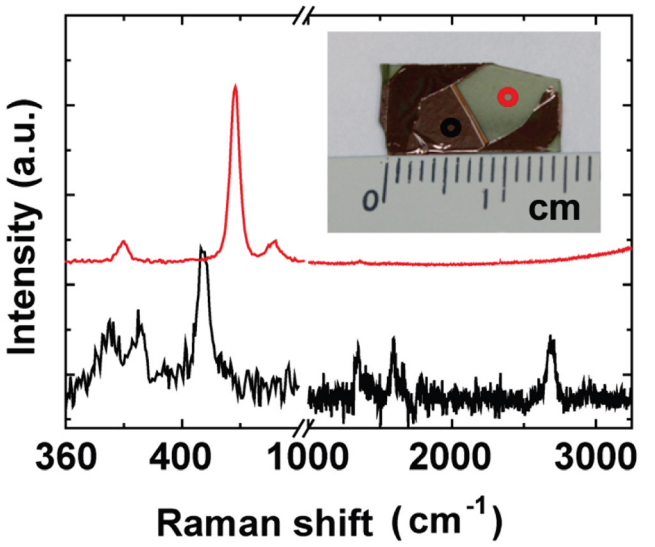


FIG. 2. (a) The cross-sectional HRTEM image of the sample with single-layer MoS_2/single-layer graphene hetero-structure. The XPS spectra for the binding energy of (b) Mo 3d, (c) S 2p, and (d) C 1s of the sample. Curve fitting is done on the C 1s spectrum to show the dominating sp^2 than sp^3 bonding of C atoms.

curve of the C 1s is shown in Fig. 2(d). After curve fitting the signal, only red and blue curves located near 284.4 and 285.5 eV are observed on the spectrum. The peak observed at 284.4 eV is resulted from the sp^2 bonding structure of the underlying graphene film. The C-S binding energy should locate near 286.8 eV in the C 1s spectrum.[20] However, except for the weak sp^3 bonding of C atoms near 285.5 eV, no significant peak can be observed on the spectrum. This result indicates that no significant C-S bond could be observed so that the MoS_2 and graphene layers are simply stacked by the van der Waals force.

The potential application of the MoS_2/graphene hetero-structures is in photodetectors. To fabricate the device, the single-layer MoS_2/graphene film is peeled off from the sapphire substrate and reattached to a 300 nm SiO_2/Si substrate. The details of the film peeling procedure are discussed elsewhere.[14] To confirm if the MoS_2/graphene hetero-structure is completely peeled off from the substrate, two Raman spectra measured on the back of the peeled-off film (black curve) and on the substrate after peeling (red curve) are shown in Fig. 3(a). The inset picture shows the actual locations for Raman measurements. Raman signals of both MoS_2 and graphene are found on the peeled-off film, while only sapphire's Raman signal is observed on the substrate. Compared with Fig. 1(c), the less intense Raman peak intensities are attributed to the influence of the Cu template. The MoS_2/graphene hetero-structure can be peeled off instead of removing only the MoS_2 film. This indicates that the adhesive force between MoS_2/graphene is much stronger than that of graphene/sapphire. Such strong interfacial van der Waals force will affect the phonon structure of MoS_2/graphene and it also explains the reduction of ΔK discussed in Fig. 1(e). Further, investigations are still required in the future to confirm this attribution.

After standard photolithography and O_2 plasma etching procedure, a back-gated MoS_2/graphene transistor is fabricated with gold electrodes. The I_D-V_{GS} characteristics of the device under dark and illuminated conditions are shown in Fig. 3(b). The inset photograph in Fig. 3(b) shows the actual device with the source, drain electrodes, and the channel. The derived hole mobility in the darkness is 445 $cm^2\ V^{-1}\ s^{-1}$ and reduces to 435 $cm^2\ V^{-1}\ s^{-1}$ under light illumination. These values are compatible with other devices made of CVD-grown graphene channels.[21] As shown in the figure, V_{GS} with lowest drain currents shifts from +12 V to −36 V under light irradiation condition. Similar transition from p-type to n-type has also been observed elsewhere in MoS_2/graphene transistors fabricated by using sequentially film attachment.[12] In our device architecture, the graphene layer acts as a current path when drain voltages are applied since graphene is more conductive than MoS_2 and is directly contacted with the Au electrodes. However, due to its low absorption coefficient, the graphene channel mobility would not change with or without light irradiation. Since our MoS_2/graphene hetero-structure is sequentially grown in the CVD chamber, there is no chemical contamination at the interfaces. In such case, the photo-excited electrons in the MoS_2 layer would effectively hop to the graphene channel and turn the original p-type channel into n-type. This will result in the large shift of the lowest-drain-current V_{GS} under light illumination since the observation of lowest



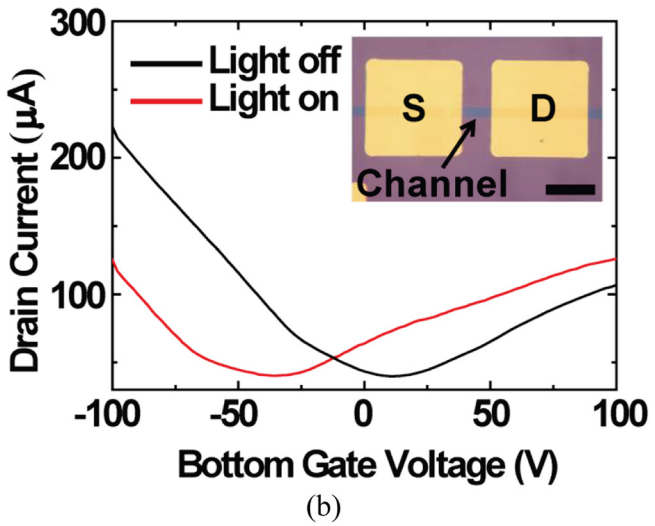


FIG. 3. (a) Raman spectra measured on the back side of the peeled-off film (black curve) and on the substrate after peeling (red curve). The inset picture shows the actual locations for Raman measurements. (b) The I_D-V_{GS} characteristics of the device under dark and illuminated conditions. The inset optical microscope image shows the device architecture labeled with the source (S), drain (D), and channel with a scale bar of 50 μm.

drain currents in graphene transistors correspond to the crossover of Fermi levels with the Dirac point.

With the demonstration of epitaxially grown MoS_2/graphene single hetero-structure, the next target is the growth of 2-D material double hetero-structures. Based on the MoS_2/graphene hetero-structure, the second graphene layer is epitaxially grown on it. The growth condition is controlled at reduced temperature around 800 °C concerning the thermal stability of the MoS_2 layer at high temperature. The cross-sectional HRTEM image of the graphene/MoS_2/graphene double hetero-structure is shown in Fig. 4. The inset of the figure shows the schematic diagram of the double hetero-structure. Layer-by-layer graphene and MoS_2 are observed but the structure of the second graphene film is not as organized as the bottom graphene. This is due to the reduced growth temperature of the second graphene film to prevent any thermal desorption of MoS_2.

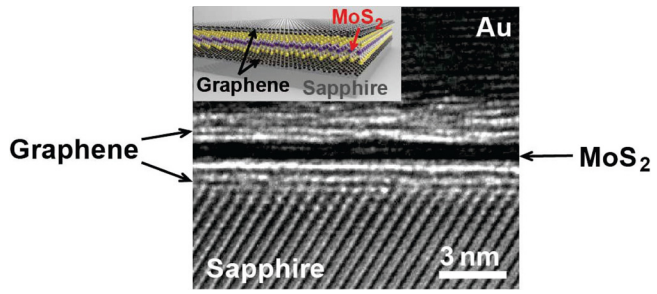


FIG. 4. The cross-sectional HRTEM image of the graphene/MoS_2/graphene double hetero-structure. The inset of the figure shows the schematic diagram of the double hetero-structure.

In conclusion, uniform large-size MoS_2/graphene hetero-structures fabricated directly on sapphire substrates are demonstrated with layer-number controllability by CVD. Photo-excited electron induced Fermi level shift of the graphene channel are observed on the single MoS_2/graphene hetero-structure transistors. At this stage, we are still trying to optimize the growth conditions of the graphene/MoS_2/graphene double hetero-structures. So far, our results open the possibility of epitaxially growth of multi-hetero-structures on sapphire substrates. The following work would be the growth optimizations for each layer in the hetero-structures without bringing damages to the other layers and the development of mass-production CVD chambers, as we have done on the fabrication and applications of laser diodes in the past 50 yr.

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