An Investigation in Phase Transition of MoTe₂ Film with Continuous Tellurization Reaction

Leijie Sun*, Manman Ding*, Jie Li, Li Yang, Xun Lou, Zijian Xie, Wenfeng Zhang, Haixin Chang*

Quantum Matter and Device Lab, Center for Joining and Electronic Packaging, State Key Laboratory of Material Processing and Die and Mold Technology, School of Materials Science and Engineering, Huazhong University of Science and Technology (HUST) Wuhan 430074, China.

*Corresponding author E-mail: hxchang@hust.edu.cn
+ These authors contributed to this work equally

Abstract. Molybdenum ditelluride (MoTe₂), as a member of two dimensional transition metal dichalcogenides (2D TMDCs), has been drawing scientists’ attention due to its susceptible phase transition. Here, we studied the phase transition process of MoTe₂ with tellurization reaction step by step. In the process of tellurization reaction, the 1T’ MoTe₂ would firstly convert to an intermediate phase (1T’@2H MoTe₂) and then slowly convert to 2H MoTe₂ instead of forming a direct phase transition from 1T’ MoTe₂ to 2H MoTe₂. This result might inspire the phase engineering of other 2D TMDCs and the exploration of potential device design.

1. Introduction

MoTe₂, as a novel two dimensional material, has drawn more and more attention for its unique properties in recent years [1-4]. The MoTe₂ usually have two phases: 1T’ MoTe₂ and 2H MoTe₂ which belongs to semi-metal and semiconductor, respectively. Monolayer 2H MoTe₂ has a direct band gap of 1.1 eV, which is close to silicon that the basement of electronic components. However, the large schottky barrier between TMDCs and metal electrode restrict the realistic application of TMDCs in electronic devices [5-8]. Hence, how to reduce the schottky barrier is becoming an urgent issue. Montejo et al[9] adopted a way of oxidizing the interface between MoS₂ and metal electrode to reduce the contact barrier. However, this method may introduce a new component (MoO₃), which would affect the intrinsic properties of the materials. On the other hand, in-situ phase transition of TMDCs can result in a high quality homogeneous heterostructure between semi-conducting and the metallic TMDCs. If the work function between the semi-conducting and the metallic TMDCs is compatible, an ideal two-dimensional ohmic contact will be formed between the metal-semiconductor homogeneous heterostructure.

Previous studies have shown that the energy difference between the 2H MoTe₂ and the 1T’ MoTe₂ is only 44 meV, which is much smaller than other TMDCs. The small energy difference indicates that the phase transition between the metallic state and the semi-conducting state of MoTe₂ is more likely to occur. Suyeon Cho et al. have reported the transformation from 2H MoTe₂ to 1T’ MoTe₂ by laser irradiation[10]. The formed homogenous heterostructure forms an ohmic contact, whose carrier mobility increased by 50 times and the switching ratio reaches to 10⁵. Meanwhile, Jin Cheol Park et al.
demonstrated that the 1T’ MoTe$_2$ could be converted to 2H MoTe$_2$ when they prolong the reaction time under excessive tellurium atmosphere[11]. Besides, the 2H MoTe$_2$ can also be converted to 1T’ phase by annealing 2H MoTe$_2$. Yang li et al. also pointed out that the content of hydrogen in carrier gas also has a significant influence on the phase transition of MoTe$_2$[12].

However, the phase transition of MoTe$_2$ in the above mentioned reports lacks of details investigation in the process of 1T’ MoTe$_2$ to 2H MoTe$_2$ or the thickness of MoTe$_2$ is relative large. In this paper, we studied the process of phase transition of 1T’ MoTe$_2$ thin film by conducting a tellurization reaction every 30 minutes. We found that the 1T’ MoTe$_2$ doesn’t translate directly to 2H MoTe$_2$ in the process of continuous tellurization reaction. First, the 1T’ MoTe$_2$ translates to an intermediate phase (1T’@2H MoTe$_2$), and then the intermediate phase would slowly convert to 2H MoTe$_2$.

2. Experimental Section

The preparation of 1T’ MoTe$_2$ film: The experimental method is shown in Figure 1. First, MoO$_x$ (x<3) film as the precursor is prepared by evaporating MoO$_3$ powder to the SiO$_2$/Si substrate. MoO$_x$ film is placed in the center of the heating zone, and 0.2 g tellurium powder was placed upstream away from the precursor. Then the furnace was heated to 650 ℃ and kept for 30 min. A mixture gas of Ar (3 sccm) and H$_2$ (4 sccm) are flowed into the tube to supply the reducing atmosphere. After the reaction is finished, the furnace is opened and cooled to room temperature.

Characterizations: X-ray diffraction (XRD) patterns were measured using an X-ray diffraction meter (PANalytical B.V., Empyrean) to identify all the prepared materials. Optical images were taken on an optical microscope (MV6100). Atomic force microscope (AFM, SPM9700) was used to examine the thickness of the as-grown samples. Raman measurements were performed using an HR800 Raman system with a 532 nm excitation laser. The laser spot focused on the samples with a 50 × 0.75 NA objective lens. All the Raman spectra were calibrated with the Si peak at 520.7 cm$^{-1}$.

![Figure 1. Schematic diagram of the experimental setup.](image)

3. Results and Discussion

The optical image of MoTe$_2$ film is shown in the Figure 2a. It can be seen that the film is uniform and smooth. As is shown in Figure 2b, the thickness of the MoTe$_2$ film is about 11 nm measured by atomic force microscopy (AFM). In the Raman spectrum, the peaks located at 110.6 cm$^{-1}$ (A$_0$), 127.8 cm$^{-1}$ (A$_2$), 162.7 cm$^{-1}$ (B$_2$), 190 cm$^{-1}$ (B$_3$) and 258.2 cm$^{-1}$ (A$_3$) can be attributed to the main characteristic peaks of 1T’ MoTe$_2$, which is in accordance with the previous report[13]. Besides, there are only diffraction peaks of (0 0 2n) planes (Figure 2d), indicating that the 1T’ MoTe$_2$ thin film has a good orientation along c axis[14].
Next, the as-prepared 1T’ MoTe$_2$ thin film was performed tellurization reaction step by step. As shown in Figure 3a, the surface of the sample is uniform after first reaction, and the corresponding Raman spectrum (Figure 3d) showed that the film is still 1T’ MoTe$_2$. Interestingly, some the white spots appear on the film after the second tellurization reaction (Figure 3b). The Raman spectra (Figure 3e) show that there is still only signal of 1T’ MoTe$_2$ in the region without white spots. However, the characteristics of both 2H MoTe$_2$ and 1T’ MoTe$_2$ in white spots are detected, and we named it as 1T’@2H MoTe$_2$. Such as, the peaks of A$_u$, B$_g$ belong to 1T’ MoTe$_2$, and the peaks of A$_1g$, E$_{2g}$ belong to 2H MoTe$_2$. Besides the Raman signals of 1T’ MoTe$_2$ in white spots have relatively blue shift compared to pure 1T’ MoTe$_2$. This is due to that the stress release when 1T’ MoTe$_2$ transforms to 2H MoTe$_2$. When another tellurization reaction for the above mentioned sample was conducted, we found the area of white spots become larger, and the color in the central region becomes heavier (Figure 3c). Expectantly, there was only 2H MoTe$_2$ Raman signal in the corresponding region. Therefore, we assume that the 1T’ MoTe$_2$ doesn’t change directly to 2H MoTe$_2$ in the process of continuous tellurization reaction. Firstly, the 1T’ MoTe$_2$ transformed to an intermediate phase (1T’@2H MoTe$_2$), and then the intermediate phase would slowly convert to 2H MoTe$_2$. 

Figure 2. (a) Optical image of 1T’ MoTe$_2$ thin film; (b) AFM image of 1T’ MoTe$_2$ thin film; (c) Raman spectrum of 1T’ MoTe$_2$ thin film; (d) XRD of 1T’ MoTe$_2$ thin film.
Figure 3. (a-c) The optical images of first, second and third telluride reaction for MoTe₂; (d-f) The Raman spectra of corresponding spot in the figure (a-c).

The Raman mapping can directly display the process of MoTe₂ phase transition. The Raman mapping image (Figure 4a) shows that there are three regions with distinct colors, which can represents three different MoTe₂ states. We take 10 points from left to right in the mapping image, and extract their corresponding Raman signals (Figure 4b). The Raman spectrum shows that dark blue region represents the 1T' MoTe₂. As the point moves to right, the characteristic peak of 1T' MoTe₂ gradually weakens. Conversely, the characteristic peaks of 2H MoTe₂ gradually appear (light blue region) and the peak intensity increasingly enhance. Finally, there is only the characteristic peak of 2H MoTe₂ (green region). The transition of Raman signals illustrate the process of the phase change for MoTe₂ as above mentioned. An intermediate phase (1T'@2H MoTe₂) is formed when 1T' MoTe₂ transforms to 2H MoTe₂.

Figure 4. (a) Raman mapping of 1T'@2H MoTe₂; (b) Raman spectra from left to right in (a).

Therefore, we believe that 1T’ MoTe₂ can fully convert to 2H MoTe₂ by continual tellurization reaction. The optical image of MoTe₂ that went through six times of tellurization reactions (Figure 5a) shows that the MoTe₂ film is almost covered with 2H phase. Figure 5b demonstrates the corresponding XRD patterns of MoTe₂ film after every tellurization reaction. With the increase of tellurization reaction times, the diffraction peak of (0 0 2) gradually shifts to the lower angle correspondingly, indicating the 1T’ MoTe₂ can gradually converts to 2H MoTe₂.
4. Conclusion
In conclusion, the 1T’ MoTe₂ thin film with good orientation can be obtained through CVD method. We studied the real phase transition process from 1T’ MoTe₂ to 2H MoTe₂ with tellurization reaction step by step. In addition, instead of translating directly to 2H MoTe₂ in the process of continuous tellurization reaction, the 1T’ MoTe₂ translates to an intermediate phase (1T’@2H MoTe₂), and then the intermediate phase would slowly convert to 2H MoTe₂. This result can help us understand the phase control engineering of other 2D TMDCs, which is critical for the potential application of 2D TMDCs in electronic devices.

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