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Degradation and Effective Encapsulation of Few-Layer 1T′-$MoTe_2$ thin Film

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Abstract

We have investigated the degradation of CVD-grown few-layer 1T′-$MoTe_2$ thin film. Surface oxidation of both Mo and Te atoms easily occurs even at room temperature, while Mo atoms show preferential oxidation in comparison with Te. Notably, Raman-active Te metalloid is identified as the byproduct of $MoTe_2$ oxidation. We further demonstrate that encapsulation by a thin PMMA coating can effectively prevent the degradation of few-layer $MoTe_2$ Film at the ambient conditions.

1. Introduction

Molybdenum- and tungsten-based transition-metal dichalcogenides (TMDCs) such as $MoTe_2$ and WTe_2 attract intense research interests owing to their fascinating properties [1-2]. Notably, recent investigations predicts distorted octahedral (1T′) TMDCs to be semimetallic topological insulators, implying their crucial application for developing topological quantum computing devices[3]. Unfortunately, 1T′ TMDCs generally exhibit severe surface chemical instability, which hampers their application possibilities. In this regard, a thorough understanding of their degradation behavior is obviously desirable while are much less investigated experimentally.

In this study, we present an oxygen-induced degradation of few-layer 1T′-$MoTe_2$ thin film grown by CVD method. We demonstrate that Surface oxidation of both Mo and Te atoms occurs at the ambient condition, and Raman-active Te metalloids would emerge and vanish relying on the oxidation temperature. By spin-coating a dense PMMA film, $MoTe_2$ thin film can be effective encapsulated. The results provide a solid understanding of $MoTe_2$ ambient instability and offer a feasible protective method, which might accelerate its future topological quantum computing related-applications.

2. Experimental

Few-layer 1T′-$MoTe_2$ film was grown by chemical vapor deposition (CVD) onto 300 nm SiO_2/Si substrate using high tellurization velocity [4]. Its structural characteristics and polymorphism were identified by Raman Spectroscopy and X-ray Photoelectron Spectroscopy (XPS). To evaluate the degradation behavior, as-synthesized 1T′-$MoTe_2$ film was kept at ambient condition for several hours, and then further annealed under the pure oxygen atmosphere for 30 min at different temperature ranging from 100°C to 400°C, respectively. Structural deterioration was evaluated by Raman Spectroscopy and XPS. To protect $MoTe_2$ thin film, a dense layer of PMMA film was spin coated onto the surface of $MoTe_2$ under the optimized condition immediately after the CVD growth. Encapsulation effect was evaluated after 1 week by removing PMMA coating using the argon ion etching in XPS.

3. Results and Discussion

The optical images of as-synthesized $MoTe_2$ thin film is shown in **Figure 1 (a)**, indicating the film is uniform and continuous across the entire area. Raman spectrum (**Figure 1 (b)**) exhibits five prominent Raman modes at 108(A_u), 127(A_g), 161(B_g), 189(B_g) and 257(A_g) cm^{-1}, respectively, verifies the film as 1T′-$MoTe_2$ film. The film is about five layers with a thickness ~4.33 nm characterized by atomic force spectroscopy (AFM), as shown in **Figure 1(c)**). **Figure 1(d)** shows the chemical states by XPS, which the prominent Mo 3d and Te 3d peaks can be assigned to Mo−Te bonds. The Mo/Te atomic ratio was determined to be around 1:2 by XPS, indicating the as-grown $MoTe_2$ film possesses a good stoichiometry.

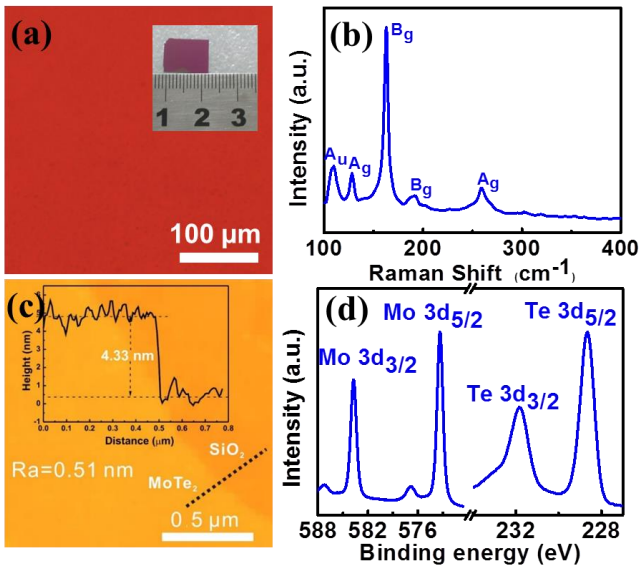

Figure 1. Characterization of CVD-grown 1T′-$MoTe_2$ thin film. (a) Optical images of 1T′-$MoTe_2$ film on ~1.0 × 1.0 cm SiO_2/Si substrates; (b) Representative Raman spectrum taken at several different locations; (c) Atomic force microscopy (AFM) image to reveal the thickness and roughness; (d) Mo 3d and Te 3d XPS analysis.

To reveal the oxygen-induced degradation, XPS analysis of 1T′-$MoTe_2$ film before and after O_2 annealing at different temperature for 30 min was performed, as shown in **Figure 2.** For pristine 1T′-$MoTe_2$, only Mo $3d_{5/2}$ (228.5 eV) together with Mo $3d_{3/2}$ (231.6 eV) and Te $3d_{5/2}$ (573.1

eV) together with Te $3d_{3/2}$ (583.5 eV) can be observed, which are assigned to the Mo-Te bonds. When the pristine 1T′-$MoTe_2$ film was exposed at the ambient condition, new Mo-O bonds (233.15 eV and 236.25 eV), and Te-O bonds (576.89 eV and 587.26 eV) obviously arise, suggesting $MoTe_2$ surface is easily oxidized to form MoO_x-TeO_2 layer. The intensity of both Mo-O bonds and Te-O bonds was found to increase with the increase of oxygen annealing temperature, confirming the enhanced oxidation behavior of $MoTe_2$ surface. Interestingly, another new doublet peaks of Te 3d (584.3 and 573.9 eV) appears at 350 ℃, which can not be assigned as Mo-Te band or Te-O band, while is more close proximity to Te-Te bonds**.** Such observation implies that Te metalloids might be another byproduct of $MoTe_2$ oxidation relying on the degradation condition. We also noticed that only Mo-O bonds and Te-O bonds can be observed with further increase of annealing temperature to 400 ℃, indicating the Te metalloids should be decomposed and the 1T′-$MoTe_2$ film has been fully oxidized into MoO_x-TeO_2 layer at 400 ℃.

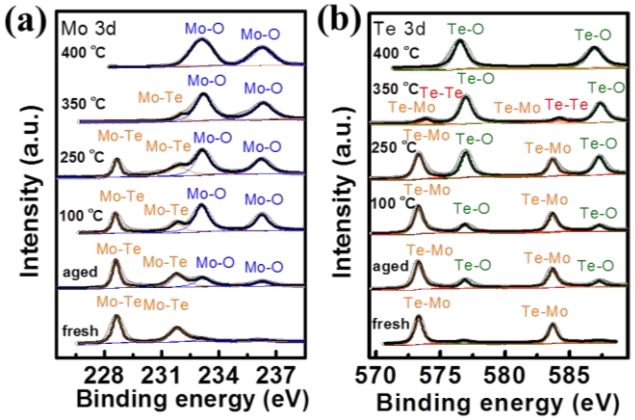

Figure 2. Mo 3d (a) and Te 3d (b) XPS analysis of few-layer 1T′-$MoTe_2$ film before and after O_2 annealing with a constant flow rate (50 sccm) at different temperature for 30 min.

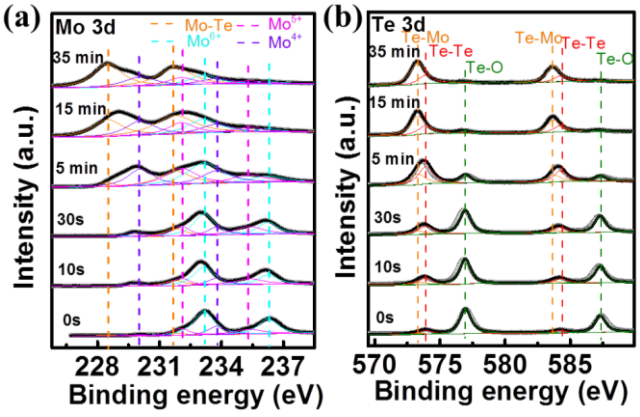

Figure 3. Mo 3d (a) and Te 3d (b) XPS spectra evolution as a function of argon ion etching time to remove the surface oxide layer for the oxidized 1T′-$MoTe_2$ film.

To clarify the oxidation behavior of 1T′-$MoTe_2$ film, XPS analysis of oxidized 1T′-$MoTe_2$ film as a function of argon ion etching time to remove the MoO_x-TeO_2 layer was further performed, as shown in **Figure 3**. Both the intensities of MoO_{3-x} (x≤3) and TeO_2 doublet peaks gradually decrease with the etching time increases, suggesting the oxide film is gradually thinned. Significantly, the intensity of MoO_{3-x} (x≤3) is always higher than the TeO_2 after etching, and even small amount of MoO_{3-x} still remain on the $MoTe_2$ surface although TeO_2 has been completely removed after etching 35 min. Such observation implies a preferential oxidation of Mo in $MoTe_2$ film compared with Te atoms.

Furthermore, the emergence and decomposition of Te metalloids were identified by Raman analysis. As shown in **Figure 4 (a)**, no significant change of Raman-active modes is observed for pristine and degraded 1T′-$MoTe_2$ film exposed at ambient the condition and annealed at 100 ℃, while two new peaks (A and B) at 123 cm^{-1} and 143 cm^{-1} similar with Raman features of Te particles show up when the annealing temperature is above 250 ℃. Such observation further confirms the Te metalloids as oxidation byproduct, which is consistent with XPS analysis above. We also found the intensity of 1T′-$MoTe_2$ Raman peaks gradually decreases till to completely vanishes, and the intensity of peaks A and B obviously increases when the annealing temperature increases from 250 ℃ to 350 ℃. Such results suggest Raman analysis is an feasible way to characterize the Te metalloids during the degradation of $MoTe_2$ film compared with XPS. Similar with XPS analysis, Raman peaks A and B cannot be observed at 400 ℃, which confirms the decomposition of Te metalloids.

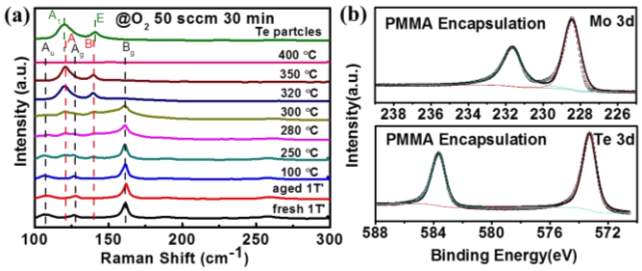

Figure 4. (a) Raman-active modes of 1T′-$MoTe_2$ film before and after O_2 annealing with a constant oxygen flow rate (50 sccm) at different temperature for 30 min. (b) Mo 3d and Te 3d XPS analysis to evaluate the effect of PMMA encapsulation.

To protect the $MoTe_2$ film, a dense layer of PMMA was spin coated onto the $MoTe_2$ surface immediately after the CVD growth. After exposure to ambient condition with PMMA protection for 1 week, PMMA layer was removed by argon ion etching for XPS characterization. As shown in **Figure 4(b)**, both Mo 3d and Te 3d spectrum show no Mo-O and Te-O bonds, suggesting an effective encapsulation of $MoTe_2$ with the coated PMMA film.

4. Conclusion

We have demonstrated a preferential oxidation of Mo in few-layer 1T′-$MoTe_2$ film at the ambient condition. Raman-active Te metalloid is identified as the byproduct of $MoTe_2$ oxidation. A thin PMMA coating was verified to be an effective way to prevent the degradation of $MoTe_2$ Film at ambient condition.

Acknowledgements

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References

[1] A.A. Soluyanov et al, Nature, 527, 495-498 (2015).

[2] M. Chhowalla et al, Nat. Chem., 5, 263-275 (2013).

[3]X. Qian et al, Science, 346, 1344 -1347(2014).

[4] L. Yang et al, ACS Nano., 11, 1964 -1972(2017).