

## NANOMATERIALS

## Selective control of electron and hole tunneling in 2D assembly

Dongil Chu,<sup>1\*</sup> Young Hee Lee,<sup>2,3</sup> Eun Kyu Kim<sup>1†</sup>

Recent discoveries in the field of two-dimensional (2D) materials have led to the demonstration of exotic devices. Although they have new potential applications in electronics, thermally activated transport over a metal/semiconductor barrier sets physical subthermionic limitations. The challenge of realizing an innovative transistor geometry that exploits this concern remains. A new class of 2D assembly (namely, “carristor”) with a configuration similar to the metal-insulator-semiconductor structure is introduced in this work. Superior functionalities, such as a current rectification ratio of up to 400,000 and a switching ratio of higher than  $10^6$  at room temperature, are realized by quantum-mechanical tunneling of majority and minority carriers across the barrier. These carristors have a potential application as the fundamental building block of low-power consumption electronics.

## INTRODUCTION

Performance improvements have led state-of-the-art silicon-based electronics to face challenges in continuing to fulfill Moore’s law as a result of leakage current and electrostatic degradation (1). Fortunately, these challenges are expected to be met by an abundance of atomically thin, two-dimensional (2D) materials (2–4). Considering the natural advantages of 2D materials (3, 4), new transistor architectures could be realized by assembling diverse van der Waals materials into a 3D structure with superior performance in terms of the on/off ratio and the subthreshold swing. A popular van der Waals heterojunction, graphene/transition metal dichalcogenides (TMDs) (5–10), mimics a graphene barristor developed and named by Yang *et al.* (11) and has displayed Schottky-limited transport, revealing current on/off ratio values ranging widely from 10 to  $10^6$  under the modulation of the Schottky barrier height  $\phi_B$  (5–7, 9, 10). However, these devices have a critical weakness in the thickness of the active layer [TMDs or hexagonal boron nitride (hBN)], which exhibits either a strong temperature dependence or an unacceptably small switching ratio. The off-state current  $I_{\text{off}}$  is especially pronounced and is conceptually comparable to that of the conventional field-effect transistor (FET) (5, 6, 8, 11, 12) because it eventually results in either direct tunneling transport in thin devices (similar to channel shrinkage in FETs) (9, 10, 13) or thermionic emission transport with a thick active layer (long channel) by majority carriers (which are electrons in most devices) (7, 8, 11). Therefore, the challenge is to create and characterize a device that simultaneously has pure quantum tunneling transport in both the on and off states, a weak temperature dependence, and fast switching.

As a promising approach for achieving these goals, a metal-insulator-semiconductor (MIS) capacitor-like device is developed by sandwiching an insulating hBN tunnel barrier between a multilayer graphene (MGr) and an n-type tungsten disulfide ( $\text{WS}_2$ ) nanosheet. Device operation relies on the tunability of the surface potential  $\phi_s$  of  $\text{WS}_2$  at the atomically abrupt interface that is switchable between the inversion of holes and accumulation of electrons, as controlled by the tunneling process across the insulator (Fig. 1A). Thus, a high current on/off ratio is robust for the

controllability of  $\phi_s$  by means of a Fermi level shift  $\Delta E_{\text{FG}}$  in the electrostatically gated MGr. To date, a triode device based on band-to-band tunneling currents via the transition from minority to majority carriers has not been achieved; thus, we refer to our device as a “carristor” to reflect the carrier-controlled nature of the device. We have demonstrated that the proposed carristor (denoted below by MIS-C) can be created when the hBN thickness is intentionally reduced for operations away from thermodynamic equilibrium (Fig. 1B and fig. S1). In the overall study, we also fabricated alternative devices (barristors) composed of MGr-TMDs (denoted by GW-B and GM-B for  $\text{WS}_2$  and  $\text{MoS}_2$  active layers, respectively) for systematic comparison.

## RESULTS

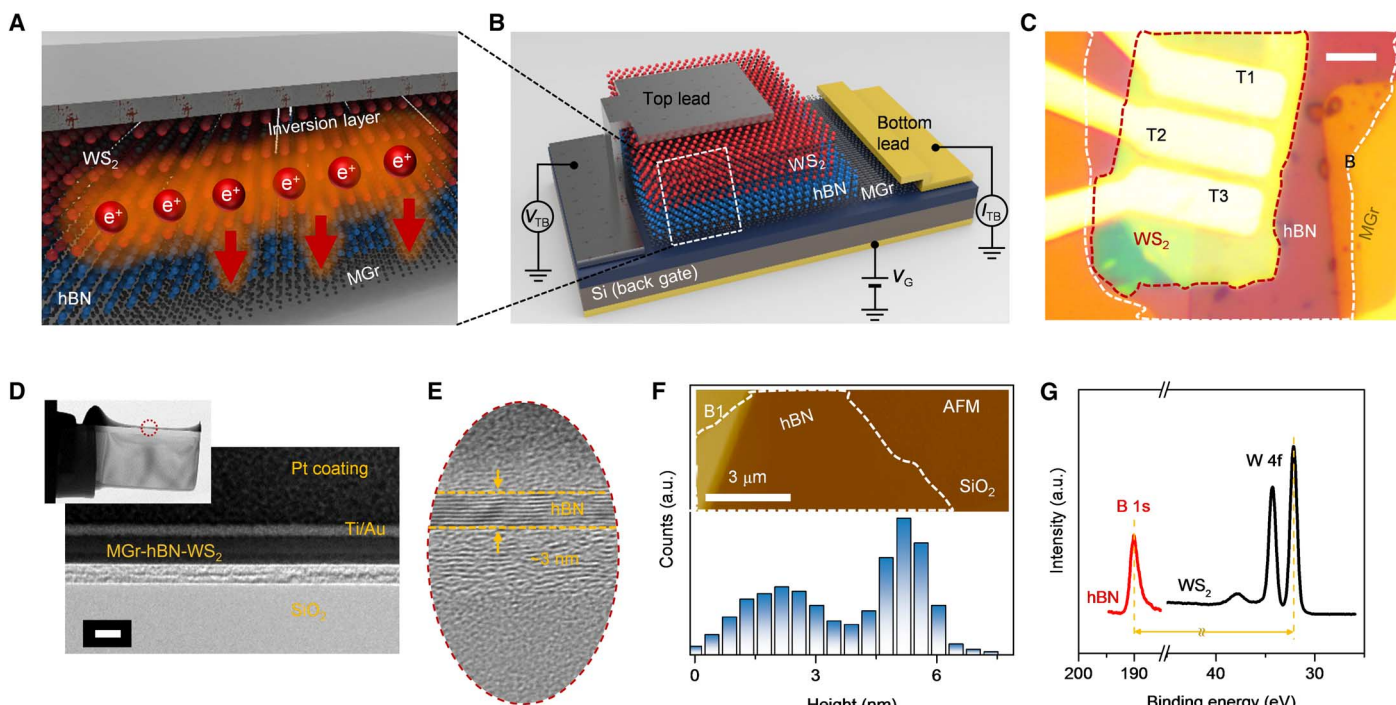
Figure 1C shows an optical image of one of the investigated carristors fabricated on a thermally oxidized 280-nm-thick layer of  $\text{SiO}_2$  on a Si substrate (fig. S2). Briefly, a vertically assembled MGr-hBN- $\text{WS}_2$  stack was generated by the dry transfer of exfoliated nanosheets from individual bulk crystals and sandwiched by electrodes, namely, top (T1 to T3) and bottom (B) leads, to establish electrical interconnections. The details of the tunneling device fabrication procedure and the material characterization are presented in Materials and Methods. High-resolution transmission electron microscopy (TEM) allows us to verify the atomic sharpness of the interface (Fig. 1D), with a thin uniform tunnel layer of approximately 3 nm appearing both in the magnified TEM image and in the statistical histogram (for hBN/ $\text{SiO}_2$  steps) acquired from atomic force microscopy (AFM) (Fig. 1, E and F). To construct the band lineup in the heterostructures, a conventional x-ray photoelectron spectroscopy (XPS) technique was used, which reveals a straddling heterojunction (Fig. 1G and fig. S4). When performing electrical transport measurements, the degenerately doped  $n^+$ -type silicon acted as a back gate for the modulation of  $V_G$ , and a dc bias voltage  $V_{\text{TB}}$  was applied to one of the top leads while measuring the vertical tunnel current flow  $I_{\text{TB}}$  (B is ground).

Carrier transport through the MIS system is often regarded as a leakage current in FETs (1, 14, 15). However, Fig. 2A shows that such a current becomes useful when a  $V_{\text{TB}}$  value between  $-3$  and  $3$  V is applied. The output curve reveals strong asymmetric behavior that has characteristics analogous to that of a p-n junction diode or a typical Schottky diode. Therefore, the Shockley diode equation  $I_{\text{TB}}(V_{\text{TB}}) = I_0[\exp(eV_{\text{TB}}/\eta k_B T) - 1]$  can be used for quantitative characterization, where  $I_0$ ,  $e$ ,  $\eta$ ,  $k_B$ , and  $T$  are the saturation current, the elementary

<sup>1</sup>Quantum-Function Research Laboratory and Department of Physics, Hanyang University, Seoul 04763, South Korea. <sup>2</sup>IBS Center for Integrated Nanostructure Physics, Institute for Basic Science (IBS), Sungkyunkwan University, Suwon 440-746, South Korea. <sup>3</sup>Department of Energy Science, Sungkyunkwan University, Suwon 440-746, South Korea.

\*Previously known as Dongri Kiu.

†Corresponding author. Email: ek-kim@hanyang.ac.kr



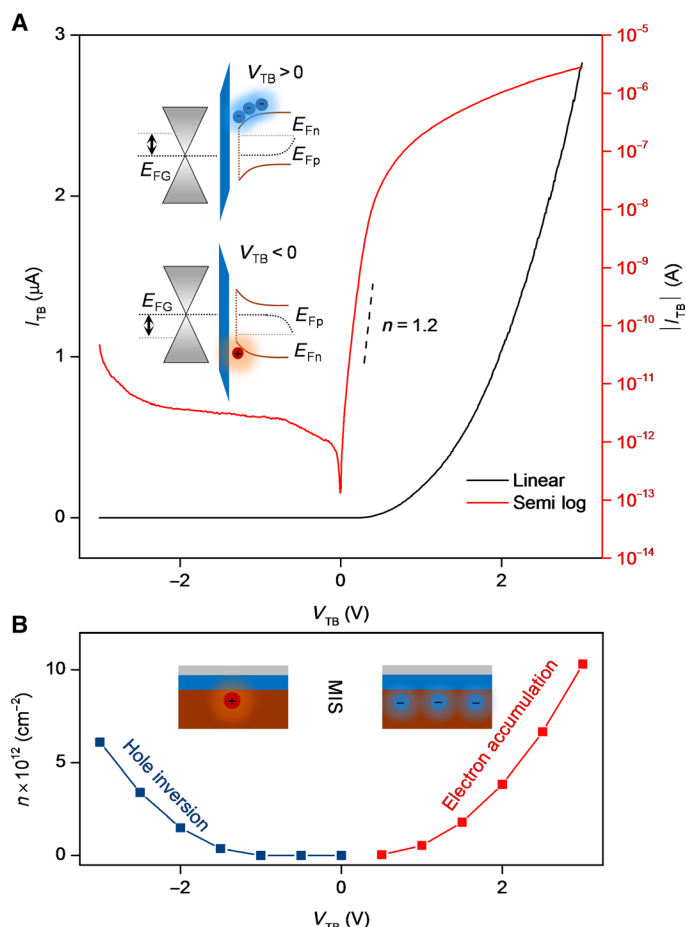
**Fig. 1. Illustration of MIS-C and the characterization of the device structure.** (A) Schematic illustration of an MIS-C under the state of forming an inversion of holes for tunneling. “ $e^+$ ” represents the hole carrier. (B) Schematic representation of the carristor layout and electrical connections for electrical transport measurements. (C) Optical image of a typical MIS-C with Ti/Au top and bottom contacts. Scale bar, 5  $\mu\text{m}$ . (D) High-resolution TEM image of an MGr-hBN-WS<sub>2</sub> heterostructure fabricated on a SiO<sub>2</sub>/Si substrate with a titanium metal capping layer (corresponding to the top lead). The layer thicknesses of the MIS-C are 10.5 and 13.1 nm for WS<sub>2</sub> and MGr, respectively. Scale bar, 10 nm. (E) High-magnification TEM image of the ultrathin hBN tunnel barrier with a thickness of  $\sim 3$  nm between the WS<sub>2</sub> and the graphene. (F) Measured histogram of the height distributions for hBN on SiO<sub>2</sub>, confirming a height profile of  $< 3$  nm. Inset: AFM topographic image acquired from the device in (C) showing SiO<sub>2</sub> covered by hBN. a.u., arbitrary units. (G) XPS spectra of W 4f and B 1s core levels, located at 30 to 40 eV and 190 eV, respectively.

charge, the ideality factor, the Boltzmann constant, and the absolute temperature, respectively. In this way, a rectification ratio  $R_R$  of approximately 100,000 and  $\eta = 1.2$  can be calculated. The  $R_R$  value obtained in our carristors represents at least a 10,000-fold improvement compared to other works investigating a p-n junction based on layer-by-layer stacked TMDs (16). We note that GW-B and GM-B performed within the limit in  $R_R$ , with a typical range of  $< 10^2$  (fig. S5), which is consistent with previous reports (6, 7, 9). The  $\eta$  value was found to be much smaller than that of TMD-based barristors (6), implying an optimal interface density of states (DOS) at the hBN-WS<sub>2</sub> interface. Such remarkable enhancements are expected to be a consequence of the substantial differences in the underlying principles of device physics.

The current rectifying behavior can be understood by examining the inset of Fig. 2A for  $V_{TB} > 0$  (electron accumulation mode) and  $V_{TB} < 0$  (hole inversion mode) biasing. The associated surface carrier density plot shown in Fig. 2B is consistent with this surface mode transition (see the Supplementary Materials for the calculation). Inversion- and accumulation-induced quasi-bound states, together with quantum confinement in the narrow quantum well near the WS<sub>2</sub> interface, were not characterized in this work but are probably the cause of the momentum-conserved transmission phenomenon. This part of the field is still relatively unexplored.

Although the electron wave function can penetrate a several-atom-thick hBN barrier resulting in a tunneling phenomenon due to barrier height  $e\chi_{TB}$  being much larger than the thermal energy, the conduction mechanism still needs to be elucidated and demonstrated using

temperature-dependent transport measurements, as shown in Fig. 3A (the corresponding output data for GW-B are shown in fig. S6). The nearly flat out-of-plane resistivity of  $\sim 10^8$  ohm- $\mu\text{m}^2$  [defined as  $\rho^T = 1/(dJ_{TB}/dV)$ , where  $J_{TB}$  is the current density] with decreasing temperature observed in Fig. 3B (MIS-C, blue squares) clearly indicates the tunneling behavior under the overall bias (10, 14). Alternatively, GW-B (yellow squares) shows a significant decrease in  $\rho^T$  by more than four orders of magnitude from 230 to 90 K with semiconducting behavior and from 245 K to room temperature with strong metallic behavior. These two temperature regimes have also been observed by Georgiou *et al.* (5). Metal-semiconductor contact could be responsively adapted for the barristor and has indeed been extensively described by thermionic emission (6–8, 11), thermionic field-emission (8), and FET models (8). Figure 3C presents an Arrhenius plot of  $\ln(I_{TB})$  versus  $T^{-1}$  for the carristor (blue) and the barristor (yellow). It is interesting to note that that MIS-C has an ultralow activation energy  $E_A$  of 13 meV that is evidently smaller than  $k_B T$  ( $T = 300$  K).  $E_A$  has a certain correlation with the temperature-dependent on/off ratio. The current component, owing to the disorder-assisted generation-recombination (G-R) effect in the depletion region (with width  $W_D$ ) governed by Shockley-Read-Hall statistics, is expected to be temperature-sensitive (14) because it is proportional to  $en_i(T)W_D/\tau$ , where  $\tau$  is the carrier lifetime and  $n_i(T)$  is the intrinsic carrier density (see the Supplementary Materials). The measured  $E_A$  of the MIS-C is 100 times smaller than the half bandgap of WS<sub>2</sub>; thus, the insignificant generation of G-R current is suggestive (17). We attribute the nonzero  $E_A$  to the



**Fig. 2. Room temperature electrical characteristics of an MIS-C and energy band diagram.** (A)  $I_{TB}$ - $V_{TB}$  output curve measured across the heterostructure (between leads T1 and B) showing an ideality factor of 1.2; the silicon back gate was set to ground during the measurements. Inset: Schematic of the energy band diagram of a vertically stacked MIS-C under forward (top) and reverse (bottom) bias conditions.  $E_{FG}$ , graphene Fermi level;  $E_{Fn}$  ( $E_{Fp}$ ), quasi-Fermi level for electrons (holes). (B) Calculated density of generated hole inversion and electron accumulation at the interface as a function of  $V_{TB}$  for an n-type  $WS_2$ . Note that the surface has weak inversion states at zero bias due to  $\phi_{ms}$ .

bandgap reduction with temperature because of the intensified electron-phonon interaction at high temperatures that may alter the height of the barrier.

More surprisingly, the external electric field resulting from the silicon back gate determines the output characteristics. Figure 3D presents representative  $I_{TB}$ - $V_{TB}$  curves for a  $V_G$  range of  $-7$  to  $7$  V, allowing us to obtain  $R_R$  versus  $V_G$  over a range of 10 to 400,000 (inset of Fig. 3E). The nonlinear  $I$ - $V$  curves are divided into two distinctive signatures, namely, current multiplication for  $V_{TB} < 0$  and a plateau pattern for  $V_{TB} > 0$ . When  $V_{TB} < 0$ , we observed a marked current enhancement by more than five orders of magnitude. When  $V_{TB} > 0$ , as  $V_G$  is increased, a plateau can be clearly observed for each curve near zero  $V_{TB}$  that becomes more pronounced at large positive  $V_G$ . This plateau corresponds to the raising of the depletion layer in  $WS_2$ ; that is, it provides evidence of  $(V_{TB}, V_G)$ -dependent  $\phi_s$ . We note that a flat form of  $\phi_s$  weakens the generation of electron density at the  $WS_2$  surface, leading to a nearly constant current region. Moreover, as

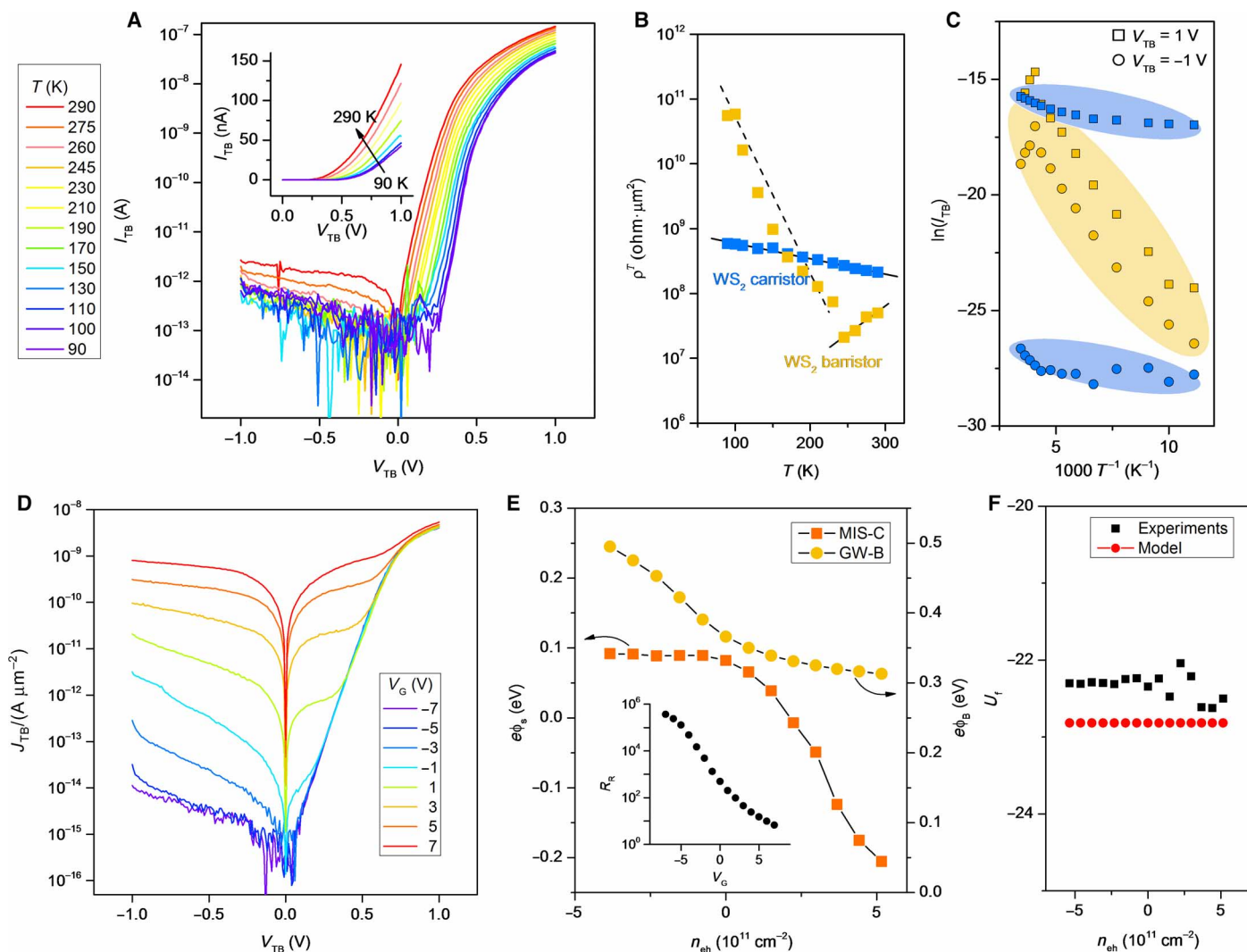
$\phi_s$  departs from the flat band to shift down as  $V_{TB}$  increases, a large population of electrons allows all the curves to converge for a finite transmission coefficient  $T_E$  (18). We hypothesize that  $V_{TB}$ ,  $V_G$ , variations in  $\phi_s$ , and (constant)  $T_E$  play major roles in our MIS-C, as will be discussed in more detail. Generally, the amount of surface DOS acts as G-R centers and as an extra tunneling path between graphene and  $WS_2$ . Green *et al.* (18) have shown that the influence of surface DOS is substantial when the MIS-C is positively biased. However, the existence of a plateau confirms that the localized DOS has no detectable effect on the bandgap of the semiconductor, consistent with a recent study by Braga *et al.* (19). By contrast, GW-B and GM-B do exhibit current multiplication behavior (figs. S7A and S8A) that has been observed in other studies, but such behavior lacks the current-plateau feature.

Charge transport in MIS structures has been studied extensively because it is related to the planar MISFET (metal-insulator-semiconductor field-effect transistor) and is of primary importance to the reliability and stability of integrated circuit technology. By incorporating the Wentzel-Kramers-Brillouin approximation for rectangular barrier, the expression for the band-to-band current  $I_{TB}(V_{TB}, V_G) \propto T_E \exp[-e\phi_s(V_{TB}, V_G)/k_B T]$  was used to analyze the characteristics of the MIS-C (see the Supplementary Materials). We note that the MIS-C mimics the conventional MIS capacitor in that the band bending effectively depends on work function difference  $\phi_{ms}$ , as mentioned above. Notably, we could electrostatically adjust the work function of graphene  $W_G$  to generate an undoubted transition in  $\phi_s(V_{TB}, V_G)$ . It appears more directly, as displayed in Fig. 3E (left axis). Remarkably, by sweeping the polarity of  $V_G$ ,  $e\phi_s$  can be sensitively changed from 92 meV at  $V_G = -7$  V to  $-205$  meV at  $V_G = 7$  V, suggesting the significant influence of  $\phi_s(V_G)$  to form hole inversion and electron accumulation (see the Supplementary Materials for the  $\phi_s$  extraction method). However, in the case of the GW-B, a positive value of  $e\phi_B$  (from 459 to 313 meV) can be found over the entire range of  $V_G$  because the majority carrier transport is restricted only by  $\phi_B$  (7–9, 11). This finding for the GW-B complies with theoretical predictions (20, 21) and experimental observation (10).

We define a barrier function  $U_f = \ln(A^*AT^2T_E)$ , where  $A^*$  and  $A$  are the Richardson constant and active contact area, respectively. Figure 3F shows that the measured value of  $U_f$  in our MIS-C is nearly independent of gate modulation at room temperature. Assuming the effective mass of a hole in hBN,  $m_{BN}^* = 0.5m_0$  (13, 22, 23), and taking barrier thickness  $d_{BN}$  to be 2.8 nm, the theoretical model describes a calculated  $U_f$  (red circles in Fig. 3F) close to the measured value without the gating dependence, as expected, demonstrating an effective  $d_{BN}$  that is slightly smaller than  $\sim 3$  nm (Fig. 1E). This observation reflects the lowering of the hole barrier behavior. Recent experimental efforts on tunnel devices with an hBN barrier embedded within different electrodes (graphene, graphite, and metal) have revealed discrepancies. The pronounced negative differential resistance with momentum transfer by aligning the crystal orientation of two graphene (24, 25) or defect-assisted (26) Coulomb blockade signatures with defect-mediated tunneling (27) and that of the sublinear  $I$ - $V$  curve with direct tunneling (22) is relatively ambiguous, although some of these devices contain identical graphene electrodes. Nevertheless, we did not observe resonant tunneling or single-electron charging effects in our samples;  $T_E$  exhibited the expected behavior of exponential dependence on  $d_{BN}$  and negligible barrier deformation as a function of  $V_G$  (see the Supplementary Materials).

We now explore the “transistor-like” operation of the MIS-C for the first time. Figure 4A illustrates the transfer characteristics ( $I_{TB}$ - $V_G$ )



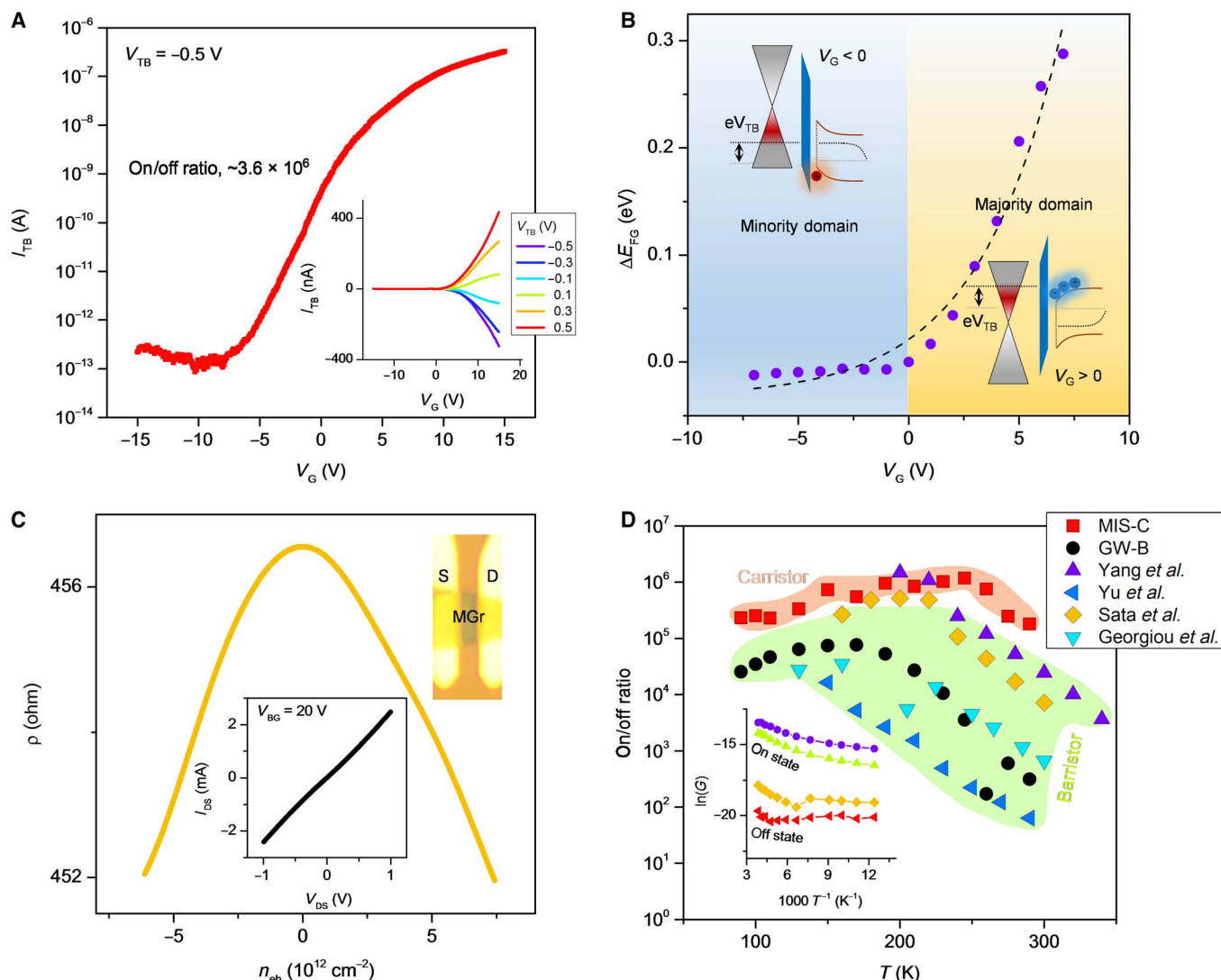


**Fig. 3. Temperature- and electrostatic gating-dependent  $I$ - $V$  characteristics.** (A) Semilog  $I_{TB}$ - $V_{TB}$  output curves of an MIS-C for temperatures between 90 and 290 K. Inset: The corresponding linear scale data. (B) Out-of-plane resistivity versus temperature curve for an MIS-C (blue) and a GW-B (yellow) at  $V_{TB} = 1$  V. (C) Arrhenius plot of  $I_{TB}$  at  $V_{TB} = -1$  V (circle) and 1 V (square) for a MIS-C (blue) and a GW-B (yellow).  $E_A$  of 108 meV for semiconducting and  $-155$  meV for metallic behavior are extracted to yellow circles that are correlated to  $\phi_B$ . (D) Semilog scale of  $I_{TB}$ - $V_{TB}$  output curves for different back-gate voltages with an active contact area of  $50 \mu\text{m}^2$ . (E) Surface potential (left axis) and Schottky barrier height (right axis) as functions of  $V_G$  modulation for MIS-C and GW-B, respectively. Note that  $\phi_s$  has a saturation regime at  $V_G < 0$  and becomes negative at  $V_G > 0$ . Inset: Rectification ratio as a function of  $V_G$  extracted from the data (D) at  $V_{TB} = \pm 1$  V. (F) Barrier function as a function of  $1000 T^{-1}$  in the temperature range from 90 to 290 K.

for a typical sample measured at  $V_{TB} = -0.5$  V. A linear scale  $I_{TB}$ - $V_G$  plot with various  $V_{TB}$  is displayed in the inset of Fig. 4A. We find that  $I_{TB}$  has an exponential dependence on  $V_G$  and a high on/off ratio of  $3.6 \times 10^6$  at  $V_{TB} = -0.5$  V even at room temperature (see fig. S10 for different  $V_{TB}$  voltages), which is 100 to 100,000 times higher than the values reported in previous reports of graphene/TMD-based barristors (see figs. S7B and S8B for the results of our barristors) (5–7, 9–11, 13). Figure 4B depicts the corresponding asymmetric variation in  $\Delta E_{FG}$  as a function of  $V_G$ . The asymmetry is probably caused by the unbalanced hole doping because the carrier counteraction occurs between the hole carriers doped by the negative polarity of  $V_G$  and the small amount of electron carriers created by negative  $V_{TB}$  (note that charge neutrality requires an equal charge at both sides of the semimetal and the semiconductor) (14). In addition, the preceding

discussions assumed the ability to control the sequential tunneling of the double carriers. To further address this point, we fabricated MGr-based conventional FETs on  $\text{SiO}_2/\text{Si}$  wafer. The inset of Fig. 4C (top right) shows an optical image of the MGr-FET. A linear output behavior [inset of Fig. 4C (bottom)] confirms metal-to-MGr contact before in-plane resistivity  $\rho$  analysis. The associated  $\rho$  as a function of  $V_G$  presented a peak at the Dirac point voltage corresponding to the vanishing of the DOS as  $E_{FG}$  approached the Dirac point (Fig. 4C). Although different MGr FETs display different peak positions due to oxide charges and unintentional doping, the  $E_{FG}$  of MGr crosses over to the Dirac point (28, 29). This behavior is similar to that of single-layer graphene (28).

On the basis of the benefits for the tunneling transport of MIS-C, as shown in Fig. 3A, weak temperature-dependent transfer characteristics



**Fig. 4. Transfer characteristics of the carristor.** (A) Room temperature semilog  $I_{TB}$ - $V_G$  transfer characteristics of an MIS-C at  $V_{TB} = -0.5$  V. Inset: The corresponding linear scale  $I_{TB}$ - $V_G$  at various  $V_{TB}$ . (B) Fermi level shift of graphene versus  $V_G$ . These data are extracted from  $V_G$ -dependent surface potential variations and converted by applying the Schottky-Mott model based on the following expression:  $\phi_s = W_G + \Delta E_{FG} - W_s$  (where  $W_s$  is the  $WS_2$  work function). Inset: Energy band diagram under different gate polarities. Effect of p-doping (top;  $V_G < 0$ ); the shifting of  $E_{FG}$  to a lower level results in  $\phi_s$  forming an inversion layer; thus,  $I_{TB}$  is dominated by holes. Effect of n-doping (bottom;  $V_G > 0$ ); the shifting of  $E_{FG}$  to an upper level results in  $\phi_s$  forming an accumulation of electrons;  $I_{TB}$  is dominated by the abundance of electrons. (C) In-plane resistivity as a function of the gate voltage in an MGr channel FET measured at  $V_{SD} = 10$  mV under room temperature. Insets: Output curve of the same device at a back-gate voltage  $V_{BG} = 20$  V (bottom) and an optical image of a 10-nm-thick MGr with source/drain (S/D) contact (top right). (D) On/off ratio versus temperature for carristors and barristors. Inset: Plot of  $\ln(G)$  versus  $1000 T^{-1}$  for an MIS-C at on and off states, where conductance  $G$  is defined as  $1/\rho^T$ . The barristor data are extracted from previous studies (5, 6, 9, 11).

should also be available. The electrostatic gating from the Si substrate is effectively screened by MGr (29, 30) and only generates n- or p-doping in MGr.  $I_{off}$  and the on-state current  $I_{on}$  are similar to the current corresponding to negative and positive  $V_{TB}$ , respectively. The inset of Fig. 4D shows a plot of  $\ln(G)$  versus  $1000 T^{-1}$  in both on and off states, indicating that the observed behavior is in agreement with that of Fig. 3A. By using  $\ln(I_{on}/I_{off}) \propto -E_A/k_B T$ , the measured  $E_A$  in Fig. 4D (red squares) corresponds to approximately 11 meV, which is very close to the data extracted from Fig. 3C. In contrast, the GW-B exhibits an exponential decay with  $T$  (black circles) and a similarity in the decay slope to the results of other barristors (5, 6, 9, 11). Their  $I_{off}$  response to temperature is analogous to the subthreshold conduction of silicon MISFETs

(12). The expression  $\ln(I_{on}/I_{off}) \propto -e\phi_B/k_B T$  is valid for describing Fig. 4D for barristors (31). We could roughly extract  $e\phi_B$  of the barristors; typical values lay in the range of 148 to 303 meV.

## DISCUSSION

To summarize, assembly of 2D crystals with atomic precision enables the creation of a novel carristor via layer-by-layer construction with materials having a distinctive electronic structure. Our assembly, the so-called carristor, exhibits current rectification and switching features and could open new routes for constructing electronic devices by taking advantage of the small active area (lack of double contact space

for S/D) and ultrafast direct tunneling time, which could enable the direct rectification of infrared radiation.

## MATERIALS AND METHODS

### Device fabrication

For the vertically stacked MGr-hBN-WS<sub>2</sub> (MIS-C) and MGr-TMD (GW-B and GM-B) devices, we used the standard Scotch tape-based cleavage technique for each 2D bulk crystal in combination with a contamination-free transfer method to avoid wet chemicals and even deionized water (32, 33). Single-crystalline graphite was purchased from Graphene Supermarket, and hBN, WS<sub>2</sub>, and MoS<sub>2</sub> were purchased from 2D Semiconductors. First, the bottom contact was prepatterned onto a degenerately doped Si substrate, followed by a 280-nm-thick SiO<sub>2</sub> capping layer, as shown in fig. S2A. Then, we applied mechanical exfoliation to obtain an MGr nanosheet that was deposited on a polydimethylsiloxane (PDMS) layer. Thick pieces of graphene with a typical thickness of 10 to 27 nm were chosen to create the bottom contacts, fully suppressing any underlying electric field screening (screening length of 1.2 nm) (29, 30). This intermediate PDMS layer acted as a supporting framework for the transfer of 2D nanosheets by means of a micro-manipulation system (33). After the MGr was placed at the desired location on the silicon substrate, we transferred an hBN nanosheet so that it overlapped the underlying MGr flake (fig. S2B). Subsequently, the top layer (WS<sub>2</sub> nanosheet) was placed onto the high-quality hBN that was used as both a tunnel barrier and an ultrasoother, defect-free substrate (fig. S2C) (34). A 1.4- $\mu$ m-thick layer of negative-tone photoresist was spin-coated onto the sample and patterned using a photomask through a photolithography process (fig. S2D). We metallized three separate top Ti/Au (10/60 nm) contacts for the vertical device using a thermal evaporator with a deposition rate of 5 Å/s. GW-B and GM-B have the same fabrication procedures but without inserting an hBN tunnel barrier for the direct MGr-TMD contact (fig. S3, A to D). Dozens of devices were fabricated and studied in the process of completing this study.

### Materials characterization

High-resolution TEM images were obtained with a JEOL JEM-2100F operating at 200 kV. Before the TEM analysis, a focused ion beam (Quanta 3D FEG, FEI) was used to prepare site-specific samples (inset of Fig. 1D). The focused ion beam cutting and lift out were performed after the deposition of a carbon/Pt coating. The cross-sectional specimen was extracted from the studied device and used to determine the individual thicknesses of the layered materials and to verify the atomic sharpness of the interfaces. Topographic image and histogram statistics were carried out using an AFM (XE-100, Park Systems) in the noncontact mode of operation with an AR5-NCH (Nanosensors) cantilever. XPS core-level and valence band spectra were collected using an XPS (angle-resolved XPS, Thermo Fisher Scientific), incorporating a monochromatic Al K $\alpha$  source (1486.6 eV). Energies of the spectra were calibrated against the C 1s peak set at 284.5 eV.

### Electrical measurement

*I-V* characteristics were conducted using a semiconductor parameter analyzer (HP 4156A) and measured in a liquid nitrogen-cooled cryostat (ASK, 700 K) at a pressure of approximately 10<sup>-3</sup> torr in a dark environment.

## SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/3/4/e1602726/DC1>

Supplementary Text

fig. S1. The 3D schematic structure of the carristor.

fig. S2. Optical images of MIS-C fabrication steps.

fig. S3. Optical images of GW-B (or GM-B) fabrication steps.

fig. S4. Band alignment of MIS-C and XPS spectra.

fig. S5. Schematic representation and *I-V* curves.

fig. S6. *I<sub>TB</sub>-V<sub>TB</sub>* curve for GW-B at different temperatures from 90 to 290 K  $V_G = 0$ .

fig. S7. Electrical transport characteristics of GW-B.

fig. S8. Electrical transport characteristics of GM-B.

fig. S9. Highly nonlinear dependence of *I<sub>TB</sub>* as a function of *V<sub>TB</sub>* for experimental (black line) and calculated data (red dots) under zero gate field and *T* = 300 K.

fig. S10. Semilog *I<sub>TB</sub>-V<sub>G</sub>* curves for MIS-C at different *V<sub>TB</sub>* from -0.1 to -0.5 V at room temperature.

table S1. List of symbols and descriptions used in the study.

References (35–41)

## REFERENCES AND NOTES

- M. Lundstrom, Moore's law forever? *Science* **299**, 210–211 (2003).
- A. K. Geim, I. V. Grigorieva, Van der Waals heterostructures. *Nature* **499**, 419–425 (2013).
- A. D. Franklin, Nanomaterials in transistors: From high-performance to thin-film applications. *Science* **349**, aab2750 (2015).
- G. Fiori, F. Bonaccorso, G. Iannaccone, T. Palacios, D. Neumaier, A. Seabaugh, S. K. Banerjee, L. Colombo, Electronics based on two-dimensional materials. *Nat. Nanotechnol.* **9**, 768–779 (2014).
- T. Georgiou, R. Jalil, B. D. Belle, L. Britnell, R. V. Gorbachev, S. V. Morozov, Y.-J. Kim, A. Gholinia, S. J. Haigh, O. Makarovskiy, L. Eaves, L. A. Ponomarenko, A. K. Geim, K. S. Novoselov, A. Mishchenko, Vertical field-effect transistor based on graphene-WS<sub>2</sub> heterostructures for flexible and transparent electronics. *Nat. Nanotechnol.* **8**, 100–103 (2013).
- W. J. Yu, Z. Li, H. Zhou, Y. Chen, Y. Wang, Y. Huang, X. Duan, Vertically stacked multi-heterostructures of layered materials for logic transistors and complementary inverters. *Nat. Mater.* **12**, 246–252 (2013).
- Y.-F. Lin, W. Li, S.-L. Li, Y. Xu, A. Aparecido-Ferreira, K. Komatsu, H. Sun, S. Nakaharai, K. Tsukagoshi, Barrier inhomogeneities at vertically stacked graphene-based heterostructures. *Nanoscale* **6**, 795–799 (2014).
- J. Y. Kwak, J. Hwang, B. Calderon, H. Alsalm, N. Munoz, B. Schutter, M. G. Spencer, Electrical characteristics of multilayer MoS<sub>2</sub> FETs with MoS<sub>2</sub>/graphene heterojunction contacts. *Nano Lett.* **14**, 4511–4516 (2014).
- Y. Sata, R. Moriya, T. Yamaguchi, Y. Inoue, S. Morikawa, N. Yabuki, S. Masubuchi, T. Machida, Modulation of Schottky barrier height in graphene/MoS<sub>2</sub>/metal vertical heterostructure with large current on-off ratio. *Jpn. J. Appl. Phys.* **54**, 04DJ04 (2015).
- T. Yamaguchi, R. Moriya, Y. Inoue, S. Morikawa, S. Masubuchi, K. Watanabe, T. Taniguchi, T. Machida, Tunneling transport in a few monolayer-thick WS<sub>2</sub>/graphene heterojunction. *Appl. Phys. Lett.* **105**, 223109 (2014).
- H. Yang, J. Heo, S. Park, H. J. Song, D. H. Seo, K.-E. Byun, P. Kim, I. Yoo, H.-J. Chung, K. Kim, Graphene barristor, a triode device with a gate-controlled Schottky barrier. *Science* **336**, 1140–1143 (2012).
- F. H. Gaensslen, V. L. Rideout, E. J. Walker, J. J. Walker, Very small MOSFETs for low-temperature operation. *IEEE Trans. Electron Devices* **24**, 218–229 (1977).
- L. Britnell, R. V. Gorbachev, R. Jalil, B. D. Belle, F. Schedin, A. Mishchenko, T. Georgiou, M. I. Katsnelson, L. Eaves, S. V. Morozov, N. M. R. Peres, J. Leist, A. K. Geim, K. S. Novoselov, L. A. Ponomarenko, Field-effect tunneling transistor based on vertical graphene heterostructures. *Science* **335**, 947–950 (2012).
- S. M. Sze, K. K. Ng, *Physics of Semiconductor Devices* (John Wiley & Sons, ed. 3, 2006).
- P. S. Davids, R. L. Jarecki, A. Starbuck, D. B. Burckel, E. A. Kadlec, T. Ribaudo, E. A. Shaner, D. W. Peters, Infrared rectification in a nanoantenna-coupled metal-oxide-semiconductor tunnel diode. *Nat. Nanotechnol.* **10**, 1033–1038 (2015).
- M. M. Furchi, A. Pospischil, F. Libisch, J. Burgdörfer, T. Mueller, Photovoltaic effect in an electrically tunable van der Waals heterojunction. *Nano Lett.* **14**, 4785–4791 (2014).
- C.-C. Lin, J.-G. Hwu, Performance enhancement of metal-oxide-semiconductor tunneling temperature sensors with nanoscale oxides by employing ultrathin Al<sub>2</sub>O<sub>3</sub> high-k dielectrics. *Nanoscale* **5**, 8090–8097 (2013).
- M. A. Green, F. D. King, J. Shewchun, Minority carrier MIS tunnel diodes and their application to electron- and photo-voltaic energy conversion—I. Theory. *Solid State Electron.* **17**, 551–561 (1974).
- D. Braga, I. Gutiérrez Lezama, H. Berger, A. F. Morpurgo, Quantitative determination of the band gap of WS<sub>2</sub> with ambipolar ionic liquid-gated transistors. *Nano Lett.* **12**, 5218–5223 (2012).

20. A. Avsar, J. Y. Tan, T. Taychatanapat, J. Balakrishnan, G. K. W. Koon, Y. Yeo, J. Lahiri, A. Carvalho, A. S. Rodin, E. C. T. O'Farrell, G. Eda, A. H. Castro Neto, B. Özyilmaz, Spin-orbit proximity effect in graphene. *Nat. Commun.* **5**, 4875 (2014).
21. Z. Wang, D.-K. Ki, H. Chen, H. Berger, A. H. MacDonald, A. F. Morpurgo, Strong interface-induced spin-orbit interaction in graphene on WS<sub>2</sub>. *Nat. Commun.* **6**, 8339 (2015).
22. L. Britnell, R. V. Gorbachev, R. Jalil, B. D. Belle, F. Schedin, M. I. Katsnelson, L. Eaves, S. V. Morozov, A. S. Mayorov, N. M. R. Peres, A. H. C. Neto, J. Leist, A. K. Geim, L. A. Ponomarenko, K. S. Novoselov, Electron tunneling through ultrathin boron nitride crystalline barriers. *Nano Lett.* **12**, 1707–1710 (2012).
23. Y.-N. Xu, W. Y. Ching, Calculation of ground-state and optical properties of boron nitrides in the hexagonal, cubic, and wurtzite structures. *Phys. Rev. B* **44**, 7787–7798 (1991).
24. B. Fallahazad, K. Lee, S. Kang, J. Xue, S. Larentis, C. Corbet, K. Kim, H. C. P. Movva, T. Taniguchi, K. Watanabe, L. F. Register, S. K. Banerjee, E. Tutuc, Gate-tunable resonant tunneling in double bilayer graphene heterostructures. *Nano Lett.* **15**, 428–433 (2015).
25. A. Mishchenko, J. S. Tu, Y. Cao, R. V. Gorbachev, J. R. Wallbank, M. T. Greenaway, V. E. Morozov, S. V. Morozov, M. J. Zhu, S. L. Wong, F. Withers, C. R. Woods, Y.-J. Kim, K. Watanabe, T. Taniguchi, E. E. Vdovin, O. Makarovskiy, T. M. Fromhold, V. I. Fal'ko, A. K. Geim, L. Eaves, K. S. Novoselov, Twist-controlled resonant tunnelling in graphene/boron nitride/graphene heterostructures. *Nat. Nanotechnol.* **9**, 808–813 (2014).
26. L. Britnell, R. V. Gorbachev, A. K. Geim, L. A. Ponomarenko, A. Mishchenko, M. T. Greenaway, T. M. Fromhold, K. S. Novoselov, L. Eaves, Resonant tunnelling and negative differential conductance in graphene transistors. *Nat. Commun.* **4**, 1794 (2013).
27. U. Chandni, K. Watanabe, T. Taniguchi, J. P. Eisenstein, Evidence for defect-mediated tunneling in hexagonal boron nitride-based junctions. *Nano Lett.* **15**, 7329–7333 (2015).
28. A. Das, S. Pisana, B. Chakraborty, S. Piscanec, S. K. Saha, U. V. Waghmare, K. S. Novoselov, H. R. Krishnamurthy, A. K. Geim, A. C. Ferrari, A. K. Sood, Monitoring dopants by Raman scattering in an electrochemically top-gated graphene transistor. *Nat. Nanotechnol.* **3**, 210–215 (2008).
29. Y. Sui, J. Appenzeller, Screening and interlayer coupling in multilayer graphene field-effect transistors. *Nano Lett.* **9**, 2973–2977 (2009).
30. H. Miyazaki, S. Odaka, T. Sato, S. Tanaka, H. Goto, A. Kanda, K. Tsukagoshi, Y. Ootuka, Y. Aoyagi, Inter-layer screening length to electric field in thin graphite film. *Appl. Phys. Express* **1**, 034007 (2008).
31. F. Xia, D. B. Farmer, Y.-m. Lin, P. Avouris, Graphene field-effect transistors with high on/off current ratio and large transport band gap at room temperature. *Nano Lett.* **10**, 715–718 (2010).
32. J. Song, F.-Y. Kam, R.-Q. Png, W.-L. Seah, J.-M. Zhuo, G.-K. Lim, P. K. H. Ho, L.-L. Chua, A general method for transferring graphene onto soft surfaces. *Nat. Nanotechnol.* **8**, 356–362 (2013).
33. D. Qiu, D. U. Lee, C. S. Park, K. S. Lee, E. K. Kim, Transport properties of unrestricted carriers in bridge-channel MoS<sub>2</sub> field-effect transistors. *Nanoscale* **7**, 17556–17562 (2015).
34. C. R. Dean, A. F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K. L. Shepard, J. Hone, Boron nitride substrates for high-quality graphene electronics. *Nat. Nanotechnol.* **5**, 722–726 (2010).
35. J. A. Baglio, G. S. Calabrese, E. Kamieniecki, R. Kershaw, C. P. Kubiak, A. J. Ricco, A. Wold, M. S. Wrighton, G. D. Zoski, Characterization of n-type semiconducting tungsten disulfide photoanodes in aqueous and nonaqueous electrolyte solutions: Photo-oxidation of halides with high efficiency. *J. Electrochem. Soc.* **129**, 1461–1472 (1982).
36. F. S. Ohuchi, W. Jaegermann, C. Pettenkofer, B. A. Parkinson, Semiconductor to metal transition of WS<sub>2</sub> induced by K intercalation in ultrahigh vacuum. *Langmuir* **5**, 439–442 (1989).
37. A. Kumar, P. K. Ahluwalia, Tunable dielectric response of transition metals dichalcogenides MX<sub>2</sub> (M=Mo, W; X=S, Se, Te): Effect of quantum confinement. *Phys. B* **407**, 4627–4634 (2012).
38. A. A. Mitioglu, P. Plochocka, J. N. Jadczyk, W. Escoffier, G. L. J. A. Rikken, L. Kulyuk, D. K. Maude, Optical manipulation of the exciton charge state in single-layer tungsten disulfide. *Phys. Rev. B* **88**, 245403 (2013).
39. H. C. Card, E. H. Roderick, Studies of tunnel MOS diodes I. Interface effects in silicon Schottky diodes. *J. Phys. D Appl. Phys.* **4**, 1589–1601 (1971).
40. H. P. Hughes, H. Starnberg, *Electron Spectroscopies Applied to Low-Dimensional Structures* (Springer Science & Business Media, 2001), vol. 24.
41. Y.-J. Yu, Y. Zhao, S. Ryu, L. E. Brus, K. S. Kim, P. Kim, Tuning the graphene work function by electric field effect. *Nano Lett.* **9**, 3430–3434 (2009).

#### Acknowledgments

**Funding:** This work was supported by a National Research Foundation of Korea grant funded by the Korean government (Ministry of Science, ICT and Future Planning) (NRF-2016R1A2B4011706). **Author contributions:** E.K.K. proposed the research and supervised the overall study. D.C. discovered the tunneling effect of the carrier, conceived and designed the experiments, and performed device fabrication, electrical characterization, and TEM analysis. E.K.K. and Y.H.L. supervised the analysis of the results. D.C. wrote the manuscript and prepared the data representation, with all authors participating in discussions. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

Submitted 4 November 2016

Accepted 17 February 2017

Published 19 April 2017

10.1126/sciadv.1602726

**Citation:** D. Chu, Y. H. Lee, E. K. Kim, Selective control of electron and hole tunneling in 2D assembly. *Sci. Adv.* **3**, e1602726 (2017).

## Selective control of electron and hole tunneling in 2D assembly

Dongil Chu, Young Hee Lee and Eun Kyu Kim

*Sci Adv* 3 (4), e1602726.

DOI: 10.1126/sciadv.1602726

### ARTICLE TOOLS

<http://advances.sciencemag.org/content/3/4/e1602726>

### SUPPLEMENTARY MATERIALS

<http://advances.sciencemag.org/content/suppl/2017/04/17/3.4.e1602726.DC1>

### REFERENCES

This article cites 39 articles, 5 of which you can access for free  
<http://advances.sciencemag.org/content/3/4/e1602726#BIBL>

### PERMISSIONS

<http://www.sciencemag.org/help/reprints-and-permissions>

Use of this article is subject to the [Terms of Service](#)

---

*Science Advances* (ISSN 2375-2548) is published by the American Association for the Advancement of Science, 1200 New York Avenue NW, Washington, DC 20005. The title *Science Advances* is a registered trademark of AAAS.

Copyright © 2017, The Authors