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# Hidden Surface Channel in Two-dimensional Multilayers

- 3 Youkyung Seo<sup> $\S, \uparrow, \#$ </sup>, Soo Yeon Kim<sup> $\S, \uparrow, \#$ </sup>, Yeeun Kim<sup> $\uparrow, ¥$ </sup>, Chulmin Kim<sup>II</sup>, Byung Chul Lee<sup>II</sup>, Yoon Hee
- 4 Park<sup>§</sup>, Minji Chae<sup>§</sup>, Youjin Hong<sup>§</sup>, Min Kyung Seong<sup>§</sup>, Changhyun Ko<sup> $\dagger$ , §, ‡</sup>, Alessandro Cresti<sup> $\Delta$ </sup>,

5 Christoforos Theodorou<sup>4</sup>, Gyu Tae Kim<sup>II</sup>, and Min-Kyu Joo<sup>†,§,‡,\*</sup>

- 6 <sup>§</sup>Department of Applied Physics, Sookmyung Women's University, Seoul 04310, Republic of
- 7 Korea
- 8 <sup>†</sup>Department of Physics, Sookmyung Women's University, Seoul 04310, Republic of Korea
- <sup>9</sup> <sup>¥</sup>Department of Physics and Astronomy, Seoul National University, Seoul 08826, Republic of
- 10 Korea
- 11 <sup>II</sup>School of Electrical Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul
- 12 02841, Republic of Korea
- <sup>13</sup> <sup>‡</sup>Institute of Advanced Materials and Systems, Sookmyung Women's University, Seoul 04310,
- 14 Republic of Korea
- 15 <sup>A</sup>Univ. Grenoble Alpes, Univ. Savoie Mont Blanc, CNRS, Grenoble INP, IMEP-LAHC, 38000
- 16 Grenoble, France
- 17
- 18 \*E-mail: mkjoo@sookmyung.ac.kr
- <sup>#</sup>These authors contributed equally to this work.
- 20
- 21 **KEYWORDS**: two-dimensional materials, multilayers, carrier transport, surface doping,
- 22 interlayer resistance
- 23

1 Abstract: Numerous carrier scatterers, such as atomic defects, fixed oxide charges, 2 impurities, chemical residues, and undesired surface adsorbates, including oxygen and water 3 molecules, strongly degrade the carrier mobility of atomically thin two-dimensional (2D) 4 materials. However, the effect of surface adsorbates and surface oxidation on the carrier density 5 profile along the thickness of 2D multilayers is not well known, particularly for a substantial 6 interruption in the formation of the top-surface channel. Here, we uncover a hidden surface 7 channel in *p*-type black phosphorus and *n*-type rhenium disulfide multilayers originating from 8 undesired ambient adsorbates and surface oxides that not only populate hole density (or reduce 9 electron density) but also suppress carrier mobility. The absence of a second peak in the 10 transconductance curve under ambient conditions indicates the disappearance of the top-11 surface channel inside the 2D multilayers, which is a possible indicator for the cleanliness of the top surface and can be used in gas sensor applications. Moreover, the negligible variation 12 13 in the drain bias polarity-dependent turn-on voltage for the bottom channel under ambient 14 conditions validates the exclusive contribution of surface adsorbates to the formation of the top 15 channel in 2D multilayers. Our results provide a novel insight into the distinct carrier transport 16 in 2D optoelectronic devices and diverse sensors.

#### 1 **1. Introduction**

2 Atomically thin two-dimensional (2D) materials, such as graphene, black phosphorus (BP), 3 and transition-metal dichalcogenides (TMDs), have demonstrated unique low-dimensional 4 physical properties with chemically inert surfaces (without out-of-plane dangling bonds), such 5 as quantum phase transition [1], Coulomb drag [2], exciton condensation [3], quantum 6 interference [4], and quantum spin Hall effect [5]. However, these novel 2D physical properties 7 are often hampered and even distorted by various Coulomb impurities, such as atomic defects, 8 fixed oxide charges, impurities, chemical residues, and undesired surface adsorbates, including 9 oxygen and water molecules [6–10], resulting in undesired excess carrier doping [11], surface 10 oxidation [12], and mobility degradation [13,14]. In addition to these vulnerabilities of 2D 11 monolayers, theoretical studies have predicted that the effective mass increases as the number 12 of layers decreases in most 2D materials [15], leading to a relatively low intrinsic carrier 13 mobility in 2D monolayers. This phenomenon limits their various pragmatic applications 14 compared with their multilayer counterparts.

15 2D multilayers, which consist of multiple monolayers, not only exhibit a higher carrier 16 mobility but also demonstrate a better immunity to surrounding Coulomb scatterers than those 17 of monolayers [14,16,17]. These merits render them promising candidates for low-power, low-18 noise, and high-energy-efficient electronic devices and multifunctional sensors [18]. 19 Nonetheless, unlike a monolayer platform, the interlayer resistance  $(R_{Int})$  and the Thomas-20 Fermi charge screening length strongly influence on the carrier density profile along the *c*-axis 21 of 2D multilayers and the layer-dependent in-plain carrier mobility, which makes this 22 multilayer system have complex carrier transport mechanism [19]. For example, when the 23 carrier density populates inside 2D multilayers with increasing gate potential at a given  $R_{\text{Int}}$ ,

1 the layer demonstrating the highest conductivity in the layers shifts from bottom- to top-surface 2 in a conventional back-gate configuration due to the interplaying between  $R_{\text{Int}}$  and the layer-3 dependent in-plain carrier mobility [19]. Similarly, a variation of drain bias and temperature 4 could alter the amplitude of  $R_{\text{Int}}$ , resulting in a change of carrier density profile inside 2D 5 multilayers and leading to exhibit two humps in its corresponding transconductance curve  $(g_m)$ 6 [20]. It is worth to note that one prevailing assumption in such a scenario is that carrier mobility 7 corresponding to top-surface channel is always higher than that of bottom-channel mainly 8 because of the enhanced Coulomb scattering effects stemming from an underlying dielectric 9 substrate [11]. On the contrary, when the carrier mobility corresponding to top-surface channel 10 is degraded by undesired surface adsorbates including oxygen and water molecules and 11 structural atomic defects during device fabrication or surface oxidation, the carrier transport 12 via top-surface channel is significantly restricted. This suggests that the presence of top-surface 13 channel can be a possible indicator for the cleanness of top-surface of 2D multilayers. Nevertheless, the importance implication of the shape of transconductance is rarely explored 14 in 2D optoelectronic devices. For instance, since the photocurrent (IPH) strongly relies on 15 carrier mobility  $(I_{PH} \propto \mu \propto g_m)$ , thereby  $g_m$  simply guides us how to maximize  $I_{PH}$  and 16 photoresponsivity ( $R = I_{PH}/P \propto g_m$ , where P denote the laser power) [21,22]. 17

Thus far, numerous 2D van der Walls (vdW) materials have been reported with interesting optoelectronic properties mainly originating from their atomically thin nature (Nat. Rev. Mater. 2, 17033 (2017)). Among them, a black phosphorus (BP) multilayer is known to be extremely sensitive to ambient conditions, whereas a rhenium disulfide (ReS<sub>2</sub>) is relatively very stable comparing to BP. This contrasting feature makes them ideal platform to study the effects of surface adsorbates and surface oxidation on top of 2D materials. Moreover, an ambipolar BP is an attractive material for future electronics which provides a chance to observe both *n*- and *p*-type conduction mechanism at the same time. Meanwhile, an *n*-type 2D ReS<sub>2</sub> multilayers has been suggested as a promising candidate for optoelectronic applications, mainly because of its thickness-independent all direct bandgap and decoupled vdW interaction. The larger interlayer resistance of ReS<sub>2</sub> compared to that of other vdW materials such as MoS<sub>2</sub> and graphene facilitates the conducting channel migration under electrostatic bias conditions [23].

7 In this work, we reveal the presence of a top-surface channel hindering from undesired 8 ambient adsorbates and surface oxides in a multilayer p-type black phosphorus (BP) and n-9 type rhenium disulfide (ReS<sub>2</sub>) as representative materials. The surface adsorbates and oxides not only reduce the electron density  $(1.26 \times 10^{12} \text{ cm}^{-2} \sim 2.88 \times 10^{12} \text{ cm}^{-2}$  in ReS<sub>2</sub> multilayers) 10 but also suppress the field-effect mobility (about 27.6 % for holes in BP and 26.3 % for 11 electrons in ReS<sub>2</sub> multilayers at  $V_D = 5$  V), prohibiting the presence of second hump in a 12 13 transconductance  $(g_m)$  under ambient conditions. In particular, the field-effect mobility of ReS<sub>2</sub> 14 increases with drain bias  $(V_{\rm D})$  at a high vacuum condition, meanwhile this mobility decreases 15 with  $V_D$  at ambient conditions. This contradictory carrier mobility reliance on  $V_D$  further 16 supports the restricted formation of conducting top-surface channel and limited spatial channel migration along the thickness. We confirmed additionally the negligible variation in drain bias 17 18 polarity-dependent turn-on voltage for the bottom-channel of ReS2 multilayer under ambient 19 conditions, supporting an exclusive contribution of surface adsorbates to the formation of top-20 channel in 2D multilayers.

21 **2.** Materials and device fabrications

1 For this study, we fabricated 2D multilayer BP and ReS<sub>2</sub> transistors using a conventional dry 2 transfer method [24,25] as illustrated in Figures 1a-b. The properly chosen mechanically 3 exfoliated BP and ReS<sub>2</sub> flakes were first placed on a 120 nm SiO<sub>2</sub>/ $p^+$ -Si substrate. To define 4 active channel area using metal electrodes, a bilayer poly (methyl methacrylate) (PMMA: EL11 5 and C4) was spread evenly on multilayer flakes by spin-coater and selective electron-beam 6 lithography (Elphy Quantum, Raith) was performed. Au (280 nm) metal deposition was carried 7 out using an electron-beam evaporator after the development of PMMA. The optical images of 8 the fabricated BP and ReS<sub>2</sub> devices are displayed in Figures 1c-d, respectively (Eclipse LV 9 150N, Nikon). The thicknesses of the multilayer BP ( $\approx 22.1$  nm) and ReS<sub>2</sub> ( $\approx 22.6$  nm) were 10 confirmed via atomic force microscopy (AFM, Park Systems, NX10) under ambient conditions. The channel length and width ratios were also confirmed ( $L/W = 4.5 \mu m/13.2 \mu m$  for BP and 11  $= 5.5 \ \mu m/5.5 \ \mu m$  for ReS<sub>2</sub>). 12

13 The fabricated devices were thermally annealed in two steps, that is, i) for 9 h at 423 K and ii) for 1 h at 656 K, under a high-vacuum condition ( $< 10^{-6}$  Torr) to obtain a clean surface and 14 15 low metal-to-semiconductor Schottky barrier. Notably, the multilayer devices were placed in a high-vacuum chamber for one month before the electrical characterization to exclude 16 17 unnecessarily physisorbed surface adsorbates on the top surface of the materials. The 18 effectiveness of our thermal treatment under the high-vacuum condition is discussed further in 19 supporting information (see Figure S1). In addition, to ensure the formation of adsorbates on 20 the surface of 2D materials in addition to surface oxidation, all electrical characterizations (B1500A, Keysight) under ambient conditions were conducted within a day after 1.5 h of air 21 22 venting. Figures 1e-f present the optical Raman spectra (XperRAM C series, Nanobase) 23 measured from the BP and ReS<sub>2</sub> flakes with a laser excitation wavelength ( $\lambda_{EX}$ ) of 532 nm at a power of 3.3 mW, respectively. The observed dominant vibration modes of A<sup>1</sup><sub>g</sub> (≈ 359.0 cm<sup>-1</sup>),
A<sup>2</sup><sub>g</sub> (≈ 463.6 cm<sup>-1</sup>), and B<sub>2g</sub> (≈ 435.4 cm<sup>-1</sup>) peaks indicate the multilayer BP, whereas the
obtained E<sub>g</sub> (≈ 150–160 cm<sup>-1</sup>) and A<sub>g</sub>-like (≈ 208.6 cm<sup>-1</sup>) peaks indicate the multilayer ReS<sub>2</sub>.
The characteristic frequencies for both flakes were consistent with those in previous reports
[20,23,26,27].



Figure 1. Device structure and optical Raman spectra of multilayer TMDs. Device schematics
of multilayer (a) BP and (b) ReS<sub>2</sub> transistors. AFM images of our (c) BP and (d) ReS<sub>2</sub> devices
to confirm the thickness profile with 5 μm scale bar. The corresponding optical images with
10 μm scale bar are presented in the inset. Representative Raman spectra for the (e) BP and (f)
ReS<sub>2</sub> multilayers.

#### 1 **3. Results and discussion**

#### 2 3.1 Electrical properties of p-type BP multilayers

3 The  $V_{\rm D}$ -dependent drain current ( $I_{\rm D}$ ) output characteristic curves of the multilayer BP under high-vacuum and ambient conditions are directly compared for representative back-gate bias 4 5  $(V_{\rm G})$  values ranging from -10 V to -40 V in steps of -10 V, as displayed in Figure 2a. The 6 observed pseudolinear tendency indicates an ohmic-like contact property at the Au-ReS2 7 interface regardless of the case, demonstrating the effectiveness of our two-step annealing 8 process. In addition, the measured I<sub>D</sub> under ambient conditions was less than that under high-9 vacuum conditions. We attributed this suppression of conductance to the effects of numerous 10 Coulomb impurities on top of the BP in addition to surface oxidation, which modifies the 11 carrier density profile along the thickness of the BP.

12 Previous theoretical and experimental studies have revealed that the V<sub>D</sub>- and/or V<sub>G</sub>-dependent 13 interlayer resistance or energy barrier enables the modification of the carrier density profile 14 along the c-axis of 2D multilayers [28,29]. This results in the presence of two plateaus in their 15 transconductance  $(g_m = (\partial I_D / \partial V_G))$  and derivative of  $g_m (dg_m = \partial g_m / \partial V_G)$  curves after  $V_D$ 16 normalization with a single gate configuration [23]. To explore the effects of surface adsorbates 17 including surface oxidation on the carrier transport system in 2D multilayer BP, the  $V_{\rm D}$ -18 normalized  $V_{\rm G}$ -dependent  $I_{\rm D}$  transfer curves  $(I_{\rm D}/V_{\rm D})$  for a high-vacuum condition are displayed 19 in Figure 2b. The enhancement of  $I_{\rm D}$  with decreasing  $V_{\rm G}$  indicates p-type carrier transport in 20 the BP transistor. The corresponding  $g_m$  and  $dg_m$  curves are shown in Figure 2c. In this figure, 21 two humps can be observed, and they merge with increasing  $|V_D|$  at high  $V_D$  conditions ( $|V_D|$  > 22 1 V), manifesting the shift of most conducting channel from the bottom to the top surface driven 23 by reduced interlayer resistance regardless of  $V_D$  (see Figure S2) [28,30]. In addition, the two1 peak of dg<sub>m</sub> is exhibited at almost the same  $V_{\rm G}$  values at all given  $V_{\rm D}$ , indicating a multichannel 2 carrier transport in the BP device (see Figures S3a-b). Meanwhile, under ambient conditions, 3 the second peak of dg<sub>m</sub> gradually disappears at high  $V_D$  ( $|V_D| > 1$  V), as shown in Figures S3c-4 d. This anomalous feature indicates the disappearance of the top channel in the BP multilayers 5 owing to undesired adsorbates on the surface under ambient conditions in addition to surface 6 oxidation. The two unexpected peaks in the relatively low  $V_D$  regime ( $V_D < 1$  V) under ambient 7 conditions appear to be mainly due to the high contact resistance caused by adsorbate invasion 8 into the Au-BP interface (see Figure S4) [31].

9 We also examined the  $V_{\rm D}$ -dependent field-effect mobility ( $\mu_{\rm FE} = g_{\rm m} \cdot (L/W) \cdot C_{\rm OX}^{-1} \cdot V_{\rm D}^{-1}$ , where 10  $C_{\rm OX}$  denotes the oxide planar capacitance per unit area) for both conditions (Figure 2d), to 11 discuss the carrier scattering effects arising from surface adsorbates. The  $\mu_{\text{FE}}$  increases with 12  $|V_{\rm D}|$  up to 1 V and drops abruptly at  $|V_{\rm D}| > 1$  V for both cases. We ascribed the enhancement of 13  $\mu_{\rm FE}$  to the reduction of the interlayer resistance with increasing  $|V_{\rm D}|$ . Meanwhile, the observed dramatic suppression of  $\mu_{\text{FE}}$  in the high  $V_{\text{D}}$  regime, which is closely associated with the 14 15 cleanliness of the top channel, can be attributed to the undesired adsorbate effects in addition 16 to surface oxidation, hiding the formation of the top-surface channel. As expected, the  $\mu_{FE}$  of 17 BP under ambient conditions declines more rapidly than that under high-vacuum conditions, 18 demonstrating the effects of surface adsorbates and surface oxidation on the carrier mobility 19 and/or contact resistance [11]. Furthermore, the higher values of  $\mu_{\rm FE}$  under high-vacuum conditions than those under ambient conditions, regardless of V<sub>D</sub>, support the scenario that 20 21 carrier scattering from impurities resulted in mobility suppression, particularly on the top 22 surface. Despite the different features between high-vacuum and ambient conditions, the 23 instability of BP causing the inevitable degradation of the device hampers the apparent

manifestation of the importance of the cleanliness of the top channel for its formation, requiring
 additional evaluation with other 2D materials.







5 **Figure 2**. Electrical characterization of the *p*-type BP multilayers. (a)  $I_D-V_D$  output 6 characteristic curve comparison at high-vacuum and ambient conditions.  $V_D$ -normalized (b) 7  $I_D-V_G$  transfer curves, (c)  $g_m = ((\partial I_D/\partial V_G)/V_D)$  curves, and  $dg_m (= \partial g_m/\partial V_G)$  curves at the high-8 vacuum condition, respectively. (d)  $V_D$ -dependent  $\mu_{FE}$  for both high-vacuum and ambient 9 conditions.

10

#### 1 *3.2 Electrical properties of n-type ReS*<sub>2</sub> *multilayers*

2 We performed similar measurements (e.g., output characteristic curves, transfer curves, the 3 corresponding  $g_m$  and  $dg_m$  curves, field-effect mobility, and turn-on voltage ( $V_T$ )) on the *n*-type 4 ReS<sub>2</sub> multilayers to demonstrate the similar distinctive carrier transport as in the *p*-type BP 5 counterparts. The V<sub>D</sub>-dependent output characteristic curves show a high linearity of the 6 multilayer ReS<sub>2</sub> under both high-vacuum and ambient conditions (Figure 3a), indicating the 7 negligible Schottky barrier effects in the observed  $V_{\rm G}$  regime. In addition, the measured  $I_{\rm D}$ 8 under high-vacuum conditions is superior to that measured under ambient conditions, which is 9 consistent with the aforementioned BP behavior, manifesting Coulomb impurity effects on the top channel of 2D materials under ambient conditions. 10



11

**Figure 3.** Electrical characterization of the *n*-type ReS<sub>2</sub> multilayers. (a)  $I_D-V_D$  output characteristics at high-vacuum and ambient conditions.  $V_D$ -normalized (b)  $I_D-V_G$  transfer curves, and (c)  $g_m$  and  $dg_m$  curves at the high-vacuum condition for the low  $V_D$  and (d) high  $V_D$ regimes. (e)  $V_D$ -normalized  $g_m$  and  $dg_m$  curves at the ambient condition.

1 The  $V_{\rm G}$ -dependent  $I_{\rm D}$  transfer curves normalized by  $V_{\rm D}$  ( $I_{\rm D}/V_{\rm D}$ ) are presented in Figure 3b for 2 both conditions. The observed enhancement of  $I_D$  with increasing  $V_G$  at the given  $V_D$  values 3 indicates a typical *n*-type behavior. As mentioned in the previous section, the two plateaus of 4  $g_{\rm m}$  indicate different carrier densities along the *c*-axis in 2D multilayer devices, indicating both 5 bottom- and top-channel formation. In Figures 3b-3d, we can observe these distinct features in 6 the multilayer ReS<sub>2</sub> device under high-vacuum conditions. In these figures, we can observe the 7 shape change of  $V_{\rm D}$ -dependent conductance and the anomalous humps exclusively under high-8 vacuum conditions, which is in contrast to that under ambient conditions. In addition, as  $V_{\rm D}$ 9 increases, the two peaks of g<sub>m</sub> gradually extend and merge (see Figure 3d), indicating channel 10 migration from the bottom to the top surface driven by reduced interlayer resistance [20]. As 11 this anomalous signature reveals not only conduction channel migration but also the important 12 role of surface cleanliness for the formation of top-surface channels in 2D multilayers, the absence of a second peak in the  $g_m$  and  $dg_m$  curves under ambient conditions indicates the 13 14 vanished top-surface channel inside the 2D multilayers (see Figure 3e). Furthermore, the observed almost-identical V<sub>D</sub>-normalized g<sub>m</sub> curves regardless of the conditions demonstrate a 15 negligible Au-metal-to-ReS<sub>2</sub> Schottky barrier effect, particularly for small  $V_D$  regimes ( $V_D < 1$ 16 V) (see Figures 3c-e). 17



Figure 4. (a)  $V_D$ -dependent  $\mu_{FE}$  and (b)  $V_T$  of our ReS<sub>2</sub> devices at high-vacuum and ambient conditions.

4

5 Subsequently, we investigated the  $V_{\rm D}$ -dependent  $\mu_{\rm FE}$  in both conditions to confirm the 6 important role of top-surface cleanliness in top-channel formation in 2D multilayers. As the 7 increment of  $V_{\rm D}$  reduces the effect of interlayer resistance in addition to the conduction channel 8 migration, the determined maximum  $\mu_{\rm FE}$  increases with increasing  $V_{\rm D}$  in terms of the total 9 conductance of the device, as displayed in Figure 4a. Meanwhile, the  $\mu_{FE}$  obtained under 10 ambient conditions decreases with  $V_{\rm D}$ , again suggesting the substantial effect of Coulomb 11 impurities on the top of ReS<sub>2</sub>, which interferes with the channel migration. The  $\mu_{\text{FE}}$  suppression 12 in ReS<sub>2</sub> devices exclusively under ambient conditions, which is consistent with the aforementioned  $\mu_{\text{FE}}$  tendency in BP in the high  $V_D$  regime ( $|V_D| > 1$  V), restricts carrier transport 13 14 properties owing to the unclean surface. Moreover, these impurities induce an undesired 15 surface p-doping effect on the top of  $\text{ReS}_2$ , not only leading to the shift of  $V_T$  positively but 16 also masking the formation of the top-surface channel inside the 2D multilayers (see Figure 17 4b). In particular, the observation of i) almost constant  $V_{\rm T}$  values for the top-channel ( $V_{\rm T}$  Top  $\approx$  1 0.5 V) regardless of  $V_D$  and ii) increasing  $V_T$  values for the bottom channel ( $V_T$  Bottom = -34 V--25 V) with increasing V<sub>D</sub> indicating the bottom-channel migration to achieve a minimum 2 3 resistive path inside the ReS<sub>2</sub> multilayers under the high-vacuum condition. However, the 4 obtained V<sub>D</sub>-dependent V<sub>T\_ambient</sub> ( $\approx$  -18.5 V) under ambient conditions is almost pinned, 5 indicating that the restricted channel migration is mainly driven by the numerous surface 6 adsorbates on the top of ReS<sub>2</sub>, overwhelming the advantages of the channel migration and 7 reduced interlayer resistance in the ReS<sub>2</sub> multilayers. The electron density is suppressed by  $\approx$  $1.26 \times 10^{12}$  cm<sup>-2</sup>- $2.88 \times 10^{12}$  cm<sup>-2</sup> (=  $C_{OX}/q \times (\Delta V_T)$ ), where q denotes the electronic unit charge) 8 9 and  $\mu_{\rm FE}$  is decreased to  $\approx 26.3$  % at  $V_{\rm D} = 5$  V in ReS<sub>2</sub>.

#### 10 3.3 Drain bias polarity effects on carrier transport in 2D multilayers

11 In addition, we present the  $I_D$ ,  $g_m$ , and  $dg_m$  curves as a function of the polarity of  $V_D$  for both 12 conditions to clarify the formation of the top surface in 2D multilayers. Indeed, when an insignificant Schottky barrier effect exhibits on the channel migration, there is a negligible 13 14 difference among them regardless of the conditions. Figures 5a-f demonstrate the  $I_D/V_D$ ,  $g_m/V_D$ , 15 and  $dg_m/V_D$  curves for positive and negative  $V_D$ , respectively, under high-vacuum conditions. 16 In these figures, most of the curves are almost identical when  $V_D$  is less than  $\pm 1$  V. However, as  $V_{\rm D}$  decreases further, the  $g_{\rm m}/V_{\rm D}$  curve broadens and merges faster than when  $V_{\rm D}$  is positive 17 (see Figure 5d), which is observed in the corresponding  $dg_m/V_D$  curves (see Figure 5f). We 18 19 ascribed this quick channel migration to a strong effective gate-to-drain electrostatic bias ( $V_{G}$ -20  $_{\rm D} = V_{\rm G} - V_{\rm D}$ ) condition, enhancing consequently the channel migration with the suppressed interlayer resistance. It should be underlined that when  $V_{\rm D}$  is negative,  $V_{\rm G-D}$  is always higher 21 22 than that when  $V_{\rm D}$  is positive. In addition, the  $V_{\rm G}$  position corresponding to the second 23 maximum  $dg_m/V_D$  shifts negatively when  $V_D$  is negative, which indicates the spatial

1 modification of the conducting channel, and more importantly, results in an enhanced carrier 2 mobility. Meanwhile, the observed  $I_D/V_D$ ,  $g_m/V_D$ , and  $dg_m/V_D$  curves under ambient conditions 3 are similar to each other regardless of the polarity of  $V_{\rm D}$ , demonstrating the considerable 4 adsorbate effects on the top of ReS<sub>2</sub> on the formation of the top channel in the 2D multilayers 5 (see Figures 5g-i). More specifically, when surface adsorbates causing an undesired *p*-doping 6 effect are placed onto the surface of *n*-type multilayer ReS<sub>2</sub>, the Fermi level of the top channel 7 would be down-shifted, limiting the large modulation of  $R_{\text{Int}}$  under electrostatic  $V_D/V_G$  bias 8 conditions. Consequently, the top channel formation and channel migration would be strongly 9 restricted as demonstrated in Figures 5g-i under ambient conditions. To observe the surface 10 adsorbate effects on 2D multilayers, the presence (or not) of top channel with regards to the 11 conditions (ambient or high vacuum) is demonstrated by presenting a conceptual illustration of 12 the vanished top-surface channel under ambient conditions, as shown in Figure 6. Additionally, 13 we confirmed another ReS<sub>2</sub> channel locating the upper part on the same ReS<sub>2</sub> flake, 14 demonstrating consistent results (see Figure 1d and S5).



1

Figure 5.  $V_D$  polarity effects on the carrier transport mechanism.  $V_D$ -normalized (a-b)  $I_D-V_G$ transfer curves, (c-d)  $g_m$  curves, and (e-f)  $dg_m$  curves for the high-vacuum condition. Sample plots for the ambient condition; (g)  $I_D-V_G$  transfer curves, (h)  $g_m$  curves, and (i)  $dg_m$  curves.



1

Ambient condition

- Figure 6. Conceptual illustration of the vanished top-channel in BP and ReS<sub>2</sub> due to surface
  adsorbate effects
- 4

### 5 4. Conclusions

We report the surface effect of 2D devices in terms of Coulomb impurities, such as atomic defects, oxide fixed charges, impurities, chemical residues, surface oxides and undesired surface adsorbates, including oxygen and water molecules. Identical electrical 1 characterizations were conducted under both high-vacuum and ambient conditions on BP and 2 ReS<sub>2</sub> devices to elucidate the conductivity reduction due to undesired surface adsorbates. It 3 was observed that the charge density was reduced and the mobility decreased under ambient 4 conditions. We attribute these electrical performance degradations to the disappearance (or 5 decline) of the top channel due to undesired Coulomb scatters and the *p*-doping effect on the 6 top surfaces in addition to surface oxidation. Our findings can provide a better understanding 7 of distinct carrier transport features in addition to the importance of top surface cleanliness, not 8 only for BP and ReS<sub>2</sub>, but also for all types of 2D multilayered devices.

#### 9 Data availability statement

10 The data that support the findings of this study are available upon reasonable request from theauthors.

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#### 16 **Conflicts of interest**

17 The authors declare no conflicts of interest.

#### 18 Supplementary information

- 19 Figure S1. (a) Optical image of 10 nm-thick multilayer BP multilayers. (b) Semi-logarithmic
- 20 scaled transfer characteristic curves ( $I_D$ - $V_G$ ) at  $V_D = 1.0$  V after the thermal annealing process
- 21 at high-vacuum condition with a different sweep direction. (c) V<sub>D</sub>-dependent transfer curves.

- 1 Figure S2. (a) Measurement schematic to obtain interlayer resistance  $(R_{Int})$  of ReS<sub>2</sub> multilayers
- 2 via c-AFM. (b) Current-voltage characteristics at Au substrate. (c) Determined  $R_{Int}$  of ReS<sub>2</sub>
- 3 multilayer as a function of voltage.
- 4 Figure S3. V<sub>D</sub>-normalized derivative of transconductance under (a) high vacuum and (b)
- 5 ambient conditions.
- 6 Figure S4. 3D illustrations presenting surface adsorbates effects on both channel and contact
- 7 property.
- 8 Figure S5. (a) AFM image of the confirmed  $\text{ReS}_2$  device locating the upper part on the same
- 9 ReS<sub>2</sub> flake.  $V_D$ -normalized (b)  $I_D V_G$  transfer curves, and (c)  $g_m = ((\partial I_D / \partial V_G) / V_D)$  curves at the
- 10 high-vacuum and ambient conditions, respectively.

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