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Epitaxial growth of monolayer $PdTe_2$ and patterned $PtTe_2$ by direct tellurization of Pd and Pt surfaces

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Abstract

Two-dimensional (2D) palladium ditelluride ($PdTe_2$) and platinum ditelluride ($PtTe_2$) are two Dirac semimetals, which have fascinating quantum properties such as superconductivity, magnetism and topological order and show the promising applications in future nanoelectronics and optoelectronics. However, the synthesis of PdTe2 and PtTe2 monolayers (MLs) is hindered by a strong interlayer coupling and orbital hybridization. In this study, we demonstrate an efficient synthesis of PdTe₂ and PtTe₂ MLs Large-area and high quality MLs of PdTe₂ and patterned PtTe₂ were epitaxially grown on the Pd(111) and Pt(111) surfaces by direct telurization in ultra-high vacuum. This was confirmed by x-ray photoelectron spectroscopy, low energy electron diffraction and scanning tunnelling microscopy. PdTe₂ ML demonstrated high thermal stability showing no decomposition sign after annealing at 470 °C. A well-ordered (2×2) PtTe₂ structure with Kagome lattice was observed on Te/Pt(111) surface following annealing at 200 °C in UHV, where the (2×2) pattern was formed by Te atom vacancies. PtTe₂ multilayer film was prepared as well, and it demonstrated the excitation of the Dirac plasmons as measured by high-resolution electron energy loss spectroscopy. The direct tellurization offers the simple and reliable protocol for the preparation of the ML of PdTe₂ and patterned PtTe₂, and this opens new opportunities for quantum phenomena research and for practical optoelectronics applications.

1. Introduction

Two-dimensional (2D) noble transition metal dichalcogenides (NTMDs) are a subgroup of the 2D transition metal dichalcogenides (TMDCs), which exhibit the drastically different properties from most TMDCs [1]. NTMDs demonstrate a strong thicknessdependence of the band structure, high mobility, inplane anisotropy and high air stability; these offer the exciting opportunities in nanoelectronics, optoelectronics and catalysis [2–9]. Type II Dirac fermions with superconductive properties were shown in PdTe₂, the coexistence of the superconductivity and the topological states at the 2D level creates a possibility to observe Majorana fermions [10-13]. The excitation of the 3D Dirac plasmons was observed in PtTe₂; and this makes this material a promising candidate for optoelectronic applications [14-16]. Both PdTe₂ and PtTe₂ show thickness-dependence of the band structure [17], which gives an opportunity to tune the electrical and optical properties of the materials. It is highly desirable to scale down the highqualitive PdTe₂ and PtTe₂ to a monolayer (ML).

Unlike other TMDCs, $PdTe_2$ and $PtTe_2$ show a strong interlayer interaction due to their specific electronic configurations, where the *d* levels are nearly full occupation and the *p* levels are highly hybridized [17, 18]. This makes challenging to obtain ultrathin

2D layers using the 'top-down' methods such as a mechanical exfoliation. The traditional methods such as molecular beam epitaxy (MBE), chemical vapor deposition (CVD) and pulsed laser deposition were successfully used to grow different 2D materials demonstrating the promising 'bottom-up' approach [19–21]. Recently, the PdTe₂ and PtTe₂ flakes were synthesized by MBE, CVD and laser-assisted synthesis [22-25]. However, as prepared 2D flakes have the size in micrometre scale and present multilayer materials. Therefore, the synthesis of large-area, highquality ML 2D films attracts significant attention. Large-area and high-quality ML of PtSe2 was realized on the Pt(111) by selenium evaporation and sequential annealing in ultra-high vacuum (UHV) [26, 27]. A (3×3) superstructure was detected pointing to a strong interaction between PtSe₂ ML and the substrate [27]. Also, the intrinsically patterned 1T/1H PtSe₂ ML was observed during the epitaxial growth by controlling the concentration of defects [26].

Here we report in the first time the synthesis of the large-area PdTe₂ and PtTe₂ ML films by direct tellurization of the Pd(111) and Pt(111) surfaces. Using a one-step approach, we obtained highquality ML films as confirmed by scanning tunnelling microscopy (STM), x-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED). In the case of PtTe₂, a (2×2) structure with Kagome lattice was observed demonstrating the well-ordered vacancies of Te atoms in the topmost layer of PtTe₂. Multilayer of PtTe2 was also obtained by this method and the excitation of Dirac plasmons was detected by high-resolution electron energy loss spectroscopy (HREELS). The reliable synthesis of the PdTe₂ and patterned PtTe2 MLs open new application opportunities in electronics and optoelectronics.

2. Method

All experiments were performed using an Omicron Surface Analysis Cluster, which was described elsewhere [28-30]. The setup consists of an UHV preparation chamber and UHV μ -metal analysis chamber with base pressures of 1×10^{-9} mbar and 5×10^{-11} mbar, respectively. Pd(111) and Pt(111) single crystals with 9 mm of diameter, 1 mm of thickness and with orientation accuracy <0.5° (MaTecK GmbH) were cleaned by repeated cycles of Ar⁺ sputtering and annealing in UHV at 780 °C. The surface cleanliness was monitored by XPS, LEED, and STM. For each deposition experiment, the single crystals were freshly cleaned. Tellurium (99.999%, Sigma-Aldrich) was thermally evaporated using a home-built evaporator in the preparation chamber. The tellurium temperature in the evaporation regime was in the range of 290 °C-300 °C and the evaporation rate was controlled by the heater power. The substrate was kept at room temperature (RT) during Te deposition. The amount of deposited tellurium was verified by XPS. The details of thickness of deposited Te and deposition time are shown in figure S1 (available online at stacks.iop.org/2DM/8/045033/ mmedia). The sample temperature was measured by a K-type thermocouple attached to the manipulator part with which a sample holder was in a good thermal contact. To complete the telluride synthesis, a single crystal was annealed at the specified temperature for 10 min in UHV.

STM images (Omicron ambient temperature UHV STM) were collected at RT using electrochemically etched W and Pt-Ir tips at constant current (topographic) mode. In all experiments reported here, the tip was electrically grounded, meaning that at positive bias the electrons flowed from the tip to the sample. The STM images were analyzed using WSxM software [31].

XPS was acquired using a non-monochromatic Mg K α x-ray radiation ($h\nu = 1253.6$ eV) at 150 W. High resolution spectra were recorded at constant pass energy of 20 eV using the electron energy analyzer-Omicron EAC 125 and the analyzer controller-Omicron EAC 2000. The resolution of the instrument/sample system, which was measured as the full width at half maximum of Pt 4f_{7/2} peaks of the clean Pt(111) crystal, was approximately 1.2 eV. Photoelectrons were collected at a 45° angle with respect to the surface normal. The parameters used for the calculation of practical electron attenuation lengths (EALs) using NIST database tool [32] are shown in table S1 in the supporting information (SI).

LEED measurements were conducted in the analyst chamber straight after sample preparation with a four-grid optics (Omicron LEED).

3. Results and discussion

PdTe₂ and PtTe₂ MLs were grown by deposition of Te on the Pd(111) and Pt(111) surfaces followed by annealing under UHV conditions. The schematic cartoon of the process is shown in figure 1. HREELS spectra confirm the formation of PdTe₂ and PtTe₂ (figure S2). On PdTe₂, HREELS losses were observed at 15 meV and 25 meV in agreement with the optical modes reported for PdTe₂ bulk crystal [33]. The mode of PtTe₂ shows a single vibration at 21 meV, which also follows the phonon dispersion features of PtTe₂ [34].

The different annealing temperature is required for PdTe₂ and PtTe₂ to get a flat and high-quality surface. Thus, a large-area PdTe₂ ML film was obtained after annealing at 470 °C (figure 2(b)), whereas the reasonably flat surface of PtTe₂ was obtained following annealing at 200 °C (figure 2(f)). For PdTe₂, the surface annealed at low temperatures was covered **IOP** Publishing



by small irregularly shaped islands although STM showed the atomic arrangement corresponding to $PdTe_2$ (figure S3(a)). Below we focus on the conditions giving the best growth results, which corresponds to the annealing temperature of 470 °C. LEED of PdTe₂ ML obtained following 470 °C annealing shows a hexagonal diffraction pattern confirming a high crystallinity the (1×1) PdTe₂ structure over a large area (insets of figures 2(b) and S4(a)). Moreover, LEED analysis performed at the multiple spots is fully consistent with this conclusion (figure S4). LEED indicates that the PdTe₂ film has the same crystalline orientation across the entire surface. This allows to conclude that a large area of PdTe2 ML of several mm size was prepared. The high-resolution STM image in figure 2(c) demonstrates the atomic structures of PdTe₂ with a hexagonal arrangement of the Te atoms in the topmost layer. An interatomic distance of 4.7 Å (figure 2(d)) corresponds to $\sqrt{3} \times \sqrt{3}$ arrangement for Pd(111) ($\sqrt{3} \times 2.75 = 4.76$ Å). The PdTe₂ lattice is rotated by 30° with respect to the underlying Pd(111) substrate, aligning one of the unit vectors of PdTe₂ with the $[\overline{1}12]$ direction of the Pd(111) substrate (figure S5). The $\sqrt{3} \times \sqrt{3}$ arrangement could be thermodynamically driven to match the fcc or hcp sites of underlying Pd(111) substrate.

In the case of PtTe2, a ML film was obtained following annealing at the temperature of 200 °C. The prepared surface was flat, only a few nanoparticles and the decoration of a monoatomic step was observed by STM (figure 2(f)). Unlike the (1×1) structure observed on PdTe₂/Pd(111), LEED displays a hexagonal diffraction (2×2) pattern on the PtTe₂ surface (inset of figure 2(f)). The STM image in figure 2(g) shows atomic vacancies, which look like dark spots, forming the hexagonal structure with a periodicity of 8.2 Å (the line profile in figure 2(h)), which is approximately two times by the expected lattice parameter for PtTe₂ [35, 36]. This (2×2) PtTe₂ represents the Kagome lattice as shown by two green triangles in figure 2(g). These atomic vacancies are the ordered defects due to missing Te atoms in the topmost layer of PtTe₂. The size of the (2×2) PtTe₂ structure approximately matches three times of Pt(111) lattice $(2 \times 4.1 \text{ Å} \approx 3 \times 2.77 \text{ Å} = 8.31 \text{ Å})$. The (2×2) $PtTe_2$ is aligned with the underlying Pt(111) having one of the unit cell vectors parallel with the $|\overline{1}10|$ direction of Pt(111). This was concluded based on the LEED observation (figure S6). Therefore, we can suppose that the generated Te vacancies rearrange into the (2×2) pattern, which is driven thermodynamically to match the fcc or hcp sites of the underlying Pt(111) lattice. According to STM, in the (2×2) structure, one of four Te atoms of the topmost layer is missing, therefore, the formal stoichiometry should be PtTe_{1.75}. The (2 $\,\times\,$ 2) structure demonstrates high thermal stability. LEED does not change and remains the (2×2) patterns following annealing at 500 °C in UHV (figure S7(a)). The atomic resolution STM image shows that the (2×2) PtTe₂ is still mainly intact although a few defects are generated (figures S7(b)-(d)). We would like to underline that the (2×2) structure is unique and only observed for PtTe₂ and not for PdTe₂. To the best of our knowledge, the (2×2) structure was not reported before.

Chemical sensitivity of XPS was used to confirm the formation of PdTe₂ and PtTe₂. Following Te deposition at RT on Pd(111), the centroids of the Pd $3d_{5/2}$ and Pd $3d_{3/2}$ peaks were at 335.6 eV and 340.9 eV, respectively, which shift towards higher binding energies (BEs) by 0.5 eV with respect to those of clean Pd(111) (figures 3(a) and S8(a)). This indicates the formation of the Pd-Te chemical bond right after Te deposition, and it points to a low activation barrier for the reaction between Pd and Te. The surface cleanliness is an important factor to promote the reaction. Impinging tellurium atoms can easily interact with the surface of the noble metal creating the chemical bond. The formation of $PdTe_x$ particles with the size of approximately 2 nm was detected following deposition as shown in figure S9. The annealing at 470 °C in UHV leads to the decreasing of the Te amount and, the centroid of the Pd 3d_{5/2} peak shifts back to 335.1 eV. This is because the contribution of Pd(111) bulk dominates in the XPS signal and the contribution of PdTe₂ ML is difficult to be separated. On the other hand, the annealing results in the shift of the Te 3d peaks towards lower BEs by 0.2 eV, which points to the further transfer of the electron density from Pd to Te confirming the formation of PdTe₂ (figure 3(b)). In the case of Te/Pt(111), the annealing at 200 °C does not lead to the shift of the Pt 4f and Te 3d peaks (figures 3(c), (d) and 8(b)). For both PdTe₂ and PtTe₂, the Te $3d_{5/2}$ peak at 573.3 eV (figures 3(a)and (c) is higher by approximately 0.5 eV comparing to the bulk materials [23, 24]. This could be attributed to charge transfer between the epitaxial grown MLs and the substrates due to differences in the work functions [37, 38].

The thickness of the as-grown films was calculated using XPS data analysed with a XPS Thickness Solver tool from Nanohub [39]. XPS thickness model is discussed in detail elsewhere [30, 40]. This



Figure 2. Epitatial growth of monolayer Parle2 and patterned PTe2: (a), (c) cartoon presentation (top and side views) of Parle2 and patterned PTe2, respectively. The missing Te atoms in the patterned PtTe2 are marked with the black dashed circles in the side view of (e). (b), (f) Typical STM images of the PdTe2 and patterned PtTe2 films, respectively. The scanning parameters for (b) were $V_b = 0.8$ V, $I_t = 0.7$ nA and for (f) were $V_b = -0.5$ V, $I_t = 1.6$ nA. Insets: LEED patterns of PdTe2 and patterned PtTe2, respectively; the blue dashed circles indicate the reflexes for the (1 × 1) PdTe2 corresponding to the unit cell (blue diamond) in (c); the red dashed circles in (f) are for the unit cell of PtTe2 drawn as a red diamond in (g) and the yellow dashed circles are for the (2 × 2) arrangements of the holes in (g). (c), (g) Atomic resolution STM images of PdTe2 and PtTe2, respectively, the scanning parameters were similar to (b), (f). (d), (h) Line profiles of PdTe2 and patterned PtTe2 corresponding to the blue and red dashed lines in (c) and (g), respectively. The green triangles in (g) represent the Kagome lattice of the patterned PtTe2.

approach was proposed by Fadley [41]. The equation for the overlayer thickness, *t*, can be written as

$$\frac{N_{\rm l}(\theta)}{N_{\rm s}(\theta)} = \frac{\rho_{\rm l} \times \frac{d\sigma_{\rm l}}{d\Omega} \times \Lambda_{\rm l}(E_{\rm l}) \times \cos\theta}{\rho_{\rm s} \times \frac{d\sigma_{\rm s}}{d\Omega} \times \Lambda_{\rm s}(E_{\rm s}) \times \cos\theta} \\ \times \frac{\left(1 - \exp\left(\frac{-t}{\Lambda_{\rm l}(E_{\rm l}) \times \cos\theta}\right)\right)}{\left(\exp\left(\frac{-t}{\Lambda_{\rm l}(E_{\rm s}) \times \cos\theta}\right)\right)} \tag{1}$$

where $N_{\rm l}(\theta)$ and $N_{\rm s}(\theta)$ are the photoemission peak areas of the overlayer (l is for Te 3d in our case) and the substrate (s is for Pd 3d or Pt 4f in our case) at the given photoemission angle, θ , measured in respect to the surface normal. ρ_l and ρ_s are the numbers of atoms per unit volume (density) for the overlayer and substrate. $(d\sigma_l/d\Omega)$ and $(d\sigma_s/d\Omega)$ are differential cross-sections for the overlayer and substrate photoemission peaks. This numbers can be calculated using the Scofield cross sections [42] and the Reilman asymmetry parameter [43]. Instead of the inelastic mean free paths in the original [41], we use the EAL: $\Lambda_1(E_1)$ for the photoelectrons originated in the overlayer and attenuated in the overlayer, $\Lambda_s(E_s)$ for the photoelectrons originated in the substrate and attenuated in the substrate, and $\Lambda_1(E_s)$ for the photoelectrons originated in the substrate and attenuated in the overlayer. All EALs were calculated using NIST SRD-82 [32]. Equation (1) was solved numerically using the Nanohub tool [39]. In the [40], the Nanohub tool was validated for the thickness calculation of TMDC materials such as MoS_2 , and the results were crosschecked by transition electron microscopy.

The intensity ratio between the photoemission peaks obtained from the MoS₂ films such as Mo 3d, S 2s and S 2p and the Al 2p peaks from the substrate was used as the primary input parameter for the thickness calculation in the [40]. In our case, the photoemission peaks of Pt and Pd from NTMDs cannot be separated from substrates. Therefore, we have simplified the system. For the calculation, we have considered the PdTe₂ (PtTe₂) overlayer as Te overlayer as shown in figure S10. The as-calculated thicknesses of the Te overlayers were 2.37 Å and 2.48 Å for PdTe2 and PtTe₂, respectively. To verify if these numbers correspond to ML, the ML PtSe₂ on Pt(111) was used as a reference because of the similar structural construction with our system. By following the recipe from [26, 27], ML PtSe₂ was grown on Pt(111) confirmed by STM, LEED and XPS (figure S11). Using the same calculation method, the thickness of Se overlayer was 2.26 Å, which corresponds to the PtSe₂ ML on Pt(111) and can be used as a reference value for our system. The ratio between 2.37 Å and 2.26 Å is 1.05, corresponding to 1.05 ML for PdTe₂ on Pd(111). The PtTe₂ on Pt(111) estimated in the same way is 1.10 ML. Therefore, the conclusion is that in both cases the MLs of PdTe₂ and PtTe₂ were successfully grown. On the other hand, no bilayer or multilayer areas were detected by STM, also confirming the ML natures. The step height was approximately 2.2 Å (figure S12), matching a monoatomic step of Pd(111) or Pt(111) and



Figure 5. APS spectra of Pd le₂ (the top row) and patterned PtTe₂ (the bottom row). (a), (b) The Te 3d and Pd 3d peaks obtained after deposition of Te (blue) and following annealing at 470 °C (red), respectively. (c), (d) Te 3d and Pt 4f peaks obtained after deposition of Te (blue) and following annealing at 200 °C (red), respectively.

pointing to that PdTe₂ or PtTe₂ was grown epitaxially as a single layer.

The annealing temperature plays an important role in the PdTe₂ and PtTe₂ synthesis. Following the annealing at the temperature of 100 °C, the Te/Pd(111) and Te/Pt(111) surfaces are not flat and are covered with islands (figures 4(a) and S3(a)). The formation of the islands with an irregular shape indicates a non-thermodynamic equilibrium growth. Atomic structures of PdTe₂ can be resolved on top of the islands and on the terraces following the annealing even at of 100 °C (inset of figure S3(a) in the SI), further confirming the low activation barrier of the reaction between Pd and Te. Likely, the PdTe₂ ML film covers the surface as a 'carpet'.

The Pt–Te interaction is more complex. Following the annealing at 100 °C, two atomic structures labelled with 'I' and 'II' were detected by STM (figure 4(a) and (b)). Structure I exhibits hexagonal atomic arrangements with the periodicity of 4.1 Å (figures 4(c) and (e)), which corresponds to the normal PtTe₂ lattice [35, 36], and we refer to this structure as a (1 × 1) PtTe₂. Typically, this phase is observed outside of the islands on the terraces. Structure II is the discussed above (2 × 2) PtTe₂ L Liu et al



Figure 4. (a) A typical STM image of the PtTe₂ monolayer obtained at annealing temperature of 100 °C. (b) A zoom-in STM image of (a) and the inset shows the observed LEED pattern. The white dashed lines are 'guide for the eye' of the boundary between structure I and structure II on the terrace. Structure II exists both inside and outside of the islands. The red and yellow circles indicate in the LEED pattern the (1 × 1) and (2 × 2) reflexes, respectively. (c), (d) Atomic resolution STM images of the (1 × 1) and (2 × 2) PtTe₂ structures, respectively. The green triangles in (d) show the Kagome lattice. The insets of (c) and (d) demonstrate fast Fourier transform (FFT) of each image. (e) A line profile corresponding to the red dashed line in (c). The tunnelling conditions were $V_{\rm b} = -1.1$ V, $I_{\rm t} = 0.9$ nA.

Kagome lattice (figure 4(d)). LEED patterns show bright (1×1) and weak (2×2) diffraction spots, confirming the coexistence of the two structures across a large area (inset of figure 4(b)). The (1×1) phase of PtTe₂ has higher surface density of Te comparing to the (2×2) structure. However, the latter is more thermodynamically stable: the (2×2) phase dominates completely following the annealing at 200 °C. Moreover, the 500 °C annealing in UHV did not affect much the (2×2) PtTe₂ phase, STM detects only a few atomic defects appeared on the surface (figure S7).

The PtTe₂ multilayer film was grown by the substantial increasing of the deposited amount of Te (figure 5(a)). The thickness calculated based on the XPS results was estimated to be approximately four PtTe₂ layers. The height of the step of multilayer PtTe₂ is 5.0 Å, (inset of figure 5(a)) corresponding to *c* lattice constant of PtTe₂ [14]. The PtTe₂ multilayer is characterized by the Pt $4f_{7/2}$ and $4f_{5/2}$ peaks at 71.6 eV and 74.9 eV, respectively (figure S13). These positions are shifted towards the higher BEs by 0.4 eV comparing to the ML case. Meanwhile, the Te 3d_{5/2} and $3d_{3/2}$ peaks are at 572.8 eV and 583.2 eV, which are shifted towards lower BEs by 0.5 eV comparing to the ML case. The BEs of the Te 3d peaks are consistent with the values reported in the literature for PtTe₂ [23]. This also confirms our hypothesis about the charge transfer between the Pt(111) substrate and the PtTe₂ ML. The atomic structure of the PtTe₂ multilayer has the periodicity of 4.1 Å (figure 5(b)) corresponding to the lattice constant of PtTe₂ [36]. LEED shows the typical (1×1) diffraction patterns (inset of figure 5(b) indicating the high crystallinity across



Figure 5. Multilayer PtTe₂. (a) A STM topographic image of multilayer PtTe₂. The tunnelling conditions are $V_b = -1.1$ V, $I_t = 0.8$ nA. Inset: a height profile along the black dashed line in (a). (b) Atomic resolution STM image of the multilayer PtTe₂. The blue rhombus indicates a unit cell. The tunnelling conditions are $V_b = 0.9$ V, $I_t = 0.7$ nA. Inset: LEED patterns of the multilayer PtTe₂. The blue dashed circles indicate the (1×1) reflexes. (c) HREELS spectrum of the multilayer PtTe₂ (after background subtraction). The blue line is 'guide for the eye'. The kinetic energy of the electron beam (E_i) is 5 eV. The incident angle (α_i) and scattering angle (α_s) for the HREELS measurement are 60° and 54°, respectively.

a large surface area. Notably, the excitation spectrum of multilayer $PtTe_2$ was obtained by HREELS (figure 5(c)) and it shows potential excitation of Dirac plasmons (figure S14). This confirms the high quality of the $PtTe_2$ multilayer and demonstrates its potential in the optoelectronics application. The successful growth of ML and multilayer of $PtTe_2$ provides a significant platform for investigating the unique layer-dependent properties of this material.

4. Conclusions

We demonstrate the epitaxial growth of the ML of PdTe2 and patterned PtTe2 by direct tellurium deposition on the Pd(111) and Pt(111) surfaces; the synthesis was established by STM, XPS and LEED. The large-area high quality PdTe₂ and patterned PtTe₂ ML films were prepared following the annealing in UHV at the temperatures of 470 °C and 200 °C, respectively. The PdTe₂ exhibits the hexagonal structure with the atomic spacing of 4.7 Å. This ML was fully formed following the annealing at 470 °C. Contrary to the 'single' (1×1) PdTe₂ structure, PtTe₂ demonstrates two phases. The (2×2) PtTe₂ structure was more thermodynamically stable than the (1×1) PtTe2 phase, the latter of which was observed after the annealing at 100 °C. The (2 \times 2) pattern was formed by well-ordered Te atomic vacancies arranged as the Kagome lattice and it completely dominated following the 200 °C annealing. This structure did not show the signs of degradation following the annealing at 500 °C. XPS confirms the ML nature of the epitaxial-grown films. High quality PtTe₂ multilayer film was obtained by the increasing of the amount of the deposited Te. HREELS measured the excitation of plasmons on the multilayer film of PtTe₂. This simple and robust synthesis of the large area 2D materials opens new opportunities for novel quantum phenomena research and for the potential applications in optoelectronics.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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References

- Pi L, Li L, Liu K L, Zhang Q F, Li H Q and Zhai T V 2019 Recent progress on 2D noble-transition-metal dichalcogenides Adv. Funct. Mater. 29 1904932
- [2] Chia X, Adriano A, Lazar P, Sofer Z, Luxa J and Pumera M 2016 Layered platinum dichalcogenides (PtS₂, PtSe₂, and PtTe₂) electrocatalysis: monotonic dependence on the chalcogen size *Adv. Funct. Mater.* 26 4306–18
- [3] Ciarrocchi A, Avsar A, Ovchinnikov D and Kis A 2018 Thickness-modulated metal-to-semiconductor transformation in a transition metal dichalcogenide *Nat. Commun.* 9 919

- 141 8928–36
 [5] Jiang S *et al* 2019 Anisotropic growth and scanning tunneling microscopy identification of ultrathin
 - even-layered PdSe₂ ribbons *Small* **15** 1902789
- [6] Avsar A, Ciarrocchi A, Pizzochero M, Unuchek D, Yazyev O V and Kis A 2019 Defect induced, layer-modulated magnetism in ultrathin metallic PtSe₂ Nat. Nanotechnol. 14 674–8
- [7] Yu X *et al* 2018 Atomically thin noble metal dichalcogenide: a broadband mid-infrared semiconductor *Nat. Commun.* 9 1545
- [8] Hu D et al 2019 Unveiling the layer-dependent catalytic activity of PtSe₂ atomic crystals for the hydrogen evolution reaction Angew. Chem., Int. Ed. 58 6977–81
- [9] Okogbue E, Ko T J, Han S S, Shawkat M S, Wang M, Chung H S, Oh K H and Jung Y 2020 Wafer-scale 2D PtTe₂ layers for high-efficiency mechanically flexible electro-thermal smart window applications *Nanoscale* 12 10647–55
- [10] Xue H, Yang H, Wu Y, Yao G, Guan D, Wang S, Zheng H, Liu C, Li Y and Jia J 2019 Molecular beam epitaxy of superconducting PdTe₂ films on topological insulator Bi₂Te₃ *Sci. China: Phys. Mech. Astron.* 62 076801
- [11] Clark O J et al 2018 Fermiology and superconductivity of topological surface states in PdTe₂ Phys. Rev. Lett. 120 156401
- [12] Wang M X *et al* 2012 The coexistence of superconductivity and topological order in the Bi₂Se₃ thin films *Science* 336 52–55
- [13] Timmons E I et al 2020 Electron irradiation effects on superconductivity in PdTe₂: an application of a generalized Anderson theorem Phys. Rev. Res. 2 023140
- [14] Politano A, Chiarello G, Ghosh B, Sadhukhan K, Kuo C N, Lue C S, Pellegrini V and Agarwal A 2018 3D Dirac plasmons in the type-II Dirac semimetal PtTe₂ Phys. Rev. Lett. 121 086804
- [15] Yan M et al 2017 Lorentz-violating type-II Dirac fermions in transition metal dichalcogenide PtTe₂ Nat. Commun. 8 257
- [16] Zeng L, Wu D, Jie J, Ren X, Hu X, Lau S P, Chai Y and Tsang Y H 2020 Van der Waals epitaxial growth of mosaic-like 2D platinum ditelluride layers for room-temperature mid-infrared photodetection up to 10.6 microm Adv. Mater. 32 2004412
- [17] Villaos R A B, Crisostomo C P, Huang Z Q, Huang S M, Padama A A B, Albao M A, Lin H and Chuang F C 2019 Thickness dependent electronic properties of Pt dichalcogenides NPJ 2D Mater. Appl. 3 2
- [18] Yang H, Kim S W, Chhowalla M and Lee Y H 2017 Structural and quantum-state phase transitions in van der Waals layered materials *Nat. Phys.* 13 931–7
- [19] Liu C W *et al* 2020 Substrate-induced strain in 2D layered GaSe materials grown by molecular beam epitaxy *Sci. Rep.* 10 12972
- [20] Yi K, Liu D, Chen X, Yang J, Wei D, Liu Y and Wei D 2021 Plasma-enhanced chemical vapor deposition of two-dimensional materials for applications Acc. Chem. Res. 54 1011–22
- [21] Yao J D, Zheng Z Q and Yang G W 2019 Production of large-area 2D materials for high-performance photodetectors by pulsed-laser deposition *Prog. Mater. Sci.* 106 100573
- [22] Ma H et al 2018 Thickness-tunable synthesis of ultrathin type-II Dirac semimetal PtTe₂ single crystals and their thickness-dependent electronic properties *Nano Lett.* 18 3523–9
- [23] Fu L, Hu D, Mendes R G, Rummeli M H, Dai Q, Wu B, Fu L and Liu Y 2018 Highly organized epitaxy of Dirac

semimetallic PtTe_2 crystals with extrahigh conductivity and visible surface plasmons at edges ACS Nano 12 9405–11 $\,$

- [24] Li E et al 2018 High quality PdTe₂ thin films grown by molecular beam epitaxy Chin. Phys. B 27 086804
- [25] Nguyen D A, Park D Y, Lee J, Duong N T, Park C, Nguyen D H, Le T S, Suh D, Yang H and Jeong M S 2021 Patterning of type-II Dirac semimetal PtTe₂ for optimized interface of tellurene optoelectronic device *Nano Energy* 86 106049
- [26] Lin X et al 2017 Intrinsically patterned two-dimensional materials for selective adsorption of molecules and nanoclusters Nat. Mater. 16 717–21
- [27] Wang Y et al 2015 Monolayer PtSe₂, a new semiconducting transition-metal-dichalcogenide, epitaxially grown by direct selenization of Pt Nano Lett. 15 4013–8
- [28] Paul R, Reifenberger R G, Fisher T S and Zemlyanov D Y 2015 Atomic layer deposition of FeO on Pt(111) by ferrocene adsorption and oxidation *Chem. Mater.* 27 5915–24
- [29] Gharachorlou A, Detwiler M D, Mayr L, Gu X K, Greeley J, Reifenberger R G, Delgass W N, Ribeiro F H and Zemlyanov D Y 2015 Surface chemistry of trimethylaluminum on Pd(111) and Pt(111) J. Phys. Chem. C 119 19059–72
- [30] Gharachorlou A, Detwiler M D, Nartova A V, Lei Y, Lu J, Elam J W, Delgass W N, Ribeiro F H and Zemlyanov D Y 2014 Palladium nanoparticle formation on TiO₂(110) by thermal decomposition of palladium(II) hexafluoroacetylacetonate ACS Appl. Mater. Interfaces 6 14702–11
- [31] Horcas I, Fernandez R, Gomez-Rodriguez J M, Colchero J, Gomez-Herrero J and Baro A M 2007 WSXM: a software for scanning probe microscopy and a tool for nanotechnology *Rev. Sci. Instrum.* 78 013705
- [32] Powell C J and Jablonski A 2011 NIST Electron Effective-Attenuation-Length Database, Version1.3, SRD 82 (Gaithersburg, MD: National Institute of Standards and Technology)
- [33] D'Olimpio G, Guo C, Kuo C-N, Edla R, Lue C S, Ottaviano L, Torelli P, Wang L, Boukhvalov D W and Politano A 2020 PdTe₂ transition-metal dichalcogenide: chemical reactivity, thermal stability, and device implementation *Adv. Funct. Mater.* **30** 1906556
- [34] Kim K, Kim S, Kim J S, Kim H, Park J-H and Min B I 2018 Importance of the van Hove singularity in superconducting PdTe₂ Phys. Rev. B 97 165102
- [35] Kliche G 1985 Far-infrared and x-ray investigations of the mixed platinum dichalcogenides PtS_{2-x}Se_x, PtSe_{2-x}Te_x, and PtS_{2-x}Te_x *J. Solid State Chem.* **56** 26–31
- [36] Hao S et al 2018 Low-temperature eutectic synthesis of PtTe₂ with weak antilocalization and controlled layer thinning Adv. Funct. Mater. 28 1803746
- [37] Xiong W, Huang K and Yuan S 2019 The mechanical, electronic and optical properties of two-dimensional transition metal chalcogenides MX₂ and M₂X₃ (M = Ni, Pd; X = S, Se, Te) with hexagonal and orthorhombic structures *J. Mater. Chem.* C 7 13518–25
- [38] Michaelson H B 1977 The work function of the elements and its periodicity J. Appl. Phys. 48 4729–33
- [39] Smith K C, Saenz D A, Zemlyanov D and Voevodin A 2012 XPS thickness solver
- [40] Zemlyanov D Y et al 2018 Versatile technique for assessing thickness of 2D layered materials by XPS Nanotechnology 29 10
- [41] Fadley C S 1978 Electron Spectroscopy: Theory, Techniques and Applications (New York: Academic) pp 1–156
- [42] Scofield J H 1976 Hartree-slater subshell photoionization cross-sections at 1254 and 1487 eV J. Electron Spectros. Relat. Phenomena 8 129–37
- [43] Yeh J J and Lindau I 1985 Atomic subshell photoionization cross sections and asymmetry parameters: $1 \le Z \le 103$ At. Data Nucl. Data Tables 32 1–155