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Chemical Vapor Transport Growth and Characterization of WTe_2 Crystals †

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Abstract: Tungsten ditelluride (WTe_2) is a transition metal dichalcogenide (TMD) with physical and electronic properties that make it attractive for a variety of applications. The synthesis of this material in practically important monolayer or few layers' form is rather difficult therefore the growth of high quality bulk crystals as source for exfoliation of 2D samples is of prime importance. In our study WTe_2 single crystals are grown by chemical vapor transport (CVT) method using bromine (Br) as a transport agent. Following the synthesis, the powdered and bulk crystals were characterized by X-ray diffraction (XRD), Raman spectroscopy and AFM. The synthesis of Td crystal phase of WTe_2 with high crystalline quality is confirmed by XRD analyses. The surface morphology and Raman analyses additionally support the phase and structure identification and crystalline quality evaluation. The reliability of the CVT method using Br transport for growth of crystal materials with high quality is thus validated.

Keywords: WTe_2; Crystal Growth; Chemical Vapor Transport; XRD; AFM; Raman spectroscopy

1. Introduction

WTe_2 is a type-II Weyl semimetal material [1] which among TMDs is unique, as it crystallizes in a distorted 1T' phase, also known as the Td phase (orthorhombic crystal structure) in contrast to the commonly observed 2H and IT structures in this materials class. In the Td phase, the tungsten atoms are octahedrally coordinated by the tellurium atoms and the successive layers in between are rotated by 180° [2]. Its unique electronic nature leads to very diverse electrical, magnetic, thermal and optical properties. Specially to note: strong anisotropic electrodynamics [3], extremely large, non-saturated magnetoresistance [4] "negative" magnetoresistivity (at specific conditions) [5], room temperature ferroelectric semimetal [6], superconductivity [7] and plasmon polariton activity [8]. In addition, one of the contemporary research trends for WTe_2 is directed towards the realization in 2D form with many perspectives for topological, spintronic and opto-electronic applications. The material is very challenging chemically (due to low chemical reaction activity of W with Te), especially for various synthesis techniques as Chemical Vapor Deposition (CVD) and Molecular Beam Epitaxy (MBE). Consequently, the majority of contemporary WTe_2 studies aiming in 2D limit relied on mechanically-exfoliated samples from single crystals. In this context, there is a necessity for an improvement of the synthesis and growth techniques for preparation of high quality crystals closer to the structural perfection. In this study we present specific details of WTe_2 crystal growth via Chemical Vapor Transport (CVT) and corresponding morphological and structural quality control

and characterization via XRD (X-ray Diffraction), Raman spectroscopy and Atomic Force Microscopy (AFM).

2. Materials and Experimental Methods

2.1. Chemical Vapor Transport method

WTe_2 single crystals were prepared by CVT method using Br as transport agent. As first step WTe_2 compound was sintered from stoichiometric quantities of W and Te powders both with high purity (99.999) in quartz ampoule. The ampoule was evacuated to 10^{-4} torr, sealed and placed in one heating zone-furnace and heated to 725°C with 20°C/hour. The synthesizing process was kept at 725°C for 3 days (72 hours). Once the process completed, the synthesized material was removed from the ampoule, crushed, homogenized, and placed in another quartz ampoule together with transport agent Br (3 mg/ml volume). The ampoule was evacuated and sealed as immersed in liquid N_2 in order to prevent any evaporation loss of the transport agent. The evacuated and sealed ampoule with total 5 g mixture of W, Te and bromine was placed in a 2-zone thermal gradient furnace with the temperatures in the zones of 780 and 680 °C respectively. The growth process takes 7-8 days. The thermal regime is selected considering the W-Te system phase diagram [9]. The WTe_2 single crystals obtained were with dimensions up to 1 cm^2, elongated rectangular shape reflecting the typical orthorhombic crystal structure and flat metallic surface. The CVT process is visualized on Fig. 1.

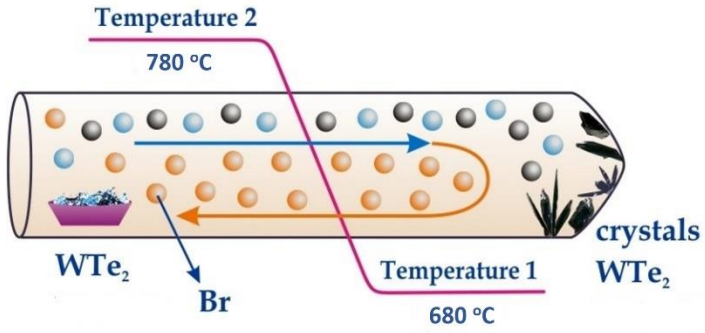


Figure 1. Schematics of WTe_2 single crystals growth process by CVT method.

2.2. Characterization instruments details

The crystal structure of WTe_2 crystals was analyzed by single crystal and powdered X-ray diffraction collected within the range of 5.3° to 80° of 2θ with a constant step of 0.02°, using a Bruker D8 Advance diffractometer with Cu Kα radiation and a LynxEye detector.

The Raman spectra was studied (backscattering geometry) using HORIBA Jobin Yvon Labram HR visible spectrometer equipped He-Ne-laser (633-nm excitation line) with a Peltier-cooled charge-coupled device (CCD) detector.

The surface morphology is analyzed by Atomic Force Microscope MFP-3D, Asylum Research, Oxford Instruments.

3. Results and Discussion

The crystal structure of TMDs materials as WTe_2 is typically layered with a van der Waals stacking and strong anisotropy even in the a-b plane. The XRD data for WTe_2 are presented on Fig. 2, the main crystal lattice parameters are identified – orthorhombic, space group Pmn21 (space group

number 31) with a = 3.4830 Å, b = 6.2780 Å and c = 14.0540 Å. Calculated density (g/cm^3): 9.44; volume of cell (10^6 pm^3): 307.31; Z: 4.00.

The main diffraction peak (002) is detected at 12.60° 2θ degrees, while due to layered structure the other characteristic peaks are with minor intensity - (004), (006), (008), (112) and (113). The preferential (00l) crystallographic orientation is excellent confirmation of the highly crystalline nature of the samples and effectiveness of CVT growth.

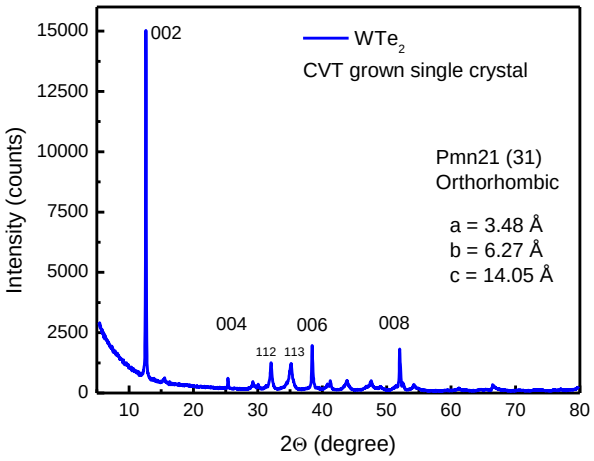


Figure 2. XRD analysis of WTe_2 single crystals. Lattice parameters and characteristic crystallographic directions are identified.

The Raman spectra of WTe_2 crystals were acquired in an ambient environment. The Raman data are presented on Fig. 3, with five of the typical vibrational modes for WTe_2 detected and designated as A_1^9 ~ 210 cm^{-1}, A_1^7 ~ 163 cm^{-1}, A_1^4 ~ 132 cm^{-1}, A_1^3 ~ 111 cm^{-1} and A_2 ~ 90 cm^{-1} confirming the desired chemical composition. Moreover, the sharp peaks with strong intensity, clearly marks the high degree of crystallinity of the material in accordance with the XRD data.

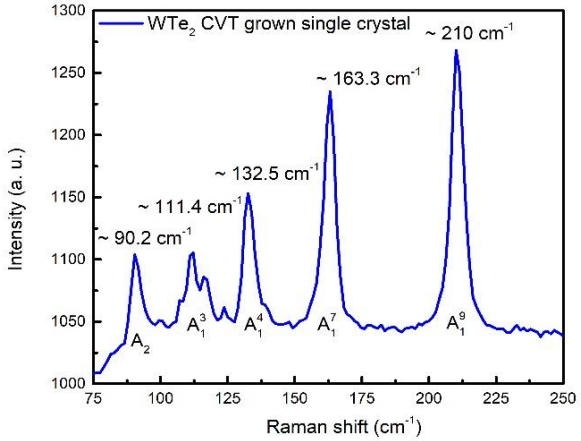
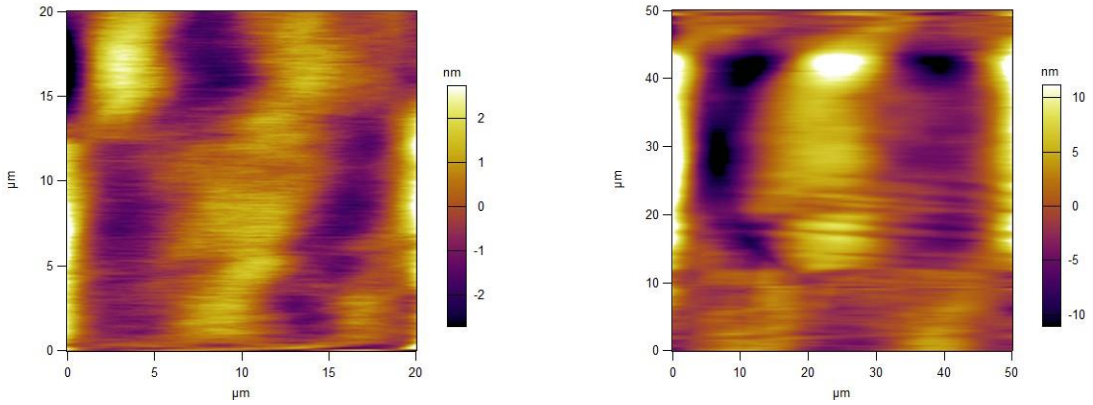


Figure 3. Raman spectra and characteristic vibration modes for WTe_2 single crystal.

The WTe_2 crystals surface morphology was analyzed by means of AFM - in tapping mode. Scans over areas of 20μm x 20μm and 50μm x 50μm have been performed and 2D topology gradient map of the surface was constructed (Fig. 4 a and b). The data revealed that the surface topology is also close to the structural perfection even on a nanoscale level, since the RMS roughness relief varies within 1 nm to 4 nm. This is a fine verification of the quality of the crystal which will be suitable for further alterations as mechanical exfoliation for instance.



(**a**) (**b**)

Figure 4. AFM analysis of two separate sectors from WTe_2 single crystal surface topology.

5. Conclusions

We have presented a detailed description of the preparation stages, technical considerations and growth procedure of WTe_2 by means of Chemical Vapor Transport method. The obtained crystals were characterized by XRD and Raman spectroscopy verifying excellent crystallinity. In addition, we have analyzed the surface topology of WTe_2 crystal via AFM analysis with construction of topography 2D map revealing a few nanometers variation of the morphology features.

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Conflicts of Interest: The authors declare no conflict of interest.

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