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Formation of In-Plane Semiconductor-Metal Contacts in 2D Platinum Telluride by Converting PtTe_2 to Pt_2Te_2

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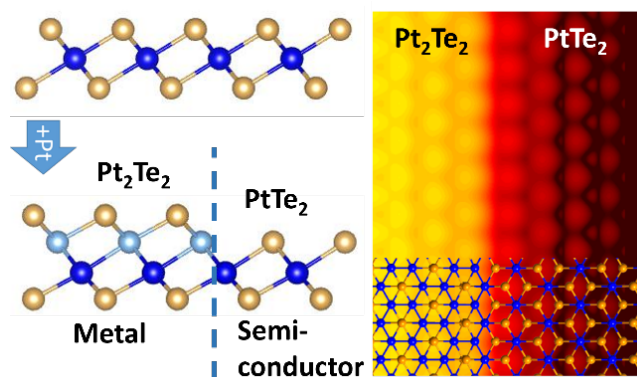
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Abstract:

Monolayers of platinum tellurides are particularly interesting 2D materials because they exhibit phases with different stoichiometries and electronic properties. Specifically, PtTe_2 is a narrow gap semiconductor while Pt_2Te_2 is a metal. Here we show that the former can be transformed into the latter by reaction with vapor-deposited Pt atoms. Owing to low surface diffusion barriers of Pt ad-atoms, the transformation occurs by nucleating the Pt_2Te_2 phase within the PtTe_2 islands, so that a metal-semiconductor lateral junction is formed. Using scanning tunneling microscopy/spectroscopy, the electronic structure of this lateral junction is studied. A flat band structure is found with the Fermi-level of the metal aligning with the Fermi-level of the intrinsically p-doped PtTe_2 suggesting low contact resistance. This flat band is achieved by an interface dipole that accommodates the ~ 0.2 eV shift in the work functions of the two materials. First-principles calculations indicate that the origin of the interface dipole is the atomic scale charge redistributions at the heterojunction. The demonstrated compositional phase transformation of a 2D semiconductor into a 2D metal is a promising approach for making in-plane metal contacts that are required for efficient charge injection and is of particular interest for semiconductors with large spin-orbit coupling, like PtTe_2 .

TOC-graphic:



[§] Contributed equally

Phase transformations in 2D materials and development of heterostructures based on the compounds with the same chemical composition have recently received considerable attention due to the possibility of post-synthesis modifications of existing structures. In particular, switching between semiconducting and metallic phases of 2D sheets of transition metal dichalcogenides (TMDs) has been accomplished by structural phase changes from the 2H-semiconducting to 1T'-metallic phase in group VIB TMDs.¹ Such phase transformations can be achieved by increasing vacancy concentration due to thermal treatment,² electron irradiation,³ or charge doping by alkali metal atom adsorption.^{4,5,6,7,8} Since in most cases a structural switch occurs from the lower energy H-phase to a higher energy T'-phase,^{9,10} these transformations are reversible, and the system can return back to the more stable H-phase. In contrast, compositional phase changes in 2D materials^{11,12,13} are not spontaneously reversible and thus the produced phases are stable. However, there are few examples of compositional control of contacts and usually these are mixtures of 2D and 3D crystal structures.¹⁴

PtTe₂ is an intriguing material with strongly layer dependent electronic properties. Only the monolayer is semiconducting while multi-layers and bulk materials are metallic.¹⁵ Moreover, the platinum-tellurium system exhibits various layered compositional phases, including PtTe₂ and Pt₂Te₂.^{16,17,18,19} While monolayer PtTe₂ is semiconducting with a band gap of ~0.5 eV,¹⁵ Pt₂Te₂ is metallic. Both phases possess a hexagonal structure with very closely matched lattice constants, so that a heterojunction between the two phases can be constructed with virtually no interface strain and defects. Here we demonstrate a low temperature process that enables the transformation of PtTe₂ into Pt₂Te₂ by incorporation of vapor deposited Pt atoms into PtTe₂ monolayer. The partially converted monolayer flakes exhibit PtTe₂/Pt₂Te₂ heterojunctions, which enables the spectroscopic analysis of the semiconductor/metal interface in a planar system. In contrast to previous modifications of TMDs with excess transition metal atoms,^{20,21,22,23} we consider here stable extended 2D phases, *i.e.*, the transformation from one known 2D phase to a 2D phase with another stoichiometry of the same elements. The transformation of PtTe₂ to Pt₂Te₂ may be referred to as an introduction of an additional layer of Pt as schematically illustrated in Fig. 1, without the need for rearrangement of the Pt-atoms in PtTe₂. This close structural relationship between PtTe₂ and Pt₂Te₂ is expected to facilitate a compositional transformation by incorporation of excess Pt and the formation of well-defined heterojunctions.

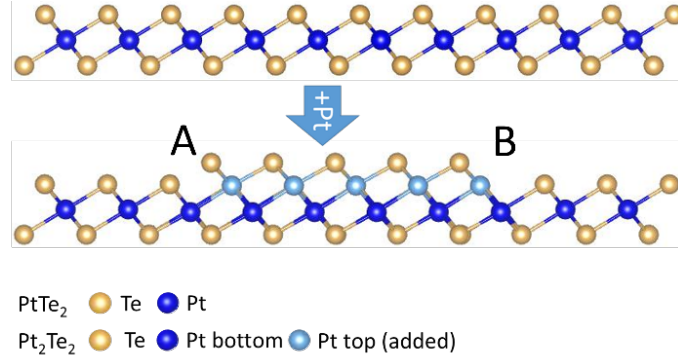


Fig.1: Schematic illustration of the phase transformation of PtTe_2 to Pt_2Te_2 by adding Pt-atoms. PtTe_2 has a 1T-TMD structure and the Pt_2Te_2 phase has two layers of Pt in between the tellurium layers. For partial transformation of a PtTe_2 layer, two kinds of phase-boundaries between the PtTe_2 and Pt_2Te_2 phases can be formed along the zig-zag direction of the 1T-structure. These two phase-boundaries are labeled 'A' and 'B'.

PtTe_2 was grown by molecular beam epitaxy. This approach has been shown by several groups to result in high quality PtTe_2 films down to monolayer thickness if grown at low (250°C) temperatures.^{24,25} Growth at temperatures above 300°C favors formation of bilayer thick islands.²⁶ Figure 2 shows the as grown PtTe_2 film, that consists of both mono- and bi-layer islands. The Pt-4f XPS spectrum shows a single doublet, which is consistent with a single PtTe_2 phase sample.¹⁹ The sample was then exposed to Pt-vapor at 200°C . The results of the STM and XPS measurements with increasing Pt-exposure are also shown in Fig. 2. In the STM images, the Pt_2Te_2 phase can be distinguished from the PtTe_2 phase by a difference of their layer height as indicated in the line profiles. The Pt_2Te_2 phase is imaged as being 0.2-0.3 nm thicker than the PtTe_2 phase. In addition to the contrast change in STM images the nucleation and growth of Pt_2Te_2 by reaction of PtTe_2 with Pt, can also be followed in XPS. The two phases have distinct Pt-4f peaks with a chemical shift of ~ 1.2 eV between the two phases.¹⁹ Fig. 2 also shows the variation of the Pt-4f components with increasing exposure. It is apparent that the component assigned to PtTe_2 decreases while the Pt_2Te_2 component increases indicating the transformation of PtTe_2 to Pt_2Te_2 . However, the transformation is incomplete and some PtTe_2 remains on the surface. From STM images it is apparent that the monolayer has completely transformed so that the remaining PtTe_2 observed in XPS is likely due to second layer PtTe_2 in the bilayer regions. The STM images also reveal the nucleation of Pt clusters on the surface with increasing Pt-deposition. Initially these clusters are primarily present in between Pt-telluride islands on the bare substrate. Once the Pt-telluride has transformed to Pt_2Te_2 , Pt-clusters also nucleate

on the PtTe_2 terraces. This suggests that vapor deposited Pt preferably incorporates into the PtTe_2 phase and only nucleates Pt-clusters once all the PtTe_2 is converted into Pt_2Te_2 .

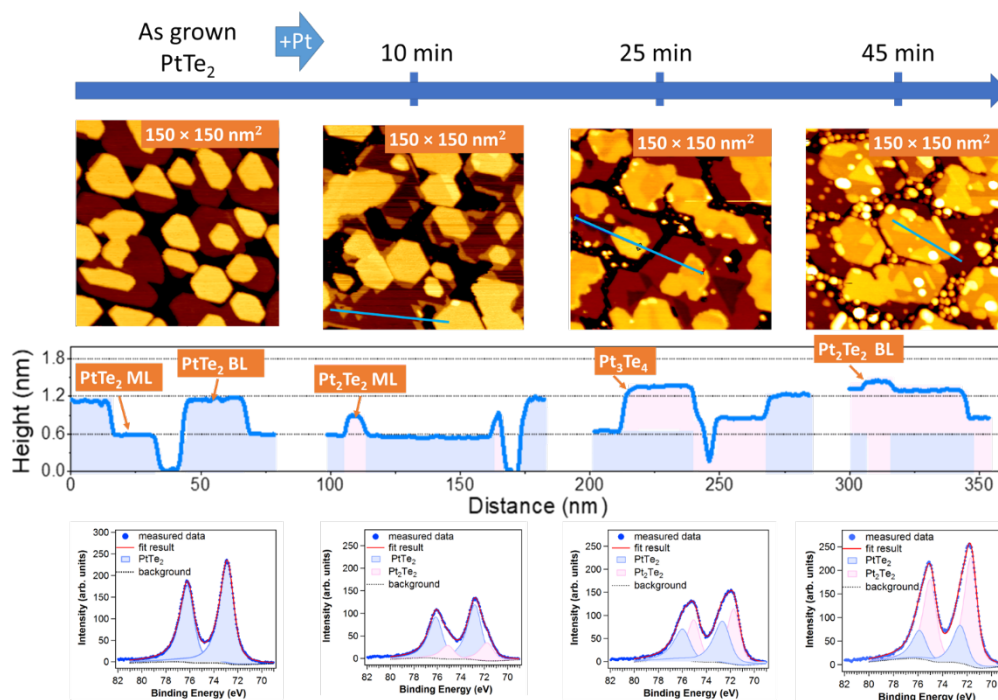


Fig. 2: Sample evolution in STM and XPS with increasing Pt-deposition. STM images and indicated line profiles show the conversion of PtTe_2 into Pt_2Te_2 . The deposition of Pt on the sample is indicated on the top. Pt was deposited at a rate of $\sim 0.01 \text{ nm/min}$. The as grown PtTe_2 sample exhibits both mono- and bi-layer PtTe_2 islands that convert into Pt_2Te_2 as Pt is deposited. Pt_2Te_2 phase exhibits slightly higher contrast as evident in the STM images and highlighted by the line profile. In the line profiles the different phases are indicated by light blue for PtTe_2 and light pink for Pt_2Te_2 regions. For higher Pt-exposures, Pt clusters are observed to form on the surface and the bare substrate region between the Pt-telluride islands. The conversion of PtTe_2 to Pt_2Te_2 is also observed in the Pt-4f core levels measured by XPS and show at the bottom of the image for different Pt-exposures. The Pt-4f is fitted with two doublets with the color of the components corresponding to Pt in a PtTe_2 environment (blue) and Pt_2Te_2 environment (pink).

First-principles calculations support the observed transformation processes. Excess Pt adsorbed on the surface of PtTe_2 strongly interact with the system giving rise to the destabilization of the Pt-Te bonds in the PtTe_2 phase (shown in Fig. S1). Such a distortion of PtTe_2 by excess Pt shows that Pt will strongly react with the substrate and form 'distorted' structures shown in Fig. S1b. For a certain concentration of Pt added to PtTe_2 , the Pt_2Te_2 phase can form, which is the lowest energy structure for this composition. Specifically, using appropriate Pt chemical potentials our calculations show that formation of Pt_2Te_2 is

favored over the nucleation of metallic Pt-clusters, as illustrated in Fig. S2. Moreover, Pt-diffusion barriers on PtTe_2 have been calculated to be around 260 meV (Fig. S1c). A low diffusion barrier facilitates the growth of the Pt_2Te_2 phase from a few nucleation sites in PtTe_2 islands. Further inspections of the STM images indicates that the Pt_2Te_2 preferentially nucleates at one edge orientations of the hexagonal PtTe_2 islands as shown in Fig. 3. For extended islands nucleation and growth of Pt_2Te_2 phases are also observed. The nucleation sites for the latter are not known, i.e., if it is homogenous or heterogenous nucleation. Nucleation density may be sensitively dependent on the kinetic parameters of deposition rate and sample temperature and these parameters have not been systematically varied in this study. The Pt_2Te_2 phase has generally a triangular shape within the PtTe_2 phase. Preferred edge nucleation and Pt_2Te_2 domain shape indicate that there is an energetically preferred phase boundary between Pt_2Te_2 and PtTe_2 . DFT calculations of the phase boundaries suggest that the phase boundary labeled 'B' in Figure 1 is energetically preferred and thus is expected to be observed in the experiments.

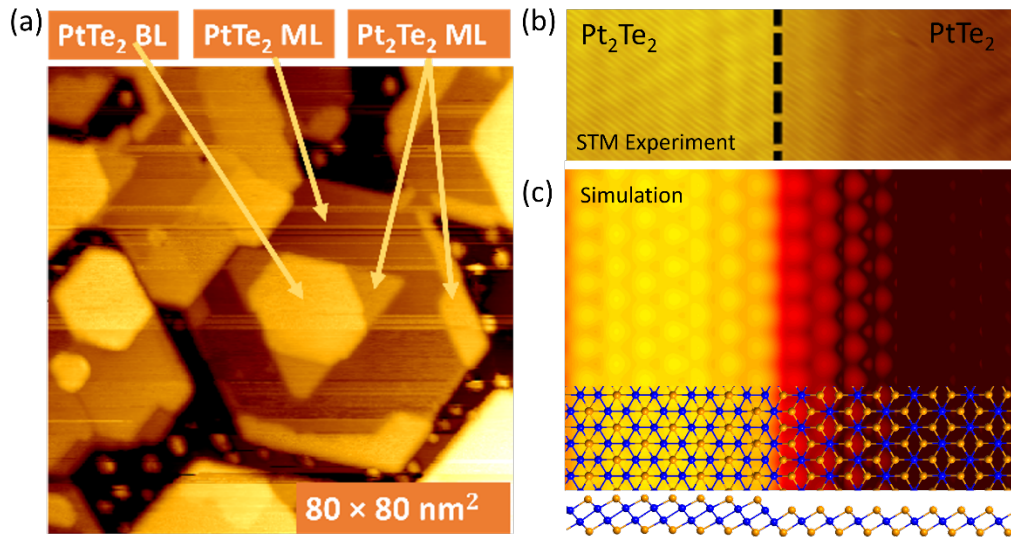


Fig. 3: STM of $\text{Pt}_2\text{Te}_2/\text{PtTe}_2$ phase coexistence. (a) STM image of a partially conversion of PtTe_2 into the Pt_2Te_2 phase. It is apparent that the initial PtTe_2 islands have hexagonal shapes. For monolayer 1T phase the two zigzag edges are identical if the substrate does not play an important role and thus a hexagonal shape is expected. Formation of Pt_2Te_2 , however preferentially occurs at only one of the two edges. Similarly, Pt_2Te_2 embedded within the PtTe_2 phase island, form preferentially triangularly shaped Pt_2Te_2 phases. As shown in Fig. 1, two different phase boundaries exist and the preference of one phase boundary over another explains the orientation of the phase boundaries in the STM image. (b) Atomically resolved STM image of interface. (c) Simulated STM image of the interface.

Making efficient electronic contacts to 2D semiconductors remains a challenge^{27,28,29,30} with covalently-bonded in-plane side-contacts generally considered to allow for better charge injections as compared to metal top contacts, because top contacts exhibit an inevitable tunnel barrier across the van der Waals gap that increases the contact resistance.³¹ High quality covalently-bonded side contacts of metals to 2D materials are, however, much more challenging to engineer and thus have mostly been studied by theoretical calculations.³¹ Detailed atomic-scale characterization and assessments of electronic properties of such side contacts are absent. The phase transformation of PtTe_2 into Pt_2Te_2 described above suggests that Pt-deposition onto PtTe_2 would not result in just a top-contact to PtTe_2 but instead a transformation of PtTe_2 into Pt_2Te_2 occurs even at low deposition temperatures. This implies the formation of a side contact of semiconducting monolayer PtTe_2 with a metallic Pt_2Te_2 phase. The structural similarity between the two phases ensures an atomically sharp contact and absence of dislocation-type defects at the interface, as the STM images of the phase-contact indicate. The controlled formation of this phase contact enables us to study the electronic structure of such a 2D metal/semiconductor side contact. In contrast to traditional buried metal/semiconductor contacts the purely 2D lateral contact is exposed to vacuum and thus can be investigated by scanning tunneling spectroscopy. To obtain the interface band alignment, both the position of the band edges relative to the Fermi-level and the work function (WF) alignment across the interface need to be determined. The former is measured directly by I-V (dI/dV) spectroscopy, while the WF differences across the interface can be assessed by field emission resonance (FER) measurements. FER spectroscopy has been widely used to determine WF modulations in 2D monolayer materials on metal substrates, e.g., for hex-BN,^{32,33} graphene,³⁴ oxide layers,^{35,36} NaCl,³⁷ or CuN³⁸. Briefly, in FER the bias voltage between an STM-tip and the sample surface is chosen such that the Fermi-level of the STM-tip lies above the vacuum level of the sample. The drop of the potential in the tunnel junction gives rise to a triangular potential well between the tip and the sample surface with discrete image potential states that are probed in the FER spectroscopy. Local changes in the substrate WF shifts these image potential states corresponding to the WF changes and thus a shift of the resonance states is a direct measure of the WF changes along the surface. While absolute WFs are difficult to extract, because of unknown STM-tip conditions, the relative difference in the WF and the spatial extent of the WF modulation can be measured accurately and this is the critical information required for the interface band alignment.

Fig. 4 shows the dI/dV spectra and FER across a $\text{Pt}_2\text{Te}_2/\text{PtTe}_2$ interface. In dI/dV spectra the Fermi-level is the reference energy at 0 eV and thus the Fermi-level of the metal is always aligned with the Fermi-level in the semiconductor. What is important is the level of the semiconductor band edges at the metal contact

and its comparison with the band edges before contact has been made, which presumably is the same as far away from the contact. For an as grown pristine PtTe_2 film the dI/dV spectrum is shown in Fig. 4(d) as the red spectrum. The calculated local density of states near the interface is presented in Fig. S3, and it is in a qualitative agreement with the experimental results. This film is p-type with the Fermi-level ~ 0.1 eV above the valence band edge. This band edge position is unaltered after contacting Pt_2Te_2 , indicating that there is no significant shift of the Fermi-level and thus no band bending, or Schottky contact. The field emission resonance, shown in Fig. 4 (b), on the other hand, indicate a shift of the WF across the interface by 0.2 eV. This shift is very sharp and occurs over less than a nanometer at the interface, indicating that the difference in the WF is accommodated by an interface dipole on the atomic scale. These measurements are summarized in an interface band diagram shown in Fig. 4(e). The calculated band edge positions relative to the vacuum level are shown in Fig. S4 for the two materials. Consistent with the experiment, a shift of the WF by about 0.2 eV is needed to obtain the observed band alignment.

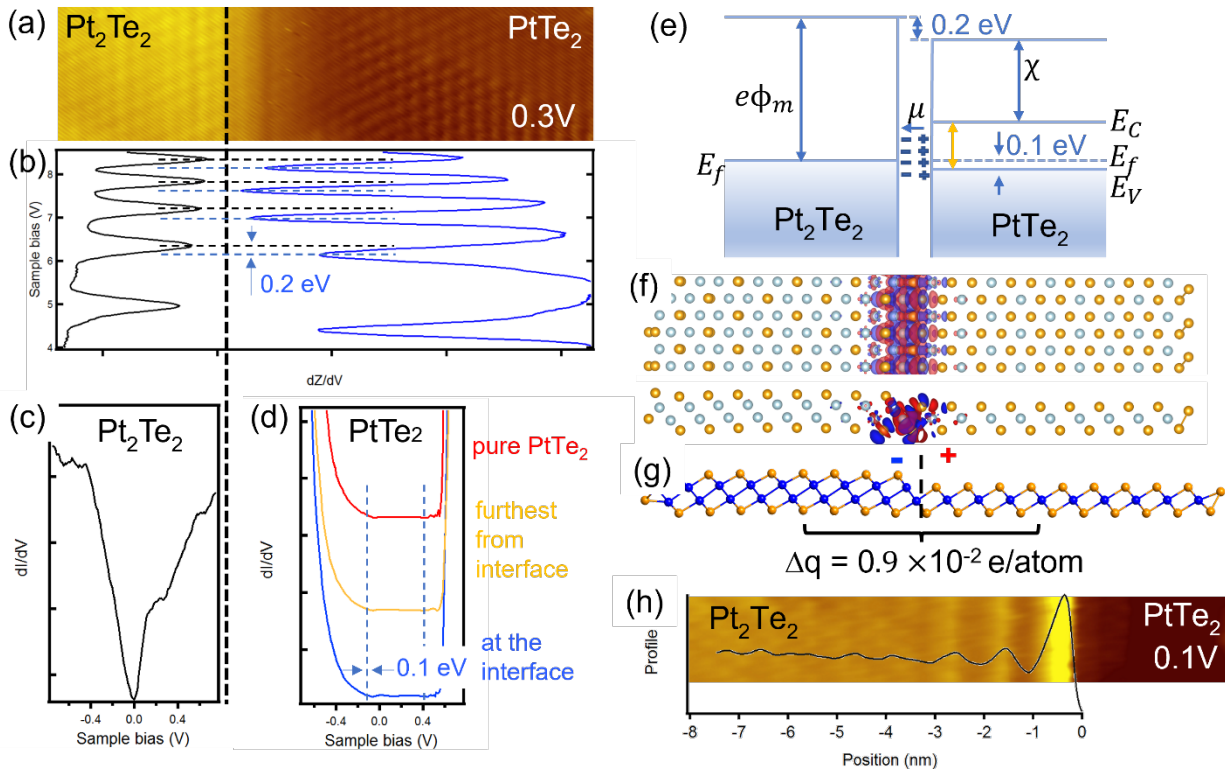


Fig. 4: Determination of electronic structure of Pt_2Te_2 - PtTe_2 metal/semiconductor interface by low temperature (20 K) STM/STS measurements and DFT. (a) atomically resolved STM image of interface. (b) Field emission resonance spectroscopy, showing a 0.2 eV lower WF of the semiconducting PtTe_2 compared to the metallic Pt_2Te_2 side of the heterojunction. (c) dI/dV spectra showing the metallic properties of Pt_2Te_2

and (d) a 0.5 eV band gap of PtTe₂. For PtTe₂ spectra of a pure PtTe₂ sample (without the presence of interfaces with Pt₂Te₂) is shown by the red spectrum, which indicates an intrinsic p-type doping level. The blue and yellow spectra are taken close and far away (~10 nm) from the interface with Pt₂Te₂. All spectra show a very similar Fermi-level position and thus indicating a flat band alignment at the interface. (e) Schematic interface electronic structure derived from the STS data. The 0.2 eV WF offset between the metal and semiconductor implies an interface dipole as indicated. (f) Charge densities derived from DFT calculations (red region = increase blue region = decrease) indicating the atomic scale of the charge redistribution. at the interface. Bader charge integration shown in (g) indicate that more electrons are 'lost' (moved to the atoms exactly at the interface) from the PtTe₂ region than for the Pt₂Te₂ region giving rise to the interface dipole. (h) STM images at low bias voltage across the Pt₂Te₂/PtTe₂ interface exhibit oscillation at the interface in the metallic PtTe₂ phase. These oscillations may be associated with Friedel oscillations due to screening of the charges at the interface.

In the simplest model of a metal-semiconductor band alignment, the Schottky-Mott model, both the WF and Fermi-level are aligned at the interface and the required band offset in the semiconductor to achieve this band alignment causes an extended charge depletion layer in the semiconductor. In contrast to metal-semiconductor contacts in 3D materials, the reduced charge screening in 2D materials is expected to give rise to a reduced charge equilibration process at 2D- heterojunctions and a carrier delocalization.³⁹ Nevertheless, the WF offset measured here at the interface implies an atomic scale interface dipole. Interface dipoles can be caused for various reasons.⁴⁰ Spillover of metal Bloch states into the semiconducting gap (like surface dipoles on metal surfaces) would cause a dipole opposite to the one measured and thus can be excluded as the main reason for the dipole. Therefore, an atomic-scale charge transfer at the interface is most likely associated with this dipole. To get further insight into the charge redistribution at the interface, we carried out DFT calculations of the difference in the electronic charge upon contact formation. It should be pointed out that contrary to the interface made from completely different materials, the Pt₂Te₂/PtTe₂ system can be split into separate Pt₂Te₂ and PtTe₂ semi-infinite sheets in several different ways, as shown in Fig. S5, which gives rise to different binding energies between the subsystems and different charge transfer. For each division of the system, the charge transfer is confined to a few atom spaces at the interface, as illustrated in Fig. 4 (f) for the division giving the highest energy release upon interface formation. To avoid the ambiguity related to the choice of the subsystems, we adopted another strategy to assess the charge redistribution. The Bader charges in the areas (four primitive cells for each material) close to the interface were calculated and compared to those in infinite Pt₂Te₂/PtTe₂ systems. The results indicated that the decrease in the electronic charge is larger in PtTe₂

system, giving rise to a difference of 0.9×10^{-2} e/atom, with positive charge accumulated in Pt₂Te₂, in agreement with the experimental data.

In general, excess charges at metal/semiconductor interfaces must be screened and giving rise to Friedel oscillations. In this 2D system such Friedel oscillations may be imaged directly by STM. At low bias voltages oscillations are observed in STM images in the metallic Pt₂Te₂ along the interface as shown in Fig. 4 (h) and these oscillations are consistent with the screening of the excess charges at the interface.

In conclusion, a compositional phase transformation in PtTe₂ is enabled by on-surface reaction with vapor deposited Pt. This implies that vapor deposition of Pt on monolayer PtTe₂ causes its transformation into metallic Pt₂Te₂ and a side-metal contact to semiconducting PtTe₂. We have shown that this configuration results in a barrier-less flat band configuration where the WF differences between metal and semiconducting part are compensated by an interface dipole at the atomic scale. Thus, the heterojunction between Pt₂Te₂ and PtTe₂ can be understood by a modified Schottky Mott rule, with the only change being to replace the WF of the free metal edge with the new effective WF. The effective interface WF is the metal WF minus the interface dipole. Similar effective WFs due to interface dipoles were invoked in metal-graphene contacts.⁴¹ Interestingly, this interface dipole is just large enough to allow for a flat band alignment and thus a barrier less metal-semiconductor junction. However, the Fermi-level of the metal lies within the semiconducting gap and thus does not pin the band edges. Thus, in applications that allow shifting of the Fermi-level in the semiconductor by gating may induce charge injection barriers. Such effects should be studied in future experiments by transport measurements and/or nano-beam photoemission studies. Enabling efficient charge injection into a material with large spin-orbit coupling like PtTe₂ is a prerequisite for making efficient spin and charge devices. The unique compositional transformation from one ordered 2D phase to another may play an important role in the development of future nano-devices. The process demonstrated here of transforming one 2D compound into another by on surface reaction with vapor deposited elements, should not be limited to the Pt-telluride system only. Other 2D materials may be transformed by similar surface reactions and thus enable a new pathway for 2D material synthesis and formation of in plane 2D heterojunctions.

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Supporting Information:

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/XXXXXXXXXXXX>

- Computational details and methods

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