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Doping of MoTe₂ via Surface Charge Transfer in Air

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we investigate by means of Kelvin probe force microscopy (KPFM) and density functional theory calculations (DFT) the doping of MoTe₂ via surface charge transfer occurring in air. Using DFT, we show that oxygen molecules physisorb on the surface and increase its work function (compared to pristine surfaces) toward p-type behavior, which is consistent with our KPFM measurements. The surface charge transfer doping (SCTD) driven by adsorbed oxygen molecules can be easily controlled or reversed through thermal annealing of the entire sample. Furthermore, we also demonstrate local control of the doping by contact



electrification. As a reversible and controllable nanoscale physisorption process, SCTD can thus open new avenues for the emerging field of 2D electronics.

KEYWORDS: surface charge transfer doping, molybdenum ditelluride, 2D materials, work function, Kelvin probe force microscopy

INTRODUCTION

Due to the plethora of properties revealed when the material dimensionality is reduced, tremendous interest was generated by the discovery and integration of graphene and other twodimensional (2D) layered materials into new structures for advanced electronic,¹⁻⁴ optoelectronic,^{5,6} and sensing applications.⁷⁻¹⁰ Enabled by recent developments in the synthesis of high-quality 2D sheets,¹¹ transition metal dichalcogenides (TMDCs) show remarkable flexibility in terms of composi-tion,^{12,13} crystal structures,^{14–16} mechanical,¹⁷ electronic,¹⁸ and optoelectronic properties.^{19,20} For example, molybdenum dichalcogenides display unique properties such as high electronic mobilities,^{3,21} excellent on/off current ratios,³ indirect to direct band gap transition as a function of thickness,²² and ambipolar field-effect transistor behavior,^{23,24} among others. Full integration of TMDCs in device applications requires a reliable control and tuning of their electronic properties. Also, being intended exclusively for 2D applications, it is essential to understand the interface properties of such materials, e.g., how the charge transport is affected by layer thickness, doping, and Schottky contact barrier. Due to a strong Fermi level pinning near the conduction band (promoted especially by sulfur vacancies), the MoS₂ exhibits *n*-type conduction, independent of the metal contact.²⁵ In contrast, MoTe₂ manifests ambipolar behavior in part due to the energy level of the Te vacancies located in the middle of the bandgap.²⁵ Therefore, a more effective and versatile control of the polarity and Fermi level tuning could be expected for MoTe₂ via surface processes, in particular through surface charge-transfer doping (SCTD).²⁶⁻²

For bulk semiconductors, substitutional doping is the method of choice to control the charge transport by replacing host atoms with impurities of different valence. However, producing charge doping by substitutional impurities is inadequate for TMDCs due to the lack of control over the dopant concentration in each layer of the material. A viable and nondestructive alternative for charge doping in 2D materials is SCTD, in which a charge transfer occurs to or from the atoms or molecules adsorbed on the surface of the material. This charge transfer is driven by the inequality between the electrochemical potential of the surface adsorbates and the Fermi level of the material. Depending on the reducing or oxidizing action of the adsorbates with respect to that material, an *n*-type or *p*-type doped surface region can be formed. The SCTD was extensively investigated on graphene for controllable charge doping²⁹ and band gap opening,³⁰ with





ACS Applied Materials & Interfaces Research Article www.acsami.org (a) (b) $\Phi_{tip} - \Phi_{surf}$ Φ_{surf}-Φ_s Evac $\Phi_{surf} \Phi_s$ Evac EC Φtip Φ_{tip} Φ_{s} EC EF V_{dc} Φ_{s} EF E۷ tip tip (d) (c) surface surfac (f) (e) Amplitude (a.u.) Amplitude (a.u.) $+ 2\omega_{..}$ 58 60 62 56 58 60 62 . 56 Frequency (kHz) Frequency (kHz)

Figure 1. Schematic of the PeakForce KPFM operation at the contact between a metallic tip and a semiconductor sample. Energy band alignment is shown (a) when there is no applied bias between the tip and the sample and (b) under a dc bias V_{dc} applied on the tip to compensate for the work function difference between the tip and the surface. Mechanical and electrical modulations of the PeakForce KPFM in the lift mode, (c) with and (d) without the applied feedback. Panels (e) and (f) show the frequency spectra of the cantilever deflection corresponding to (c) and (d), respectively. The sidebands due to the electrical modulation are at $\omega_1 \pm \omega_m$ and $\omega_1 \pm 2\omega_m$ when no feedback is applied (e) and remain only at $\omega_1 \pm 2\omega_m$ when feedback is acting on the ones at $\omega_1 \pm \omega_m$ (f).

applications in electronic devices³¹ and sensors.⁷ SCTD is also relevant for tuning the electrical and optical properties from the perspective of fabricating complementary integrated circuits, sensors, optoelectronic, photovoltaic, and other devices.^{32–34} In terms of materials, SCTD doping was reported for MoS_2 ,^{35,36} $MoTe_2$,^{37–41} and black phosphorus.⁴² Due to air adsorption, a gradual change in conductivity (from ambipolar to *p*-type) was also observed over a period of 100 days on $MoTe_2$ field-effect transistors exposed to air.⁴³ Similarly, the ambient exposure for a prolonged period was found to be responsible for the surface charge accumulation in MoS_2 flakes due to a slow oxidation of the outer layers;^{44,45} in this last case, the surface charge accumulation was in terms of electrons, making the MoS_2 surface highly *n*-doped and promoting a surface-dominant 2D current transport.

In previous works, the effect of SCTD on TMDCs was inferred mostly from transport measurements^{37-39,41} and photoelectric characterizations, e.g., Raman, photolumines-cence, and XPS measurements, ^{35,36,43,44} which predominantly show the bulk response of materials. As device miniaturization continues, the surface contribution to the electrical response of low-dimensional materials becomes comparable or even surpasses the bulk contribution. Moreover, in device-level measurements the electronic properties of the 2D TMDCs may often be compounded with those of the contacts, and it is not straightforward to distinguish or control the extent to which the surface alone contributes to electrical characteristics. Therefore, it is crucial to understand how 2D TMDCs can be doped reliably, controllably, and inexpensively via SCTD; a recent report by Luo et al. 38 also identifies a need for direct work function measurements to complement device-level studies. Here, we bring key evidence of inducing and tuning the p-doping of MoTe₂ via exposure to ambient air by

measuring and analyzing the work function variations of this TMDC as the surface adsorbate coverage is varied globally (via annealing) or locally (via contact electrification). On the basis of corroborating density functional theory (DFT) results with experimental measurements, we argue that the main mechanism of *p*-doping is the adsorption of oxygen molecules accompanied by electron transfer from the substrate, rather than the oxygen–water redox couple reported in other SCTD studies.^{26,46}

RESULTS AND DISCUSSION

The work function of a surface is directly related to its electric properties; specifically, its variations are proportional to the areal density of electrostatic dipoles formed by surface charge transfer in the presence of adsorbates (see the "Materials and Methods" section). We have used Kelvin probe force microscopy (KPFM) to observe in detail the effects of SCTD on MoTe₂ flakes of various thickness, ambient exposure, and nanoscale electrostatics. KPFM is an extension of the electrostatic force microscopy,⁴⁷ designed for more versatile measurements of the contact potential difference (CPD) between a conductive AFM tip and a sample. CPD is defined as $(\Phi_{tip} - \Phi_S)/e$, where Φ_{tip} and Φ_S are the work functions of the tip and the sample, respectively, and *e* is the elementary charge. The work function of the sample depends on a variety of parameters, including adsorption layers, surface charges, doping, and surface band bending. In Figure 1, these surface changes in the work function of a semiconductor probed by KPFM are described generically as a surface potential, Φ_{surf} . Figures 1a,b show the alignment of the energy bands of a metallic tip and an *n*-type semiconductor when the KPFM balances the CPD between the tip and the surface of the semiconductor. This balancing is the main functionality of



Figure 2. (a) Schematic stacking of $MoTe_2$ sample on Au substrate deposited on a silicon chip, as used in the KPFM measurements. (b) AFM topography (25 μ m × 25 μ m) of a 45 nm thick $MoTe_2$ flake. (c) AFM image at a smaller height scale, revealing few-layer $MoTe_2$ flakes next to the thick flake, shown in black. The lower panel of (c) shows the height profile taken along the dashed line, wherein the red line levels show the height differences between various layers of the thin flakes. (d, e) Maps of the surface potential difference (d) before annealing and (e) after annealing, with the lower panels indicating surface potential variations along the dash lines in (d) and (e), respectively. The surface potential measurements are with respect to that of the Au substrate, considered as reference. (f) Map of the tip-sample adhesive force over the scanned area shown in (a).

the technique and translates into a direct current (dc) voltage measurement, V_{dc} , that cancels out the electrostatic potential difference between the tip and surface through the feedback loop of the KPFM. In the following, the scans are discussed in terms of V_{dc} measured by PeakForce KPFM method (see the "Materials and Methods" section and section 1 in the Supporting Information).

The 2H-phase MoTe₂ flakes were mechanically exfoliated and deposited on Au-coated Si chips [Figures 2a-f]. Variations in the thickness of the flakes were observed under $100 \times$ optical magnification and measured precisely from AFM topographical scans. Figure 2b shows a typical AFM topography image around a 45 nm thick MoTe₂ flake (blue) on Au (yellow). Zooming to a smaller scale [Figure 2c] reveals image contrast due to other thinner flakes of MoTe₂ either on their own or on top of others. Indeed, small triangular layers on top of larger and thinner MoTe₂ layers can be resolved in the topography image and in height profiles [Figure 2c]. Further details of the topographic characterization, including a schematic color map of the domains of different thickness, are presented in section 4 of the Supporting Information. The MoTe₂ flakes also give contrast in the adhesion map obtained in the PeakForce tapping (PFT) mode [Figure 2f], where they are easily identified on the Au substrate due to the difference in adhesive properties.

The topography images in Figure 2 were acquired in the first pass of the PeakForce KPFM scans. In the second pass of these scans, the KPFM maps provided the CPD contrast between the tip and the scanned surface. Because Φ_{tip} is the same over the entire scan, the measured contrast corresponds in fact to the CPD between the Au substrate and the MoTe₂ flake [refer to Figure 2d]. We note that the surface potential of the flakes varies with their thickness, both before and after annealing. This dependence may not solely be attributed to the number of layers, because it involves the effect of the substrate as well. For small numbers of layers, it is expected that the Au substrate effect dominates. Indeed, the measured values [Figures 2d,e] indicate that the thin flakes (2-3 layers; 2L and 3L) have a surface potential comparable to that of the Au substrate (5.1 eV), and the single layer (1L) is at a surface potential above that of the Au substrate by 0.1 eV. For the 45 nm thick $MoTe_{2}$, we record a surface potential around 4.9 eV, indicating that the effect of the Au substrate has not decayed significantly, since the surface potential values for MoTe₂ flakes are still well above the 4.1 eV work function of bulk MoTe2.48 After annealing, some adsorbates leave the surface of the flake, and the surface potential decreases. Figures 2d,e for a 45 nm thick flake show a decrease (via annealing) of the work function by 0.2 eV. The 1L and 2L work function decrease is \sim 50 meV, i.e., 4 times smaller than that of the 45 nm thick flake. Recent works have addressed the effect of ambient environment and thickness on the *n*-type versus *p*-type response of FET made of MoTe₂,³⁸ but no quantitative reasoning was developed in detail in connection to their surface and electronic properties. Evidence of doping by surface charge transfer in common TMDCs^{35–39} and other systems⁴² suggests that surface charge transfer may play a role in determining the electronic properties of MoTe₂. We investigate here the physical origins of the variations in work function and conduction type occurring in MoTe₂ in ambient air, as well as possible ways to control such variations, locally or at the scale of the entire surface.

Focusing first on the effects of the ambient environment, we assess the role of surface adsorbates by modifying their surface coverage (experimentally) and by computing their electronic and adsorption properties. To vary the coverage on the surface, we performed annealing experiments during which the samples were held at 150 °C for 30 min to remove some of the adsorbates. The duration of 30 min was sufficient to produce significant variations of the surface potential. The annealing temperature was chosen not only to be smaller than the temperature of the 2H to 1T' phase transition (~850 $^\circ$ C)⁴⁹ but also to be safely below temperatures at which surface defects could be generated (~ 200 °C).⁴⁰ We performed KPFM on the same flakes before and immediately after annealing, with the same AFM tip and settings. The pre- and postannealing KPFM maps are shown in Figures 2d,e, respectively; the main difference immediately after annealing is a decrease of about 0.2 eV in the surface potential of the 45 nm thick MoTe₂ flake [Figure 2e]. Despite substrate effects, we observed that there is a measurable decrease in surface potential after annealing for any of the layer thicknesses investigated. The surface potential of the flakes does not reach its bulk value even after annealing, which indicates that not all the adsorbates had been removed during annealing. These observations of surface potential [Figures 2d,e] amount to a reduction of the *p*-doping of the surface via annealing, suggesting that the adsorbates control the doping.

To further test that adsorbates affect the surface properties and doping, we have monitored the surface potential of a thick, large flake (125 nm thick, covering an area of about 15 μ m × 15 μ m) for a month after annealing to see whether it recovers the values before annealing, which would happen if the adsorbate coverage reaches the level it had prior to annealing. The sample was maintained in ambient at 20 °C and 45% humidity without any extra gas pumping, and the PeakForce-KPFM scanning was performed with the same tip and settings. We have indeed found that the surface potential recovers its preannealing value and does so in an exponential manner with a characteristic time of the order of 20 days (Figure 3). Such slow recovery suggests that the large variation measured in the surface potential of the MoTe₂ flakes exposed to air is primarily due to SCTD from weakly adsorbed molecules, rather than to the surface states of MoTe₂ that would be caused by Te vacancies.⁵⁰

To gain insight into the role played by potential Te vacancies and potential chemical oxidation (either at vacancies

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Figure 3. (a) Variation in the surface potential of a 125 nm thick $MoTe_2$ flake after it was annealed at 150 °C for 30 min. The surface potential of the flake before annealing (green area) was about 4.8 eV and the slow recovery of the surface potential to its preannealing value was tracked over a time of 25 days (blue region). As shown, the recovery dependence was fitted by an exponential decay with $\Phi_0 = 4.87 \pm 0.05$ eV, $\Delta \Phi = 0.21 \pm 0.03$ eV, and $\tau = 20.5 \pm 5.7$ days. All uncertainties represent one standard deviation of the calculated values. The statistics is based on at least 50 000 measurements extracted from surface potential maps (512 pixels ×512 pixels) of areas encompassing the flake. (b) Variation in the surface potential of MoTe₂ flakes of various thickness before and after annealing at 150 °C for 30 min (1L and ML denote single- and multilayer flakes, respectively). The encircled points correspond to the flake measured in (a).

or on Te sites on the surface) in the doping of our samples, we perform XPS measurements on MoTe₂ samples before and after annealing. The details of XPS characterization and analysis are described in the "Materials and Methods" section. The main results of this XPS analysis are summarized in Figure 4 and Table 1. Figure 4 shows the XPS spectra Mo 3d, Te 3d, and O 1s levels for a typical sample, before and after the thermal annealing. XPS reveals that there is a significant amount of oxygen on the surface, as indicated by the O 1s electrons observed for the sample before annealing. The Te:Mo atomic ratio is very close to the stoichiometric 2:1, indicating a negligible amount of vacancies on the surface. Even if there were Te vacancies, then these would be passivated quickly by oxygen or perhaps OH, since the energy released in such passivation is very large (Table S2). The samples we used, however, do not oxidize easily. This observation was reported in previous work⁵¹ that we carried out on samples from the same batch. The Mo and Te abundances were not affected by the annealing. As summarized in Table 1, our analysis of XPS peaks gives binding energy peaks at ~228 eV for Mo $3d_{5/2}$, ~573 eV for Te $3d_{5/2}$, and \sim 532 eV for O 1s. These values are very close to the literature reported values for pure 2H phase MoTe₂, where the Mo $3d_{5/2}$ peak is at ~228.5 eV and Te $3d_{5/2}$ at ~573.0 eV.⁵² There is no molybdenum oxide [Mo $3d_{5/2}$ peak located at ~230 eV, vertical dashed line in Figure 4a]⁵³ or tellurium oxide [vertical



Figure 4. Typical XPS spectra for core (a) Mo 3d, (b) Te 3d, and (c) O 1s levels, before and after thermal annealing. The spectra indicate the absence or near absence of Mo-O and Te-O bonds, which would correspond to Mo $3d_{5/2}$ and Te $3d_{5/2}$ peaks at 229.6 and 576.5 eV, respectively; the vertical dash lines represent the binding energy values from literature⁵²⁻⁵⁴ corresponding to (a) Mo-O bonds and (b, c) Te-O bonds.

lines in Figures 4b,c corresponding to the Te $3d_{5/2}$ peak at ${\sim}576.5~eV$ and the O 1s peak at 530 $eV]^{52,54}$ observed on the surface, neither before nor after annealing. The elemental analysis is summarized in Table 1. This analysis reveals that after annealing, the oxygen was largely removed from the surface, as the O/Mo atomic ratio was reduced from \approx 24:1 to \approx 5:1 (Table 1). This oxygen may be in the form of O₂ and water molecules, but also can be bound in organic molecules left on the surface from the exfoliation process. Our analysis also shows that the atomic ratio between Te and Mo is very close to the ideal 2:1 value, both before and after annealing (Table 1), which is another indication that oxides (Mo–O and Te-O bonds) are not present in a significant amount.

Next, we investigate the possible physical origin of the pdoping in our experiments. Since the samples do not depart significantly from the ideal Te:Mo stoichiometry, there are no Te vacancies and hence no catalytic sites. Thus, the oxygen reduction reaction⁵⁵ in gas-phase oxygen cannot occur, so this reaction is not a factor in removing electrons from the sample. Another possible avenue for doping modulation is surface charge transfer doping^{29,46,56} enabled by oxygen solvated in the water wetting the surface, which leads to a H_2O/O_2 redox couple that drains electrons from the surface in order to achieve reaction equilibrium. Under our well-controlled conditions (ambient temperature 20.0 ± 0.1 °C, humidity 45.0 \pm 1%), the dew point for water vapor is 8.3 °C,⁵⁷ meaning that if the temperature of the MoTe₂ surface were to drop below 8.3 °C then water molecules would condense forming either liquid droplets or liquid film on MoTe2. In our experiments, the temperature of the substrate with MoTe₂ flakes never drops below 19.9 °C; therefore, any water adsorbates must be in gaseous state because the flakes are

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To provide insight into which adsorbates may contribute to doping and how, we have carried out DFT calculations (Materials and Methods) of structure, charge transfer, induced dipole density, and work function for MoTe₂ samples in the presence of H₂O, OH, and O₂. Oxygen and water molecules are ubiquitous in air in our experimental conditions, while hydroxyls could be formed if water molecules were split due to reactions with possible surface defects (Te vacancies or flake edges) that expose Mo atoms. XPS analysis revealed that nitrogen could be present, but at a significantly lower concentration than oxygen; hence, we did not carry out DFT calculations for nitrogen molecules on the surface. For samples without Te vacancies, we expect H_2O and O_2 to be physisorbed, while hydroxyls may only be chemisorbed due to their high reactivity. These expectations are born out in the DFT calculations carried out for situations corresponding to 25% adsorbate coverage (this choice for coverage value was made to keep calculations simpler). Figures 5a-c show some possible adsorption configurations for H₂O, hydroxyl, and O₂, along with the adsorption energies and relevant distances from the adsorbates to the surface. We are not necessarily looking for the most stable configurations as much as we are interested in finding situations where adsorption (i) is energetically favorable, and (ii) produces a charge transfer that is consistent, at least qualitatively, with the work function changes determined in our experiments. This is because in our samples at room temperature and ambient conditions it is unlikely that one type of adsorbate in only one configuration is present on the surface; rather, a mixture of water and oxygen will be present in various configurations with favorable adsorption energies, amounting collectively to an overall induced surface dipole pointing into the surface.

We adopt the convention that a positive adsorption energy indicates binding with the surface, i.e., adsorption energy is defined as the difference between (i) the energy of the surface and a separate molecule (or radical) and (ii) the energy of the surface with the adsorbate on it (section 2 in the Supporting Information). The strongest binding occurs for OH (chemisorbed at a distance of 2.06 Å), and the weakest binding occurs for H_2O (physisorbed at a distance of 3.67 Å). The oxygen molecule has a stronger adsorption than water, but it is still physisorbed at a distance of 3.56 Å. Tables listing distances and adsorption energies for 1-3 ML of MoTe₂ are included in section 2 in the Supporting Information.

We have also calculated the change in work function due to the presence of each adsorbate on the surface. Not surprisingly,

Table 1. Results of XPS Spectra Analysis Showing the Peak Positions of Core Electrons and Atomic Ratio to Mo before and after Sample Annealing

element	level	peak position before annealing (eV)	peak position after annealing (eV)	atomic ratio to Mo (before)	atomic ratio to Mo (after)
Mo 3 Mo 3 Te 30	Mo $3d_{5/2}$	228.18 ± 0.05	228.30 ± 0.03	1	1
	$Mo \ 3d_{3/2}$	231.27 ± 0.04	231.41 ± 0.04	1	1
Те	Te $3d_{5/2}$	572.87 ± 0.05	572.98 ± 0.04	199 ± 0.17	2.01 ± 0.07
10	Te 3d _{3/2}	583.23 ± 0.04	583.40 ± 0.04	1.77 ± 0.17	2.01 + 0.07
0	O 1s	532.07 ± 0.07	532.22 ± 0.05	24.2 ± 1.87	5.14 ± 0.43



Figure 5. Possible favorable adsorption configurations for (a) H_2O , (b) OH, and (c) O_2 on a 3 ML MoTe₂ surface at 25% coverage (only the top MoTe₂ layer is shown, for clarity); the isosurfaces show the transferred electron density, with positive and negative values colored yellow and blue, respectively. The adsorption energy, distance, and work function change are included under each potential energy. For reference, the work function of the bare MoTe₂ 3 ML surface is 4.7 eV at the level of theory used here. Work function changes (from the bare surface value) can be understood from the competition between the dipole density **D** due to the permanent moment of the adsorbate (pointing away from the surface) and the induced dipole density **p** (pointing into the surface, and due to the electron transfer to the adsorbate). (d-f) Plane-averaged electron density $\Delta \rho(z)$ transferred in the presence of (d) H_2O , (e) OH, and (f) O_2 . (g-i) Dipole integral $\eta(z)$ ("Materials and Methods" section) for (g) H_2O , (h) OH, and (i) O_2 on MoTe₂. The dipole density induced at the surface is $p = e \lim_{z \to \infty} \eta(z)$. Negative values for p signify that the induced dipoles point into the surface. The vertical dotted lines in (d-i) corresponds to the location of the top Te layer, and the vertical colored bands show the extent of the adsorbates along z.

the polar adsorbates OH and H₂O decrease the work function due to their permanent electric dipole oriented away from the surface. While for either OH and H₂O there maybe be an effective charge transfer with the surface, its effect on the work function is obliterated to a large extent by their permanent dipole pointing outward. In general, the calculated and the measured values of the work function are the result of a competition between the density of permanent dipoles [D in Figures 5a,b] and the surface dipole created via electron transfer to or from the adsorbates [p in Figures 5a-c]. In the case of adsorbed water (configuration in Figures 5), the value of the induced dipole density p is rather small, and the contribution of permanent dipoles to the work function dominates and decreases the work function. For OH, the (opposite) permanent and induced dipole densities are of similar magnitude at this coverage, which is why in this case the work function is close to that of the bare surface and hence inconsistent with the KPFM measurements. The presence of

OH on the surface is also ruled out by the XPS measurements, which show no shift in the O 1s level and no Te-O bonds, i.e., no shifts in the Te 3d peaks (Figure 4). The O_2 molecule is not polar, so no permanent dipole exists (D = 0). From the DFT calculations, we have found that physisorption of oxygen molecules on the MoTe₂ surface significantly increases the work function (from 4.7 eV without oxygen, to 5.3 eV for 25% oxygen coverage). This work function change is consistent with an electron transfer from the surface to the adsorbate. When computing the electron transfer density (Materials and Methods), we have found that for all adsorbates the transferred electron density has an oscillatory character [Figures 5d-f], which makes it difficult to assess whether electrons were (or were not) effectively transferred to or from the surface. Certainly, our computed work function variations point to that conclusion, but a direct, independent confirmation based on the induced surface dipole and its direction is still necessary. To this end, we have computed the density of the induced



Figure 6. Time evolution of a +10 V charged patch over an $MoTe_2$ flake: (a) Topography of the flake with an extra monolayer delimited by crosses and dashed border in the upper part of the flake. (b) KPFM surface potential over (a). (c) Relaxation of the surface potential after contact electrification over the black and red triangle shown in (a) and (b); (d-g) KPFM surface potential evolution after contact electrification.

dipoles, which is proportional to the asymptotic value of the dipole integral (see the "Materials and Methods" section) plotted in Figures 5g-i. For the case of water, the dipole integral is nearly zero, as the electron density transferred is 2 orders of magnitude smaller than those for OH or O₂ [Figures 5d-f]. For OH and O₂, the dipole integrals are negative [Figures 5h,i], providing direct evidence that electron transfer occurs from the surface to OH and O₂, hence rendering the surface p-type. By comparing the computed work function variations with those from experiments, we note that only the adsorption of O2 increases the work function, which is explained by the lack of a permanent dipole for oxygen. Although we have not carried out an extensive study of all possible energy configurations for O2 on MoTe2 oxygen is more electronegative than Te (bounded to Mo); hence, some electronic charge will always transfer from MoTe₂ to O₂ molecules, rendering the surface p-doped. The computed work function increase of 0.6 eV at 25% oxygen coverage is higher than that recorded experimentally (0.15 eV difference before and immediately after annealing in Figure 3), likely because in experiments the coverage associated with physisorbed oxygen molecules is smaller than that assumed in the DFT calculations. Nevertheless, the DFT-calculated increase of Φ_{MoTe_2} is comparable with the average difference (0.7-0.8 eV) between the work function of long-term airexposed flakes measured by KPFM and the reported bulk value of the work function of MoTe₂.

Inherently modified by the electronic state of the surface, the surface potential of the air-exposed $MoTe_2$ flakes shows significant variations as the $MoTe_2$ flakes change in thickness. At very small thickness, the electron-depleted regions created by SCTD can extend across the flake's thickness and morph

into an inversion region, with the Fermi level pushed very close to the valence band. Indeed, the surface potential showed a monotonous increase with the decrease in thickness, from about 4.8 eV on flakes thicker than 100 nm to about 5.0 eV on flakes of 5 nm in thickness (refer to the preannealing values in Figure 3). Furthermore, the surface potential measured over monolayers was slightly above that of the Au substrate, which suggests a complete screening of the monolayer MoTe₂ flakes by the adsorbed molecules. A decrease of ~200 meV was measured in the surface potential of few MoTe₂ flakes of various thickness right after annealing (refer to Figure 3). The fact that the change in the surface potential after annealing was independent of thickness indicates an exclusive surface response expressed by the outer layers of the flakes. These observations are consistent with the previous field-effect transistor characteristics⁵¹ measured on MoTe₂ flakes from the same batch as the ones investigated in this study. As a function of thickness, it was found that the field-effect transistors made on flakes thicker than 65 nm are *n*-type. On flakes with thickness in between 65 and 15 nm, they show an ambipolar response, and on flakes thinner than 10 nm, they are p-type.⁵⁸

Being restricted to the top layers of the flakes, SCTD can be controlled not only globally (by annealing, as discussed above) but also locally. One way to do this would be using scanning probe microscopy. A conductive AFM tip brought into contact with a flake will inject (remove) electric charges to (from) the flake, depending on the bias voltage between the tip and sample. The AFM mode used for contact electrification was PFT AFM that operates in an intermittent contact mode to reduce the contact time as much as possible and avoid the damage that would be produced by friction in a full-contact

diminish the adsorbate coverage.

scanning mode. Over a scanned area, a positively biased tip (with the sample grounded) will release the negatively charged adsorbates, which in turn will induce charge redistribution in the subsurface region. With the molecular layer removed from the scanned area, the surface potential will experience a decrease from the value set initially by SCTD, signaling a less *p*-doped region. The minimum bias voltage at which notable changes in the surface potential of the charged area were observed was about 3 V, and most of our contact electrification experiments were done with +10 V on the tip. No changes in the surface potential were made when negative biases up to -10 V on the tip (sample grounded) were tried on long-time air-exposed flakes. This is likely because the surface is already negatively charged, and a negatively biased tip would not

Figure 6 shows the contact electrification of a MoTe₂ flake over a rectangular patch of 0.5 μ m \times 0.5 μ m that was performed at +10 V on the tip and flake grounded through direct contact with the Au substrate. From regular scanning, a single layer was found to sit on top of large flake (50 nm thick, 10 μ m² large) and loosely detached around its edges; this monolayer is marked by crosses and particles along its border in Figure 6a. Further topographic and KPFM analysis, including average height profiles and surface potential profiles, demonstrate that there is indeed one monolayer in the region marked by crosses in Figure 6a (refer to section 5 in the Supporting Information). The charging patch was written halfand-half over the monolayer and the nearby compacted flake black triangle over the thick flake, and red triangle over the top monolayer in Figure 6a]. Prior to contact electrification, the KPFM mapping [Figure 6b] indicates a slight increase in the surface potential over the monolayer due to the extra charges brought by the adsorbates underneath the monolayer. After contact electrification, the change in the surface potential was monitored for few days by repeatedly performing KPFM scanning over a large area containing the charged patch, with the same tip and at the same conditions. Selected KPFM maps are shown in Figures 6d-g, documenting the recovery of surface adsorbates over time. The adsorbates recover faster over the detached monolayer compared to the compacted flake area of the patch, presumably due to their access to flake edges and under the surface. The entire process is summarized in Figure 6c, where the measured changes in the surface potential over the two halves of the charged patch are shown separately. It is also interesting to note that the recovery process exhibits two different time scales in both cases. In the first stage, a faster recovery of about 100 meV in the surface potential occurs over a time interval of about 0.5 days [left side of Figure 6c]. A second, slower stage occurs over a time scale of 10-15 days after the first day from charging and recovers by 25 to 50 meV [refer to the right side of Figure 6c]. The associated time constants are included in Figure 6c for both triangular areas during both stages of recovery. The physical origin of the twostage recovery process after contact electrification likely stems from the fact that large voltages (+10 V) lead to two kinds of charging: the first by removing the oxygen molecules physisorbed on the surface and the second by having electrons tunneling from the sample to the tip. When the tip is removed, the faster process is the equilibration of the electronic density across the sample, whereby electrons from regions next to the charged patch and from the lower layers flow toward the depleted patch. The spatial charge redistribution induced by contact electrification was also probed by the tip-to-sample

contact current measurements (section 3 in Supporting Information). The second process is a slow readsorption of oxygen molecules, which is similar to that encountered after annealing. While the reabsorption was not monitored daily after 8 days from the contact electrification, we have confirmed that surface potential was back to the original values [as in Figure 6b] in a KPFM scan made after 25 days.

Once some of the adsorbates are partially removed from MoTe₂ surfaces by either thermal annealing or contact electrification and the surface charge is decreased to a certain degree, the contact electrification can be used to modulate up and down the local surface potential. To illustrate that the recovery process could be accelerated, we have carried out additional contact electrification experiments in which we applied bias voltages in several stages and analyzed the maps of the surface potential after each stage. The recovery occurs on a faster time scale (less than 2 h), as shown in section 4 of the Supporting Information. Another possible way to carry out restoration could be to give up the strictly controlled environment (temperature and humidity) and flow oxygen in argon carrier gas in the vicinity of the surface; this would target recovery for the entire surface. Such approach, however, would require tedious calibration of the oxygen content and time/ exposure to ensure similar adsorption on the surface. Unlike the air-exposed MoTe₂ surface on which only positively biased AFM tips had induced changes in the surface potential, on partially adsorbate-saturated areas, it was possible to either decrease (by a positively biased tip) or increase (by a negatively biased tip) the local surface potential as illustrated in section 4 of Supporting Information. This demonstrates the possibility of creating adjacent rewritable regions of different charge density and variable surface potential that can be used for nanoscale complementary logic electronics.⁵⁹⁻⁶

CONCLUSION

The results presented here complement the current literature on controlled doping TMDCs in several ways. First, our results demonstrate controlled *p*-type doping by physisorbed oxygen on stoichiometric surfaces (with no vacancies). In contrast, previous works³⁹ attributed *n*-type doping on MoTe₂ to Te vacancies, and the switch to p-type doping to H₂O/O₂ redox couple occurring in air. While vacancies are effectively *n*-type dopants, we have shown here via XPS characterization that there is no significant amount of vacancies (passivated or not by oxygen) and, using DFT calculations, that physisorbed neutral O₂ molecules on a MoTe₂ surface with no vacancies drain electron density from the surface, making it *p*-type. We have performed DFT calculations for the case with vacancies as well (section 2 in Supporting Information), and found that the adsorption energy of O₂ is significantly larger on a Te vacancy, 3.47 eV, compared to 0.13 eV adsorption energy of O_2 on pristine MoTe₂. Such a large value of the computed adsorption energy of O_2 on a Te vacancy ensures that a temperature of 150 °C cannot lead to any desorption of the O_2 molecules from the vacancies; hence, there would not be any reversibility of the SCTD process such as that we have shown in Figure 3a.

Another aspect in which this work complements the literature is that we present a direct assessment of the charge transfer at the MoTe₂ surface, both experimentally (via work function measurements) and theoretically (via DFT calculations). Most literature reports use more "downstream" measurements such as transport measurements (or I/V characteristics)³⁷⁻³⁹ or photoelectric characteriza-

tions.^{35,36,43,44} As such, our results provide an important piece of the puzzle in that it is a direct evidence of SCTD process and its tunability via oxygen concentration on the surface. Furthermore, we also illustrate local control of the surface charge doping by contact electrification using the probe of an electrostatic force microscope as a floating gate. After annealing or contact electrification, the air-exposed MoTe₂ surfaces exhibit a slow reversal processes of readsorption of oxygen, restoring of the *p*-type doping. These investigations can complement typical field effect transistor measurements used to extract electronic transport properties of devices based on 2D materials. As a reversible and controllable nanoscale physisorption process, SCTD can thus open new avenues for the emerging field of 2D-TMDC electronics.

MATERIALS AND METHODS

Sample Preparation. $MoTe_2$ flakes used in this work were mechanically exfoliated from bulk single crystals that were grown by chemical vapor transport (CVT) method using polycrystalline $MoTe_2$ powder and $TeCl_4$ (ca. 5 mg/cm³) transport agent sealed in evacuated quartz ampules. Temperature in the hot and cold zones was 800 and 700 °C, respectively. Growth duration of $MoTe_2$ crystals was 140 h. This method produced pure 2H phase of $MoTe_2$ as confirmed by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), and Raman spectroscopy.⁵⁸

KPFM. The PF-KPFM mode implemented on MultiMode Bruker AFM (Bruker, Santa Barbara, CA, USA) was used in this work to perform surface potential measurements. A detailed description and illustration of the mechanical and electrical modulations driven during a PF-KPFM is discussed in section 1 of Supporting Information. In all the measurements, the Au substrate supporting the MoTe₂ flakes was ground, and the KPFM signals were routed through the conductive AFM probe. The quantitative assessment of the KPFM measurements was probed on scans on a reference sample consisting of strips of Au and Al patterned on an n-doped Si substrate (Bruker, Santa Barbara, CA, USA). The average CPD between Au and Al was 0.80 eV with a standard deviation of 0.05 eV, which is close to the difference between the work functions of the two metals, 5.1 eV for Au and 4.2 eV for Al. Several conductive AFM probes were used during the measurements. They were either PtIr probes (SCM-PIT from Bruker, Santa Barbara, CA, USA, with nominal frequency around 60 kHz and spring constant around 1 N/m) or diamond-coated probes (DCP from K-TEK, Wilsonville, OR, USA, with nominal first resonance frequency around 150 kHz and spring constant around 10 N/m). No significant differences were observed in the measured CPD with the two sets of the AFM probes used, and systematic checks were performed on the Au/Al reference sample to ensure the consistency of the measurements. Unless specified, most of the contact electrifications were performed by applying +10 V on the tip (sample ground) during PeakForce tapping (PFT) scans over delimited areas at 1 s per scan line and 512×512 pixels per scan. The PFT mode was preferred to the contact mode because of its intermittent contact operation; no material damage was observed over the biased areas. In each KPFM scan, the lift height was minimized as much as possible such that the AFM tip was just few nanometers above the surface during its oscillation in the lift mode.

X-ray Photoemission Spectroscopy (XPS) Measurements. All of the XPS spectra were acquired on mechanically exfoliated flakes placed on Au substrates. In the mechanical exfoliation process, organic species adhere to the sample and have been analyzed separately: The peak locations of Mo and Te 3d levels remain the same regardless of the annealing, which indicates that the organic species play no significant role in chemical passivation or doping. XPS data were acquired with a Kratos Axis UltraDLD XPS/UPS system, using the monochromatic Al K α line. The base pressure of the analysis chamber is 10⁻⁸ Torr. Calibration of XPS spectra in the pristine sample was done with the C–C bond in C 1s peak and set to BE = 284.5 eV with all the spectra shifting to lower binding energy by 0.4 eV. The peak positions for the after annealing sample were shifted by the same amount for consistency. The C peak comes from the adventitious carbon contamination and it is commonly observed in noncarbonous samples. The C 1s peak before the annealing shows the presence of organics in the form of C–C, C–O, and C=O bonds. Thermal annealing largely removes the C=O bonds and C–O, indicating the removal of surface oxide, while the C–C components are still present on the surface. All samples were characterized at normal takeoff angle. The XPS spectra are fit using GL(30) (70% Gaussian, 30% Lorentzian functions). The Fermi level was calibrated using atomically clean gold, and the presented spectra were calibrated with respect to the Fermi level at zero binding energy. Thermal annealing at 150 °C for 15 min was performed inside the transfer chamber with a base pressure of $\approx 10^{-7}$ Torr.

Density Functional Theory Calculations. We have performed all the DFT calculations within the framework of the generalized gradient approximation (GGA) as implemented in the Vienna Ab-initio Simulation Package (VASP).⁶² We have also incorporated the D3 functional of Grimme et al.⁶³ to describe the van der Waals interactions between layers and those between the adsorbates and the MoTe₂ slab; the adsorbates are placed symmetrically on each side of the slab. As such, no dipole corrections are necessary. All calculations were carried out without spin polarization; we have repeated some of the calculations using spin-polarization, and found no significant changes in the results. We use projector-augmented wave (PAW) pseudopotentials⁶⁴ to perform structural relaxations, as well as work function calculations. We use a plane-wave energy cutoff of 540 eV (600 eV) and Γ -centered 5 × 5 × 1 grid (10 × 10 × 1 grid) for the structural relaxations (work function calculations), and a force criterion of $10^{-2}~eV/{\rm \AA}$ for ionic convergence. We introduce a vacuum spacing of 18 and 27 Å along the c-axis for the structural relaxations and work-function calculations, respectively, in order to avoid undue interaction effects between adjacent periodic images of the computational cell.

In order to compute the work function, we calculate the surface average electrostatic potential V(z) in the supercell as a function of the coordinate z perpendicular to the surface. The value of this potential in the middle of the vacuum spacing represents the potential far away from the surface $z \to \infty$), from which we subtract the energy of the Fermi level E_{Fermi} to obtain the work function, $\Phi = \lim_{z\to\infty} V(z) - E_{\text{Fermi}}$ We compute the transferred electronic density $\Delta \rho(\mathbf{r})$ in the presence of adsorbates as

$$\Delta \rho(\mathbf{r}) = \rho_{\rm ads/MoTe_2}(\mathbf{r}) - \rho_{\rm pristine MoTe_2}(\mathbf{r}) - \rho_{\rm ads}(\mathbf{r})$$

where $\mathbf{r} = (x, y, z)$ is the location in the computational cell, and the terms of the right-hand side correspond to the relaxed adsorbate on the surface $(\rho_{\rm ads/MoTe})$, to the surface alone with the adsorbate removed and no relaxation ρ_{MoTe_2}), and adsorbate alone with the surface removed and no relaxation (ρ_{ads}) . Since the transferred electron density usually displays oscillations van der Waals bonded systems^{65–67} [also shown in Figure 5d–f], it is necessary to compute the electrostatic dipole density in order to investigate if indeed net electronic charge has been transferred upon adsorption of adsorbates. Following approaches similar to those in other 2D literature,^{65,68} we first compute the function (dubbed here the dipole integral) $\eta(z) = -\int_0^\infty z\Delta \rho(z) dz$, in which $\Delta \rho(z)$ is the plane-averaged transferred density and the integration limits are from the middle of the surface slab (lower limit 0) to the middle of the vacuum spacing in the supercell (upper limit, symbolically written as ∞). The induced dipole moment density will then be $p = e \lim \eta(z) = e \eta(c/2)$, where e is the elementary charge and the last equality assumes that the

domain of z coordinates in the supercell ranges from 0 to c (both these values representing the midpoint of the surface slab). With the above definition for the dipole integral, a positive (negative) induced dipole density p implies that electrons are transferred to the surface (to the adsorbate), and the dipole points away (toward) the surface. In the absence of permanent dipoles, the change in work function

from a bare surface to one with adsorbates is proportional to the induced dipole density $\Phi_{ads/MoTe_2} - \Phi_{pristineMoTe_2} = -\frac{p}{\epsilon_0}$ where ϵ_0 is the permittivity of vacuum.

DISCLAIMER

Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c04339.

PeakForce Kelvin probe force microscopy (PF-KPFM) measurements; density functional calculations of $MoTe_2$ with adsorbates; current mapping over surface charge-transfer doped areas; nanoscale patterning of the surface potential of $MoTe_2$ flakes; stack structure of $MoTe_2$ flakes from KPFM contrast (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A. Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, *306*, 666–669.

(2) Schwierz, F. Graphene Transistors. Nat. Nanotechnol. 2010, 5, 487-496.

(3) Radisavljevic, B.; Radenovic, A.; Brivio, J.; Giacometti, V.; Kis, A. Single-Layer MoS₂ Transistors. *Nat. Nanotechnol.* **2011**, *6*, 147–150.

(4) Akinwande, D.; Petrone, N.; Hone, J. Two-Dimensional Flexible Nanoelectronics. *Nat. Commun.* **2014**, *5*, 5678.

(5) Wang, Q. H.; Kalantar-Zadeh, K.; Kis, A.; Coleman, J. N.; Strano, M. S. Electronics and Optoelectronics of Two-Dimensional Transition Metal Dichalcogenides. *Nat. Nanotechnol.* **2012**, *7*, 699– 712.

(6) Xia, F. N.; Wang, H.; Jia, Y. C. Rediscovering Black Phosphorus as an Anisotropic Layered Material for Optoelectronics and Electronics. *Nat. Commun.* **2014**, *5*, 5.

(7) Schedin, F.; Geim, A. K.; Morozov, S. V.; Hill, E. W.; Blake, P.; Katsnelson, M. I.; Novoselov, K. S. Detection of Individual Gas Molecules Adsorbed on Graphene. *Nat. Mater.* **2007**, *6*, 652–655.

(8) Li, H.; Yin, Z.; He, Q.; Li, H.; Huang, X.; Lu, G.; Fam, D. W. H.; Tok, A. I. Y.; Zhang, Q.; Zhang, H. Fabrication of Single- and Multilayer MoS₂ Film-Based Field-Effect Transistors for Sensing NO at Room Temperature. *Small* **2012**, *8*, 63–67.

(9) Koppens, F. H. L.; Mueller, T.; Avouris, P.; Ferrari, A. C.; Vitiello, M. S.; Polini, M. Photodetectors Based on Graphene, Other Two-Dimensional Materials and Hybrid Systems. *Nat. Nanotechnol.* **2014**, *9*, 780–793.

(10) Choi, W.; Choudhary, N.; Han, G. H.; Park, J.; Akinwande, D.; Lee, Y. H. Recent Development of Two-Dimensional Transition Metal Dichalcogenides and Their Applications. *Mater. Today* **2017**, *20*, 116–130.

(11) Kim, S. K.; Kwak, J.; Ciobanu, C. V.; Kwon, S. Y. Recent Developments in Controlled Vapor-Phase Growth of 2-D Group 6 Transition Metal Dichalcogenides. *Adv. Mater.* **2019**, *31*, 1804939.

(12) Zhang, H. Ultrathin Two-Dimensional Nanomaterials. ACS Nano 2015, 9, 9451-9469.

(13) Novoselov, K. S.; Mishchenko, A.; Carvalho, A.; Castro Neto, A. H. 2d Materials and Van Der Waals Heterostructures. *Science* **2016**, 353, No. aac9439.

(14) Duerloo, K. A. N.; Li, Y.; Reed, E. J. Structural Phase Transitions in Two-Dimensional Mo- and W-Dichalcogenide Monolayers. *Nat. Commun.* **2014**, *5*, 4214.

(15) Cho, S.; Kim, S.; Kim, J. H.; Zhao, J.; Seok, J.; Keum, D. H.; Baik, J.; Choe, D. H.; Chang, K. J.; Suenaga, K.; Kim, S. W.; Lee, Y. H.; Yang, H. Phase Patterning for Ohmic Homojunction Contact in $MoTe_2$. Science **2015**, 349, 625–628.

(16) Wang, R.; Yu, Y.; Zhou, S. Y.; Li, H.; Wong, H.; Luo, Z.; Gan, L.; Zhai, T. Adv. Funct. Mater. 2018, 28, 1802473.

(17) Bertolazzi, S.; Brivio, J.; Kis, A. Stretching and Breaking of Ultrathin Mos2. ACS Nano 2011, 5, 9703–9709.

(18) Cheng, R.; Jiang, S.; Chen, Y.; Liu, Y.; Weiss, N.; Cheng, H. C.; Wu, H.; Huang, Y.; Duan, X. F. Few-Layer Molybdenum Disulfide Transistors and Circuits for High-Speed Flexible Electronics. *Nat. Commun.* **2014**, *5*, 5143.

(19) Lopez-Sanchez, O.; Lembke, D.; Kayci, M.; Radenovic, A.; Kis, A. Ultrasensitive Photodetectors Based on Monolayer MoS₂. *Nat. Nanotechnol.* **2013**, *8*, 497–501.

(20) Octon, T. J.; Nagareddy, V. K.; Russo, S.; Craciun, M. F.; Wright, C. D. Fast High-Responsivity Few-Layer MoTe₂ Photo-detectors. *Adv. Opt. Mater.* **2016**, *4*, 1750–1754.

(21) Podzorov, V.; Gershenson, M. E.; Kloc, C.; Zeis, R.; Bucher, E. High-Mobility Field-Effect Transistors Based on Transition Metal Dichalcogenides. *Appl. Phys. Lett.* **2004**, *84*, 3301–3303.

(22) Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F. Atomically Thin MoS_2 : A New Direct-Gap Semiconductor. *Phys. Rev. Lett.* **2010**, 105, 136805.

(23) Zhang, Y. J.; Ye, J. T.; Matsuhashi, Y.; Iwasa, Y. Ambipolar MoS₂ Thin Flake Transistors. *Nano Lett.* **2012**, *12*, 1136–1140.

(24) Lin, Y. F.; Xu, Y.; Wang, S. T.; Li, S. L.; Yamamoto, M.; Aparecido-Ferreira, A.; Li, W. W.; Sun, H. B.; Nakaharai, S.; Jian, W. B.; Ueno, K.; Tsukagoshi, K. Ambipolar MoTe₂ Transistors and Their Applications in Logic Circuits. *Adv. Mater.* **2014**, *26*, 3263–3269.

(25) Kim, C.; Moon, I.; Lee, D.; Choi, M. S.; Ahmed, F.; Nam, S.; Cho, Y.; Shin, H. J.; Park, S.; Yoo, W. J. Fermi Level Pinning at Electrical Metal Contacts of Monolayer Molybdenum Dichalcogenides. *ACS Nano* **2017**, *11*, 1588–1596.

(26) Strobel, P.; Riedel, M.; Ristein, J.; Ley, L. Surface Transfer Doping of Diamond. *Nature* **2004**, *430*, 439–441.

(27) Qi, D.; Chen, W.; Gao, X.; Wang, L.; Chen, S.; Loh, K. P.; Wee, A. T. S. Surface Transfer Doping of Diamond (100) by Tetrafluoro-

Tetracyanoquinodimethane. J. Am. Chem. Soc. 2007, 129, 8084–8085.

(28) Ristein, J. Surface Transfer Doping of Semiconductors. *Science* **2006**, 313, 1057–1058.

(29) Levesque, P. L.; Sabri, S. S.; Aguirre, C. M.; Guillemette, J.; Siaj, M.; Desjardins, P.; Szkopek, T.; Martel, R. Probing Charge Transfer at Surfaces Using Graphene Transistors. *Nano Lett.* **2011**, *11*, 132–137.

(30) Ohta, T.; Bostwick, A.; Seyller, T.; Horn, K.; Rotenberg, E. Controlling the Electronic Structure of Bilayer Graphene. *Science* **2006**, *313*, 951–954.

(31) Yu, W. J.; Liao, L.; Chae, S. H.; Lee, Y. H.; Duan, X. F. Toward Tunable Band Gap and Tunable Dirac Point in Bilayer Graphene with Molecular Doping. *Nano Lett.* **2011**, *11*, 4759–4763.

(32) Zhang, X. J.; Shao, Z. B.; Zhang, X. H.; He, Y. Y.; Jie, J. S. Surface Charge Transfer Doping of Low-Dimensional Nanostructures toward High-Performance Nanodevices. *Adv. Mater.* **2016**, *28*, 10409–10442.

(33) Shao, Z. B.; Jie, J. S.; Jiang, T. H.; Wu, X. F.; Li, K.; Xia, F. F.; Zhang, X. J.; Zhang, X. H. Cds Nanoribbon-Based Resistive Switches with Ultrawidely Tunable Power by Surface Charge Transfer Doping. *Adv. Funct. Mater.* **2018**, *28*, 1706577.

(34) Shao, Z. B.; Jiang, T. H.; Zhang, X. J.; Zhang, X. H.; Wu, X. F.; Xia, F. F.; Xiong, S. Y.; Lee, S. T.; Jie, J. S. Memory Phototransistors Based on Exponential-Association Photoelectric Conversion Law. *Nat. Commun.* **2019**, *10*, 1294.

(35) Mouri, S.; Miyauchi, Y.; Matsuda, K. Tunable Photoluminescence of Monolayer MoS_2 Via Chemical Doping. *Nano Lett.* **2013**, *13*, 5944–5948.

(36) Tongay, S.; Zhou, J.; Ataca, C.; Liu, J.; Kang, J. S.; Matthews, T. S.; You, L.; Li, J. B.; Grossman, J. C.; Wu, J. Q. Broad-Range Modulation of Light Emission in Two-Dimensional Semiconductors by Molecular Physisorption Gating. *Nano Lett.* **2013**, *13*, 2831–2836.

(37) Qu, D. S.; Liu, X. C.; Huang, M.; Lee, C.; Ahmed, F.; Kim, H.; Ruoff, R. S.; Hone, J.; Yoo, W. J. Carrier-Type Modulation and Mobility Improvement of Thin MoTe₂. *Adv. Mater.* **2017**, *29*, 1606433.

(38) Luo, W.; Zhu, M. J.; Peng, G.; Zheng, X. M.; Miao, F.; Bai, S. X.; Zhang, X. A.; Qin, S. Q. Carrier Modulation of Ambipolar Few-Layer MoTe₂ Transistors by Mgo Surface Charge Transfer Doping. *Adv. Funct. Mater.* **2018**, *28*, 1704539.

(39) Liu, J. K.; Wang, Y. Y.; Xiao, X. Y.; Zhang, K. A.; Guo, N.; Jia, Y.; Zhou, S. Y.; Wu, Y.; Li, Q. Q.; Xiao, L. Conversion of Multi-Layered Mote2 Transistor between P-Type and N-Type and Their Use in Inverter. *Nanoscale Res. Lett.* **2018**, *13*, 291.

(40) Zhu, H.; Wang, Q. X.; Cheng, L. X.; Addou, R.; Kim, J. Y.; Kim, M. J.; Wallace, R. M. Defects and Surface Structural Stability of MoTe₂ under Vacuum Annealing. *ACS Nano* **2017**, *11*, 11005–11014.

(41) Wu, E. X.; Xie, Y.; Zhang, J.; Zhang, H.; Hu, X. D.; Liu, J.; Zhou, C. W.; Zhang, D. H. Dynamically Controllable Polarity Modulation of MoTe₂ Field-Effect Transistors through Ultraviolet Light and Electrostatic Activation. *Science Advances* **2019**, *5*, eaav3430.

(42) Xiang, D.; Han, C.; Wu, J.; Zhong, S.; Liu, Y.; Lin, J.; Zhang, X.-A.; Ping Hu, W.; Ozyilmaz, B.; Neto, A. H. C.; Wee, A. T. S.; Chen, W. Surface Transfer Doping Induced Effective Modulation on Ambipolar Characteristics of Few-Layer Black Phosphorus. *Nat. Commun.* **2015**, *6*, 6485.

(43) Wang, S. P.; Zhang, R. J.; Zhang, L.; Feng, L. F.; Liu, J. Accurate Change of Carrier Types within Ultrathin $MoTe_2$ Field-Effect Transistors with the Time Exposed to Ambient Air. J. Mater. Sci. 2019, 54, 3222–3229.

(44) Siao, M. D.; Shen, W. C.; Chen, R. S.; Chang, Z. W.; Shih, M. C.; Chiu, Y. P.; Cheng, C. M. Two-Dimensional Electronic Transport and Surface Electron Accumulation in MoS₂. *Nat. Commun.* **2018**, *9*, 1442.

(45) Peto, J.; Ollar, T.; Vancso, P.; Popov, Z. I.; Magda, G. Z.; Dobrik, G.; Hwang, C. Y.; Sorokin, P. B.; Tapaszto, L. Spontaneous Doping of the Basal Plane of MoS₂ Single Layers through Oxygen Substitution under Ambient Conditions. *Nat. Chem.* **2018**, *10*, 1246– 1251.

(46) Chakrapani, V.; Angus, J. C.; Anderson, A. B.; Wolter, S. D.; Stoner, B. R.; Sumanasekera, G. U. Charge Transfer Equilibria between Diamond and an Aqueous Oxygen Electrochemical Redox Couple. *Science* **2007**, *318*, 1424–1430.

(47) Nonnenmacher, M.; O'Boyle, M. P.; Wickramasinghe, H. K. Kelvin Probe Force Microscopy. *Appl. Phys. Lett.* **1991**, *58*, 2921–2923.

(48) Shimada, T.; Ohuchi, F. S.; Parkinson, B. A. Work Function and Photothreshold of Layered Metal Dichalcogenides. *Jpn. J. Appl. Phys., Part 1* 1994, 33, 2696–2698.

(49) Oliver, S. M.; Beams, R.; Krylyuk, S.; Kalish, I.; Singh, A. K.; Bruma, A.; Tavazza, F.; Joshi, J.; Stone, I. R.; Stranick, S. J.; Davydov, A. V.; Vora, P. M. The Structural Phases and Vibrational Properties of $Mo_{1-x}W_xTe_2$ Alloys. 2d Materials 2017, 4.

(50) Chen, B.; Sahin, H.; Suslu, A.; Ding, L.; Bertoni, M. I.; Peeters, F. M.; Tongay, S. Environmental Changes in MoTe₂ Excitonic Dynamics by Defects-Activated Molecular Interaction. *ACS Nano* **2015**, *9*, 5326–5332.

(51) Zhang, F.; Zhang, H. R.; Krylyuk, S.; Milligan, C. A.; Zhu, Y. Q.; Zemlyanov, D. Y.; Bendersky, L. A.; Burton, B. P.; Davydov, A. V.; Appenzeller, J. Electric-Field Induced Structural Transition in Vertical MoTe₂- and Mo_{1-x} W_x Te₂-Based Resistive Memories. *Nat. Mater.* **2019**, *18*, 55–61.

(52) Ueno, K.; Fukushima, K. Changes in Structure and Chemical Composition of α -MoTe₂ and β -MoTe₂ During Heating in Vacuum Conditions. *Appl. Phys. Express* **2015**, *8*, 095201.

(53) Baltrusaitis, J.; Mendoza-Sanchez, B.; Fernandez, V.; Veenstra, R.; Dukstiene, N.; Roberts, A.; Fairley, N. Generalized Molybdenum Oxide Surface Chemical State Xps Determination Via Informed Amorphous Sample Model. *Appl. Surf. Sci.* **2015**, *326*, 151–161.

(54) Kong, H.; Yeo, J. B.; Lee, H. Y. A Study on the Properties of Tellurium-Oxide Thin Films Based on the Variable Sputtering Gas Ratio. *J. Korean Phys. Soc.* **2015**, *66*, 1744–1749.

(55) Zhang, C. L.; Hwang, S. Y.; Trout, A.; Peng, Z. M. Solid-State Chemistry-Enabled Scalable Production of Octahedral Pt-Ni Alloy Electrocatalyst for Oxygen Reduction Reaction. *J. Am. Chem. Soc.* **2014**, *136*, 7805–7808.

(56) Aguirre, C. M.; Levesque, P. L.; Paillet, M.; Lapointe, F.; St-Antoine, B. C.; Desjardins, P.; Martel, R. The Role of the Oxygen/ Water Redox Couple in Suppressing Electron Conduction in Field-Effect Transistors. *Adv. Mater.* **2009**, *21*, 3087–3091.

(57) Wood, L. A. The Use of Dew-Point Temperature in Humidity Calculations. J. Res. Natl. Bur. Stand., Sect. C 1970, 74C, 117–122.

(58) Rani, A.; DiCamillo, K.; Krylyuk, S.; Debnath, R.; Taheri, P.; Paranjape, M.; Korman, C. E.; Zaghloul, M. E.; Davydov, A. V. Control of Polarity in Multilayer MoTe₂ Field-Effect Transistors by Channel Thickness. *Low-Dimensional Materials and Devices* **2018**, *10725*, 41.

(59) Chang, Y. M.; Yang, S. H.; Lin, C. Y.; Chen, C. H.; Lien, C. H.; Jian, W. B.; Ueno, K.; Suen, Y. W.; Tsukagoshi, K.; Lin, Y. F. Reversible and Precisely Controllable P/N-Type Doping of $MoTe_2$ Transistors through Electrothermal Doping. *Adv. Mater.* **2018**, *30*, 1706995.

(60) Kim, S.; Kim, T. Y.; Lee, K. H.; Kim, T. H.; Cimini, F. A.; Kim, S. K.; Hinchet, R.; Kim, S. W.; Falconi, C. Rewritable Ghost Floating Gates by Tunnelling Triboelectrification for Two-Dimensional Electronics. *Nat. Commun.* **2017**, *8*, 15891.

(61) Seo, S.-Y.; Park, J.; Park, J.; Song, K.; Cha, S.; Sim, S.; Choi, S.-Y.; Yeom, H. W.; Choi, H.; Jo, M.-H. Writing Monolithic Integrated Circuits on a Two-Dimensional Semiconductor with a Scanning Light Probe. *Nat. Electron.* **2018**, *1*, 512–517.

(62) Kresse, G.; Furthmuller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54*, 11169–11186.

(63) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (Dft-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, 132, 154104.

(64) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 1758–1775.

(65) Murata, Y.; Nie, S.; Ebnonnasir, A.; Starodub, E.; Kappes, B. B.; McCarty, K. F.; Ciobanu, C. V.; Kodambaka, S. Growth Structure and Work Function of Bilayer Graphene on Pd(111). *Phys. Rev. B: Condens. Matter Mater. Phys.* **2012**, *85*, 205443.

(66) Ebnonnasir, A.; Kodambaka, S.; Ciobanu, C. V. Strongly and Weakly Interacting Configurations of Hexagonal Boron Nitride on Nickel. *Surf. Rev. Lett.* **2015**, *22*, 1550078.

(67) Ebnonnasir, A.; Narayanan, B.; Kodambaka, S.; Ciobanu, C. V. Tunable MoS_2 Bandgap in MoS_2 -Graphene Heterostructures. *Appl. Phys. Lett.* **2014**, *105*, 031603.

(68) Giovannetti, G.; Khomyakov, P. A.; Brocks, G.; Karpan, V. M.; van den Brink, J.; Kelly, P. J. Doping Graphene with Metal Contacts. *Phys. Rev. Lett.* **2008**, *101*, 026803.

SUPPORTING INFORMATION:

Doping of MoTe₂ via surface charge-transfer in air

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1. PeakForce Kelvin probe force microscopy (PF-KPFM) measurements

The KPFM used in this work was the frequency modulation KPFM implementation in the peakforce tapping (PFT) mode of a Bruker Multimode AFM (Bruker, Santa Barbara, CA, USA), the so-called PeakForce KPFM.¹ A detailed description and illustration of the mechanical and electrical modulations driven during a PF-KPFM scan line are shown in Figure S1. PeakForce KPFM works in a dual-pass scanning line mode, with topography and mechanical tip-sample tapping interaction resolved in the first pass and V_{dc} measurement in the second pass when the tip is lifted at some height above the surface and follows the topographical profile determined in the first pass. In the first scanning pass, the AFM operates in PFT mode with the piezo scanner mechanically vibrated in the z-direction at a set frequency (e.g., 2 kHz)and feedback on the peak magnitude of the contact force. In the second pass, the cantilever is mechanically oscillated at its first resonance frequency ω_1 and electrically modulated by an ac bias at ω_m (usually 2 kHz), $V_{ac}\sin(\omega_m t)$. As the result of this modulation, two sidebands emerged at $\omega_1 \pm \omega_m$ in the frequency spectrum of the cantilever deflection and their cancelation is made by adjusting the dc component, V_{dc}, of the bias voltage on the cantilever. This is in fact the nullification of the electrostatic force (in amplitude modulation KPFM) or its force gradient (in frequency modulation KPFM) between the plates of the tipsample capacitor. The voltage V_{dc} measured by PeakForce as KPFM potential was with the frequency modulation applied on the tip and the Au substrate grounded, so $V_{CPD} = -V_{dc}$. In this configuration, an increase (decrease) in the measured V_{dc} corresponds to a decrease (increase) in the surface potential.



Figure S1. Schematic of PF-KPFM operation with signals from one of the scans over a MoTe₂ flake on Au substrate. In the main scan line, the piezo scanner is driven by a 2 kHz mechanical oscillation with feedback on the peak force experienced by the cantilever. Extra resonances (due to the compliance of the cantilever used) appear in between taps at the first resonance of the cantilever with no influence on scanning. In the lift scan, the cantilever is raised at a given height and follows the topography acquired in the main scan. Additionally, during the lift, the cantilever is driven mechanically at its first resonance frequency ω_1 and electrically at a modulation frequency of $\omega_m = 2$ kHz and a dc KPFM voltage. The KPFM voltage is obtained from the feedback signal that cancels out the components at $\omega_1 \pm \omega_m$.

In the KPFM measurement configuration described above, the CPD between the tip and sample, the CPD between MoTe₂ flakes and Au can be directly obtained from a KPFM map over a region encompassing MoTe₂ flakes and exposed Au areas, without the need of knowing the work function of the AFM probe. The quantitative assessment of the KPFM measurements was probed on scans on a reference sample consisting of strips of Au and Al patterned on an n-doped Si substrate (Bruker, Santa Barbara, CA, USA).¹ The average CPD between Au and Al was 0.80 eV with a standard deviation of 0.05 eV, which is close to the difference between the work functions of the two metals, 5.1 eV for Au and 4.2 eV for Al.

Several conductive AFM probes were used during the measurements. They were either PtIr probes (SCM-PIT from Bruker, Santa Barbara, CA, USA, with nominal frequency around 60 kHz and spring constant around 1 N/m) or diamond coated probes (DCP from K-TEK, Wilsonville, OR, USA, with nominal first resonance frequency around 150 kHz and spring constant around 10 N/m). The PtIr probes have sharper tips and provide a better spatial resolution, whereas the diamond coated probes are more robust and were used in contact electrification measurements. No significant differences were observed in the measured CPD with the two sets of the AFM probes used, and systematic checks were performed on the Au/Al reference sample to ensure the consistency of the measurements. Unless specified, most of the contact electrifications were performed by applying ± 10 V on the tip (sample grounded) during PeakForce Tapping scans over delimited areas (either micrometer or half-micrometer size) areas at 1 s per scan line and 512×512 pixels per scan. The PeakForce Tapping mode was preferred to the contact mode because of its intermittent contact operation; no material damage was observed over the biased areas. In each KPFM scan, the lift height was minimized as much as possible such that the AFM tip was just few nanometers above the surface during its oscillation in the lift mode.

2. Density functional calculations of MoTe₂ with adsorbates

We have performed DFT calculations at the level of generalized gradient approximation² with the D3 van der Waals correction³ for H₂O, OH, and O₂ adsorbed on MoTe₂ in order to assess the effect of these adsorbates on work function of surfaces with 1, 2, and 3L, at 25% areal coverage. The adsorbates are disposed on both faces of the slab, and slabs with vacancies were considered as well; in the latter case, the adsorbates were placed directly above the vacancy and allowed to relax. 1 L with vacancies on both sides is unstable at this coverage. The main text reports only the values for 3L. We include here the work function (Table S-I), adsorption energies (Table S-II), and distances to the upper Te atomic plane (Table S-III) for the all computed cases. The adsorption energy ΔE_{ads} is defined here as

 $\Delta E_{ads} = E_{\text{pristine MoTe}_2} + E_{ads} - E_{ads/MoTe}_2,$

where $E_{\text{pristine MoTe}_2}$, E_{ads} and $E_{ads/MoTe}_2$, are the energy of the slab without adsorbate, the energy of the adsorbate by itself (in the absence of substrate), and the energy of the system consisting in the adsorbate relaxed on the substrate, respectively. By this convention, the adsorption energy is positive if adsorption is thermodynamically favorable.

	bare	H ₂ O	OH	O ₂	vac	vac+H ₂ O	vac+OH	vac+O ₂
1 L	4.79	3.29	4.58	5.88	4.58	-	-	-
2 L	4.74	3.15	4.55	5.81	4.44	4.74	4.44	5.45
3 L	4.66	3.12	4.46	5.25	4.52	5.66	4.52	5.25

Table S1. Calculated work functions (eV) for MoTe₂ slabs.

Table S2. Adsorption energies (eV) for MoTe₂ slabs.

	H ₂ O	OH	O ₂	vac+H ₂ O	vac+OH	vac+O ₂
1 L	0.037	1.53	0.13	-	-	-
2 L	0.040	1.89	0.13	0.33	5.10	3.47
3 L	0.040	1.22	0.13	0.25	5.12	3.47

Table S3. Distances (Å) to the Te atomic place for $MoTe_2$ slabs. Distances are measured from the top Te atomic plane to the closest O atom. A negative value signifies that the (closest) O atom is below the Te plane.

	H_2O	OH	O_2	vac+H ₂ O	vac+OH	vac+O ₂
1 L	3.653	1.969	3.488	-	-	-
2 L	3.700	2.059	3.501	1.691	-0.396	-0.741
3 L	3.670	2.059	3.559	1.839	-0.396	-0.742

The water molecule relaxed with the O atom towards the surface for bare surfaces. When the H_2O molecule was placed above the vacancy, it relaxed with the H atoms pointing down, i.e. reverted the direction of its permanent dipole. This is reflected in the work function change from 3.12 eV (H_2O on 3 L)

to 5.66 eV (H₂O on a Te vacancy, 3 L, flipped dipole) values in Table S-I. The work function values of MoTe₂ determined in Table S-I are in reasonable agreement with a recent experimental estimation,⁴ as well as with our own measurements. The work function decreases with the number of layers, and increases when oxygen adsorbed: molecules are these trends are seen in our experiments, and the numerical differences stem primarily from the fact the oxygen coverage in experiments and DFT calculations are not the same.

3. Current mapping over surface charge-transfer doped areas

The removal of the negative charges and negatively charged adsorbates during scanning with a positivelybiased tip (sample grounded) has also been confirmed by current-AFM mapping (Figure S2). After the topography of the top of a thick MoTe₂ flake was PeakForce imaged in Tapping (Figure S2.a), a



Figure S2. (a) AFM topography of a thick unannealed MoTe₂ flake. (b) KPFM surface potential after charging over a 1 μ m × 1 μ m patch (tip bias at +10 V); the change in the surface potential is shown with respect to the uncharged area. (c) Averaged-contact PF-TUNA current map over the area shown in (a) and (b) with clear reduction in the contact current over the charged area. (d) Average profile of the contact current over the box highlighted in (c). (e) Schematic of the current measurement and charge distribution for an unannealed area with negatively charged adsorbates (left) and an area where the negative charges were removed via scanning with a positively-biased tip (right).

1 μ m × 1 μ m area was selected and scanned again with a +10 V biased tip. Subsequently, the decrease in the surface potential over the charged area was demonstrated by imaging the surface potential over a region that includes the charged area (Figure S2.b). As discussed in the main text, the decrease in the surface potential indicates a removal of the surface adsorbates. Along with the adsorbates, some of the negative charges are also removed. As a result, a reduction in the tip-sample contact current is expected; indeed, this was observed in current-AFM mapping (Figure S2.c) over the same area imaged by KPFM (Figure S2.b). The current-AFM mapping was performed with the PeakForce Tunneling AFM (PF-TUNA)⁵ module of the MultiMode AFM (Bruker, Santa Barbara, CA, USA).¹ A diamond coated AFM probe (DCP from K-

TEK, Wilsonville, OR, USA) was used for the PF-TUNA current mapping under a bias voltage of -8 V on the sample (Figure S2.e).

4. Nanoscale patterning of the surface potential of MoTe₂ flakes

As detailed in the main text, on long-term air-exposed MoTe₂ flakes, the surface potential can only be decreased by contact electrification with positively biased tip, through the removal of the negativelycharged adsorbates. No increase in the surface potential was obtained with negatively biased tips on longterm air-exposed MoTe₂ flakes. However, when some of the adsorbates were removed by thermal annealing (150 °C for 30 minutes), it was possible to either decrease (positively biased tip and sample grounded) or increase (negatively biased tip and sample grounded) the surface potential of the flakes (refer to Figure S3). This is because, once some of the adsorbed molecules were removed and the surface potential reduced by annealing, it was possible to modulate the surface potential further by contact electrification: more negatively charged adsorbates were removed with positive voltages on the tip and some negative charges were transferred from the tip to the sample with negative voltages on the tip. The extra negatively charged patch (dark square in Figure S3.c) has a shorter lifetime than the positively charged patches (light yellow squares in Figure S3.b, c, and d). This demonstrates the possibility of creating adjacent rewritable regions of different charge density and variable surface potential that can be used for nanoscale complementary logic electronics.⁶⁻⁸



Figure S3. KPFM surface potential over an annealed MoTe₂ flake on Au substrate (with Au as zero reference): (a) before charging; (b) after 30 min from +10 V charging (brighter patch on the flake); (c) after 2 h and 40 min from +10 V charging (brighter patch on the flake) and 10 min after -10 V charging (darker patch on the flake); (d) after 5 h from + 10 V charging (brighter patch on the flake) and 3 h and 30 min after the -10 V charging (no visible contrast at the negatively charged location). Each image covers an area of 16 μ m x 4 μ m and all images share the same color scale bar shown on the right side of the figure.

Furthermore, the surface potential of the same area of a MoTe₂ flake can be modulated back and forth by contact electrification performed at various bias voltages. Figure S4a shows the surface potential over a region of $5 \ \mu m \ x \ 5 \ \mu m$ of a long-term air-exposed MoTe2 flake right after a +10 V contact electrification. The contact electrification was done in PFT (tip biased at +10 V and sample grounded) over an area of $1 \ \mu m \ x \ 1 \ \mu m$ (the upper left corner of the image). After the contact electrification, the surface potential of the scanned area decreased by about 300 meV (bright patch in Figure S4a) with respect to the surface potential of the uncharged flake. The surface potential of the charged area was then mostly restored by a subsequent contact electrification performed over the same area, but with the tip biased at $-5 \ V$. As shown in Figure 4Sb, the restoration of the surface potential was not complete, and some alterations were still present even after a subsequent -10 V electrification over the same area (refer to Figure S4c). It was only after a second contact electrification at -10 V that no differences were observed anymore between the charged and uncharged areas (Figure S4d). It is therefore possible to modulate back and forth the surface potential of a free-absorbent MoTe₂ surface by different voltages of positive and negative polarity and control the local surface charge doping. Each PFT scan for contact electrification mapping was performed in about 8 min and each KPFM scan for surface potential imaging in about 16 min.



Figure S4. KPFM surface potential over a 90 nm thick and long-term air-exposed MoTe₂ flake (no annealing): (a) right after +10 V charging. The charging was done by contact electrification with the AFM tip biased at +10 V while scanning in PFT over an 1 μ m x 1 μ m area located in the upper-left corner of the image (brighter patch); (b) after -5 V charging over the charged area shown in a); (c) after an additional -10 V charging over the same area; d) after a second additional -10 V charging over the same area. Each image covers an area of 5 μ m x 5 μ m and all images have the same color scale bar. The surface potential is scaled with respect to that of the uncharged area.

5. Stack structure of MoTe₂ flakes from KPFM contrast

The stack structure of the $MoTe_2$ flakes can be easily identified from the KPFM color contrast in corroboration with topography and/or mechanical contrast (see the main text for discussion). Here we give further details for two examples that were used in the main text for the identification of some few-layer flakes.

A) One and two-layers MoTe₂ flakes.

In the example discussed in Figure 2, the KPFM image shows strong contrast between a 45 thick and onelayer (1L)/ two-layers (2L) MoTe₂ flakes. On the scale used to show this contrast (Figure S5a), there does not appear to be sufficient contrast to distinguish between 1L and 2L flakes. However, once the scale bar is reduced, the 2L regions can be easily distinguished in Figure S5b, with blue associated to 1L and red to 2L. Some enhancement (red towards yellow in Figure S5b) in the surface potential around the edges of the 2L regions can be attributed to detachments and/or charge/particle accumulation. On the reduced color scale of the Figure S5b, the KPFM contrast of the 45 nm thick flake is saturated (bright yellow). The height difference between 1L and 2L regions is shown along a scan line (dashed line in Figures S5a and b) in Figure S5c (same as in Figure 2 of the main text). By corroborating the information from topography, mechanical contrast (Figure 2b in the main text), and KPFM, the stack structure of the flakes imaged is shown in Figure S5d in the form of colored domains.



Figure S5. (a) and (b) KPFM maps over MoTe₂ flakes on Au substrate: in (a), a strong contrast is observed between Au and a 45 nm thick MoTe₂ flake and in (b) the color scale was reduced to enhance the contrast between 1L and 2L MoTe₂ flakes. (c) The height profile across the dashed line shown in (a) and (b) showing the height difference between 1L and 2L regions; (d) Color-coded stack structure of the regions identified within the area shown in (a) and (b).

B) One-layer on top of bulk MoTe₂ flake.



Figure S6. (a) Topography and (b) KPFM surface potential maps of MoTe₂ flake with an extra layer on top; (c) and (d) average profiles across the same region delimited by a rectangular box $(2.0 \ \mu m \ x \ 0.8 \ \mu m)$ in each of the maps shown in (a) and (b), respectively. The direction along the average profiles is indicated by arrows on the short sides of the box.

The extra layer on top of the bulk flake discussed in the Figure 6 of the main text is easily identified in the upper part of the KPFM map by color contrast (Figure S6b). In the topography map (Figure S6a), the layer is less visible due to the large topographical variations across the area (larger than what is shown in Figure 5a of the main text) and occasional particles. The edges of the extra layer can still be distinguished rationally in the topography maps by small ripples pointing up (these correspond to the darkest contrast in the KPFM map), and by the string of particles aligned along these edges. On some regions across the border, we made quantitative measurements of the average height profiles across rectangular boxes, on both topography and KPFM maps. In the average height profile shown in Fig. S6c, a step height of about half a nanometer was measured between the flat part of the bulk and the flat part of the extra layer. This is consistent with the height of one MoTe₂ monolayer (≈ 0.62 nm). The border is identified in Fig. S6c by a large bump, which is due to the particles aligned along the border of the monolayer that are present inside the rectangular box. Across the border, the average surface potential (Figure S6d) captured within the average box shows a variation of about 30 meV, most likely due to the extra adsorbates underneath the layer.

Disclaimer: Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

References:

1. Li, C. Z.; Minne, S.; Hu, Y.; Ma, J.; He, J.; Mittel, H.; Kelly, V.; Erina, N.; Guo, S.; Mueller, T. *Application Note #140, PeakForce Kelvin Probe Force Microscopy (Bruker Nano Surfaces)* **2013**

2. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Physical Review Letters* **1996**, 77, 3865-3868.

3. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (D F T-D) for the 94 Elements H-Pu. *Journal of Chemical Physics* **2010**, 132, Art. no. 154104.

4. Zhu, M.; Luo, W.; Wu, N.; Zhang, X.-a.; Qin, S. Engineering Few-Layer Mo Te₂ Devices by Co/Hbn Tunnel Contacts. *Applied Physics Letters* **2018**, 112, Art. no. 183102.

5. Li, C. Z.; Minne, S.; Pittenger, B.; Mednick, A.; Guide, M.; Nguyen, T.-Q. *Application Note* #132, *Simultaneous Electrical and Mechanical Property Mapping at the Nanoscale with PeakForce TUNA (Bruker Nano Surfaces)* **2011**.

6. Chang, Y. M.; Yang, S. H.; Lin, C. Y.; Chen, C. H.; Lien, C. H.; Jian, W. B.; Ueno, K.; Suen, Y. W.; Tsukagoshi, K.; Lin, Y. F. Reversible and Precisely Controllable P/N-Type Doping of Mo Te₂ Transistors through Electrothermal Doping. *Advanced Materials* **2018**, 30, Art. no. 1706995.

7. Kim, S.; Kim, T. Y.; Lee, K. H.; Kim, T. H.; Cimini, F. A.; Kim, S. K.; Hinchet, R.; Kim, S. W.; Falconi, C. Rewritable Ghost Floating Gates by Tunnelling Triboelectrification for Two-Dimensional Electronics. *Nature Communications* **2017**, *8*, Art. no. 15891.

8. Seo, S.-Y.; Park, J.; Park, J.; Song, K.; Cha, S.; Sim, S.; Choi, S.-Y.; Yeom, H. W.; Choi, H.; Jo, M.-H. Writing Monolithic Integrated Circuits on a Two-Dimensional Semiconductor with a Scanning Light Probe. *Nature Electronics* **2018**, 1, 512-517.