The Study of Atmospheric Pressure CVD Growth Process of Mo$_x$W$_{1-x}$Te$_2$ Nanobelts for Tuneable Chemical Composition

Shijian Liu$^{1,2}$, Haipeng Qiu$^{1,3}$, Shanhua Liu$^{1,2}$, Jin Zou$^3$, Zhigang Chen$^3$

$^1$ AVIC Aviation Foundation Technology Establishment, Beijing 101300, China
$^2$ AVIC Composite Corporation LTD, Beijing 10300, China
$^3$ The University of Queensland, Brisbane 4067, Australia

Tel (+86) 18911985403 (Shijian Liu); email: 331743043@qq.com

Abstract. Transition metal dichalcogenides nanomaterials with topological semimetallic phase (MoTe$_2$, WTe$_2$ and Mo$_x$W$_{1-x}$Te$_2$) are expected to realize no-consumption electronic transportation due to its Dirac point. Especially, the various structure existence in Mo$_x$W$_{1-x}$Te$_2$, like hexagonal (2H), monoclinic (1T') and orthorhombic (Td), provides opportunities for phase engineering, which is beneficial for future novel electronic and spintronic devices. Plenty works have focused on the synthesis of MoTe$_2$, WTe$_2$ and Mo$_x$W$_{1-x}$Te$_2$ nanomaterials. Unfortunately, the understanding of the growth process of Mo$_x$W$_{1-x}$Te$_2$ nanomaterials is still absent and the exact control of the atomic ratio between Mo and W in Mo$_x$W$_{1-x}$Te$_2$ nanomaterials is still a huge task up to now. Here, we study the growth process of Mo$_x$W$_{1-x}$Te$_2$ nanomaterials by the growing of binary MoTe$_2$ and WTe$_2$ nanomaterials. Through detailed structural and compositional characterization, same growth mode, crystallography, and morphology have been observed among MoTe$_2$, WTe$_2$ and Mo$_x$W$_{1-x}$Te$_2$ nanomaterials. Through analysis, we suggest that the heating temperature of Mo and W precursors during the CVD process is the key parameters to achieve the tuneable chemical composition of Mo$_x$W$_{1-x}$Te$_2$ nanomaterials. This study dissected the growth process of Mo$_x$W$_{1-x}$Te$_2$ nanomaterials and provided a possible method to control the chemical composition of Mo$_x$W$_{1-x}$Te$_2$ nanomaterials by APCVD, which is beneficial to realize the phase engineering in Mo-W-Te system and also for future topological application.

1. Introduction
During the past few years, the family of transition metal dichalcogenides (TMDs), especially the MoTe$_2$, WTe$_2$ and Mo$_x$W$_{1-x}$Te$_2$, has been studied widely and expanded constantly due to the novel topological structure and properties under nanosize. [1-3] In particular, the Mo$_x$W$_{1-x}$Te$_2$ is expected to combine the advantages of MoTe$_2$ and WTe$_2$, which may be more practicable to realize topological properties and achieve topological application.[4, 5] Determined by the atomic ratio between Mo and W, it is reported that by using chemical vapour transport (CVT) as growth method, various structures are possible for Mo$_x$W$_{1-x}$Te$_2$ bulk material, such as Hexagonal (2H), monoclinic (1T’) and orthorhombic phase (Td).[6-10] In specifically, 2H is a semiconducting phase with ~1 eV indirect band gap, while 1T’ is a conducting metal. As for T$_d$ phase, it is a semimetal with novel topological structure and properties. Various possible structure with various properties in Mo$_x$W$_{1-x}$Te$_2$ nanomaterials provides opportunities for phase engineering, which is beneficial for future novel electronic and spintronic devices. Recently,
the growth of Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanobelts were reported.[11, 12] However, the mechanism of the growth process of tuneable chemical composition of Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanomaterials and the exact control of the atomic ratio between Mo and W in Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanomaterials is still a huge task.

Here, based on the synthesis of the ternary Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanobelts, we further study the atmospheric pressure chemical vapour deposition (APCVD) growth process to reveal the growth process of Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanomaterials and find the key factor to control the atomic ratio Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanomaterials. Via scanning electron microscopy (SEM) and transmission electron microscopy (TEM), we found that under our growth condition, by removing the Mo (W) precursors, binary WTe\textsubscript{2} (MoTe\textsubscript{2}) nanobelts with same crystallography information can be fabricated successfully. Besides, the H\textsubscript{2} is found to be crucial to the successful growth of ternary Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanobelts. Through the analysis of the results, it can be concluded that the detailed chemical composition of Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanobelts is decided by the saturated vapor pressure and can be controlled by the heating temperature of each precursors, which is instructive for realizing the tuneable chemical composition of Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanomaterials.

2. Experiment

In this work, all the experiments were conducted in a horizontal single-zone tube furnace using APCVD as the synthesis method. MoO\textsubscript{3}, WCl\textsubscript{6} and Te powders were used here as precursors, and placed at the center of the tube furnace. Both MoO\textsubscript{3} and WCl\textsubscript{6} are put at the centre of the tube furnace. Te powders were put at the ~12 cm upstream from the centre of the tube furnace. A 300 nm SiO\textsubscript{2}/Si wafer was used as the substrate to collect our samples, which is needed to be cleaned carefully prior to the experiment. A mixture gas of 200 sccm Ar and 20 sccm H\textsubscript{2} were used as the carrier gas. Temperature was ramped up to 700°C in 20 minutes and held for 2 hours, following by a natural cooling. The substrates with samples were sealed under vacuum for not being oxidized. The structural information of our samples were examined by XRD patterns on Bruker D8 Advance MKII with Cu Ka radiation source. Morphology and composition of our samples were identified by JEOL JSM-7100F SEM equipped with Energy-dispersive X-ray Spectroscopy (EDS) detector. A Trans Philips Tencai F20FEG-S/TEM operating at 200 kV was employed to characterize the structure of our samples. The samples on the substrate was first dispersed in ethanol with ultrasonic and the solution was then dripped on the Cu grid for TEM characterization. TEM samples were cut by the focused ion beam (FIB) for specific characterization.

3. Results and Discussions

Figure 1(a) is the XRD spectrum of our as-synthesized samples, showing a major crystal orientation of the surface is {002}, which is consistent with the reported results.[6, 13] However, as shown in Table 1, the position of the {002} peaks are close with each other among the 2H, 1T' and T\textsubscript{d} phase. Therefore, XRD results can tell us the major upward surface is (002) facet, while the crystal structure is still remain uncertain. The inset in Figure 1(a) is the schematic diagram of the CVD experimental setup for the growth of Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanomaterials, where both Mo, W and Te precursors were added at specific temperature area in the furnace. Figure 1(b) is the typical SEM image of the Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanostructures collected on the substrates and shows an “island” growth products with high density and large scale. The inset is a high-magnification SEM image, in which rectangular nanobelts with thickness around 100 nm, width from 200 nm to 500 nm, and length at micron grade are clearly observed. The growth of the Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanostructures is reproducible and the fact of large-scale and high-density products reveals that the experimental condition is appropriate for the growth of Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanostructures. The Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanostructures grew in “island” shape corresponding to a unique growth mode called Volmer-Weber growth.[14] This is mainly decided by the wettability between the deposited atoms and the substrate as well as the diffusivity of the deposited atoms, which can be affected by the growth temperature and the growth time. Figure 1(c) is the corresponding EDS spectrum of our samples, which indicates the atomic ratio among Mo, W and Te to be around 0.9: 0.1: 2, revealing the composition of Mo\textsubscript{0.9}W\textsubscript{0.1}Te\textsubscript{2}. As the atomic ratio between O and Si is around 2:1, the
The absence of O and Si peaks can be attributed to the SiO₂/Si substrate. Figure 1(d) is the bright-field (BF) TEM image of our samples, which is cut and changed orientation by FIB, showing a width of ~200 nm. The SAED pattern from zone axis [010] showing a parallelogram shape with β=98°, which is closed to the structure of 1T’-MoTe₂. Combining the results of XRD and SAED pattern, the structure of our samples can be identified to be 1T’ (Monoclinic) phase instead of 2H (Hexagonal) phase or T_d (Orthorhombic) phase. This result is in accord with the Yangyang Lv’s and Xuejun Yan’s work,[15, 16] where the Mo₀.₉W₀.₁Te₂ bulk material grew by solid-state reaction and CVT method was determined to be 1T’ phase.

| Table 1. Standard XRD positions of (00l) peaks of 2H-MoTe₂, 1T’-MoTe₂ and T_d-WTe₂. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Structure                      | JCPDS           | 2θ (degree)     |                 |                 |                 |                 |
| 2H-MoTe₂                       | No. 72-0117     | 12.668          | 25.494          | 38.656          | 52.375          | 66.958          |
| 1T’-MoTe₂                      | No. 71-2157     | 12.793          | 25.750          | 39.052          | 52.977          | 67.765          |
| T_d-WTe₂                       | No. 71-2156     | 12.572          | 25.299          | 38.389          | 51.949          | 66.388          |

Figure 1. The growth of Mo₀.W₁xTe₂ nanobelts. (a) The schematic diagram of experimental setup. (b) The SEM image of the samples; inset is the high-magnification SEM image. (c) The EDS spectrum of the samples. (d) The BF TEM image of the samples; inset is the selected area electron diffraction (SEAD) pattern with zone axis at [010].
Figure 2. (a) The low-magnification SEM image of the samples grown without H₂. (b) is the corresponding EDS spectrum.

Figure 3. The growth of WTe₂ nanobelts. (a) The schematic diagram of experimental setup. (b) The SEM image of the samples; inset is the high-magnification SEM image. (c) The EDS spectrum of the samples. (d) The BF-TEM image of the samples; inset is the SEAD pattern with zone axis at [001].
During the synthesis of Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanobelts, it is noticed that the H\textsubscript{2} has play an important role. Figure 2(a) is a typical SEM image of the samples grown without H\textsubscript{2}, showing a large-scale and high-density round particles with a radius from 100 nm to 20 \textmu m, which is different from the results shown in Figure 1. Figure 2(b) is the corresponding EDS spectrum of the particles, showing the peaks of Mo, W, Te, Si and O. However, the signal of O is relatively higher than Si and the atomic ratio between O and Si is around 4:1, indicating that the O peaks is not only from substrates but also other sources, such as MoO\textsubscript{3} precursors. Without the inlet of H\textsubscript{2}, the more O atoms have took part in the formation of Mo-W-Te. This observation indicates that H\textsubscript{2}, not only acting as the carrier gas but also preventing the samples being oxidized, is significant for the growth of Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanobelts by APCVD.

To further understand growth process of the ternary Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2}, we removed the W and Mo precursors respectively. Figure 3(a) is the schematic diagram of the experimental setup for the growth of WTe\textsubscript{2} nanostructures without Mo precursors. Figure 3(b) is a SEM image of the as-synthesized WTe\textsubscript{2} nanostructures, showing a large scale of nanobelts in “island” shape, similar to the Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanobelts mentioned above. The inset is the high-magnification SEM image, showing the WTe\textsubscript{2} nanobelts are of similar size and shape with Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanobelts. Figure 3(c) is the corresponding EDS spectrum, which shows the atomic ratio between W and Te to be around 1:2, indicating the nature of WTe\textsubscript{2}nanobelts. The analysed atomic ratio between Si and O is around 1: 2, which is consistent with the composition of the SiO\textsubscript{2} substrate. Therefore, the signals of Si and O are arisen from the substrate. Figure 3(d) is the BF-TEM image of WTe\textsubscript{2} nanobelt, showing a width of ~100 nm. The inset is the corresponding SAED pattern, showing a rectangular shape, consistent with the T\textsubscript{d} WTe\textsubscript{2} crystal structure. Besides, the growth direction of the nanobelts is along [200], as indicated by the SAED pattern.

Figure 4(a) is the schematic diagram of the experimental setup for the growth of MoTe\textsubscript{2} nanomaterials without W precursors. Figure 4(b) is a SEM image of the as-synthesized MoTe\textsubscript{2} nanostructures, showing a large scale of nanobelts in “island” shape. Such a consistent growth mode among Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2}, WTe\textsubscript{2} and MoTe\textsubscript{2} reveals that the CVD growth mechanism is general for Mo-W-Te family. The inset is the high-magnification SEM image, showing the MoTe\textsubscript{2} nanobelts are in a rectangular shape and the thickness is ~100 nm. Figure 4(c) is the EDS spectrum of the samples, which shows the atomic ratio between Mo and Te equaling 1:2, revealing the MoTe\textsubscript{2} nature. Combining the BF-TEM image and the corresponding SAED pattern in Figure 4(d), the MoTe\textsubscript{2} nanobelt is in monoclinic (1T’) structure and grew along [200] direction.

As indicated by the results of Figure 1 to Figure 4, both Mo and W atoms can react with Te atoms individually during the CVD growth of Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanobelts. On the one hand, the growth model for Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanobelts is reported to be the vapor solid (VS) growth,[11]which means the Mo and W atoms can both bond with Te atoms during the formation of Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanobelts. On the other hand, as the electronegativity between Mo and Te is similar with W and Te, the binding force between Mo and Te should be similar with W and Te, which means to react with Te atoms, there is no privilege between Mo and W atoms. Therefore, the amount of Mo and W atoms during the growth process has become the key factor to determine the exact chemical composition of Mo\textsubscript{x}W\textsubscript{1-x}Te\textsubscript{2} nanomaterials. As indicated by the ideal gas law as shown in equation (1),[19] the amount of gas can be described as:

\[
n = \frac{PV}{RT}
\]

In equation (1), P is the absolute pressure, \( V \) is the volume, \( n \) is the amount of moles, R is a gas constant and T is the absolute temperature of the gas. In a typical CVD process, the volume of all the gases can be regarded as the same. Through deformation of equation (1), the ratio of the amount of moles between two vapour substances in CVD process can be described as:

\[
n_1 \times T_2 = n_2 \times T_1
\]
Figure 4. The growth of MoTe$_2$ nanobelts. (a) The schematic experimental setup. (b) The SEM image of the samples; inset is the high-magnification SEM image. (c) The EDS spectrum of the samples. (d) The BF-TEM image of the samples; inset is the SEAD pattern with zone axis at [001].

In our cases, the both the Mo and W precursors are solid state. The absolute pressure here should be the saturated vapour pressure of Mo and W precursors. Basically, the saturated vapour pressure of solid or liquid materials can be usually described by the Calusius-Clapeyron equation or Antoine equation,[17, 18] which are shown in equation (1) and equation (2):

$$\frac{d[\ln p]}{d[1/T]} = \frac{\Delta_{\text{sub}}H}{R}$$

$$\log_{10}p = A + \frac{B}{T + C}$$

In equation (3), $p$ is the saturated vapour pressure of solid or liquid materials, $T$ is the absolute temperature, $\Delta_{\text{sub}}H$ is the enthalpy of sublimation constant of certain material and $R$ is the gas constant. In equation (4), $p$ is the saturated vapour pressure of solid or liquid materials, $t$ is the Celsius...
temperature and A, B, C are the antoine constant, which are decided by the certain material. It can be found that the saturated vapour pressure of solid or liquid materials are related with the temperature of the materials and the choice of the materials. Therefore, throughout the analysis mentioned above, it can be concluded that the atomic ratio between Mo and W in ternary $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ nanobelts can be controlled by the saturated vapor pressure of Mo and W atoms in the CVD furnace, which is mainly controlled by the heating temperature and also the choice of Mo and W precursors.[20] This is a significant instruction for the further experimental design in the realization of tuneable chemical composition of $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ nanomaterials and even other TMDs.

4. Conclusions
In summary, with Mo, W and Te precursors, large-area and high-density of 1T$'$-$\text{Mo}_{0.9}\text{W}_{0.1}\text{Te}_2$ nanobelts can be fabricated by APCVD, which grew along [200] with the largest facet of (002). Besides, H$_2$ is proved to be significant for the growth of $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ nanobelts. Without Mo or W precursors, the binary WTe$_2$ or MoTe$_2$ nanobelts with the same crystal facet direction as $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ nanobelts can be fabricated under same growth condition, indicating the individual reactivity between Mo (W) and Te atoms. The same growth mode, growth direction and morphology of MoTe$_2$, WTe$_2$, $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ nanostructures revealing the universality growth mechanism of Mo-W-Te family, which is instructive for CVD growth of other TMDs nanomaterials. This work not only dissects the growth process of $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ nanomaterials but also demonstrates a possible way to achieve the tunable composition of $\text{Mo}_x\text{W}_{1-x}\text{Te}_2$ nanostructures and realize the phase engineering of Mo-W-Te system, which is beneficial to develop the unique topological properties for future electronic devices.

Acknowledgement
The University of Queensland is acknowledged for the support of the previous study in this work. Dr. Yichao Zou, Dr. Xiaolei Shi, Mr. Qizhen Li, Mr. Weidi Liu and Miss. Yuzhe Yang are also acknowledged for the help in this work.

References
[1] Belopolski I et al. 2016 Nat. Commun. 7 13643
[2] Wang Z J, Gresch D, Soluyanov A A, et al. 2016 Phys. Rev. Lett. 117 056805
[3] Soluyanov A A, Gresch D, Wang Z J, et al. 2015 Nature 527 495
[4] Belopolski I, et al. 2016 Phys. Rev. B 94 085127
[5] Chang T R, et al. 2016 Nat. Commun. 7 10639
[6] Keum D H, et al. 2015 Nat. Phys. 11 482
[7] Rhodes D, et al. 2017 Nano Lett. 17 1616
[8] Park J C, et al. 2015 ACS Nano 9 6548
[9] Jiang Y C and Gao J 2016 Sci. Rep. 6 19624
[10] Duerloo K N and Reed E J 2016 ACS Nano 10 289
[11] Liu S J, Zou Y C, Shi X L, et al. 2019 J. Alloy. Compd. 777 926
[12] Zou Y C, et al. 2018 Small 14 1800780
[13] Lee C H, Cruz-Silva E, Calderin L, Nguyen M A T, et al. 2015 Sci. Rep. 5 10013
[14] Puurunen R L and Vandervorst W 2004 J. Appl. Phys. 96 7686
[15] Lv Y Y, et al. 2017 Sci. Rep. 7 44587
[16] Yan X J, et al. 2017 Appl. Phys. Lett. 110 211904
[17] Nahrwold M L, Archer P G and Cohen P J 1973 Anesthesiology 39 444
[18] Oja V and Suuberg E M 1999 J. Chem. Eng. Data 44 26
[19] Cook M A 1947 J. Chem. Phys. 15 518
[20] Li H L, Zhang Q L, Duan X D, et al 2015 J. Am. Chem. Soc. 137 5284