Atomic Scale Insights into Phase Coexistence in Ternary Transition Metal Chalcogenides by Cross-Sectional (S)TEM Imaging

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2D materials including graphene and transition metal dichalcogenides (TMDs) have attracted numerous research interests recently because of their exotic mechanical, optical, thermal, and electronic properties.[1] The properties of TMDs (MX_2, M=Mo and W, X=S, Se, Te) are associated with their Van der Waals (VdW) connected layered structures and their polymorphic phases, including hexagonal 2H, monoclinic T' and orthorhombic T_d.[2,3] The existence of different phases in TMDs opens up the possibility for phase engineering, which allows the design of many novel electronic devices.[2,3] For $MoTe_2$, the alloying of $MoTe_2$ with W can reverse the phase stability between 2H and T', and access the T' or T_d phase in $Mo_{1-x}W_xTe_2$.[2,3] Previous phase determination of $Mo_{1-x}W_xTe_2$ was based on mesoscopic scale characterizations such as Raman spectroscopy and X-ray diffraction, and it remains as a controversy on whether there exists a nanoscale phase mixing.[2,3] On the other hand, aberration-corrected scanning transmission electron microscopy (STEM) provides the capability to precisely resolve the local atomic structure of TMDs.

Here, we synthesized $Mo_{1-x}W_xTe_2$ nanostructures with different compositions using chemical vapor deposition.[4] We show that cross-sectional (S)TEM imaging can be used to monitor the phase evolution in $Mo_{1-x}W_xTe_2$ with W alloying [2H (hexagonal)→T' (monoclinic)→T_d (orthorhombic)]. High-angle annular dark field (HAADF) STEM imaging (Fig. 1), coupled with electron diffraction, indicates that the $Mo_{1-x}W_xTe_2$ specimens have two categories of phases: the pure monoclinic T' phases at low W concentration ($Mo_{0.9}W_{0.1}Te_2$), and the mixed phase of monoclinic and orthorhombic at high W concentrations ($Mo_{0.5}W_{0.5}Te_2$ in Fig. 1a, $Mo_{0.2}W_{0.8}Te_2$ in Fig. 1b). The crystallographic relations between the monoclinic (denoted by m) and orthorhombic (denoted by o) phases were found to be coherent as $\{001\}_m//\{001\}_o$ (Fig. 1a) and $\{100\}_m//\{100\}_o$ (Fig. 1b). Interestingly, T' and T_d coexist with lattice-matched interfaces. This is mediated by a new orthorhombic phase T_d' (unit cell denoted by orange rectangles, Fig. 1a,b). Such T_d' phase preserves the centro-symmetry of T' and can transit to T_d with a small VdW glide of center tri-layer. Energetic calculations show T_d' has a relatively low formation energy, which provides a possible transition path for T'→T_d. Our study gives direct evidence of lattice-matched phase coexistence in ternary TMDs, and atomic-scale insights into the phase-evolution mechanism in $Mo_{1-x}W_xTe_2$.

References

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Acknowledgements

This work was financially supported by the Australian Research Council. Y.-C. Zou thanks the financial support of Overseas Travel Fellowship provided by Australian Nanotechnology Network. We thank the Progress 100 program to encourage the UQ-KU collaboration, and the Nanotechnology Platform Project for advanced nanostructure characterization. The Australian Microscopy & Microanalysis Research Facility is acknowledged for providing characterization facilities.

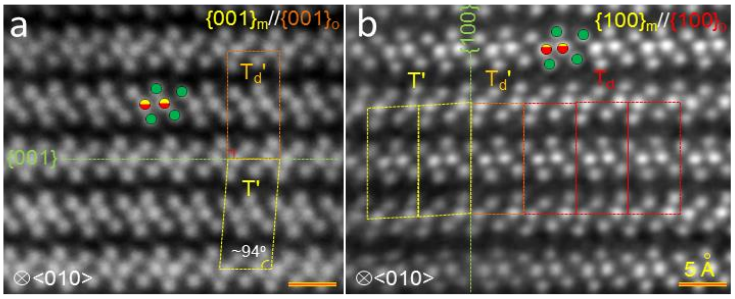

Fig. 1 HAADF STEM images taken from the phase-mixing region in <010> cross-sectional (S)TEM specimens for (a) $Mo_{0.5}W_{0.5}Te_2$ and (b) $Mo_{0.2}W_{0.8}Te_2$. The green dash lines denotes the interface between the coexisting phases. The yellow, orange, red rectangular markers respectively denote the unit cell of T', T_d', T_d. The yellow, red, green balls respectively denote Mo, W, Te occupation. Scale bars are 5 Å.