

Direct Observation at Room Temperature of the Orthorhombic Weyl Semimetal Phase in Thin Epitaxial MoTe 2

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The room temperature observation of the noncentrosymmetric orthorhombic phase of epitaxial MoTe₂ on InAs(111) substrate is reported. Due to enlarged lat-tice parameters of 1-3 ML films a type II topological Weyl semimetal is predicted with Weyl nodes located a few meV below the Fermi level, accessible to transport.

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Direct Observation at Room Temperature of the Orthorhombic ¹/₂ Weyl Semimetal Phase in Thin Epitaxial MoTe₂ 4 5

Polychronis Tsipas, Sotirios Fragkos, Dimitra Tsoutsou, Carlos Alvarez, Roberto Sant, Gilles Renaud, Hanako Okuno, and Athanasios Dimoulas*

The direct observation at room temperature of the noncentrosymmetric 13 orthorhombic topological Weyl semimetal phase in epitaxial thin films of 14 15 MoTe₂ grown on InAs(111)/Si(111) substrates by molecular beam epitaxy 16 is reported. The orthorhombic phase is typically found at lower tempera-17 tures but its observation at room temperature in this work is attributed to 18 the enlarged lattice parameters, influenced by the substrate, which sta-19 bilize an interlayer antibonding state compatible with the orthorhombic 20 21 stacking. First-principles calculations predict eight type II Weyl nodes which 22 are located below (but near) the Fermi energy making them accessible 23 to charge transport and creating the prospect for practical applications 24 exploiting the nontrivial topological properties. The orthorhombic phase 25 coexists with an unconventional triclinic layer stacking which is different 26 27 than the monoclinic or orthorhombic structures but it is centrosymmetric 28 and topologically trivial. 29

32 1. Introduction 33

35 2D group VI (Mo.W) transition metal disulphide and disele-36 nide materials, typically stabilized in the hexagonal 2H pris-37 matic structure, are semiconductors and have been extensively studied due to their great potential for diverse and versatile 38 applications.^[1-3] The Mo and W ditellurides (WTe₂ and MoTe₂) 39 are notable exceptions because structural and electronic insta-40 41 bilities drive a transformation to a lower symmetry, distorted 42 1T (often referred to as 1T') octahedral crystal structure with metallic or semimetallic properties.^[4] 43

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1T' is the most stable phase of WTe₂ 12 at room temperature (RT). On the other 13 hand, for MoTe₂ the most stable phase at 14 RT is the 2H, while the 1T' is metastable 15 lying only about a few tens of meV higher 16 in energy.^[5] The small difference in energy 17 allows the RT stabilization of 1T' utilizing 18 bulk growth methodologies^[6-10] at high 19 temperature typically followed by rapid 20 cooling to RT. The metastability of 1T' 21 implies that reversible transformations 22 from the semiconducting to the metallic 23 phase through a small energy barrier 24 could be possible^[5] by applying external 25 stimuli. This has already been demon-26 strated experimentally at RT by applying 27 strain^[11] or electrostatic doping by a gate 28 bias,^[12] rendering MoTe₂ a promising 29 candidate material for the realization of 30 useful electronic devices. 31

Moreover, MoTe₂ and WTe₂ exhibit exciting physical prop-32 erties adding functionality and significantly extending the 33 range of applications. In the limit of a monolayer with a cen-34 trosymmetric structure these materials have been predicted 35 to be 2D topological insulators (or quantum spin Hall insu-36 lators)^[13] which have been experimentally verified recently 37 for the case of WTe2.^[14] In the few layer regime, 1T' WTe2 38 adopts at RT an orthorhombic $Pmn21(T_{d})$ structure (γ -phase) 39 which lacks inversion symmetry thus becoming a topological 40 type II Weyl semimetal as first predicted^[15] and later veri- 41 fied^[16] for bulk WTe₂ material. On the other hand, few layer 42 or bulk 1T' MoTe2, at RT is typically found in a centrosym- 43 metric monoclinic $P21/m \beta$ -phase which is proposed to be 44 a quantum spin Hall state.^[17] However MoTe₂ undergoes a 45 structural phase transition from the β -phase to the noncen- 46 trosymmetric orthorhombic (T_d) γ -phase at lower tempera- 47 tures, typically below 250 or 150 K, in which case MoTe₂ 48 is predicted^[18] to become a type II topological Weyl semi- 49 metal (similar to y-WTe2), already verified by ARPES in bulk 50 MoTe₂.^[8,9,19,20] The number of Weyl nodes, their position in 51 k-space and energy, and the nature of surface states (topo-52 logical or trivial) in γ -MoTe₂ depend sensitively on the lattice 53 parameters and the strain. Theoretical values^[21] of the lattice 54 parameters differ a lot depending on the density functional 55 used and deviate from experimental values,^[6-9] which also 56 depend a lot on the fabrication method. Most of the works 57 find 8 Weyl nodes^[8,9,18,20,22] while for certain choice of small 58 lattice parameters only 4 Weyl nodes are predicted,^[23] the 59

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1 lowest number ever reported for any Weyl semimetal. In all 2 cases, MoTe₂ Weyl nodes^[8,9,18,20,22] are closer to Fermi energy 3 (E_F) compared to WTe₂,^[15,16,24,25] however they are always 4 above E_F , including those in Mo_xW_{1-x}Te₂,^[26,27] thus inhibiting 5 both their observation by ARPES and their effective use in 6 functional electronic devices.

7 To shed light on the electronic structure of γ -MoTe₂ the Weyl 8 node configuration in particular, and to exploit the topological 9 properties in practical applications, it is important to control 10 the lattice parameter and to stabilize the γ -phase of MoTe₂ at 11 RT by suitable epitaxial methods and substrates. More gen-12 erally, the ability to epitaxially grow MoTe₂ thin films by synthetic methods on cm-scale crystalline substrates is essential 13 to enable device processing. Epitaxial processes are typically 14 15 nonequilibrium and are influenced by the substrate so the most stable structural phases, layer stacking, and physical 16 17 properties of epitaxial thin films may be different compared to 18 those produced by equilibrium bulk methodologies. In most cases, CVD-grown MoTe₂ thin films are found in the RT most 19 20 stable 2H structure although 1T' structures are also obtained by postgrowth temperature treatments.^[28-30] Growing epi-21 taxial thin films of MoTe₂ (and WTe₂) by MBE is challenging 22 because Mo (W) and Te have very similar electronegativities^[31] 23 so during coevaporation of Mo (W) and Te, the material tends 24 25 to form intermetallic Mo-Mo or W-W bonds which do not 26 favor the incorporation of Te in the material resulting in poor 27 Te-deficient and highly nonstoichiometric films. Following the 28 successful growth of the stable 1T'-WTe₂ by MBE on a variety 29 of 2D substrates by employing interrupted growth methodology,^[31] a few works^[32-34] have reported the stable 2H MoTe₂ 30 31 phase by MBE but the metastable 1T' MoTe₂ phase was elusive until recently when two independent groups^[35,36] showed evi-32 dence of room temperature 1T' MBE films mixed with 2H on 33 epi-graphene/SiC substrates.^[35] However, they lack of informa-34 35 tion about the epitaxial quality and the thin film structure; it 36 is not known in particular whether they adopt the monoclinic 37 $(\beta$ -MoTe₂) or orthorhombic (γ -MoTe₂) structure. Stabilization 38 of the latter Weyl semimetal phase is highly desirable but difficult to obtain at RT as already mentioned above. An inter-39 40 esting approach is to substitute ≈8% of Mo by W to engineer 41 the γ -phase as it has already been shown using bulk single crystals.^[37] Recently, indirect evidence of RT 7-MoTe₂ has been 42 43 reported in thin films exfoliated from bulk where low dimensionality is thought to play a role.^[38] Direct observation of the 44 γ -MoTe₂ phase at RT either on bulk or epitaxial material has 45 not been reported. 46

47 In this paper we report on the direct RT observation of the important orthorhombic noncentrosymmetric Weyl semimetal 48 49 *y*-phase in epitaxial 3 ML MoTe₂ films grown layer by layer on 50 InAs(111)/Si(111) substrates by MBE. Moreover, we observe 51 an unconventional triclinic layer stacking, which is however 52 centrosymmetric, topologically predicted to be trivial with no 53 Weyl points. The measured lattice constants of our epitaxial 54 orthorhombic phase are found to be notably larger than the 55 previously reported experimental values from bulk y-phase 56 MoTe₂. We argue in this paper that the enlarged lattice parame-57 ters have important consequences on the energy position of the 58 Weyl points as well on the stabilization of the γ -phase at room 59 temperature in epitaxial thin films.

2. Results

2.1. Crystal Structure and Reciprocal Lattice

The structure details and the reciprocal lattice are described 5 in brief to facilitate the data interpretation. As already men-6 tioned, the 1T distorted (1T') structure of MoTe₂ is typically 7 found either in the RT monoclinic $P21/m \beta$ -phase or the low 8 9 temperature (T < 250 K) orthorhombic (T_d) Pmn21 γ -phase (Figure 1). Here we use the notation as follows. 1T' refers to the 10 distorted 1T without distinguising between orthorhombic and 11 monoclinic stacking. T_d-MoTe₂ refers to orhorhombic stacking 12 while β -MoTe₂ refers to monoclinic stacking. A characteristic 13 difference between the two phases is the interatomic distance *d* 14 (Figure 1b,c) which becomes larger in the orthorhombic struc-15 ture compared to the monoclinic $(d_0 > d_m)$ due to a parallel shift 16 of the second (top) layer with respect to the bottom one.^[21] The 17 undistorted 1T lattice can be described either by a primitive 18 hexagonal unit cell (solid lines in Figure 1d) or by a rectangular 19 surface nonprimitive unit cell (dashed line) which is double the 20 hexagonal primitive unit cell (solid line), with lattice parameters 21 $a_{\rm T}$ and $b_{\rm T}$ such that $a_{\rm T}/b_{\rm T} = \sqrt{3}$. On the other hand, the surface 22 rectangular primitive unit cell of 1T' has $a_{T'}/b_{T'} > \sqrt{3}$ deviating 23 from the "ideal" value of $\sqrt{3}$. Similarly, the reciprocal space or 24 1T' (Figure 1e) has a rectangular primitive unit cell with the 25 reciprocal lattice constant ratio $b_{T'}^*/a_{T'}^* > \sqrt{3}$. The deviation of 26 these ratios from ideal values produces characteristic signatures 27 in our data as will be discussed below facilitating the nanostruc-28 29 ture characterization of our films.

2.2. Sequential Layer by Layer Thin Film Epitaxial Growth and Surface Structure

In-terminated InAs(111)/Si(111) substrates are prepared by ex 35 situ chemical cleaning followed by in situ thermal annealing 36 37 and, where required, by a mild Ar⁺ sputtering (see the Experimental Section) prior to annealing, until a 2×2 reconstruction 38 pattern is obtained in reflection high energy electron diffrac-39 tion (RHEED) (Figure S1, Supporting Information), indica-40 tive of a clean, oxide-free surface. Thin 1-3 ML MoTe₂ films 41 are grown (see the Experimental Section) in a layer- by-layer 42 sequence, with each layer grown in a two-step process. First, 43 a single layer MoTe₂ is grown at a low temperature of 280 °C 44 and Te/Mo ratio of 100/1, adopting a beam-interrupted epitaxy 45 method similar to that used for the MBE growth of WTe2.^[31] 46 After 30 s of W and Te codeposition, the growth is interrupted 47 by closing the Mo shutter for about 60 s, while the film is con-48 tinually exposed to Te and then the growth continues again 49 by opening the Mo shutter for another 30 s. The process is 50 repeated until 1 ML of MoTe₂ is completed. The growth rate 51 is estimated to be 0.5 ML min⁻¹. Subsequently, the sample is 52 annealed at 400 °C in the presence of Te flux (0.5 Å s⁻¹) for 53 30 min to improve the crystallinity and the surface ordering 54 55 monitored by RHEED (Figure S1, Supporting Information). 56 Once the first layer is fully formed and optimized, the second and third layers are grown by repeating the same process, thus 57 enabling the sequential layer-by-layer growth of MoTe2 thin 58 59 films.







41Figure 1. Crystal phases for the 1T distorted (1T') MoTe2 a) along [1 100] direction and b) orthorhombic T_d -phase along the [1120] direction, c) mono-4142clinic β-phase along the [1120] direction. d-f) Top view of the direct and reciprocal lattices. Lattice parameters are indicated as *a*, *b* (direct) and *a**,4243b*(reciprocal): (d) 1T, (e) 1T', (f) 1T' reciprocal lattice. The solid lines represent the primitive unit cells. The broken line represents the nonprimitive4344unit cell for 1T [1 100] and [1120] of 1T correspond to [100] and [010] of the distorted (1T') lattice, respectively.44

46 The surface nanostructure of 1 ML 1T' MoTe₂ is imaged 47 in Figure 2a by in-situ ultrahigh vacuum scanning tun-48 neling microscopy (UHV-STM) at RT. The domains have an 49 average lateral size ≈ 40 nm and they differ in height about 50 3.5 Å (Figure 2b), which is the same as the height of mono-51 atomic steps of the underlying InAs substrate. It is therefore 52 concluded that the domain formation in MoTe₂ originates from the monatomic step nanostructure of the InAs surface, 53 54 consistent with scanning transmission electron microscopy 55 (STEM) observations shown in subsequent section (Figure 3). Deposition of a second layer results in the formation of 2D 56 57 islands (Figure 2c) with a height of ≈ 7 Å (Figure 2d) which 58 is roughly equal to the thickness of a single 1T' MoTe₂ layer 59 including the van der Waals gap between the top and the

bottom layers. The islands coalesce to form a complete second 46 layer. 47

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Atomic resolution STM images of a single domain are con-48 sistent with the symmetry of 1T' MoTe₂ surface (Figure 2e). 49 The Fourier transform in Figure 2f yields the surface reciprocal 50 space in similarity with the schematic of Figure 1f. In a dif-51 ferent part of the surface, two domains A and B rotated 60° with 52 each other are imaged (Figure 2g) resulting in a more complex 53 reciprocal space (see the Fourier transform of Figure 2h) where 54 additional periodicities (1 and 2 in Figure 2h), define a recip- 55 rocal lattice for domain B (white dashed rectangles) rotated by 56 60° with respect to the one corresponding to domain A (red 57 dashed rectangles). Consideration of the complex reciprocal 58 space composed of superimposed rotated lattices is essential 59





Figure 2. In situ room temperature UHV-STM of 1T'-MoTe₂. a,b) 1 ML MoTe₂ and the corresponding line scan, showing the influence of the substrate. c,d) Surface morphology after the deposition of an incomplete second layer MoTe₂ and the corresponding linescan showing the thickness of the top layer of about 7 Å, including the van der Waals gap with the bottom layer. e,f) Surface and Fourier pattern showing a single domain 1ML 1T'-MoTe₂. The dashed rectangles show the unit cells of real (e) and reciprocal space (f) lattices. g) Image of two domains A and B rotated by 60° between each other h) The additional intense spots marked by 1 and 2 originate from the rotated pattern B and defines the superimposed reciprocal lattice (white dotted rectangles).

for the interpretation of X-ray diffraction (XRD), angle resolved
photoelectron spectroscopy (ARPES) and RHEED measurements reported in the subsequent sections and the Supporting
Information.

2.3. Orthorhombic and Unconventional Triclinic Layer 46 Stacking Structure

The MoTe₂ thin films are evaluated in cross-section by STEM at RT to identify the film layer stacking. Figure 3 shows cross-section images for both1 and 3 ML MoTe2. In Figure 3a, two regions of 1 ML of 1T' $MoTe_2$ are shown interrupted by an atomic step in the InAs, ≈3.5 Å, hence forming domains with different heights, similar to STM observations in Figure 2a. It is worth mentioning that there is no evidence for the 2H pris-matic phase which is the most stable at RT, therefore the thin films are in a pure 1T' phase.

57 As the growth continues from 1 to 3 ML 1T' MoTe₂, two 58 dominant phases are observed, namely the orthorhombic 59 T_d -MoTe₂ phase (Figure 3c), comprising two layers in the unit

cell, which typically appears at lower temperatures (<250 K) and an unconventional triclinic stacking, containing one layer per unit cell (Figure 3e), not previously reported. A fundamental difference between the triclinic stacking of Figure 3e and the conventional room temperature stable β -MoTe₂ monoclinic phase is that the second layer is rotated by 180° with respect to the first layer. The lattice parameter along the *c*-axis in the $T_{\rm d}$ orthorhombic structure (Figure 3b,c) is measured to be between 14.1 and 14.2 Å (Figure 3d), which is significantly larger than the reported experimental c values from bulk T_d-MoTe₂ crys-tals^[6–9] found to be in the range between 13.861 and 13.8935 Å. Moreover, among the different 1T' structures (Figure 1), the most stable room temperature monoclinic stacking, known as β -MoTe₂ (Figure 1c) is absent in our films. Additionally, fast Fourier transform (FFT) patterns were calculated from the regions containing only the MoTe₂ film in the STEM images; they are shown in Figure 3f-h. The FFT patterns were analyzed and compared with corresponding simulated electron diffraction patterns to verify the different MoTe₂ crystals structures. The simulated electron diffractions patterns and this analysis are presented in Figure S3 of the Supporting Information.

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Figure 3. STEM images from epitaxial MoTe₂ thin films. a) 1 ML of 1T' MoTe₂ showing film interruption at the edge of an InAs monoatomic step b) 3 ML 1T' phase along [1 100] zone axis, c) 3ML orthorhombic (T_d) stacking along [1120] zone axis, d) intensity line plot in the c direction from images (b) and (c) in red and green, respectively, e) 3 ML of unconventional triclinic stacking along [1120] zone axis. f-h) FFT patterns from respective STEM images. The equivalent [uvw] notation for the zone axis directions are [100] for [1 100], and [010] for [1120].



Incidence X-Ray Diffraction (GIXD)

Single-layer and three-layer MoTe2 are evaluated by GIXD and the data for 3 ML films are presented in Figure 4. The in-plane reciprocal space map (RSM) in Figure 4a reveals that the MoTe₂ film is epitaxially grown on InAs in such a way that [100]_{MoTe2}// $[11-2]_{InAs}$, and $[010]_{MoTe2}//[01-1]_{InAs}$ in the plane. We observe 56 no 30° or 90° rotated domains or polycrystallinity other than 57 that arising from the Al protecting cap (rings in Figure 4a). The 58 positions of the diffraction peaks in k-space are in agreement 59 ADVANCED SCIENCE NEWS_____





Figure 4. Synchrotron GIXD from epitaxial 3 ML MoTe₂ a) reciprocal space map (RSM). The diffraction peak and crystallographic orientations corre-spond to bulk Miller indices notation. The h, k and h = k axis are high symmetry directions in hexagonal surface k-space. The open circles and rectangles denote reciprocal lattice points and unit cells, respectively, originating from three rotated domains: 0° (red), 60° (blue), 120° (black). CTR denotes crystal truncation rods. Polycrystalline rings are due to Al cap layer b) Radial scans along the h and h = k crystallographic directions shown in (a). c) In-plane rocking curves of the on-axis (020) single peak and d) the off-axis (310) peak (symbol curve) deconvoluted into two peaks (solid blue and red lines) originating from two different domains rotated by 60°.

53 with a complex reciprocal space (open circles in Figure 4a) 54 which is a superposition from 0°, 60°, and 120° rotated 55 domains. The most characteristic configuration is the triplet 56 along h = k ([01-1]_{InAs}) consisting of the on-axis (020) peak and 57 the two off-axis (310) peaks all belonging to different domains 58 rotated between each other by 60°. It should be noted that in 59 the ideal case where $b^*/a^* = \sqrt{3}$ applying to the hexagonal

symmetry of the undistorted 1T structure (see Figure 1d), all 53 three closely spaced reciprocal lattice points would be expected 54 to coincide giving a single diffraction peak. In our case though 55 of a distorted 1T' MoTe₂ lattice, where the ratio deviates from 56 ideal ($b^*/a^* > \sqrt{3}$), the peak splitting into a triplet configuration is clearly detected by GIXD (Figure 4a). Similar situation 58 arises along *h* ([11-2]_{InAs}) direction with the triplet consisting of 59

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1 the on-axis (400) peak and two off-axis (220) peaks from rotated 2 domains as well as the triplet involving (200) and two (110) 3 peaks although the latter triplet is not resolved very well. As a 4 consequence, the radial scans along h and h = k directions in 5 Figure 4b show doublets for certain diffractions.

6 In the doublet the peak due to the off axis signals superpo-7 sition have larger transversal width as seen from the rocking 8 curves of Figure 4c and d because they have the contributions 9 from two off-axis diffraction peaks (see the deconvolution of (310) diffraction peak in Figure 3d). From the FWHM of the 10 11 on-line single peak (020) in Figure 3c an in-plane mosaicity of 3.71° is estimated which is substantially higher than that 12 of the InAs substrate (0.79°); also higher than the mosaicity of 13 1.79° observed in epitaxial ZrTe₂ on InAs(111) substrate.^[39] 14

Considering only the well resolved on-axis single peaks 15 (020), (300), and (400), the reciprocal (a^*, b^*) and direct (a, b)16 17 lattice parameters can be accurately determined from the RSM and the radial scans as follows. The position of the 020 peak 18 19 in the q space is q = 3.5894 Å⁻¹ and it is equal to two times the 20 reciprocal space unit cell lattice constant b (Figure 4b). There-21 fore $b^* = q/2 = 1.7947$ Å⁻¹ and $b = 2\pi/b^* = 3.501$ (±0.003) Å. 22 Looking along the h and k directions in Figure 4a, the (300) 23 and (400) peaks are $3a^*$ and $4a^*$, respectively, and by considering their location in *k*-space from Figure 4b, $a^* = 0.99105 \text{ Å}^{-1}$ 24 25 (averaged over the four peaks, two along each direction h and 26 k) and $a = 2\pi/a^* = 6.340 \ (\pm 0.005)$ Å are obtained. These values are in reasonably good agreement with the ones deduced from 27 28 RHEED (Figure S1, Supporting Information).

It is worth noting that the values *a*, *b* (determined from GIXD) and *c* (determined from STEM) in our epitaxial thin films are larger than the ones measured from bulk T_{d} -MoTe₂ crystals.^[6–9] This is attributed to the influence of the substrate and the layer-by-layer sequential growth adopted in the present work.

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37 2.5. Electronic Band Structure of 1T' MoTe₂ Epitaxial Thin Films

39 The electronic band structure of 1 ML 1T' MoTe₂ imaged by 40 in situ ARPES is given in Figure 5, in direct comparison with 41 1 ML density functional theory (DFT) first-principles calculations using the experimental lattice parameters deduced from 42 43 our epitaxial thin films. In contrast to exfoliated single crystal 1T' MoTe2, our epitaxial material contains rotated domains dif-44 45 fering by 60° between each other (see also discussion of STM, 46 XRD, and RHEED in Figures 2 and 4 and Figure S1, Supporting 47 Information). This gives rise to a complex Brillouin zone (BZ) 48 configuration (Figure 5d) resulting in an overlap of the elec-49 tronic band structure along two different directions in the BZ, 50 as for example ΓY and ΓS directions, in the ARPES spectrum 51 of Figure 5a, yielding a complex dispersion adversely impacting 52 energy and momentum resolution. By employing second derivative of the energy dispersion the resolution is improved 53 54 (Figure 5b,c) yielding a reasonably good agreement with DFT 55 simulations along the high symmetry lines in the BZ which are indicated by thick (blue and red) arrows in Figure 5d. Notably, 56 57 the feature at around $k_{11} \approx 1 \text{ Å}^{-1}$ in Figure 5b is located at the Γ point of the neighboring BZ (indicated by broken line in 58 59 Figure 5d) and is effectively a replica of the band at $k_{II} = 0$ Å⁻¹. There is also evidence for the existence of electron pockets 1 near the Γ point along ΓX as predicted by DFT in Figure 5c 2 (blue line). 3

In principle, by applying ARPES to thicker films, it should 4 be possible to distinguish between orthorhombic T_{d} -phase and 5 triclinic stacking and therefore identify the most dominant 6 configuration however the ARPES spectra for 2 and 3 ML (not 7 shown here) are very similar to the ones for 1 ML (Figure 5). 8 This could be explained by considering that 21.22 eV ARPES 9 known to be a surface sensitive technique probes the topmost 10 layer which is coupled weakly to the bottom layers showing the 11 behavior of a single layer in ARPES. 12

Using the measured set of lattice parameters in our epitaxial 13 thin films (a = 6.340 Å, b = 3.501 Å, c = 14.15 Å) we have per-14 formed DFT bulk band structure calculations for the noncen-15 trosymmetric orthorhombic $(T_{\rm d})$ structure with the aim to pre-16 dict the existence of Weyl nodes and find their location in energy 17 and k-space. By considering the topmost valence band and the 18 next (conduction) band we find eight Weyl nodes as a result of 19 broken inversion symmetry (Figure 6), which are all located in 20 the $k_{z} = 0$ plane and are symmetrically placed in k-space with 21 respect to the high symmetry directions X– Γ –X and Y– Γ –Y as 22 shown in the schematic of Figure 6a. Their exact coordinates 23 in k-space and energy are as follows: W1⁻: $(k_x = 0.18707 \text{ Å}^{-1})$, 24 $k_{\gamma} = 0.0456$ Å⁻¹, $k_z = 0$ Å⁻¹) at $E-E_{\rm F} = -1.1$ meV, W2⁺ 25 $(k_x = 0.1871 \text{ Å}^{-1}, k_y = 0.0351 \text{ Å}^{-1}, k_z = 0 \text{ Å}^{-1})$ at $E - E_F = -12.9 \text{ meV}$. 26 The Weyl nodes in each pair have opposite chirality and are 27 located below the Fermi level but very close to it (Figure 6b). The 28 Fermi arc connecting the Weyl nodes with opposite chirality (+, -)29 is shown as part of the surface state passing through them in 30 Figure 6b. It should be noted that this set of lattice parameters 31 deduced from our epitaxial thin films yields Weyl nodes which 32 are closer to the Fermi level than any other reported^[8,9,18,20,23,24] 33 Weyl nodes for MoTe₂ in the literature. While in all of these 34 cases, they are typically located a few tens of meV above $E_{\rm F}$, in 35 our epitaxial thin films the Weyl nodes are predicted just below 36 the Fermi level which facilitates observations by ARPES and 37 makes them accessible to transport, thus suitable for electronic 38 applications where topological properties can play a critical role. 39

The unconventional triclinic layer stacking as evidenced by 40 STEM in Figure 3d, yields a calculated bulk band structure 41 (Figure S4, Supporting Information) with no Weyl points, a 42 result which is expected since this structure is centrosymmetric. 43

To gain more insight about the possible role of the enlarged 44 lattice parameters on the stabilization of the orthorhombic 45 $T_{\rm d}$ -phase at room temperature in our epitaxial thin films we 46 analyze our first-principles calculations which have been per-47 formed using two different sets of experimental lattice para-48 meters (Figure 7) following similar methodology and reasoning 49 as in ref. [21] Set #1 (*a* = 6.3341 Å, *b* = 3.4751 Å, *c* = 13.8816 Å) 50 in Figure 7a is an average obtained from experimentally 51 reported values for bulk, free standing T_{d} -MoTe₂,^[6-9] detected 52 at low temperatures and Set #2 (a = 6.340 Å, b = 3.501 Å, 53 c = 14.15 Å) in Figure 7b is from our measured T_d -MoTe₂ epi-54 taxial films at RT. In both band structures (Figure 7a,b), the 55 uppermost valence band B1 along TA consists of hybridized 56 Te p_x and Mo d_{xz} orbitals while the lower band B2 consists 57 of hybridized Te p_z and Mo d_{z2} orbitals. From the plot of the 58 wavefunctions of B1 and B2 at Γ for Set #2 (our experimental 59 SCIENCE NEWS ______ www.advancedsciencenews.com

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(a) compared with DFT simulations for 1 ML 1T' MoTe₂. Blue line is along Γ Y, red line is along Γ S c) 2nd derivative of spectra along Γ X compared 41 41 with DFT simulations for 1 ML 1T' MoTe₂. e) Schematic illustration of k-space constructed by the superposition of orthorhombic Brillouin zones (BZ) 42 42 originated from of 0° (blue solid line) 60° or 120° rotated domains (red solid lines). The dashed lines denote neighboring Brillouin zones. The Γ point 43 43 of the neighboring 0° BZ nearly coincides with the S point of the rotated BZs. The horizontal thick arrows shows the paths along which the ARPES 44 spectra in (a) and (b) are recorded. Note that ARPES images simultaneously the bands along ΓY (blue arrow) and ΓS (red arrow) paths since these 44 two paths are parallel due to the overlapping of rotated domains. The thick vertical arrow shows the paths along which the ARPES in (c) is recorded. 45 45 46 46

parameters) in Figures 7c,d, it is inferred that interlayer cou-47 48 pling occurs through an antibonding configuration along 49 interlayer distance *d* between inner Te atoms having large and 50 opposite sign wavefunction values. Since B2 is fully occupied 51 in both cases the degree of occupancy of the interlayer antibo-52 nding band B1 along ΓA and near Γ determines the tendency of MoTe₂ to stabilize in the T_d phase. For Set #1 of the experi-53 54 mental bulk parameters obtained from the literature (Figure 7a; 55 Figure S4, Supporting Information), a significant portion of the uppermost valence band B1 near Γ point along ΓA is unoccu-56 57 pied. In contrast, for Set #2 of our epitaxial thin film enlarged 58 experimental parameters in Figure 7b, B1 is fully occupied thus strengthening the interlayer antibonding state which favors 59

an elongated interlayer distance *d* (Figure 7c). This elongation stabilizes T_d stacking configuration at RT since $d(=d_o)$ for 48 orthorhombic stacking is large and indeed larger than the corresponding monoclinic distance d_m (see Figure 1b,c). 50

3. Discussion

In this work we use MBE to grow the distorted 1T (1T') phase 55 of MoTe₂ epitaxially on InAs(111)/Si(111) substrates. Adopting 56 an interrupted growth methodology at low growth temperatures 57 (≈ 280 °C) first applied to the MBE growth of WTe₂ on MoS₂ 58 and HOPG substrates,^[31] we show by STEM and GIXD that a 59

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Figure 6. Calculated Weyl node configuration for the bulk orthorhombic T_d -MoTe₂ using the experimental parameter sets deduced from our epitaxial films a) Positions of Weyl nodes in the first Brillouin zone. The blue and red points closely spaced between each other indicate pair of Weyl nodes with opposite chirality. b) Theoretical energy dispersion along a path KK' shown by broken line in (a), passing through the pair of Weyl points. Theoretical constant energy contour plots for two different energies c) E = -1.1 meV and d) E = -12.9 meV corresponding to the energy location of the Weyl node pairs. e⁻ and h⁺ denote the touching electron and hole pockets, respectively.

32 pure 1T' MoTe₂ phase can be obtained with improved crystallinity after postgrowth annealing at 400 °C. Despite the fact the 33 34 2H prismatic phase of MoTe₂ is more stable at RT, a pure 1T' 35 MoTe₂ phase is observed here attributed to the influence of the 36 substrate due to tensile biaxial strain and/or electron doping. 37 Tensile strain between 0.3% and 3% under uniaxial conditions as theoretically predicted^[5] or 0.2% as experimentally dem-38 39 onstrated^[11] is thought to drive the transition from the stable 2H to the metastable 1T' $MoTe_2$ phase at or near RT. In our 40 case, the in-plane a and b lattice parameters of the epitaxial 41 films are accurately measured by synchrotron GIXD (Figure 4) 42 and found to be larger than those obtained in free standing 43 films exfoliated from bulk,^[6,9] indicating a relatively small epi-44 taxial tensile strain configuration with $\varepsilon_{xx} = \delta a/a \approx +0.1\%$ and 45 46 $\varepsilon_{vv} = \delta b/b \approx +0.7\%$, which may partly explain the transformation 47 to 1T' phase at RT in our epitaxial thin films. It has also been 48 predicted^[17] that electron doping $\approx 0.1e^{-1}$ per unit cell induces 49 the $2H \rightarrow 1T'$ transition in MoTe₂. Electron doping could be a 50 possible scenario in our case, since the electronic charge can be 51 provided by the InAs substrate which is known to have strong 52 n-type semiconductor character at the surface due to the accu-53 mulation of a dense electron gas.^[40]

54 MBE, a typically far from equilibrium process, can produce 55 thin film structures which cannot be obtained under equilib-56 rium conditions. Beyond the substrate effects (strain, doping) 57 already discussed above, the ability to sequentially grow one 58 layer on top of another as in the present work, allows different 59 stacking configurations which cannot be obtained in films exfoliated from bulk. Such a layer stacking, namely a triclinic 32 structure is observed here by STEM (Figure 3e; Figure S2, Sup-33 porting Information), where all layers are in phase presenting 34 a fundamental difference compared to the typical monoclinic 35 or orthorhombic structures where two consecutive layers are 36 180° out of phase (Figure 1). Hints of such in-phase layer 37 stacking are found also in MBE-grown WTe2^[31] but not suf- 38 ficiently emphasized. Although the triclinic structure is cen- 39 trosymmetric with trivial topology (no Weyl nodes found), it is 40 very interesting that here the important noncentrosymmetric 41 orthorhombic (T_d) Weyl semimetal phase is observed by STEM 42 coexisting with the triclinic structure. This orthorhombic phase 43 is typically reported in the literature below 250 or 150 K so 44 questions are raised about the possible origin of its stability at 45 RT as observed in our work. The reduced dimensionality anal-46 ysis previously proposed to explain the indirect observation^[38] 47 of RT T_d -MoTe₂ in 12 nm thick films exfoliated from bulk does 48 not directly apply to our ultrathin (1–3 ML) films. Our DFT 49 analysis for T_d -MoTe₂ (Figure 7) shows that the enlarged lattice 50 parameters of our epitaxial thin films result in a characteristic 51 band structure where the uppermost valence band B along ΓA 52 is fully occupied dispersing well below the Fermi level similar 53 to what is observed for T_d -WTe₂.^[21] It should be noted that in 54 the case of T_d -WTe₂, the full occupation of this band is corre- 55 lated with the absence of a barrier in the energy profile for the 56 transition from β to T_d -phase^[21] which explains the stability 57 of T_d -phase at RT. A similar situation could apply for the epi- 58 taxial MoTe₂ in this paper. Expressing it in a different way, it 59





Figure 7. DFT calculations for bulk T_d -MoTe₂ for two different lattice parameter sets: a) averaged experimental lattice parameters from bulk T_d -MoTe₂ taken from refs. [6–9], b) experimental lattice parameters from epitaxial thin films in this work. The symbols in both (a) and (b) represent the projections of the bands in the Te and Mo orbitals. c,d) Wavefunctions at the Γ point are plotted for valence bands B1 and B2, respectively, corresponding to T_d -MoTe₂ calculated with the experimental parameters reported in this work (Set #2). The wavefunction sign (+) and (-) is indicated by blue and green color, respectively.

55 can be said that this fully occupied band B (Figure 7) is related 56 to an antibonding state^[21] along the interlayer distance *d* (see 57 Figure 1), then the T_d -MoTe₂ is favored because this phase is 58 compatible with an enlarged *d* ($d_o > d_m$ in Figure 1) as it would 59 be expected for an antibonding state. This analysis shows that the enlarged lattice parameters in the epitaxial thin films could 1 explain the observation at RT of the orthorhombic T_d -MoTe₂ 2 instead of the monoclinic phase. 3

The RT orthorhombic MoTe₂ reported here lacks inversion symmetry so it is expected to be a topological Weyl semimetal. Using the enlarged experimental lattice parameters found in this work, a DFT analysis (Figure 6) for the T_d -MoTe₂ predicts eight type II Weyl nodes which are located very close to the Fermi level and just below it, in notable difference with previous results where all Weyl points were found above $E_{\rm F}$. The occupation of states near the Weyl nodes makes them visible in ARPES electronic band imaging and accessible to transport which means that epitaxial thin films of T_d -MoTe₂ on InAs(111) substrates can be used to fabricate devices which could exploit the nontrivial topological properties of these films in practical RT applications.

Future work should focus on improving the epitaxial quality of these films. Although there is a very good in-plane epi-taxial alignment between MoTe₂ and InAs substrate such that $[100]_{MoTe2}//[11-2]_{InAs}$, and $[010]_{MoTe2}//[01-1]_{InAs}$ (Figure 4), with no signs of polycrystallinity, the in-plane mosaicity of 3.71° is substantially higher than the InAs one (0.79°) and higher than the 1.79° mosaicity of epitaxial ZrTe₂ on InAs.^[39] Moreover, the MoTe₂ epilayer, similar to the case of ZrTe₂,^[39] follows the landscape of the InAs surface (STEM in Figure 3) which shows monatomic steps of 3.5 Å, producing a MoTe₂ nanostructure with domain size in the order of a few tens of nm as also seen by STM in Figure 2. The presence of 60° and 120° rotated domains is widely evidenced by STM, RHEED, and GIXD data, which is a distinct characteristic of our thin epitaxial films compared to single crystals obtained from bulk where such domains are absent. While these rotated domains in the hex-agonal undistorted 1T or 2H MoTe₂ structure are equivalent, in 1T' MoTe₂ result in a complex k-space and Brillouin zone, mixing the energy dispersion along different directions thus adversely affecting resolution, inhibiting clear observation of Weyl node configuration in ARPES. Domain rotation may be facilitated at the step edges, where also the continuity of the film may be interrupted (Figure 3), which could be harmful for electrical transport. By improving the surface treatment of InAs prior to growth we may be able to minimize the density of monatomic steps and increase the domain size in an attempt to obtain a single crystalline epitaxial film. Although the use of single crystal InAs(111) could resolve some of the issues related to the step and domain formation and improve the mosaicity of MoTe₂, the effort should focus on the improvement of epitaxial InAs on Si substrates since the availability of large area wafers (200 and 300 mm) of this kind is essential for a manufacturable technology of MoTe₂ and other 2D materials in the future.

4. Conclusion

In this work epitaxial thin films of $MoTe_2$ with the distorted 1T' 54 structure are grown by molecular beam epitaxy on InAs(111)/ 55 Si(111) substrates. The films are rotationally commensurate with the substrate such that $[100]_{MoTe2}//[11-2]_{InAs}$ and 57 $[010]_{MoTe2}//[01-1]_{InAs}$ although 60° and 120° rotational domains are present, detected by STM, synchrotron GIXD, and RHEED. 59



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1 Using STEM cross-sectional measurements in 3 ML MoTe₂ we 2 identify two different phases coexisting in the layer. The first 3 phase shows an orthorhombic (T_d) stacking (or γ -MoTe₂) and the second phase is a triclinic stacking not reported before. 4 5 From GIXD and STEM we measure lattice parameters values 6 a = 6.340 Å, b = 3.501 Å and out of plane parameter for the 7 orthorhombic T_d -phase c = 14.1-14.2 Å which are larger com-8 pared to freestanding thin films exfoliated from bulk as a result 9 of the influence from the substrate.

10 The MoTe₂ orthorhombic T_d -phase typically found at temper-11 atures lower than 250 K, here is observed at room temperature 12 which is attributed to an interlayer antibonding state compatible with the orthorhombic T_d -phase as a result of the enlarged 13 14 lattice parameters of our epitaxial thin films. The orthorhombic 15 T_{d} -MoTe₂ is noncentrosymmetric yielding a topological type II Weyl semimetal phase. Eight Weyl nodes calculated by DFT a 16 17 few meV below the Fermi level are accessible to transport cre-18 ating the prospect for room temperature electronic applications 19 where the topologically nontrivial properties of MoTe₂ epitaxial 20 layers could play a role. 21

23 5. Experimental Section

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24 Surface Preparation and Film Growth Details: The InAs(111)/Si(111) 25 substrates were chemically cleaned in a 5N HF solution in isopropyl 26 alcohol for 5 min to etch the surface oxide and subsequently rinsed in 27 isopropyl alcohol for 30 s in order to avoid reoxidation of the substrate. 28 An annealing step at 400° C in UHV follows to get a clean and flat InAs(111) surface as evidenced by RHEED (Figure S1, Supporting 29 Information) and X-ray photoelectron spectroscopy. Where appropriate, 30 mild Ar+ sputtering was used ($E \approx 1.5$ keV, $p \approx 2 \times 10^{-5}$ mbar, $t \approx 30$ s) 31 prior the annealing step to obtain a clean surface as evidenced by 32 a 2 \times 2 reconstruction in RHEED pattern (Figure S1a,b, Supporting 33 Information) attributed to In surface vacancies.[41]

34 ARPES Measurements: In-situ ARPES was conducted at room 35 temperature in a μ -metal analytical chamber equipped with a 100 mm hemispherical electron analyzer (SPECS PHOIBOS 100) and a 2D CCD 36 detector. The energy resolution of the detection system was better than 37 40 meV using a 21.22 eV photons from a He discharge source (SPECS 38 UVS35/10), although, since the measurement is performed at RT, the 39 resolution is limited by thermal effects and is about 100 meV.

40 STM Characterization: After MoTe₂ films growth, the samples were transferred to the STM (OMICRON) chamber without breaking the 41 vacuum for in situ STM characterization. STM images were obtained in 42 UHV conditions (base pressure $\approx 10^{-9}$ mbar) at room temperature using 43 a Pt/Ir tip at the following conditions: V = 0.1 mV, I = 1 nA for high 44 resolution images (Figure 2e-h) and V = 0.4 mV, I = 400 pA for the rest. 45

STEM Characterization: STEM measurements have been carried out 46 using a Cs-corrected FEI Themis at 200 keV. HAADF-STEM images were 47 acquired using a convergence semiangle of 18 mrad and collecting 48 scattering >65 mrad. STEM specimens were prepared by the FIB lift-out technique using an FEI dual-beam Strata 400S at 30 kV. 49

Synchrotron GIXD Measurements: Diffraction measurements were 50 performed at the European Synchrotron Radiation Facility by means 51 of the UHV-MBE CVD diffractometer installed at the BM32 CRG/IF 52 beamline and optimized for GIXD. The experimental setup energy and 53 incident angle were set at 11 keV (1.13) and 0.2°, the latter set slightly 54 below the critical angle value for total reflection in order to enhance the 2D film signal while minimizing the background. 55

First-Principles Calculation: The first-principles calculations were 56 performed using the Vienna Ab initio Simulation Package^[42,43] and 57 projector-augmented waves.^[44] The generalized-gradient approximation 58 with Perdew–Burke–Ernzerhof^[45] parameterization was used as exchange 59 correlation functional. The kinetic energy cutoff was set at 450 eV, using the Monkhorst–Pack scheme^[46] employing a $12 \times 10 \times 6$ k-point mesh 1 for bulk calculations. The experimental lattice constants were used and 2 the atomic positions were fully optimized by conjugate gradient, using 3 a force threshold of 1×10^{-3} eV Å^-1. Van der Waals corrections were 4 used by applying the semiempirical DFT-D3 Grimme's method.^[47] The 5 Maximally-Localized Wannier functions are fitted based on Mo's s and d and Te's p orbitals using the Wannier90 code^[48] and the surface states, 6 7 topological Fermi arcs, and Weyl points calculations were carried out by the WannierTools software.^[49] Spin-orbit coupling was included in band 8 structure calculations. 9

Supporting information

13 Supporting Information is available from the Wiley Online Library or 14 from the author. 15

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

2D materials, molecular beam epitaxy, orthorhombic MoTe₂, 35 transmission electron microscopy, Weyl semimetal 36

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