Molecular switching operation in gate constricted interface of MoS₂ and hBN heterostructure

Rahul Tripathi^a, Pritam Bhattacharyya^b, Sukanta Nandi^a, Alok Shukla^b, Abha Misra^{a,*}

^a Department of Instrumentation and Applied Physics, Indian Institute of Science, Bangalore, Karnataka 560012, India

^b Department of Physics, Indian Institute of Technology Bombay, Powai, Mumbai 400076 India

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ABSTRACT

Combined with diverse two-dimensional (2D) materials for semiconductor interfaces are attractive for electrically controllable carrier confinement to enable excellent electrostatic control. We investigated the transport characteristic in heterointerface of multilayer molybdenum disulfide and hexagonal boron nitride (MoS₂/h-BN) to reveal that the charge transfer switching (CTS) is highly dependent on both the local gate constriction and bias applied across the channel. Notably, the CTS is controlled at a molecular level through electro-tunable gated constriction. The resulting significant change in conductance due to exposing 100 parts-per-billion of nitrogen dioxide molecules led to a high on/off ratio of 10² for completely switching off the channel thus, acting as a molecular switch. First-principle calculations further explained the mechanism of molecular CTS in the device. The molecular tunability of CTS has not been previously reported in any of the hetero semiconductor interfaces. Our finding opens avenues to exploit various atomically thin heterostructures for the mesoscopic transport phenomena towards molecular switching operation at room temperature.

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1. Introduction

The electrically modulated switches are one of the most elementary components in electrical circuitry. Molecular-scale switches not only need miniaturization of the devices but also enable multifunctionalities, e.g., robotics, memory, and neuromorphic computing, that are stable, reversible, writable, and addressable in solid-state devices. [1–4] So far, it has been challenging without the chemical process to achieve an efficient molecular switching by any external electrical field to switch the tunnel junction between two stable conductance states in the solid-state devices. [5–7] Moreover, the reported molecular switches for memory applications with large on/off ratios (10²–10³) do not provide a non-volatile memory, thus cannot be used in applications that require all-electrically driven nanocircuit components. [2,5–8] Therefore, there is a need for switching elements, which can be useful for the dual-functionality of electrical tunability and high on/off ratio. The heterostructure composed of two-dimensional (2D) materials are regarded as promising for the next generation nanodevices because of their unique band structure, enhanced features, and performance. [9,10] The deterministic order of assembly with unpre-

cedented control and accuracy to fabricate complex device architecture constitutes a remarkable paradigm to obtain unusual physical phenomena not observed in the pristine atomic layer. [11,12] Importantly, controlling electron transport with gate-defined constriction allows electrical detection and manipulation of spin, charge, or valley degrees of freedom in these heterostructures. [13–15] Among the family of 2D materials, transition metal dichalcogenides (TMDCs), represented by molybdenum disulfide (MoS₂), provide a promising platform due to their distinct electronic and chemical properties. [16–19] In MoS₂, the formation of tunneling barriers through nanostructures offers a unique perspective in terms of both carrier-confinement strength and the device geometry, which has been demonstrated recently in many experiments. [15,20,21] Confining charge carriers in MoS₂ and forming one-dimensional transport channel by electrostatic gating has been performed by Riccard et al. [21] Lateral stacking of TMDCs offers the electrically controllable carrier confinement, combined with the diverse nature of 2D materials. [14,20–28] The combination of different 2D materials into van der Waals heterostructures creates unprecedented physical phenomena, acting as a powerful tool for future devices. An exhaustive study of the band alignment and relativistic properties of a heterostructure is done by Pierucci et al. [29] Furthermore, strong hybridization effects arising between the constitutive layers of a SnS₂/WSe₂ hetero-bilayer structure was studied by Zirbi et al. [30] The atomic flatness and lack of dangling bonds

* Corresponding author.

E-mail address: abha.misra1@gmail.com (A. Misra).

at the surface of 2D insulators such as hexagonal boron nitride (h-BN) pave the way for a strongly coupled gate-defined quantum devices. [31–33] The ability to manipulate exciton dynamics by creating electrically reconfigurable confinement in MoS₂-WSe₂ vdWH led to an optical switch at room temperature. [34] Furthermore, such a local electrostatic gating enables a fine-tuning of the motion of electron near the channel with small external perturbation. [15] Layer dependent study of MoS₂ transistors for molecular-sensing performances in the presence of gate bias and light irradiation is demonstrated by Late et al. [35] Furthermore, density functional theory (DFT) calculations on single-layer and bilayer MoS₂ showed that the dependence of the charge transfer process on the applied electric field. The MoS₂ field-effect transistor-based gas sensor has been widely studied because of the field-dependent nature of its electronic states, offering them optimal sensitivity by controlled gating of the sensors. [36–39] The first principle calculation done by Yue et al. demonstrates that all molecules are physisorbed on monolayer MoS₂ with small charge transfer, acting as either charge acceptors or donors. [36] The application of a perpendicular electric field can also consistently modify the charge transfer between the adsorbed molecule and the MoS₂ substrate. A unique device architecture is designed by Sun et al. to induce tensile strain in bilayer graphene to prevent its mechanical deflection onto the substrate by electrostatic force. [39] Furthermore, the adsorption rate can be controlled by the electric field introduced by applying a back-gate voltage. The significant change in conductance due to quantum confinement is observed earlier in a confined nanostructure in the proximity of an adsorbed molecule. [40,41] In a report by Zhang et al., a large number of gates are employed for the enhanced electrostatic coupling between molecules and the active channel in a single-molecule transistor. [20,42–44] Further, in another report, the combination of single-electron transistors with local gates provides a unique way of charge interaction with an external molecule observed in terms of quantum transport behavior of the system. [45,46] However, electrical manipulation at room temperature is difficult due to the thermal excitation energy ($k_B T$) of the carriers. So far, precise carrier confinement is either enabled through the various arrangement of TMDC layers or controlling the carrier transport by a narrow gating to sense small perturbations. [41] However, far less attention is given to understand the deterministic role of fine-tuned mutually independent gate architecture without applying a narrow pulse. Therefore, independent gates are essential for electrical field-dependent molecular interaction in the presence of external perturbation at room temperature operation.

We report a well-controlled charge transfer switching (CTS) upon molecular interaction in a few-layer MoS₂ on top of the h-BN layer through electrotunable gated constriction. A thin layer of h-BN is employed on pre-patterned electrodes with variable separations for a fine controlled potential barrier in the channel of MoS₂. It enables precise control of electron transport properties upon molecular interaction by independently controlling the local gates. The gate combination is essential to separately tune the position of the Fermi level and the carrier density in the channel. Furthermore, the combination of local gates allows defining an electron channel with an off-state when depleted. Transport characteristic revealed that the CTS is a bias dependent conductance phenomenon in the channel due to the gating constriction. The channel conductance can be modulated up to three orders using source-drain bias. Furthermore, the gate combination allows a stepwise change in the conductance across the MoS₂ channel, which is observed for a fixed barrier width, and the magnitude is modulated using molecular interaction. Interestingly, the large-conductance variation (10^2) due to 100 parts-per-billion (ppb) of gas concentration leads to a complete switching off the channel acting as a molecular switch. The electrical field-dependent tunability of CTS has not been previously reported in any atomically

thin 2D materials. This observation opens avenues to utilize the variable gate architectural device to investigate mesoscopic transport phenomena for molecular interaction.

2. Results

Devices were prepared by standard mechanical exfoliation of bulk MoS₂ and h-BN using the scotch tape technique, as shown schematically in Fig. 1(a). A trilayer MoS₂ flake (~2 nm thick) is placed on top of a few-layer h-BN (~25 nm thick) flake using the standard dry transfer technique. [47] The bottom h-BN flake is thick enough to ensure an atomically flat surface and separates the MoS₂ layer from phonons and charge impurities present in the SiO₂ substrate. The flake thicknesses were first determined by the optical contrast and then confirmed by atomic force microscopy, as shown in Fig. 1(b). The bottom h-BN works as a dielectric layer for local gates (V_{local}), whereas the global gate (V_{BG}) is provided with a p-Si/SiO₂ (~300 nm) substrate. The device consists of five gate electrodes as shown in Fig. 1(c) acting as the local gate with different widths that are used to create a variable potential ladder varying from 50 to 1000 nm (W_{local}), enabling to evaluate a systematic study on gate width-dependence on a single device (Figure S1). Fig. 1(d) shows the Raman spectra of MoS₂ acquired at room temperature with a 532 nm excitation laser. The position of E_{2g}^1 and A_{1g} modes agree well with the available literature on Raman spectroscopy of thin MoS₂ flake. Both modes are sensitive to the number of atomic layers in the MoS₂ flake. The separation of E_{2g}^1 and A_{1g} peaks were measured to be 22.5 cm⁻¹, which confirms the trilayer MoS₂ flake. [16] The carrier density in the MoS₂ channel is shown to be tuned by biasing V_{BG} as in Fig. 1(e). Furthermore, a threshold voltage (V_{th}) around -12 V is observed with an on/off ratio of 10^6 , ensuring a well-tuned channel with V_{BG} . The carrier concentration in the pristine channel is estimated, $n_{MoS_2} = q^{-1}C_g|V_{th}| = 9.2 \times 10^{11} \text{ cm}^{-2}$ with $q = 9.2 \times 10^{-19} \text{ C}$ and $C_g = 1.23 \times 10^{-8} \text{ Fcm}^{-2}$ for 300 nm thick SiO₂ layer.

The output characteristic (source-drain current, I_{SD} versus source-drain voltage, V_{SD}) in Fig. 2(a) is plotted with different V_{local} for the gate width of $W_{local} = 1000 \text{ nm}$ at room temperature. A dc voltage of 100 mV is applied across the channel results in a linear I - V characteristic indicating an Ohmic contact. For, $V_{local} = 0 \text{ V}$, the modulation of I_{SD} is observed with different V_{BG} from +20 to -20 V in a low bias regime, indicating a typical result for the n-doped device (Fig. 2(b)). Furthermore, at positive V_{BG} , the conduction in the channel can be monotonically tuned by the local gate (1000 nm) at room temperature, down to a completely pinched off state which can be seen in Fig. 2(c). The carrier concentration in the channel for the local gate is estimated as $n_{MoS_2}(local) = q^{-1}C_g|V_{th}| = 3.09 \times 10^{11} \text{ cm}^{-2}$ with $q = 9.2 \times 10^{-19} \text{ C}$ and $C_g = 1.41 \times 10^{-7} \text{ Fcm}^{-2}$ for 25 nm thick h-BN layer.

The variation in drain current using both the V_{BG} and V_{local} shows an interesting transition from ON state to OFF state for a fixed V_{SD} of 100 mV. To understand the phenomena, the difference in I_{SD} was carefully analyzed across the ON and OFF states of the device and extracted using $\Delta I_{SD} = (I_{(V_{local})=0} - I_{(V_{local})=-1 \text{ V}})$, as the current change is measured from the offset value ($V_{local} = -1 \text{ V}$) to observe the change in conductance with switching effect. Furthermore, ΔI_{SD} is mapped as a function of V_{BG} and V_{local} (for a local gate of 1000 nm) (Fig. 2(d)). The step-like feature is observed around -2 V of V_{local} , indicating a transition from a bulk metallic state to a bulk insulating state within the depleted locally gated region. The flow of the electrons is highly influenced by the direct application of an electric field in the channel, which can be further evaluated using the source-drain bias.

To eliminate the effect of extra carrier injection due to the applied bias, the conductance of the channel is calculated for differ-

Fig. 1. (a) Schematic of the device structure. (b) Atomic force microscopy image of the MoS₂ and h-BN flakes. (c) Microscopic optical image of the device. (d) Raman spectra of the MoS₂ flake. (e) Conductance measurement of the device with V_{BG} .

Fig. 2. (a) I - V measurement of the device. (b) Variation in the drain current with global back-gate voltage. (c) Variation in the drain current with local gate voltage. (d) Color map of the drain current tuned by both V_{BG} and 1000 nm wide local gate, V_{local} at room temperature. (e) Conductance plot of the device tuned by different S - D bias at fixed $V_{BG} = +20$ V, at room temperature.

ent V_{SD} . Interestingly, a stepwise movement of the conductance is observed in Fig. 2(e), which was not observed in the doped region. The conductance of the channel can be tuned monotonically from 10^{-3} to $5 \times 10^{-1} \mu S$ by varying V_{SD} from 250 mV to 1 V. The classical results presented in Fig. 2(e) shows an abrupt termination of the charge transfer at the local gate voltage of $V_{local} = -2$ V, indicating the formation of a locally depleted region which is assumed insulating (Figure S2(a)). However, since the region is tun-

able by electrostatic field, electron tunneling may occur, which would make the channel conductive. [48] Therefore, a quantum mechanical model to account for the electron tunneling is required. Fundamentally, there are two types of tunneling: direct tunneling and Fowler-Nordheim (FN) tunneling. [49] Direct tunneling is significant for small gaps, while FN tunneling dominates if a high electric field is present in the gap. The characteristics of potential barrier in the channel can further be evaluated with applied bias.

Fig. 3. (a) Fowler-Nordheim plots for different local gate voltages for a fixed width of $W_{local} = 1000$ nm. (b) Simulated energy potential profile for different local gate voltages. (c) Simulated potential profile for different width (d) Self-consistent carrier density distribution for local gated geometry at $V_{BG} = +4$ V and $V_{local} = -1.5$ V. (e) Conductance plot of the device tuned by different widths of local gate (V_{local}) for a fixed $S-D$ bias and $V_{BG} = +20$ V at room temperature. (f) CTS in the conductance with different widths at a fixed V_{SD} and $V_{local} = -1.5$ V.

Under small applied bias, the direct tunneling current through the barrier can be expressed as

$$I_{SD} \propto V_{SD} \exp\left(-\frac{2d\sqrt{2m^*\phi}}{\hbar}\right)$$

where d , m^* and ϕ are the effective barrier width, effective electron mass and tunneling barrier height, $\hbar$ is the reduced Planck constant. The contribution from direct tunneling current is negligibly small which can be seen in Fig. 3(a). At higher source drain voltage, the potential barrier in the channel originates from the vertical electric field and the barrier becomes narrower, consequently leading to the Fowler-Nordheim (FN) tunneling. [50] The FN tunneling current is modeled by

$$I_{SD} \propto V_{SD}^2 \exp\left(-\frac{4d\sqrt{2m^*\phi^3}}{3\hbar eV}\right)$$

From the above two equations, the plot of $\ln(I/V_{SD}^2)$ versus $1/V_{SD}$ should show a linear regime with a negative slope for the FN tunneling.

The variation in potential barrier height (ϕ) with the V_{local} can be extracted from the slope and threshold voltage in Fig. 3(a). The threshold voltage for FN tunneling is calculated for all the V_{local} ($V_{local} = -2$ to -0.5 V) which turns out to be $1/2.49$ to $1/3.67$ V respectively, corresponding to the barrier height (ϕ/e) of 0.401 to 0.240 eV in case of 1000 nm local gate width. Inset of Fig. 3(a) shows the calculation for $V_{local} = -0.5$ V where barrier is estimated to be about 0.24 eV from the slope, $\frac{4d\sqrt{2m^*\phi^3}}{3\hbar eV} = 1.02$ where $m^* = 0.5m_0$ is the effective mass of the electron in MoS₂. The effective tunneling barrier width is also calculated from the inset of

Fig. 3(a), which is $d \approx 2.2$ nm. A self-consistent electrostatics simulation has been performed to calculate the potential barrier modulation with V_{local} across the channel. Fig. 3(b) shows the modulation of the barrier height with different local gate voltages which is close to the value extracted from the fitting parameters. Interestingly, the heterostructure shows a good contrast with conventional devices where the modulation in conductance is mostly obtained in the depletion region. This strongly implies that the heterostructures can be used as the tunneling device with a choice of appropriate local gate bias. The CTS via tunneling barrier can be tuned by two different voltages i.e. tunable barrier height by V_{local} and the type of tunneling by V_{SD} (Figure S2 (b, c)). For different widths of local gate, the tunneling barrier energy-space profile is shown in Fig. 3(c). In the direct tunneling regime, when the external electric field is small, the tunneling barrier is dominated by the image charge potential. In this regime, the channel conductivity mainly depends on the barrier width as shown in Fig. 3(c). Carrier density modulation at the vicinity of the channel is extracted through the electrostatic simulation. The color mapping in Fig. 3(d) represents a low charge carrier density near the local gated region at $V_{BG} = +4$ V and $V_{local} = -1.5$ V, which is similar to the observed experimental data. To study the effect of the barrier width on the conductance, a series of different W_{local} were designed in a single channel with the same range of V_{local} . Fig. 3(e) depicts the conductance as a function of V_{local} for different local gate widths varied from 50 to 1000 nm. For the wider local gates ($W_{local} = 1000, 500$ nm), the conductance in the channel is fully controlled from an OFF-state to the ON-state, which can be explained in terms of depletion width. On the other hand, Fig. 3(e) depicts there is a stepwise movement in the conductance with lowering in W_{local} , which disappeared at $W_{local} = 50$ nm, when there is no control over the channel (Figure S3). A temperature dependent study has

Fig. 4. (a) Gate dependence of on/off state with the gas exposure. (b) Systematic change in the conductance with an increment in gas molecule concentration. (c) Switching of the channel from OFF to ON-state by lowering gas molecules concentration. (d) Change in resistance with gas exposure at different local gate voltage. (e) Molecular sensing response for different length of local gates with a non-linear fit of the experimental data.

been performed from 10 to 300 K at a fixed bias to observe the effect of temperature on the barrier (Figure S4). When the gap is small, electrons easily tunnel through the narrower barrier, the increased tunneling probability increases the tunneling electron density (channel conductivity). [51,52] The calculated channel conductance is plotted as a function of local gate width for a fixed V_{local} (Fig. 3(f)). With the gap of 50 nm, the conductance value $0.7 \times 10^2 \mu S$, large enough to support the channel conductance even at weak S-D electric fields. However, in this direct tunneling regime, the larger gap of 1000 nm does not support the charge transfer because the tunneling barrier width is too wide leading to a complete switching off the channel with a low conductance value of $\sim 6 \times 10^{-1} \mu S$ which is shown in Fig. 3(f).

As discussed earlier, the CTS operation mainly depends on the width of local gates and the external electric field on the device, thus shows a potential for the molecular switching operation at room temperature. So far, a switching of the charge carriers is shown in the channel, which is further analyzed under external perturbation, in analogy with the source-drain bias of a conventional van der waals heterostructures. The effect of CTS on the molecular sensing ability of the device was evaluated using a controlled nitrogen dioxide (NO_2) gas environment. Initially, NO_2 gas molecules are injected using mass flow controllers and the concentration of the gas is fixed for 100 ppb throughout the experiment. After 300 s, the injection was stopped. At a regular interval of time, a quick sweeping of local gate voltage was performed ($V_{local} = -2$ to $+2$ V) at fixed V_{SD} and V_{BG} . Because of the nanometer-scale potential barrier width and the inversion layer located near the channel, the molecular interaction is seemingly distinct from other van der waals heterostructures. Fig. 4(a) shows the response of the device with $W_{local} = 1000$ nm in the presence of gas molecules.

The initial condition of the device was set to ON-state with a current value of 4.7×10^{-9} A, which turns to an OFF-state after molecular exposure with $I_{SD} = 9 \times 10^{-11}$ A. The concentration dependent study is performed by controlling the injection of molecules in the system for 300 s. A systematic stepwise decrement in the conductance is observed with the increasing molecular concentration in the channel, which can be seen in Fig. 4(b). There is almost a change of 10^2 in the conductance that occurs with the $V_{local} = -2$ to -0.5 V, where the barrier plays a crucial role in the charge conduction. A shift in the V_{th} is observed with the increasing molecular concentration indicating charge transfer mechanism in the vdWHs. Furthermore, the recovery of the device is also studied after the molecule injection was stopped. Fig. 4(c) depicts a stepwise increment in the conductance with lowering the gas molecule concentration. The change in resistance [$\Delta R = (R_{Without Gas} - R_{Gas})_{V_{local} = -1V}$] was evaluated in Fig. 4(d) with respect to time in presence /absence of molecules for different values of V_{local} . Interestingly, a clear dependence of flow of electron on the potential barrier under gas exposure is observed around $V_{local} = -2$ V, which is absent for the $V_{local} = +2$ V. There is a sharp increment in the resistance after the gas exposure that persists up to 300 s and decays slowly to its base value after switching off the gas injection. The peak value of the resistance is observed at around $V_{local} = -1$ V, which vanishes at positive gate bias of $V_{local} = +2$ V. Furthermore, the doping concentration in the channel can be plotted with time which is shown in Figure S5. The value of molecular adsorption rate can be extracted by fitting the curve to an equation $n_d(t) = \frac{n_0 p_a}{a} (\exp(-t/a) + n_a)$, where n_0 is the number of molecules injected in the system, n_a is the initial adsorption density in the MoS_2 and p_a is the adsorption rate. The extracted values of $n_0 p_a$ and $1/a$ are 7.20×10^{11}

Fig. 5. (a) Schematic energy diagram without and (b) with applied source-drain bias (V_{SD}). (c) Band structure of pristine MoS₂. (d) Change in the Fermi level position for single NO₂ molecule adsorbed in a 4×4 supercell of MoS₂. (e) Schematic of Fermi level shift after a small molecular concentration (f) with increased molecular concentration. (g) Side-view of the differential charge density plot of the NO₂ adsorbed in a 4×4 supercell of monolayer MoS₂ system. The electron loss and rich regions are indicated by the cyan and yellow colors.

cm²/min and 0.104%/min, respectively, showing molecules adsorption density of 7.20×10^{11} cm²/min on MoS₂ and 0.104% of them desorbing in a minute. Consequently, the Fermi level of the system will further move towards valance band. Furthermore, the tunneling probability of electrons through the barrier will further reduce and the channel will behave as a complete insulator. The gate width dependence molecular sensing study using a series of local gates of different W_{local} is shown in Fig. 4(e). The change in resistance (ΔR) shows the width dependent sensing response with different W_{local} indicating an ON-to-OFF state transition after molecular interaction is more prominent with larger W_{local} (Figure S6). Fig. 4(e) shows the fitting of the curve using an asymmetric double sigmoid function by an equation $\Delta R = \Delta R_0 + A * (\frac{1}{1+\exp(-(t-B))}) * (1 - \frac{1}{1+\exp(-(t-C))})$, where A, B, C are the constants and ΔR_0 is the initial value of the resistance.

To understand the mechanism behind the CTS via tunneling, the quantum tunneling process is further analyzed under various scenarios. Fig. 5 shows schematically how the CTS is critically affected in the presence of molecules which is also verified by DFT calculations. The energy diagrams corresponding to the specific (hypothetical) case are drawn where the barrier height is shown without the applied bias and with the applied bias at the left contact and at $-2 V$ of V_{local} across the channel and no voltage drop at the right contact as shown in Fig. 5(a) and 5(b). Enough bias is applied for a transition from a trapezoidal barrier to a triangular barrier as in

Fig. 5(b) and the position of the Fermi level can be tuned using the fixed V_{SD} [53,54] as well as by molecular interaction at a fixed V_{SD} . Further, the first-principle calculations were performed using DFT in NO₂ adsorbed monolayer MoS₂. We considered a 4×4 supercell of monolayer MoS₂ with one, two, and four NO₂ molecules within the supercell and the band structure of the single NO₂ adsorbed system is presented in Fig. 5(c).

We observed that the red-colored band near the Fermi level derives predominant contributions from the NO₂ molecule. The band structures of the two and four NO₂ molecules adsorbed systems are almost similar except firmer shift of the Fermi level towards the valance band. Moreover, the number of energy levels between the valance and the conduction bands increases with the number of NO₂ molecules considered in the system. Fig. 5(c) shows the band structure of monolayer MoS₂, which is in good agreement with the literature. [55] It is obvious from Fig. 5(c) and 5(d) that in NO₂ adsorbed monolayer MoS₂ system, a significant shift of the Fermi level of 0.42 eV towards the valance band is observed as compared to the monolayer MoS₂.

The shift in Fermi level (ΔE_{Fermi}) with the increasing number of NO₂ molecules found out to be 0.50 and 0.57 eV for two and four NO₂ molecules, respectively. The effect of shift in Fermi level is shown schematically in Fig. 5(e) and 5(f) where a transition from a triangular barrier to a trapezoidal barrier with a prominent CTS from ON-state to OFF-state. The differential charge density plots

of a single NO₂ adsorbed monolayer MoS₂ system, depicted in Fig. 5(g), confirms the electron transfer from monolayer MoS₂ surface to the adsorbed NO₂ molecule. The transferred charge are indicated by the cyan and yellow colors, respectively, with an iso-value of $1.98 \times 10^{-4} \text{ e}/\text{\AA}^3$ from heterostructure to gas molecule and the effect of electron transfer, which also indicates the shifting of Fermi level towards the valence band. It is understood that the shift in the Fermi level increases with the concentration of NO₂ molecules, which also in accordance with our experimental study.

3. Materials and methods

3.1. Device fabrication

Heterostructure of MoS₂ and graphene was fabricated with two different process for a maximum molecular interaction. For the first process a two step lithography process was done on a clean Si/SiO₂ wafer without any flake to ensure the flatness and proper transfer of the flakes. In the first step the gate electrode was fabricated followed by deposition process of Cr/Au (5 nm/10 nm). A standard procedure of dry transfer technique using PDMS (Polydimethylsiloxane) stamp without using any sacrificial layer to ensure the good surface quality. A piece of glass was covered with a PDMS stamp (0.2–0.4 mm thick) which is transparent can be used under the microscope. Few layers of h-BN flake (HQ Graphene) were then exfoliated directly on the stamp and prepared for transfer on top of the local gate electrodes (For details see Supplementary information). Now, MoS₂ flake (varying up-to few layers) (Manchester Nanomaterial) was exfoliated onto the PDMS stamp and placed on the micromanipulator stage upside down and aligned perpendicularly with the graphene flake using the microscope. The two were brought into contact and MoS₂ flake was transferred on top of h-BN. A 2nd layer of lithography process was done to form the contact pads with a deposition of Cr/Au (10 nm/70 nm).

3.2. Electrical and gas sensing measurements

Raman spectroscopy was performed in ambient condition, at a wavelength of 532 nm and with a light spot of 1 μm in different places of the device on MoS₂-h-BN heterostructure. The electrical characterization of the devices was carried out with an Agilent B1500A semiconductor analyzer in a closed chamber with a nitrogen environment after a stabilization process. Local gate dependent measurement was done by writing a script program for the dual sweep of gate voltage measurement port. Temperature dependent measurement was done in a high-vacuum chamber using Agilent B1500A semiconductor analyzer with a ramp of 25 °C. All the gas sensing experiments were performed at room temperature and atmospheric pressure. To achieve desirable concentration before being injected into the chamber the NO₂ gas was mixed with ultra-pure nitrogen gas. The concentration was fixed to 100 ppb of molecular concentration with a total flowrate of 1000 standard cubic centimeters per minute was maintained using the mass flow controllers throughout the experiment.

3.3. Theoretical approach and computational details

The first principles calculations were performed using density functional theory [56] as implemented in the Vienna Ab-initio Simulation Package (VASP). [57,58] All the calculations were carried out using projector-augmented wave (PAW) pseudo-potentials [57,59] and Perdew-Burke-Ernzerhof (PBE) exchange correlation functional. [60] A kinetic energy cut-off of 500 eV and $5 \times 5 \times 1$ k-mesh were considered for structural optimization. The threshold for energy and force convergence was chosen to be 10^{-5} eV

and 2×10^{-2} eV/ $\text{\AA}$, respectively, while with more than single NO₂ molecule in a 4×4 supercell, the force convergence criteria was set to be 5×10^{-2} eV/ $\text{\AA}$. The density of state calculations was carried out with a tighter threshold for energy convergence, i.e. 10^{-6} eV, and using a higher density of k-mesh, i.e. $21 \times 21 \times 1$. At least, a vacuum of 25 $\text{\AA}$ was considered along the z-direction to minimize the interactions with its images. We also incorporated the DFT-D2 method of Grimme [61,62] to take into account the van der Waals force correction. To perform the band structure calculations, we employed 60 k-points in the reciprocal space. The differential charge density in single NO₂ adsorption can be defined as $\rho_{\text{ad}} = \rho_{\text{MoS}_2+\text{NO}_2} - \rho_{\text{MoS}_2} - \rho_{\text{NO}_2}$, where $\rho_{\text{MoS}_2+\text{NO}_2}$, ρ_{MoS_2} and ρ_{NO_2} are the charge densities of the monolayer MoS₂ + adsorbed NO₂, monolayer MoS₂, and isolated NO₂ molecule, respectively.

3.4. COMSOL simulation for potential barrier calculation

To complement and support our analysis of the barrier on the device, we carried out self-consistent electrostatic simulations of the carrier density in the MoS₂ plane as a function of the back-gate and local gate voltages. The geometry of the simulation is represented in Figure S7. The dimensions of the different local gate width and the thicknesses of the SiO₂ and h-BN layers are close to those of the measured device. A sigmoid function was considered for simulation of the carrier density in MoS₂ sheet (For details see supplementary information). The Poisson's electrostatic static equation was solved with proper boundary conditions for different gate voltages. The profile of the potential energy ($E = -eV$ where e is the charge of the electron and V is the applied voltage at the local gate) across the local gated region is calculated for a fixed back-gate voltage and various local gate voltages and local gate widths.

4. Conclusion

A novel approach to control the CTS in depletion region is demonstrated for the first time by engineering the device architecture. The multi-gate configuration is used to demonstrate an electrically reconfigurable type of potential landscapes in a single channel. The charge transport through the tunable potential barrier using an in-plane electric field is governed by the carrier tunneling. A strong molecular induced modulation of doping effect is observed in MoS₂/h-BN vdWHs and a microscopic description of its origin is also discussed. The carrier movement (block or allow) in the vicinity of the channel with external perturbation is demonstrated, in analogy with source-drain bias of a conventional field effect transistor. Furthermore, the spatial confinement of the charge carriers due the potential barrier leads to an electrically controlled molecular switch using CTS mechanism. The formation of potential landscapes contributes to a new route to design and study quantum phenomena emerging from vdWHs for future study in molecular interactions.

CRedit author statement

Rahul Tripathi: Design of experiments, fabrication and testing of devices, data analysis, manuscript preparation **Pritam Bhattacharyya:** Simulation and analysis, manuscript preparation. **Sukanta Nandi:** Low temperature measurements. **Alok Shukla:** Supervision. **Abha Misra:** Writing- Reviewing and Editing.

Declaration of Competing Interest

All authors declare that there are no conflict of interest with any authors.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.apmt.2021.100999.

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