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Published in:
CrystEngComm

DOI:
[10.1039/c9ce00338j](https://doi.org/10.1039/c9ce00338j)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2019

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Vermeulen, P. A., Momand, J., & Kooi, B. J. (2019). Low temperature epitaxy of tungsten-telluride heterostructure films. *CrystEngComm*, 21(22), 3409-3414. <https://doi.org/10.1039/c9ce00338j>

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Cite this: *CrystEngComm*, 2019, 21,
3409Received 8th March 2019,
Accepted 3rd May 2019

DOI: 10.1039/c9ce00338j

rsc.li/crystengcomm

Low temperature epitaxy of tungsten–telluride heterostructure films†

Paul Alexander Vermeulen, Jamo Momand and Bart Jan Kooi*

Transition-metal di-chalcogenides (TMDCs) possess exceptional properties such as a direct bandgap and strong light interaction at monolayer thickness, making them excellently suited for nanoscale devices. Even more so, TMDCs can acquire unique and improved properties by stacking them with other 2D materials in van der Waals heterostructures. Currently, the growth of TMDC crystals frequently occurs using high-temperature processes like chemical vapor deposition or the Bridgman method. To comply with industrial standards, however, it is crucial to develop low-temperature procedures that ensure clean, large-area and lattice-oriented layers. Especially for a material such as WTe_2 , where W has an extremely high melting point, this is a difficult task. In this study, we employed pulsed laser deposition (PLD) using a single-step process at low substrate temperature (210 °C) to resolve these challenges. This deposition technique circumvents the high melting temperature of W, employing an ablation process, which yields simple stoichiometry control. By employing a seed layer of Bi_2Te_3 , we perform WTe_2 epitaxy on various substrates. The resulting films are clean and high quality 1T phase, as verified with reflective high-energy electron diffraction (RHEED) and transmission electron microscopy (TEM). The reported methods allow for fabrication of TMDC thin films for devices, and furthermore shows that PLD is excellently suited for epitaxial growth of these 2D heterostructures.

Introduction

Due to the highly dissimilar nature of the component elements of a TMDC, many unusual properties arise, such as giant magnetoresistance and superconductivity and a semiconductor–metal structural transition for WTe_2 .^{1–3} Monolayers have a direct band gap, enabling applications in optics and photovoltaics.^{4–7} Furthermore, TMDCs are candidates for making transistors smaller than CMOS on Si, and are applied in spintronic devices. Heterostructures composed of multiple 2D materials are heavily investigated due to their highly promising tunability: by stacking several thin layers with carefully chosen properties, improved functionality and performance is accomplished.⁶

One TMDC monolayer consists of three atomic planes: [X–M–X], where M is a transition metal like Mo or W, and X is a chalcogenide like S or Te. The bonding within the triplet layers is predominantly covalent and strong, whereas the bonding between them is weak, because it is based on van der Waals (vdW) bonding. For tungsten-dichalcogenides two stable unit cell structures often denoted as 2H (hexagonal) and 1T (monoclinic), have been reported.⁸ When fabricating

2D-material devices, high-quality single-crystals of TMDC are usually prepared using CVD or Bridgman techniques, and then exfoliated.⁹ Due to the weak interlayer bonding however, highly dissimilar 2D-materials may be directly grown without considering lattice mismatch. This concept of vdW epitaxy provides a powerful tool to produce single-crystal-like heterostructures of 2D-bonded materials.^{10–12}

Direct multilayer growth is highly preferable to exfoliation for several reasons. Firstly, it removes the need for manual (rotational) alignment. Epitaxial growth ensures no offset or rotation is present which is crucial for the heterostructure properties.^{13,14} Secondly, no contamination or wrinkling from the exfoliation process is introduced in the film.¹⁵ Finally, deposition allows for a much larger layer surface area, which is crucial for industrial implementation. Growth using chemical deposition is usually conducted at extremely high temperatures (>700 °C) which severely limits their integration in standard Si wafer applications.¹⁶ Furthermore, these chemical methods easily introduce contamination. Using molecular beam epitaxy (MBE), a physical vapour deposition (PVD) process, textured WTe_2 and other chalcogenide growth with high purity has been reported. Usually a vdW substrate or ‘seed’ was used, such as graphene, or tetradymites at lower temperatures.^{17–24} Of the PVD techniques, MBE is the most expensive and requires careful tuning of many inter-dependent system parameters. Pulsed laser deposition (PLD)

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† Electronic supplementary information (ESI) available. See DOI: 10.1039/c9ce00338j

can yield large-area stoichiometric films of comparable quality with more ease of use, lower cost, and monolayer thickness control.²⁵ Furthermore, promise for low-temperature PLD growth of TMDC thin films is found in literature.^{26–30} In this report we describe successful growth of single-crystal like WTe₂ monolayers at low temperature using pulsed laser deposition.

Experimental

Thin tungsten-telluride (W-Te) films were grown using a PLD system produced by TSST. A KrF excimer laser (248 nm) was used with a spot size of 1.3 mm² at a 45° incidence angle, operated at 1 Hz. Single-crystal (SC) targets of WTe₂ were obtained from HQ-Graphene, and a target made from sintered powders (SP) of W and Te was obtained from K-Tech Supplies Ltd. Target homogeneity and stoichiometry after ablation was confirmed using SEM (see ESI† SI-1). The target-substrate distance was 4 cm and the background pressure was below 10^{−7} mBar. Growth was monitored using a high-pressure reflective high-energy electron diffraction (RHEED) system, operated at 30 kV.

Cross-sections of crystalline films grown on mica were prepared using a FEI Helios G4 focused ion beam (FIB) system. All transmission electron microscopy (TEM) samples such as lamellae and SiO windows were analyzed using several electron microscopes: an FEI Nova NanoSEM 650 with EDS and CBS detectors, FEI Themis-Z (for HAADF High Angle Annular Dark Field imaging), JEOL 2010 and 2010F TEM systems. Electron-dispersive spectroscopy (EDS) was performed using a Si/Li detector and fitting using the Cliff–Lorimer w/o absorbance method.

Results

The laser pulse fluence (irradiated energy per unit area) and substrate temperature were optimized for both SC and SP tar-

gets. A copper mesh grid coated with a thin amorphous carbon film was used as a substrate. Since the carbon film is electron-transparent, this allowed for direct TEM-EDS analysis without any further sample preparation. For the fluence optimization, deposition was performed at room temperature to avoid re-evaporation. For the substrate temperature optimization, a low fluence was chosen to reduce the effect of plasma energy on initial stiction. Fig. 1 shows the atomic composition of the films for varying fluence and substrate temperatures. The process pressure was kept at 10^{−7} mBar since increasing this pressure to 0.12 mBar (the value used for Bi₂Te₃ films) reduced the Te-content by ~20 at.% (see ESI† SI-2). While for increased fluence the Te content continuously reduces, increasing substrate temperature shows an almost discontinuous step to W-rich films around 300 °C.

We conclude from the reduced Te content at higher fluence and temperatures, that Te is a more volatile element. This was also indicated by slight Te-evaporation observed on the target (ESI† SI-1). The deposition parameters show a wide operating window for obtaining a stoichiometric or slightly Te-rich film is available: fluence should be kept below 1.5 J cm^{−2} (at 30 °C), and below 250 °C (at 0.8 J cm^{−2}). We expect that depositing a slightly Te-rich film may be favourable, since excess Te may be easily evaporated to regain stoichiometry.

These films are generally deposited in the amorphous phase, but some crystalline droplets of tungsten are found as well. A typical TEM bright-field image is shown in the ESI† (SI-3). Since none of the films grown on the amorphous carbon films crystallized, it is clear that a crystalline substrate is needed as a seed crystal for crystalline growth. We have used a single-crystal-like Bi₂Te₃ layer, deposited on mica, as a seed crystal (see ESI† SI-4). We chose Bi₂Te₃ for its 2D nature, which yields a naturally passivated surface which allows for vdW epitaxy.¹⁰ Furthermore, its growth has been extensively studied in our lab.^{31,32} The WTe₂ growth conditions were obtained from the previous section: 0.8 J cm^{−2}, 210 °C, 10^{−7}

Fig. 1 a.) The fluence is varied to find the optimum ablation energy to obtain stoichiometric WTe₂ at 30 °C. Composition is measured using TEM-EDS on continuous-carbon TEM grids. b.) The substrate temperature is varied and Te content is measured. Excessive evaporation starts around 300 °C. Only slight differences are observed between single crystal and powder targets.

Fig. 2 a.) RHEED trace during deposition of WTe₂ on Bi₂Te₃. The bright streaks of the Bi₂Te₃ [12–30] zone axis (red) fade during the first ML growth. The WTe₂ streaks appear after 0.5 ML (orange) and disappear after 2 ML. b–d.) RHEED pattern of the 1T'-WTe₂ crystal structure in the [100] and [010] zone axes and disordered phase. e–g.) Schematic view of three WTe₂ zone axes observed in this work. h.) Intensity profiles of the RHEED patterns in b and c. The peak positions correspond to the atomic spacing given in e and f. The red arrows indicate faint Bi₂Te₃ peaks, which shows that the WTe₂ films grow epitaxially matched to the preceding layer and substrate.

mBar. RHEED analysis of the growth of a thick WTe₂ film is shown in Fig. 2a. Initially, the bright streaks of Bi₂Te₃ are clearly visible (red arrows). After growth of 0.5 ML WTe₂, new streaks start appearing (orange arrows) while the Bi₂Te₃ intensity diminishes rapidly. A representative RHEED pattern is shown in Fig. 2b and c shows the pattern when the sample is rotated by 30°. After 2–3 ML of WTe₂, the streaks start to fade again, and the RHEED pattern starts to resemble Fig. 2d. When no Bi₂Te₃ seed layer is used but WTe₂ is deposited directly on mica, the WTe₂ a pattern, such as that in Fig. 2d (see ESI† SI-4), immediately appears. The wide rings indicate that WTe₂ is in a disordered or amorphous state. Strikingly, using the SP instead of SC target also does not yield a crystalline film. To investigate the atomic structure of WTe₂, a 2 ML film grown on Bi₂Te₃ is rotated into two different zone axes, which are 30° apart (Fig. 2b and c). Intensity profiles across both RHEED patterns were taken. The peak spacings correspond well to the literature values for the lattice plane spacing in the [100] and [010] zone axes of 1T'-WTe₂.

For post-deposition structural analysis, a plan-view TEM sample was made by growing films on a thin (electron-transparent) amorphous SiO₂ membrane. Due to the lack of texture in the substrate the Bi₂Te₃ seed layer was not single-crystal-like, but only out-of-plane textured: the *c*-axis was oriented perpendicular to the surface plane of the SiO₂ substrate.³¹ A 5 nm WTe₂ layer was deposited on a Bi₂Te₃ seed (7 nm). The bright-field TEM and large area diffraction (1.2 μm²) are shown in Fig. 3a. The film looks homogeneous but contains voids (light spots), and some grain tilt is observed (darker areas), which indicates the film is not flat but slightly wavy. Radial intensity profiles are taken from the diffraction pattern and compared to an out-of-plane textured Bi₂Te₃ film on SiO₂, and an untextured crystalline WTe₂ film (see ESI†). All diffraction peaks of the WTe₂-Bi₂Te₃ film on amorphous SiO₂ can be ascribed to *out-of-plane textured* WTe₂ and Bi₂Te₃ layers.

The atomic composition was obtained by performing EDS on the same area as the diffraction pattern, and repeated for another site (see ESI† SI-5). We obtain a film composition of Bi₁₈W₂₂Te₆₀ (at.%). Based on the measured Bi and W content and then assuming stoichiometric layers of Bi₂Te₃ and WTe₂ the film composition should be Bi₁₆W₂₀Te₆₄. This small discrepancy means the film is 4 at.% Te-deficient, and therefore almost stoichiometric within the error of the EDS system. Since both layers of the film contain Te, no statement can be made regarding the stoichiometry of the sublayers. No significant amount of contaminants is found, the films are very clean as is expected for a physical deposition technique.

A cross-section of a Bi₂Te₃-WTe₂ multilayer was investigated using HAADF-STEM (Fig. 3c) to show the capability of epitaxially incorporating WTe₂ within a vdW device structure. The multilayer contains a single and a double bi-layer WTe₂. The number of laser pulses is linearly related to the deposition rate, and is estimated as 290 pulses per nm for WTe₂. The quintuple layers of Bi₂Te₃ and triplet layers of WTe₂ as well as the vdW gaps separating them are clearly resolved. By using a high-magnification HAADF-STEM scan, the atomic structure of the WTe₂ and Bi₂Te₃ layers is resolved. From the zig-zag positioned Te-atoms in planes parallel to the vdW gap it is clear that the WTe₂-1T' phase was grown, as already indicated by RHEED. The Bi₂Te₃ and WTe₂ are epitaxially matched and possess a common zone axis. However, the WTe₂ layers are not fully flat but show some waviness. This effect has also been observed for other growth techniques and materials, and is due to the lattice mismatch between Bi₂Te₃ and WTe₂ and the weak interlayer bonding.^{21,33} The vdW gap between Bi₂Te₃ and WTe₂ is blurred in some spots, indicating the occurrence of limited intermixing. We note that even after deposition of 4 ML of WTe₂ an epitaxial relation is maintained with the subsequent Bi₂Te₃ layer. This indicates that even

Fig. 3 a.) Plan-view bright-field TEM image of a Bi_2Te_3 - WTe_2 heterostructure. White spots in the film are voids, while the darker areas indicate stronger scattering contrast caused by misaligned grains. A diffraction pattern taken from a $1.25\ \mu\text{m}$ diameter area is shown in the inset. Sharp rings are observed and the radial intensity profile is plotted in b). The profiles for textured Bi_2Te_3 , untextured WTe_2 , and a textured Bi_2Te_3 - WTe_2 heterostructure (from a) are plotted. For the heterostructure only *c*-axis texture peaks were observed for both WTe_2 and Bi_2Te_3 . c) HAADF image of a cross section of a multilayered Bi_2Te_3 - WTe_2 film grown on mica. The vdW gaps in both materials can be clearly distinguished. d.) Higher-magnification scan of the specimen in c, where the atomic structure of the Bi_2Te_3 and $1\text{T}'$ - WTe_2 is clearly resolved. The waviness of the WTe_2 is clearly observed as well.

when the RHEED pattern is extremely weak (*cf.* Fig. 2a at 4 ML), which is probably due to the waviness of the otherwise structurally ordered crystal, the crystal quality is still sufficient for enabling heterostructure growth.

Discussion

We have shown it is possible to grow biaxially textured WTe_2 with monolayer control at low temperatures, using PLD. However, the films can only be grown using two conditions: using a (1) Bi_2Te_3 seed layer and (2) SC target.

Firstly, since the lattice parameters of WTe_2 and Bi_2Te_3 are highly dissimilar (20% mismatch), it is rather unlikely that Bi_2Te_3 provides a lattice matching condition directly. However, since both compounds share bond symmetry and an outer Te layer, compatibility is higher than for a mica- WTe_2 interface.

We expect other materials with a similar trigonal telluride structure (*e.g.* Sb_2Te_3), to be equally suited as seed layers.

Secondly, since the SP target does not contain W-Te bonds yet, the one-element plasma species have to overcome an energy barrier to form two-element bonds. This barrier is not present for the SC target, where the ablated species will contain W-Te bonds. For CdTe it has been shown that ablation/evaporation mainly produces non-reactive Te_2 monomer units, which can be cracked using higher (laser) energy.^{21,34} In contrast, this effect was not observed by us; even when fluence was increased to $5\ \text{J cm}^{-2}$ no WTe_2 crystals were observed. It seems likely however that the enthalpy of mixing of the highly dissimilar W and Te atomic species is relatively low, and therefore using a SP target will not produce the desired structures. Still, it is likely that a polycrystalline target of WTe_2 would have worked as well as a single crystal, since the WTe_2 bonds are also present there.

Conclusions

We demonstrated the growth of single-crystal-like WTe₂ films at low temperatures (210 °C) using PLD. By employing TEM and RHEED techniques we have elucidated the ablation and deposition processes, and found it is crucial to use a crystal-line WTe₂ target and a Bi₂Te₃ seed layer. Furthermore, we showed post-situ cross-sectional TEM analysis of mono- and few-layer 1T'-WTe₂ heterostructures grown using the principle of van der Waals epitaxy. The presented large-area films are stoichiometric, clean, and well ordered, although WTe₂ shows a well-known tendency to become slightly wavy. Using the presented PLD process, epitaxial WTe₂ can be incorporated into thin-films and devices, and is compatible with silicon wafer technology. This implementation of a low-temperature epitaxy using a physical growth method offers many advantages over exfoliation, and may be extended to other TMDC systems.

Conflicts of interest

There are no conflicts to declare.

Notes and references

- 1 T. Asaba, *et al.*, Magnetic field enhanced superconductivity in epitaxial thin film WTe₂, *Sci. Rep.*, 2018, **8**, 1–7.
- 2 M. N. Ali, *et al.*, Large, non-saturating magnetoresistance in WTe₂, *Nature*, 2014, **514**, 205–208.
- 3 Y. Wang, *et al.*, Gate-tunable negative longitudinal magnetoresistance in the predicted type-II Weyl semimetal WTe₂, *Nat. Commun.*, 2016, **7**, 1–6.
- 4 Q. H. Wang, K. Kalantar-Zadeh, A. Kis, J. N. Coleman and M. S. Strano, Electronics and optoelectronics of two-dimensional transition metal dichalcogenides, *Nat. Nanotechnol.*, 2012, **7**, 699–712.
- 5 A. K. Geim and I. V. Grigorieva, Van der Waals heterostructures, *Nature*, 2013, **499**, 419–425.
- 6 K. S. Novoselov, A. Mishchenko, A. Carvalho, A. H. C. Neto and O. Road, 2D materials and van der Waals heterostructures, *Science*, 2016, **353**, 461.
- 7 S. J. McDonnell and R. M. Wallace, Atomically-thin layered films for device applications based upon 2D TMDC materials, *Thin Solid Films*, 2016, **616**, 482–501.
- 8 K. A. N. Duerloo, Y. Li and E. J. Reed, Structural phase transitions in two-dimensional Mo- and W-dichalcogenide monolayers, *Nat. Commun.*, 2014, **5**, 1–9.
- 9 Z. Cai, B. Liu, X. Zou and H.-M. Cheng, Chemical Vapor Deposition Growth and Applications of Two-Dimensional Materials and Their Heterostructures, *Chem. Rev.*, 2018, **118**(13), 6091–6133.
- 10 A. Koma, K. Ueno and K. Saiki, Heteroepitaxial growth by Van der Waals interaction in one-, two- and three-dimensional materials, *J. Cryst. Growth*, 1991, **111**, 1029–1032.
- 11 A. Koma, Van der Waals epitaxy—a new epitaxial growth method for a highly lattice-mismatched system, *Thin Solid Films*, 1992, **216**, 72–76.
- 12 L. A. Walsh and C. L. Hinkle, Van der Waals epitaxy: 2D materials and topological insulators, *Appl. Mater. Today*, 2017, **9**, 504–515.
- 13 C. R. Woods, *et al.*, Commensurate-incommensurate transition in graphene on hexagonal boron nitride, *Nat. Phys.*, 2014, **10**, 451–456.
- 14 H. Kumar, L. Dong and V. B. Shenoy, Limits of Coherency and Strain Transfer in Flexible 2D van der Waals Heterostructures: Formation of Strain Solitons and Interlayer Debonding, *Sci. Rep.*, 2016, **5**, 21516.
- 15 A. V. Kretinin, *et al.*, Electronic properties of graphene encapsulated with different two-dimensional atomic crystals, *Nano Lett.*, 2014, **14**, 3270–3276.
- 16 S. Z. Butler, *et al.*, Progress, Challenges, and Opportunities in Two-Dimensional Materials Beyond Graphene, *ACS Nano*, 2013, **7**, 2898–2926.
- 17 S. Vishwanath, *et al.*, Controllable growth of layered selenide and telluride heterostructures and superlattices using molecular beam epitaxy, *J. Mater. Res.*, 2016, **31**, 900–910.
- 18 S. Vishwanath, *et al.*, MBE growth of few-layer 2H-MoTe₂ on 3D substrates, *J. Cryst. Growth*, 2018, **482**, 61–69.
- 19 H. C. Diaz, R. Chaghi, Y. Ma and M. Batzill, Molecular beam epitaxy of the van der Waals heterostructure MoTe₂ on MoS₂: phase, thermal, and chemical stability, *2D Mater.*, 2015, **2**, 044010.
- 20 E. Xenogiannopoulou, *et al.*, High-quality, large-area MoSe₂ and MoSe₂/Bi₂Se₃ heterostructures on AlN(0001)/Si(111) substrates by molecular beam epitaxy, *Nanoscale*, 2015, **7**, 7896–7905.
- 21 L. A. Walsh, *et al.*, WTe₂ thin films grown by beam-interrupted molecular beam epitaxy, *2D Mater.*, 2017, **4**, 025044.
- 22 S. Tang, *et al.*, Quantum spin Hall state in monolayer 1T'-WTe₂, *Nat. Phys.*, 2017, **13**, 683–687.
- 23 A. Ghasemi, *et al.*, Van der Waals epitaxy between the highly lattice mismatched Cu-doped FeSe and Bi₂Te₃, *NPG Asia Mater.*, 2017, **9**, 402.
- 24 E. Snse, *et al.*, Epitaxial 2D SnSe 2 / 2D WSe 2 van der Waals Heterostructures, *ACS Appl. Mater. Interfaces*, 2016, **8**(35), 23222–23229.
- 25 D. H. A. Blank, M. Dekkers and G. Rijnders, Pulsed laser deposition in Twente: from research tool towards industrial deposition, *J. Phys. D: Appl. Phys.*, 2014, **47**, 034006.
- 26 Z. Yang and J. Hao, Progress in pulsed laser deposited two-dimensional layered materials for device applications, *J. Mater. Chem. C*, 2016, **4**, 8859–8878.
- 27 C. R. Serrao, *et al.*, Highly crystalline MoS₂ thin films grown by pulsed laser deposition, *Appl. Phys. Lett.*, 2015, **106**, 052101.
- 28 T. A. J. Loh and D. H. C. Chua, Origin of Hybrid 1T'- and 2H-WS₂ Ultrathin Layers by Pulsed Laser Deposition, *J. Phys. Chem. C*, 2015, **119**, 27496–27504.
- 29 M. Gao, *et al.*, Tuning the transport behavior of centimeter-scale WTe₂ ultrathin films fabricated by pulsed laser deposition, *Appl. Phys. Lett.*, 2017, **111**, 031906.
- 30 A. Bailini, *et al.*, Pulsed laser deposition of tungsten and tungsten oxide thin films with tailored structure at the nano- and mesoscale, *Appl. Surf. Sci.*, 2007, **253**, 8130–8135.

- 31 P. A. Vermeulen, J. Mulder, J. Momand and B. J. Kooi, Strain engineering of van der Waals heterostructures, *Nanoscale*, 2018, 1474–1480, DOI: 10.1039/C7NR07607J.
- 32 P. A. Vermeulen, Growth and nanostructure of tellurides, *PhD Thesis*, University of Groningen, 2019, Print ISBNs 978-94-034-1422-5, Electronic ISBNs 978-94-034-1421-8.
- 33 D. Nandwana and E. Ertekin, Ripples, strain, and misfit dislocations: Structure of graphene-boron nitride superlattice interfaces, *Nano Lett.*, 2015, 15, 1468–1475.
- 34 J. T. Cheung, Role of atomic tellurium in the growth kinetics of CdTe (111) homoepitaxy, *Appl. Phys. Lett.*, 1987, 51, 1940–1942.