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ARTICLE

Domain Aligned Growth of Molybdenum Disulfide on Various Substrates by Chemical Vapor Deposition

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ABSTRACT

We synthesized single-layer MoS_2 atomic films on various substrates by a chemical vapor deposition method. We chose three different substrates for MoS_2 synthesis in this study; SiO_2 as an amorphous substrate, Al_2O_3 or GaN as hexagonal crystalline substrates. The lattice constant of Al_2O_3 is not well matched with that of MoS_2 whereas the lattice constant for GaN is well matched with that of MoS_2. We investigated the orientation properties of the domains of single-layer MoS_2 atomic films on these three substrates and found that MoS_2 domains synthesized on lattice-matched GaN substrate are aligned better than the other MoS_2 domains synthesized on SiO_2 or Al_2O_3 substrates. Our study may provide an insight as a route to synthesize large size, single-layer, and single-domain MoS_2 atomic films.

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KEYWORDS: MoS_2, Single Domain Aligned Growth, Single Atomic Layer, Chemical Vapor Deposition.

1. INTRODUCTION

Recently, molybdenum disulfide (MoS_2) has received a great attraction in 2-dimensional atomic electronics due to its semiconducting property with intrinsic band gap in comparison with band gap-less graphene material. MoS_2 has a layered structure in which the interaction between adjacent S–Mo–S layers is van der Waals force, so the mechanical exfoliation method can be applied to peel off individual layers.[1] More importantly, MoS_2 is a semiconductor with a direct band gap of 1.8 eV for a single layer and an indirect band gap of 1.2 eV for a bulk material.[2,3] Due to its semiconducting properties, MoS_2 has been used in electronic devices such as MoS_2 field effect transistors (FETs).[4–6]

Mechanical exfoliation, often called as a scotch-tape method, is a simple method to achieve thin MoS_2 layer film on various substrates.[7] In spite of the convenience of this method, there are also many limitation such as disability of positioning of MoS_2 pieces and complex fabrication process because of its small lateral size. To overcome these problems, many researchers have developed other methods such as chemical vapor deposition (CVD) that allows the synthesis of large MoS_2 atomic films.[8,9] We have also previously demonstrated that a large size, single layer MoS_2 film can be synthesized by the CVD method.[10] However, a CVD-synthesized MoS_2 film has many grain boundaries because of rather randomly oriented domains throughout the synthesized MoS_2 film. At the boundary where different domains are merged, MoS_2 atomic structures are twisted and tilted. And these grain boundaries often degrade the electrical properties of MoS_2 films. Therefore, it is necessary to synthesize a large area MoS_2 atomic film with single domain configuration. One strategy for this is to choose a proper substrate which is a single crystal and has an atomic structure and lattice constant matched well with those of hexagonal-structured MoS_2 film.[11–13]

In this study, we synthesized MoS_2 atomic films on various substrates by the CVD method. We chose three different substrates; SiO_2 as an amorphous substrate, Al_2O_3 as a hexagonal crystalline substrate with a lattice constant not well matched that of MoS_2 film, and GaN as a hexagonal crystalline substrate with a lattice constant well matched with that of MoS_2 film. We investigated the orientations

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of domains of MoS_2 atomic film on these three substrates. Our study may provide an insight as a route to synthesize large single layer and single domain MoS_2 film.

2. EXPERIMENTAL DETAILS

Figure 1 shows the schematic illustration of the CVD system to synthesize MoS_2 films in this study. During the MoS_2 synthesis, we employed the optimized conditions of temperature, pressure, and atmosphere. We placed MoO_3 powder (99.5% Aldrich) as a Mo precursor (~10 mg) at the center of quartz tube, and we placed sulfur powder (99.98% Aldrich) as an *S* precursor on the electric heater to vaporize sulfur. To heat MoO_3 and *S* independently, we equipped dual heating components. In this setup, MoO_3 was vaporized in the furnace (at ~700 °C) and S is vaporized by the electric heater (at ~200 °C). Different substrates(SiO_2, Al_2O_3, and GaN substrates) for MoS_2 synthesis were placed in a boat containing a MoO_3 powder source. During the synthesis, Ar gas was mixed with vaporized sulfur and flowed at 150 sccm into the furnace (temperature was set to ~700 °C). The synthesis of MoS_2 films was maintained for 5 min in the Ar gas environment, and then the furnace was cooled down at room temperature for 10 hours. With these, we successfully synthesized large-scale, single-layer MoS_2 films on the substrates.

GaN is deposited on Al_2O_3 substrate with a thickness of ~2 μm to be unaffected by the Al_2O_3 substrate. Al_2O_3 substrate and GaN substrate have the lattice constant of 4.76 Å and 3.18 Å, respectively, in comparison to the lattice constant of 3.17 Å of MoS_2 films.[14–16]

The Raman spectroscopic measurements were performed with a commercial micro-Raman instrument (XperRam 200) which includes pumped solid state laser (wavelength of 532 nm). The Raman system is also equipped with a laser scanner which has a spatial resolution about 20 nm. Objective lens (Olympus, MPLFLN 40X, NA = 0.75) was used to focus the laser to about 1 μm spot size. The exposure time for each spectrum was 500 ms with an incident laser power about 2 mW.

3. RESULTS AND DISCUSSION

Raman spectroscopy has widely been used to study the vibrational properties of two-dimensional materials and to quantitatively determine their thickness.[17] It has been reported that when single-layer single-domain MoS_2 film is synthesized by CVD method, it forms as triangular shape.[8,9] Figure 2 shows Raman spectroscopic images over an area of single-layer single-domain triangular-shaped MoS_2 film that were synthesized on a SiO_2 substrate by the CVD method. The size of this triangular MoS_2 film is ~30 μm. The Raman spectra of the MoS_2 films are characterized by two major peaks. One is assigned as the E^1_{2g} mode (that corresponds to the vibrational motion of Mo and S atoms in the *x*-*y* layered plane) and the A_{1g} mode (that corresponds to the vibrational motion of two S atoms along the *z*-axis of the unit cell) of hexagonal single-crystal MoS_2.[18,19] The exact position of the peaks corresponding to the E^1_{2g} and A_{1g} vibrational modes and the ratio of their intensities depend on the layer thickness of the MoS_2 samples.

From the Raman spectroscopic frequency images (Figs. 2(a) and (b)), we observed that the E^1_{2g} peak and A_{1g} peak are positioned around 384 cm^{-1} and 405 cm^{-1}. These peak positions ensure that the synthesized triangular film is indeed MoS_2 atomic film. Also we did not observe any significant deviation regarding the peak positions in the images of Figures 2(a) and (b), which means that uniform MoS_2 films were synthesized. In particular, the frequency difference between the two Raman peaks is about 21 cm^{-1} (405 cm^{-1} – 384 cm^{-1}), suggesting that the triangular MoS_2 films are single-layer thick MoS_2 atomic film. Figures 2(c) and (d) show Raman spectroscopic intensity images obtained at 384 cm^{-1} (E^1_{2g} peak) and 405 cm^{-1} (A_{1g} peak). These images display uniform intensities at these two specific frequencies. It means that MoS_2 thin film has uniform thickness because the peak position will be changed when the thickness of MoS_2 is not uniform. We also observed some irregularity (defects) near the center

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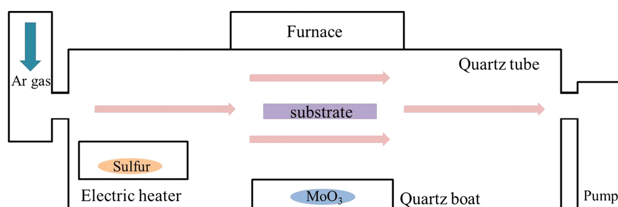

Fig. 1. Schematic illustration of the CVD setup to synthesize MoS_2 films.

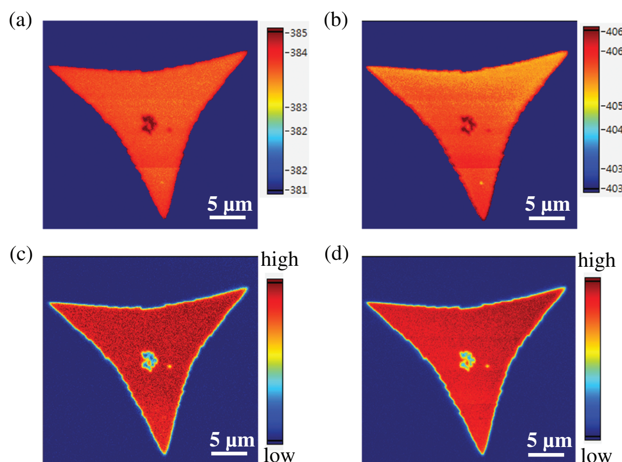

Fig. 2. (a, b) Raman spectroscopic frequency images that were obtained on a MoS_2 film synthesized on a SiO_2 substrate, indicating that the E^1_{2g} mode peak and A_{1g} mode peak are positioned around (a) 384 cm^{-1} and (b) 405 cm^{-1}. (c, d) Raman intensity images at fixed frequency of (a) 384 cm^{-1} (E^1_{2g} mode) and (b) 405 cm^{-1} (A_{1g} mode).

of MoS_2 triangular film where there was no MoS_2 signal observed. It is likely that there was some nucleation which is composed of MoO_3 in these defects.

The results of Figure 2 are Raman spectroscopic images obtained on a MoS_2 film synthesized on a SiO_2 substrate which is amorphous. We also synthesized MoS_2 films on different substrates; Al_2O_3 and GaN which are a hexagonal structured single crystal. During the MoS_2 synthesis in the quartz tube in the CVD method, the vaporized Mo and S are combined and deposited on the substrate, therefore, the crystallinity, atomic structure, and lattice constant of the substrate are important factors. The Al_2O_3 and GaN have hexagonal atomic structure which is similar to the hexagonal structure of MoS_2. If the lattice constant of the substrate is matched well with that of MoS_2, then single domains of MoS_2 is likely to tend to be aligned with less grain boundaries. As mentioned before, the Al_2O_3 and GaN have the lattice constant of 4.76 Å and 3.18 Å, respectively, in comparison to the lattice constant of 3.17 Å for MoS_2 films. So, the lattice constant of Al_2O_3 is not matched with that of MoS_2 whereas the lattice constant of GaN is matched well with that of MoS_2.

Figures 3(a)–(c) show the results of MoS_2 synthesis on SiO_2, Al_2O_3 and GaN substrate, respectively. Left images of Figure 3 are optical microscopic images and right plots are the relative angular orientation of the triangular MoS_2 individual films. For convenience, we marked dot-dashed, red-lined triangles to analyze the direction of the MoS_2 domains in the optical images. First, the results of Figure 3(a) (the case of SiO_2 substrate) indicate that there was no preference in the orientation angle. The right plot of Figure 3(a) clearly shows rather random distribution of orientation angles of MoS_2 triangular films. Here, zero degree was defined by an axis reference (marked in the left images of Fig. 3). This random orientation of MoS_2 triangular films is because the amorphous SiO_2 substrate

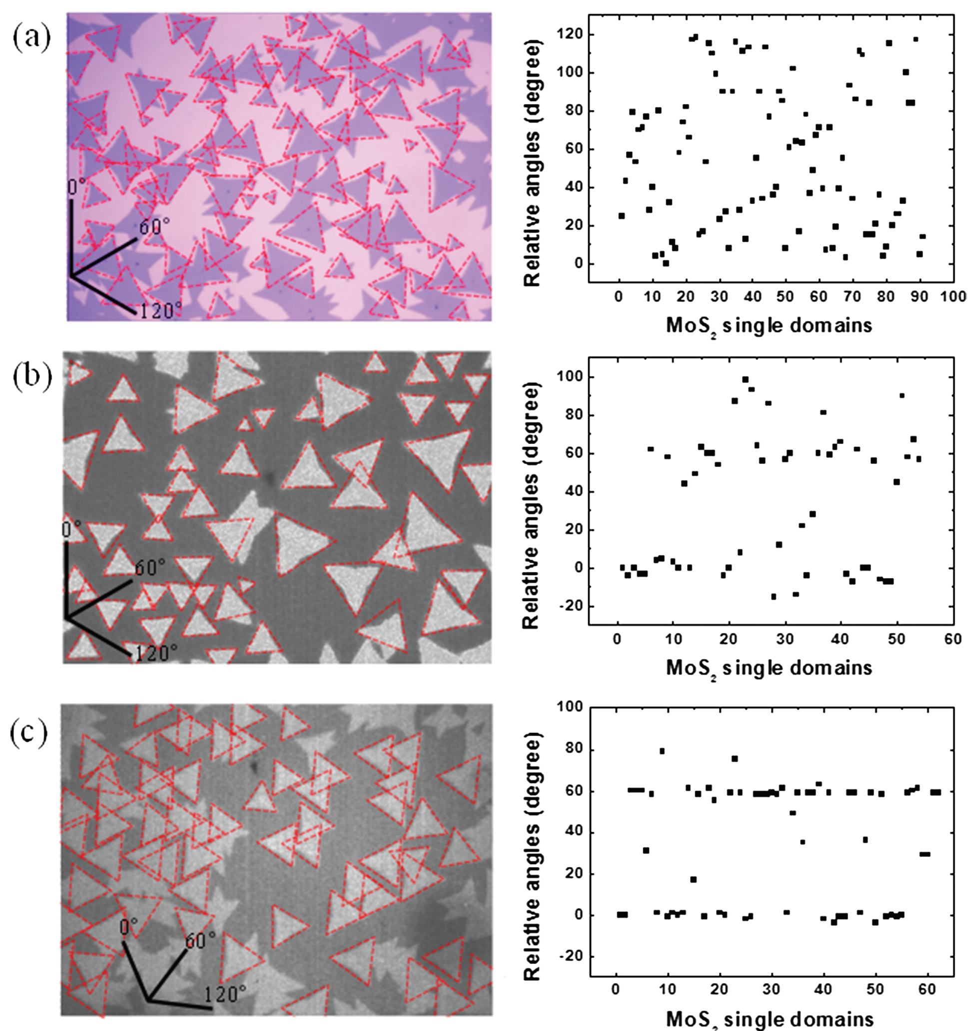

Fig. 3. (Left) Optical images and (right) relative angle analysis plot of the MoS_2 domains synthesized on (a) SiO_2, (b) Al_2O_3, and (c) GaN substrates. The insets in left images show the reference for the domain orientation direction. The right plots represent the relative orientation angles for the individual MoS_2 domains.

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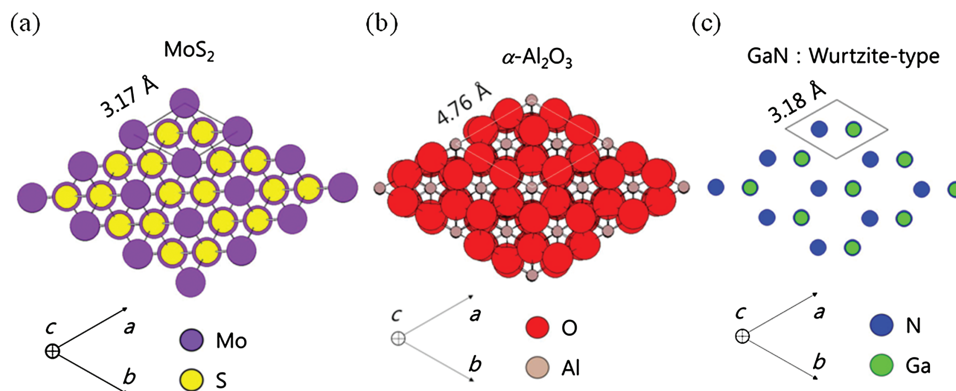

Fig. 4. Hexagonal atomic structures of (a) MoS_2, (b) Al_2O_3, and (c) GaN. The lattice constants are marked along *a*-axis of the unit cell (rhombus at the top of illustration).

has no crystal structure. The evaporated molybdenum and sulfur have no preferential growth alignment when they are synthesized on amorphous surface.

For the case of Al_2O_3 substrate as a hexagonal crystal with the lattice constant (4.76 Å) not matched with that (3.17 Å) of MoS_2 film (Fig. 3(b)), the domains of MoS_2 films had a tendency of alignment with the angle orientation of 60°, but the alignment was rather not perfect. Due to the hexagonal crystal structure of Al_2O_3, molybdenum and sulfur have preference to be deposited at particular site. However, because of the lattice strain caused by difference of lattice constant, MoS_2 domains were not aligned. In contrast, for the case of GaN substrate as a hexagonal crystal with a lattice constant (3.18 Å) matched well with that (3.17 Å) of MoS_2 film (Fig. 3(c)), the domains of MoS_2 films had a strong tendency of alignment with the angle orientation of 60°. This is because well matched lattice constant between GaN (3.18 Å) and MoS_2 (3.17 Å). This is because not only molybdenum and sulfur can be deposited on particular site at hexagonal atomic structure, but also the lattice-matched synthesis condition can reduce the lattice strain of MoS_2. Also, lattice-matched GaN can control the planar defect formation during the synthesis process.[20]

In Figure 4, we present the in-plane atomic structure of MoS_2 (Fig. 4(a)), Al_2O_3 (Fig. 4(b)), and GaN (Fig. 4(c)). In Figure 4(a), purple circles and yellow circles are molybdenum and sulfur atoms, respectively. These atoms in MoS_2 are formed as a hexagonal atomic structure. In the hexagonal crystal structure, the *a*-axis and *b*-axis constants are equal, so we refer the lattice constant along the *a*-axis on a unit cell (at the top part of atomic structural illustration). Similarly, in Figure 4(b), red circles and light red circles are oxygen and aluminum atoms, respectively. These atoms in Al_2O_3 are also formed as a hexagonal atomic structure with the lattice constant 4.76 Å. This lattice constant of Al_2O_3 is not matched with that of MoS_2. In Figure 4(c), blue and green circles are nitride and gallium atoms, respectively. These components in GaN are also formed as a hexagonal atomic structure, and particularly the lattice constant of GaN is matched well with that of MoS_2.

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4. CONCLUSION

We synthesized single-layer MoS_2 atomic films on SiO_2, Al_2O_3, and GaN substrates by a chemical vapor deposition method. Here, SiO_2 as an amorphous, Al_2O_3 as a hexagonal crystal with a lattice constant not matched with that of MoS_2 film, and GaN as a hexagonal crystal with a lattice constant matched well with that of MoS_2 film. Then, we investigated the orientation properties of the domains of MoS_2 atomic films on these three substrates. We found that the domains of synthesized MoS_2 films on the GaN substrate were aligned better than SiO_2 or Al_2O_3 due to the similarities of the crystal structure and lattice constant of MoS_2. Our study may be helpful for researches towards a possible route to synthesize large size, single-layer and single-domain MoS_2 films.

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References and Notes

1. B. Radisavljevic, A. Radenovic, J. Brivio, V. Giacometti, and A. Kis, *Nat. Nanotechnol.* 6, 147 (**2011**).
2. K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, *Phys. Rev. Lett.* 105, 136805 (**2010**).

3. S. W. Han, H. Kwon, S. K. Kim, S. Ryu, W. S. Yun, D. H. Kim, J. H. Hwang, J.-S. Kang, J. Baik, H. J. Shin, and S. C. Hong, *Phys. Rev. B* 84, 045409 (**2011**).
4. Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman, and M. S. Strano, *Nat. Nanotechnol.* 7, 699 (**2012**).
5. B. Radisavljevic, M. B. Whitwick, and A. Kis, *ACS Nano* 5, 9934 (**2011**).
6. J. Pu, Y. Yomogida, K.-K. Liu, L.-J. Li, Y. Iwasa, and T. Takenobu, *Nano Lett.* 12, 4013 (**2012**).
7. A. K. Geim and I. V. Grigorieva, *Nature* 499, 419 (**2013**).
8. S. Najmaei, Z. Liu, W. Zhou, X. Zou, G. Shi, S. Lei, B. I. Yakobson, J.-C. Idrobo, P. M. Ajayan, and J. Lou, *Nat. Mater.* 12, 754 (**2013**).
9. A. M. van der Zande, P. Y. Huang, D. A. Chenet, T. C. Berkelbach, Y. You, G.-H. Lee, T. F. Heinz, D. R. Reichman, D. A. Muller, and C. Hone, *Nat. Mater.* 12, 554 (**2013**).
10. W. Park, J. Baik, T.-Y. Kim, K. Cho, W.-K. Hong, H.-J. Shin, and T. Lee, *ACS Nano* 8, 4961 (**2014**).
11. H. J. Queisser and E. E. Haller, *Science* 281, 945 (**1998**).
12. S. Nakamura, *Science* 281, 956 (**1998**).
13. S. Mahajan, *Acta Mater.* 48, 137 (**2000**).
14. W. K. Seong, J. Y. Huh, W. N. Kang, J. W. Kim, Y. S. Kwon, N. K. Yang, and J. G. Park, *Chem. Vap. Deposition* 13, 680 (**2007**).
15. C. M. Balkas, C. Basceri, and R. F. Davis, *Powder Diffration* 10, 266 (**1995**).
16. K.-K. Liu, W. Zhang, Y.-H. Lee, Y.-C. Lin, M.-T. Chang, C.-Y. Su, C.-S. Chang, H. Li, Y. Shi, H. Zhang, C.-S. Lai, and L.-J. Li, *Nano Lett.* 12, 1538 (**2012**).
17. C. Lee, H. Yan, L. E. Brus, T. F. Heinz, J. Hone, and S. Ryu, *ACS Nano* 4, 2695 (**2010**).
18. C. Ataca, M. Topsakal, E. Aktürk, and S. Ciraci, *J. Phys. Chem. C* 115, 16354 (**2011**).
19. G. L. Frey, R. Tenne, M. J. Matthews, M. S. Dresselhaus, and G. Dresselhaus, *Phys. Rev. B* 60, 2883 (**1999**).
20. K. J. Bachmann, N. Dietz, A. E. Miller, D. Venables, and J. T. Kelliher, *J. Vac. Sci. Technol. A* 13, 696 (**1995**).

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