

Competition between bipolar conduction modes in extrinsically *p*-doped MoS₂: Interaction with gate dielectric matters

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Abstract

With reduced dimensionality and high surface area-to-volume ratio, two-dimensional (2D) semiconductors exhibit intriguing electronic properties that are exceptionally sensitive to surrounding environments, including directly interfacing gate dielectrics. These influences are tightly correlated to their inherent behavior, making it critical to examine when extrinsic charge carriers are intentionally introduced to the channel for complementary functionality. This study explores the physical origin of the competitive transition between intrinsic and extrinsic charge carrier conduction in extrinsically *p*-doped MoS₂, highlighting the central role of interactions of the channel with amorphous gate dielectrics. By providing a pristine interface to the channel and controlling the degree of such interaction using hexagonal boron nitride (h-BN) spacers of different thicknesses, we determine three distinctive interaction modes: noncontact, proximity, and direct-contact. In the direct-contact mode without an h-BN spacer, charge transfer and orbital mixing induce ambipolar conduction in few-layer *p*-doped MoS₂, showing an unexpected gate-dependent crossover between co-existing extrinsic and intrinsic conduction. Kelvin probe force microscopy and Raman spectroscopy confirm *n*-type doping in the channel through dielectric interactions, further supported by first-principles calculations identifying unpassivated silicon dangling bonds on the SiO₂ surface as the origin of *n*-doping. On the contrary, depending on the thickness of the h-BN spacers, the noncontact mode maintains degenerate *p*-type conduction in the transfer curve, while the proximity mode enables gate-responsive *p*-type conduction, emphasizing the significant role of dielectric interactions in modulating charge transport. These findings underscore the importance of dielectric engineering in optimizing 2D semiconductor devices, particularly for improving *p*-type transistor performance.

Keywords

2D semiconductors, Gate dielectric, Interface, Intrinsic and extrinsic charge carrier conduction, Charge transfer, Orbital mixing, Ambipolar conduction.

High-potential two-dimensional (2D) semiconductors offer a promising alternative to silicon in complementary metal oxide–semiconductor (CMOS) technology, especially for highly scaled process nodes.^{1–3} Their atomically smooth surfaces and lack of dangling bonds effectively address challenges encountered by bulk semiconductors at subnanometer thicknesses, commonly referred to as the thickness limit.⁴ This potential stems from optimized electron pathways and precise electrostatic control.⁵ Exceptional strides have been made in advancing *n*-type field-effect transistors (FETs) using monolayer MoS₂, positioning them closer to fulfilling industrial requirements. Developments in critical areas such as high-quality, low-temperature,^{6, 7} large-scale growth,^{8–10} improved contact engineering,^{11, 12} and the integration of high-*k* van der Waals (vdW) dielectrics^{13–15} have played pivotal roles in propelling these advancements, thereby enhancing their industrial applicability to meet market demands.

After notable success with *n*-type 2D FETs, addressing challenges in developing *p*-type counterparts has become increasingly important for realizing functional logic circuits in next-generation devices. For CMOS compatibility, substitutionally *p*-doped transition metal dichalcogenide (TMD) materials have been proposed. However, the development of *p*-doped MoS₂ FETs has progressed slowly, largely owing to inherent difficulties in controlling the polarity of the material. TMDs are highly sensitive to gate dielectric interactions, particularly through mechanisms such as charge transfer,^{16, 17} strain,¹⁸ and orbital mixing.¹⁹ Additionally, they typically tend to accumulate electrons because they utilize partially filled *d*-orbitals to accept and transport electrons. For instance, MoS₂ and MoSe₂ tend to accumulate electrons on their surfaces, rather than depleting them when exposed to air owing to interactions with external species.^{20–22} This implies that interactions between *p*-doped MoS₂ and its surrounding gate dielectric can lead to *n*-doping in the channel through mechanisms such as charge transfer or orbital mixing with dangling bonds containing unpaired electrons in the dielectric surface. Furthermore, chalcogen vacancies in doped *p*-type MoS₂ create trap states near the conduction band edge of the MoS₂,²³ which can become charged, especially in close interaction with the gate dielectric, thereby facilitating trap-assisted electron transport.^{24–27} The inadvertent role of gate dielectric in causing out-of-polarity control in *p*-doped 2D semiconductors has been somewhat overlooked.

Herein, we investigated the mechanisms underlying ambipolar behavior in *p*-doped MoS₂, focusing on how gate dielectric interactions influence charge transport in the channel. Using hexagonal boron nitride (h-BN) spacers, we examined the interaction between a six-layer *p*-doped MoS₂ channel—chosen for its ambipolar properties observed during thickness-dependent conductivity experiments—and a SiO₂ gate dielectric. We explored three distinct interaction modes based on spacer thickness: noncontact (10 nm), proximity (3 nm), and direct-contact (no spacer). Our findings reveal that noncontact mode maintains degenerate *p*-type conduction by minimizing interaction of the channel with the dielectric, while proximity mode enables gate-responsive *p*-type conduction moderated by spacer thickness. In contrast, direct-contact mode induces ambipolar conduction in the channel through charge transfer, orbital mixing, and strain effects. Surface potential modulations observed through Kelvin probe force microscopy (KPFM) and Raman spectroscopy suggest an excellent counter-doping effect in the channel driven by these dielectric interactions. Density functional theory (DFT) calculations further identify unpassivated Si dangling bonds on the SiO₂ surface as a source of *n*-doping in the channel. Electrical measurements support these findings, showing that dielectric-coupled interactions facilitate a transition from extrinsic to intrinsic charge transport in the channel, primarily through trap-related conduction and electron injection. These insights underscore the critical importance of dielectric

engineering in fine-tuning the electronic properties of *p*-type 2D semiconductors, crucial for the advancement of CMOS devices.

Results/Discussion

Thickness-dependent charge transport in doped 2D semiconductors. The carrier transport properties in extrinsically *p*-doped 2D materials are probed in a typical configuration of FET with a back gate (Fig. 1a). Throughout this study, Nb-doped MoS₂ is employed as a representative material, where Nb dopants act as substitutional acceptors, converting intrinsic pristine MoS₂ from an intrinsic *n*-type to extrinsic *p*-type semiconductor (Nb-doped MoS₂). The doping concentration (N_A) of the Nb-doped MoS₂ is fixed at 0.5 at.%, leading to degenerate a hole concentration of $3.3 \times 10^{19} \text{ cm}^{-3}$ in the channel. The substitutionality and hole density from Nb doping have been experimentally proven in our previous studies.^{28,29} Furthermore, X-ray photoelectron spectroscopy (XPS) measurements guarantee spatial uniformity of Nb dopant, with XPS depth profiling showing that Nb dopants are homogeneously distributed along the vertical depth of the channel (Supplementary Fig. 1), consistent with the formation of a solid solution Nb_{*x*}Mo_{1-*x*}S₂ over a full range of *x*.³⁰

Despite such vertical doping homogeneity, the transfer characteristics (drain current (I_{DS}) vs. gate voltage (V_{GS})) of Nb-doped MoS₂ FETs, prepared on SiO₂ (90 nm)/*p*⁺-Si substrates, exhibit a pronounced and unique dependence on thickness of the channel. Figure 1b displays the transfer curves in a semilogarithmic scale measured from devices with varying channel thicknesses at room temperature (~300 K). Thin flakes of the Nb-doped MoS₂ show a monotonically increasing gate dependence, reaching a maximum I_{ON}/I_{OFF} ratio of $\sim 10^7$ in the *p*-type conduction branch for a four-layer (4L) flake with complete electrostatic control. In addition to doping-induced *p*-type conduction, FETs with reduced thickness (<10L) begin to exhibit rather unexpected ambipolar behavior. Supplementary Figure 2 provides detailed electrical properties of Nb-doped MoS₂ FETs across different thicknesses (6L to 4L) of the channel, showing the relationship between drain current and gate-source voltage, field-effect mobility (1.9 to 0.8 cm²·V⁻¹·s⁻¹), and I_{ON}/I_{OFF} ratio (1.95×10^5 to 1.65×10^7). As thickness decreases, mobility of Nb-doped MoS₂ FETs tends to decrease while the I_{ON}/I_{OFF} ratio increases. The negligible V_{GS} dependence in thicker flakes (10L) owing to degenerate doping—caused by the presence of a shunting current path that is not controlled by electrostatic gating³¹—is further explained in Supplementary Fig. 3. We focus on the field effect region ($t_{\text{body}} \leq W_{\text{DM}}$), which is confined to regions controlled by electrostatic gating (Fig. 1c).

Such ambipolar transport characteristics, despite degenerate *p*-doping level of Nb-doped MoS₂ and sizable bandgap, indirectly imply the coexistence of bipolar conduction modes originating from intrinsic *n*-conduction in MoS₂ and extrinsic *p*-doping, which interchangeably appear depending on the applied gate voltage. Given that 2D semiconductors are sensitive to environmental factors, including dielectric media that can introduce charge transfer, strain, and orbital mixing, we conducted a series of experiments and theoretical calculations to reveal the critical role of gate dielectrics in terms of unexpected transition of conduction modes from extrinsic to intrinsic domains. To ensure a consistent ionization rate and minimize thickness-dependent variations in impurity levels and band structure, we used 6L flakes. In even thinner channels, substrate (dielectric) effects can become challenging to tell due to the expected reduced ionization of dopants, while thicker channels form shunt paths that can be superimposed on the

substrate-induced changes. Thus, 6L flakes were chosen as the optimal thickness to guarantee stable ionization and clear observation of substrate effects.

h-BN spacer for electronic decoupling. Thickness-dependent electrical transport in Nb-doped MoS₂ FETs can be explained by the presence of surface band bending near the semiconductor–dielectric interface. To study its physical origin, we designed and fabricated devices by inserting h-BN between the semiconductor and amorphous gate dielectric. With its defect-free, atomically flat surface, h-BN is ideally suited to suppress any electronic influences from the inhomogeneous topography and local charge distribution of the amorphous SiO₂ surface. As shown in the schematic illustrations of Fig. 1c, the investigated devices were co-fabricated from a single flake of even thickness to monitor the electronic influences from gate dielectric comparatively (See the Methods section for fabrication details and Supplementary Fig. 4 for additional optical images). We carefully designed the gate dielectric stack to ensure that the in-series addition of the h-BN capacitor considered their thickness and dielectric constants: h-BN ($t_{\text{h-BN}} = \text{maximum } 10 \text{ nm}$) and SiO₂ layer ($t_{\text{SiO}_2} = 300 \text{ nm}$, $C_{\text{SiO}_2} = 1.15 \times 10^{-2} \mu\text{F}\cdot\text{cm}^{-2}$, resulting in a maximum variation of $\sim 4\%$ in gate capacitance ($1.11 \times 10^{-2} \mu\text{F}\cdot\text{cm}^{-2}$), as depicted in the inset of Fig. 1d. The spacer-driven modulation of electrical transport in the Nb-doped MoS₂ is intentionally controlled by varying the spacer thickness to adjust the degree of its interaction with the gate dielectric. Specifically, the spacer thickness determines the extent of short- and long-distance charge interactions, enabling a systematic exploration and management of gate dielectric interactions.

Accordingly, three cases with different thicknesses of spacer were explored: direct-contact (no spacer), proximity (3 nm), and noncontact (10 nm), as shown in Fig. 1d. With the given channel thickness and length (thus identical extrinsic carrier concentration), the FETs built on few-layer Nb-doped MoS₂ distinctively operate under these three conditions. First, as previously discussed, the FET without an h-BN spacer shows ambipolar transport that transitions from extrinsic *p*-type to intrinsic *n*-type dominant charge transport at positive V_{GS} (direct-contact mode; Fig. 1e). In the case of a thin spacer, which still allows long-distance charge transfer via tunneling, the device predominantly exhibits *p*-FET behavior with much-enhanced gate control despite its degenerate doping level (proximity mode; Fig. 1f). It reaches a *p*-type $I_{\text{ON}}/I_{\text{OFF}}$ ratio of $\sim 10^6$ for the 6L flake through electrostatic control of Nb-doped MoS₂ FETs. Lastly, when the flake is completely isolated from the gate dielectric, the corresponding electrical transport is preserved and solely governed by extrinsic carriers, similar to its bulk counterpart (noncontact mode; Fig. 1g). Notably, the addition of the spacer readily recovers its bulk-like *p*-conduction reaching a current density of $98 \text{ kA}\cdot\text{cm}^{-2}$, which represents an order-of-magnitude increase in I_{ON} compared to the direct-contact mode. From these results, it is qualitatively evident that substantial interactions occur, including charge transfer with self-adjusted band alignments (e.g., *p*-type polarity MoS₂/CrOCl¹⁶), strain-induced spatially rugged channel (e.g., band tail near the valence band and conduction band edge^{32, 33} of the MoS₂), orbital mixing (e.g., S 3*p*–O 2*p* orbital mixing¹⁹) between the channel and gate dielectric, which will be discussed in great detail in the following subsections.

Fermi-level tuning using a gate dielectric. Depending on the presence and thickness of the spacers, the observed drastic variations in Nb-doped MoS₂ FETs may suggest a relevant modification in the concentration of extrinsically doped majority carriers and, consequently, the relative Fermi-level positions of the Nb-doped MoS₂. In amorphous SiO₂, two dominant defect in-

gap bands have been identified, with the lower defect band, often ignored for pristine *n*-type MoS₂, which is located at $\sim 0.640 \pm 0.350$ eV above its valence band maximum (VBM).³⁴⁻³⁶ For *p*-MoS₂, this band can effectively trap holes across the SiO₂–MoS₂ interface in both direct-contact and proximity device configurations, depleting the extrinsically introduced holes during the self-adjusted band alignment under an equilibrium condition (Fig. 2a). This effect can dominantly influence the threshold voltage shift in the I_{DS} vs. V_{GS} of Nb-doped MoS₂ FETs owing to such hole trapping. In contrast, the noncontact configuration with a 10 nm spacer, designed for complete decoupling, will be free from such charge transfer effects. KPFM is performed to track the corresponding Fermi-level (E_F) shift in Nb-doped MoS₂ depending on the existence of the h-BN spacer. The sample is simply prepared by inserting the spacer into a single flake in part. Fig. 2b shows the contact potential difference (CPD) across the Nb-doped MoS₂ flake (left: noncontact and right: direct-contact regions), with E_F clearly shifting upward (toward the intrinsic E_F of MoS₂) by more than 100 meV because of charge transfer. The CPD is calculated using the equation $V_{CPD} = (\phi_{surface} - \phi_{tip})/e$ where $\phi_{surface}$ is the work function of the sample surface, ϕ_{tip} is the work function of the KPFM tip, and e is the elementary charge. This equation defines the relationship between the measured contact potential difference and the relative work functions of the sample and the tip. In our analysis, the Au work function serves as the reference (0-point) to ensure consistency and clarity (see Supplementary Fig. 6 for further details on the calculations). To compare the CPD of the shunt path region, fabricated with 9L and 8L Nb-doped MoS₂ devices, Supplementary Fig. 5 displays the thickness and transfer curves of each, while Supplementary Fig. 6c illustrates the surface potential, which remains similar to the Au work function (5.1 eV), regardless of the 9L and 8L thickness, as observed in the noncontact mode. In the case of pristine MoS₂, hysteresis owing to border traps and subthreshold swing degradation notably occurs compared to devices incorporating h-BN. However, the phenomenon of charge transfer at the SiO₂ surface was not observed in surface potential measurements (Supplementary Fig. 7).

In addition, the consistency of this phenomenon was validated through Raman spectroscopy analysis, as doping and strain can induce the characteristic shifts in the main Raman peaks of MoS₂. By overlaying our measured data onto established maps illustrating the interplay between doping and strain on the peaks based on previous reports,^{18, 37} we observed clear shifts owing to the *n*-doping effect ($\Delta 0.5$ cm⁻¹, $\sim 2 \times 10^{12}$ cm⁻²) and global tensile strain effect ($\Delta 0.7$ cm⁻¹, $\sim 0.2\%$) in Nb-doped MoS₂ when transitioning from the noncontact (E_{2g} : 383.3 cm⁻¹, A_{1g} : 408.3 cm⁻¹) to the direct-contact (E_{2g} : 382.6 cm⁻¹, A_{1g} : 407.8 cm⁻¹) configurations (Fig. 2d). No noticeable variation in peak characteristics was observed for thicknesses greater than 6L (Supplementary Fig. 6d), likely because the influence of the dielectric surface diminishes with increasing thickness, while the unaffected bulk region dominates the material's behavior. Furthermore, experimental data from five points on another device exhibiting the same effect yielded consistent results, as shown in Supplementary Fig. 8 and 9. Raman spectroscopic results suggest the potential formation of tail-like band edges resulting from $\sim 0.2\%$ tensile strain, a phenomenon consistently observed and validated across numerous studies owing to the structural characteristics of MoS₂. These characteristics are attributed to the inherent reliance of MoS₂ on distance-dependent interactions between transition metal *d*-orbitals and chalcogen *3p* orbitals. Therefore, the presence of flattened h-BN spacers mitigates the effects of strain, providing an inherent characteristic of materials in optical measurement.³²

DFT analysis of SiO₂ and Nb-doped MoS₂ interactions. To investigate the interface effect, we constructed Nb-doped MoS₂/SiO₂ heterostructure models, in which we used amorphous SiO₂ structures reported in a previous study³⁸. DFT calculations with the vdW correction of Grimme-D3³⁹ were conducted to optimize the structure of the Nb-doped MoS₂/SiO₂ heterostructures and analyze the interactions between Nb-doped MoS₂ and SiO₂ (see Methods for details). Our experiments showed that in direct-contact configurations, the holes in Nb-doped MoS₂ are compensated, indicating the existence of donor states on the SiO₂ surface. We thus explored scenarios where dangling bonds with a single electron on the SiO₂ surface might contribute to *n*-doping in direct-contact configurations. By modifying the surface of a fully H-passivated SiO₂ substrate (Fig. 3a)—which, as shown in Supplementary Fig. 10, has a negligible effect on the electronic structure of MoS₂—we created dangling bonds by removing the H passivation and analyzed their impact on Nb-doped MoS₂. Actually, H-passivation has been experimentally shown to effectively reduce interface traps in MoS₂, thereby improving interfacial properties and minimizing electronic degradation.⁴⁰ Two primary configurations were examined: Si and O dangling bonds, as shown in Fig. 3b. The density of dangling bonds at the surfaces for both configurations is ~ 0.5 per nm², corresponding to known surface defects in amorphous SiO₂, as identified in previous studies.⁴¹⁻⁴⁴ DFT calculations of the Nb-doped MoS₂/SiO₂ heterostructure showed that the defect state of the Si dangling bond is positioned approximately 0.9 eV above the VBM (unless otherwise specified, VBM represents the highest occupied state contributed by the Nb-doped MoS₂ layer), denoted as VBM + 1 in Fig. 3b. This state results from orbital mixing between Si, O, and MoS₂, as illustrated in the inset of Fig. 3b. In contrast, the defect state of the O dangling bond lies slightly below the VBM, denoted as VBM – 1 in Fig. 3b, which primarily originates from the O dangling bond. The positioning of this state suggests that it is unlikely to function as a donor. Isosurface plots indicate that in the Si dangling bond configuration, the empty VBM + 1 state is localized around the unpassivated Si atom, while the fully occupied VBM state (which is empty in free-standing Nb-doped MoS₂) is delocalized in the Nb-doped MoS₂ layer and has no contribution from the dangling bond. These observations imply that the Si dangling bonds lose electrons and become positively charged, thereby influencing the electronic properties of the Nb-doped MoS₂ as a donor state. The lost electrons transfer to the MoS₂ layer and compensate for the holes introduced by the Nb dopant (Fig. 3c).

To quantify the effect of donor states in SiO₂ on Nb-doped MoS₂ in proximity, we calculated the transferred electron from the direct-contact scenario (no spacer) to a proximity distance of 3 nm. Our Bader charge analysis indicates that, in the direct-contact scenario, 0.81 *e* was transferred, while 0.12 *e* was transferred in the proximity case (Fig. 3d). This trend decreases exponentially with the distance between Nb-doped MoS₂ and SiO₂, indicating that *n*-doping effects can be controlled by the spacing between the SiO₂ and the Nb-doped MoS₂. This aligns well with our experimental observations that carrier concentration changes with the thickness of the intercalating h-BN.

Consequently, the defect state of Si dangling bonds functions as donors in SiO₂, playing a crucial role in the removal of holes in Nb-doped MoS₂. Additionally, the surface irregularity of partially passivated SiO₂ in direct-contact with MoS₂ likely contributes to the band tail of MoS₂ owing to orbital mixing with surface defects in SiO₂.

Interpreting ambipolar conduction through Bulk-limited and Body Effect. In the previous transport data, we observed ambipolar properties in the direct-contact device stemming from

bipolar *p*-type and *n*-type conduction modes of Nb-doped MoS₂ FETs. This phenomenon can be interpreted by the fact that the region near the drain electrode maintains ohmic contact owing to high *p*-doping levels of the Nb-doped MoS₂, facilitating hole injection into the channel, while areas closer to the dielectric and source electrode are depleted. Owing to its ultrathin thickness, the device allows electrons to enter through tunneling.

This inference regarding the ease of electron tunneling is supported by several observations.⁴⁵ First, the ability for tens of nanoamperes of current to flow, even with an h-BN thickness of 3.5 nm, demonstrates that electrons can readily tunnel through the thin depletion region to contribute to the channel.^{46, 47} This tunneling effect is likely even more pronounced in MoS₂, given that h-BN has a higher barrier, larger effective mass, and fewer gap states compared to MoS₂. Second, the lack of hysteresis improvement of pristine MoS₂ FETs when h-BN is inserted, except in the contact region, in contrast with the improved hysteresis when h-BN is included in the contact region, indicates that this increased hysteresis relates more to the contact region than to the channel area (Supplementary Fig. 7 and 11). Additionally, the observed hysteresis increases nonlinearly as thickness of pristine MoS₂ decreases (Supplementary Fig. 12), presumably suggesting that this mechanism is related to the injected charge in the channel, not solely to the channel carriers. Lastly, the symmetrically widening hysteresis (Supplementary Fig. 11) and its magnitude of change support this inference. The symmetrically widening hysteresis indicates that the injection of both electrons and holes is facilitated regardless of the channel type. Moreover, the trapped charge in the oxide can be quantified by the magnitude of the hysteresis, which shows a difference of 15 V. The calculated trapped charge density based on this variation (15 V , $\Delta V_{\text{FB}} = q\Delta n_{\text{t}}/C_{\text{ox}}$, where Δn_{t} is the trapped charge density in the oxide and C_{ox} is the oxide capacitance) is approximately $1.2 \times 10^{12}\text{ cm}^{-2}$. This value is comparable to the carrier concentration observed in monolayer MoS₂,^{48, 49} indicating that half of this amount of charge—whether electrons or holes—must be injected when the type of charge in the channel is opposite to that of the channel carrier.

This inference regarding the depletion of the area closer to the dielectric and source electrode is supported by simulations using COMSOL software (Supplementary Fig. 13). These simulations reveal that while the area near the source/dielectric undergoes complete depletion, the region closer to the upper channel/drain primarily exhibits a hole-rich area in the pinch-off region.

These factors collectively suggest that as the source/dielectric region depletes, an electron reservoir may form through tunneling in the adjacent area, leading to electron conduction. This conduction is likely to exhibit ohmic behavior (bulk-limited conduction). Additionally, considering the inherent traps in the channel, the presence of this large reservoir may lead to trap-related conduction, which is also bulk-limited (Supplementary Fig. 14).

These inferences help explain the observed ambipolar transport in Nb-doped MoS₂ FETs. Previous research on ambipolar behavior in TMD-based FETs has typically considered two primary approaches: the Landauer formula-based model,^{50, 51} which accounts for the Schottky junction effect and assumes ballistic transport in short channels, and the Pao–Sah model,^{52, 53} which emphasizes the channel-limited effect and easily incorporates nonideal effects in the model. However, our device behavior highly aligns with bulk conduction⁵⁴ as per bulk-charge theory, likely owing to factors such as the long channel (diffusive transport), high doping concentration (resulting in ohmic contact), the ease of electron injection through tunneling (ohmic-like behavior owing to the electron reservoir under the source electrode), along with simulation results showing a marked body effect at pinch-off.

Considering these situations, we have extended the bulk-charge model from Supplementary Note 1. According to this extended model, even when hole current flows near the upper channel/drain region, it can be explained that electrons can move through traps near the source/dielectric region owing to the body effect. This model will serve as the framework for the following electrical analysis.

Ambipolar conduction enforced via trap-related mechanisms. Based on our inference, we analyzed the output characteristics of FETs in both noncontact and direct-contact modes over a voltage range of -1 to 1 V at selected gate voltages ($V_{GS} = -80, 0$, and 80 V, as shown in Fig. 4a and b). The noncontact FET exhibits ohmic contact behavior, characterized by a slope of 1 in the output curve, which is supported by a highly doped region (Fig. 4a). In contrast, the direct-contact device exhibits a nonlinear I_{DS} vs. V_{DS} curve in the depletion and inversion regions (Fig. 4b). Such nonlinearity can be further elucidated using linear fitting in double-logarithmic scale; the slope extracted from the direct-contact Nb-doped MoS₂ flake is fitted to ~ 1.5 , implying a primary contribution from diluted T-SCLC. Additionally, at low fields (below 0.3 V), a drift-diffusion current flows when V_{GS} is 22 V, as shown in Fig 4c. In the high drain voltage range, the current initially follows ohmic behavior and then transitions to drift-dominant trap-related conduction, which plays a crucial role in the overall current flow in Nb-doped MoS₂ FETs (additional data in Supplementary Fig. 15).

The currents in both the surface-affected region (I_{SUB}) and the unaffected region (I_{FE-SUB}) can be represented as bulk-limited conduction,⁵⁵ expressed as follows (please refer to Supplementary Note 1):

$$\begin{aligned} I_{SUB} &= (9/8)\theta(W_{ch}t_{sub})\varepsilon\mu_n V_D^2/L_{ch}^3, \theta = N_c \exp(-E_T/k_B T)/N_T, \\ I_{FE-SUB} &= W_{ch}(t_{body} - t_{sub})qp\mu_p V_D/L_{ch}, p = N_v \exp(-(E_F - E_v)/k_B T). \end{aligned} \quad [1]$$

Here, I_{SUB} is the current through the channel closer to the gate dielectric, influenced by channel width (W_{ch}), effective channel thickness (t_{sub}), electron mobility (μ_n), channel length (L_{ch}), and the free-to-trap rate (θ), which depends on conduction band density of states (DOSs) (N_c), trap density (N_T), trap energy (E_T) from the trap states to the bottom of the CBM, and k_B is Boltzmann constant. Similarly, I_{FE} represents the current through the channel farther from the gate dielectric, uninfluenced by thickness ($t_{body} - t_{sub}$) of Nb-doped MoS₂, hole mobility (μ_p), and hole concentration (p), which depend on the valence band density of states (N_v), Fermi level (E_F), VBM energy (E_v), and T of Nb-doped MoS₂. Therefore, the trap-related current in the transfer curve (Fig. 4d), affecting traps considering the DOSs of MoS₂ with vacancies^{24, 56} (Fig. 4e), can be expressed as follows:

$$I_{T-SCLC} = I_{FE-SUB} + I_{SUB}. \quad [2]$$

It follows that if I_{SUB} and I_{FE-SUB} exhibit similar current levels, this would correspond to a slope of 1.5 in the linear fitting when plotted on a double-logarithmic scale. Moreover, a similar

slope has been reported in previous studies, such as the diluted T-SCLC phenomenon observed in undoped monolayer MoS₂ transistors under increased light intensity.⁵⁷

Interfacial effect in trap-related conduction. From Equation 2, we can examine the trap effect using a temperature-dependent current. Since $E_F - E_V$ is controlled via electrostatic gating, and if it is much higher than E_T , we can consider that the variation in T-SCLC current with temperature is determined using the trap-limited current itself ($\Delta I_{T-SCLC}(T) = \Delta I_{SUB}(T) + \Delta I_{FE-SUB}(T) \cong \Delta I_{SUB}(T)$). Therefore, this current can be characterized using an Arrhenius plot at the limited conduction as follows:

$$\ln(I_{T-SCLC}) \propto \frac{-E_T}{k_B T}. \quad [3]$$

To apply Equation 3, we measure the transfer curve of Nb-doped MoS₂ FETs within the temperature range of near-complete ionization of Nb (band conduction region; Supplementary Fig. 16), specifically between 190 and 300 K, to understand the trap-related conduction mechanism in detail (Fig. 5a and b). We analyzed the trap energy as a function of gate voltage, yielding crucial results that indicate a series of changes in Arrhenius plot (activation energy (E_a) vs. V_{GS}) as the energy difference between E_F and the VBM increases, eventually transitioning into differences in trap energy. These results suggest variations in the distribution of trap energy or energy distribution owing to the band tail. The peak point represents the discrete trap energy of vacancies in the Nb-doped MoS₂.

In proximity mode, the trap energy was relatively small (200 meV) but comparable to the level (260 meV) of trap energy recently extracted through deep-level transient spectroscopy⁵⁸ (Fig. 5c). In direct-contact mode, this value was considerably lower (150 meV, Fig. 5d). Additionally, the change in slope (falling rate) of E_a vs. V_{GS} as the peak value of E_a is approached was evident. The falling rates, which indicate the energy distribution of trap states,⁵⁹⁻⁶¹ were markedly low in Nb-doped MoS₂ when in direct-contact with SiO₂. The decline in slope and decrease in peak energy represent the most profound differences between the direct-contact and proximity modes. This observation suggests an increase in gap states for interface between the channel and gate dielectric attributed to orbital mixing owing to surface defects and rugged states from strain. These factors result in a reduced falling rate, low trap energy, and ultimately enhanced n -polarity of Nb-doped MoS₂ FETs.

Design of a basic logic circuit through conductivity modulation with dielectric engineering.

We confirmed conductivity modulation between SiO₂ and the inserted h-BN layer through multiple experiments (Supplementary Fig. 17). Moreover, we observed similar compensation phenomena in other doped TMDs, such as Re-WSe₂, suggesting that these effects can be generalized as a gate dielectric effect (Supplementary Fig. 18).

The incorporation of layers such as h-BN in 2D TMDs demonstrates a remarkable ability to manipulate interface properties of 2D TMDs channel, offering a pathway to control electrical characteristics.⁶² This controllable electrical behavior of 2D TMDs FETs can be summarized via

two primary mechanisms. First, the h-BN layer plays a critical role in alleviating local strains and reducing orbital mixing between the channel and gate dielectric, thereby preserving the inherent properties of the channel. Second, the h-BN layer substantially regulates the amount of charge transfer between the channel layer and SiO₂. By adjusting the thickness of the h-BN layer, both mechanisms can be finely tuned, controlling the electrical behavior of the device. Furthermore, we believe that this modulation approach extends beyond h-BN and SiO₂ to any novel gate dielectric, including vdW insulators.

Using this strategy, an Nb-doped MoS₂ 4-layer channel, which contains fewer ionized dopants than 6L, can transition the device from weak *n*-type ambipolar (direct-contact) to weak *p*-type ambipolar (noncontact) through the insertion of an h-BN layer, as illustrated in Fig. 5e. This transition enables the fabrication of an inverter, as depicted in Fig. 5f, demonstrating the versatility of this approach in device design. Detailed properties of the inverter operation can be found in Supplementary Fig. 19. However, our deliberate choice of a 300 nm-thick SiO₂ was aimed at isolating the gate dielectric-induced effects from the gating effect. While the gain of the inverter may not be high, the insights gained pave the way for future applications.

Conclusions

This study delves into the complex interactions between the channel and gate dielectric in highly *p*-doped MoS₂, particularly focusing on the impact of dielectric engineering on charge transport properties of Nb-doped MoS₂ FETs. We employed h-BN spacers of varying thicknesses to delineate three distinct interaction modes: noncontact, proximity, and direct-contact. Our results reveal that noncontact modes with thicker h-BN spacers (10 nm) preserved the degenerate *p*-type behavior inherent to the doped MoS₂. In contrast, proximity (3 nm h-BN spacer) and direct-contact (no spacer) modes exhibited gate-responsive *p*-type/ambipolar properties. This transition is attributed to the extent of interaction between the channel and the underlying gate dielectric. KPFM and Raman spectroscopy were pivotal in understanding these interactions. KPFM results indicated important modulations in surface potential of Nb-doped MoS₂ channel, while Raman spectroscopy highlighted peak shift effects, both confirming the pronounced *n*-doping effects induced by gate dielectric interactions. DFT calculations further identified critical traps within SiO₂, which facilitate charge transfer and potentially convert few-layer Nb-doped MoS₂ from *p*-type to *n*-type when in direct-contact. Electrical measurements corroborated these findings, demonstrating that gate dielectric-coupled interfaces (both proximity and direct-contact) bolster the transition from extrinsic to intrinsic charge transport. This transition is primarily driven via T-SCLC, influenced by traps near the CBM and electron injection owing to the ultrathin structure of FETs. This study underscores the critical role of precise dielectric engineering in modulating these interactions to achieve optimal electronic properties in *p*-type 2D materials.

Methods/Experimental

Device fabrication details. The top-down assembly method was adopted to design the FET. Nb-doped MoS₂ (0.5%) single crystals were received from the Der-Yuh Lin Group. To remove surface contamination, substrates (300 nm-thick SiO₂/p⁺-Si) were cleaned with a piranha solution. Few-layer Nb-doped MoS₂ flakes were exfoliated from a single crystal using the micromechanical method. The stripped flakes were transferred to polydimethylsiloxane (PDMS). Next, PDMS was used to stack exfoliated Nb-doped MoS₂ flakes half-and-half above h-BN (the self-standing h-BN was provided by the National Institute for Material Science in Tsukuba, Japan) and SiO₂ using an optical microscope and transfer system. E-beam lithography equipment (NBL NB3) was used to produce the source and drain pattern (beam current: 4.4 nA, dose: 9.3 C·m⁻²). Pd (15 nm) and Au (45 nm) were fabricated using an e-beam evaporator (Temescal FC-2000). A highly doped Si was employed as a gate.

Electrical measurement details. The semiconductor analyzer (KEITHLEY 4200-SCS), connected with a cryogenic probe station (2–300 K), was used to study the basic electrical properties and temperature-dependent transport measurement of the FET. The I vs. V characteristics between the drain and source were measured at room temperature in a vacuum environment, depending on gate voltage (transfer curve) and drain voltage (output curve). The transfer curves were also measured in the temperature range from 190 to 270 K to analyze the effect of temperature on conductivity.

Computation details. The first-principles calculations are performed using density functional theory (DFT) with Perdew-Burke-Ernzerhof (PBE) functional,⁶³ as implemented in Vienna Ab-initio Simulation Package (VASP).⁶⁴ To describe the van der Waals interactions between MoS₂ and the SiO₂ substrate, a correction of DFT-D3 with Becke-Johnson damping function is applied.³⁹ The plane-wave basis energies cutoff is set at 450 eV according to our tests, and a gamma-only grid of k -points is used for sampling the Brillouin zone. The convergence threshold for energy is set to 1×10^{-6} eV for the electronic SCF loop, while the maximum force convergence tolerance for the ionic relaxation loop is 0.03 eV·Å⁻¹. Additionally, in Bader analysis calculations, vacuum layer thicknesses exceeding 40 Å are adopted to ensure good convergence.

Materials characterization detail. All devices were measured for thickness using atomic force microscopy (AFM) (OXFORD Cypher S AFM Microscope). SKPM measurements were performed using a cantilever (ASYELEC.01-R2 $f = 75$ kHz, $k = 2.8$ N·m⁻¹). A bias voltage (drive amplitude) ranging from 1 to 3 V was applied during imaging. Raman spectroscopy and mapping were performed on a WiTec alpha 300R M-Raman system with a 532 nm excitation wavelength (2.33 eV). The laser spot measured ~640 nm with a 50× objective lens, and the laser power was set at 2 mW. The quantitative information of the Nb atom in the Nb-doped MoS₂ crystal was investigated using XPS. XPS measurements were performed on a K-alpha spectrometer (ThermoFisher) using aluminum K α nonmonochromatic X-ray excitation at a base pressure of $\sim 1 \times 10^{-9}$ mbar. The quantitative information of the Nb atom was determined by dividing the individual peak areas in a wide-scan XPS survey spectrum by their respective atomic sensitivity factor after appropriate background subtraction.

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Supporting Information

The Supporting Information is available free of charge at.

Depth dependent XPS measurements of Nb-doped MoS₂; thickness-dependent electrical properties of Nb-doped MoS₂; transfer characteristics of 10L Nb-doped MoS₂ FETs; optical microscope images of FET devices; AFM topography of MoS₂ and Nb-doped MoS₂ surfaces; CPD of MoS₂ and Nb-doped MoS₂ and Raman spectra analysis of Nb-doped MoS₂ in direct-contact and noncontact configurations; Raman analysis of E_{2g} and A_{1g} peaks in different configurations; band structure comparisons of SiO₂/MoS₂ and freestanding MoS₂; injection-dominated hysteresis trends in MoS₂ FETs; variation in hysteresis with different layer thickness; COMSOL simulations of transfer curves and charge distributions; schematic diagram of tunneling and electric field effects in device configurations; temperature-dependent transfer characteristics of Nb-doped MoS₂; transfer curve analysis of Re-doped WSe₂ FETs; operational current and gain data for inverters; modeling of ambipolar conduction through body effects in ultra-thin channels.

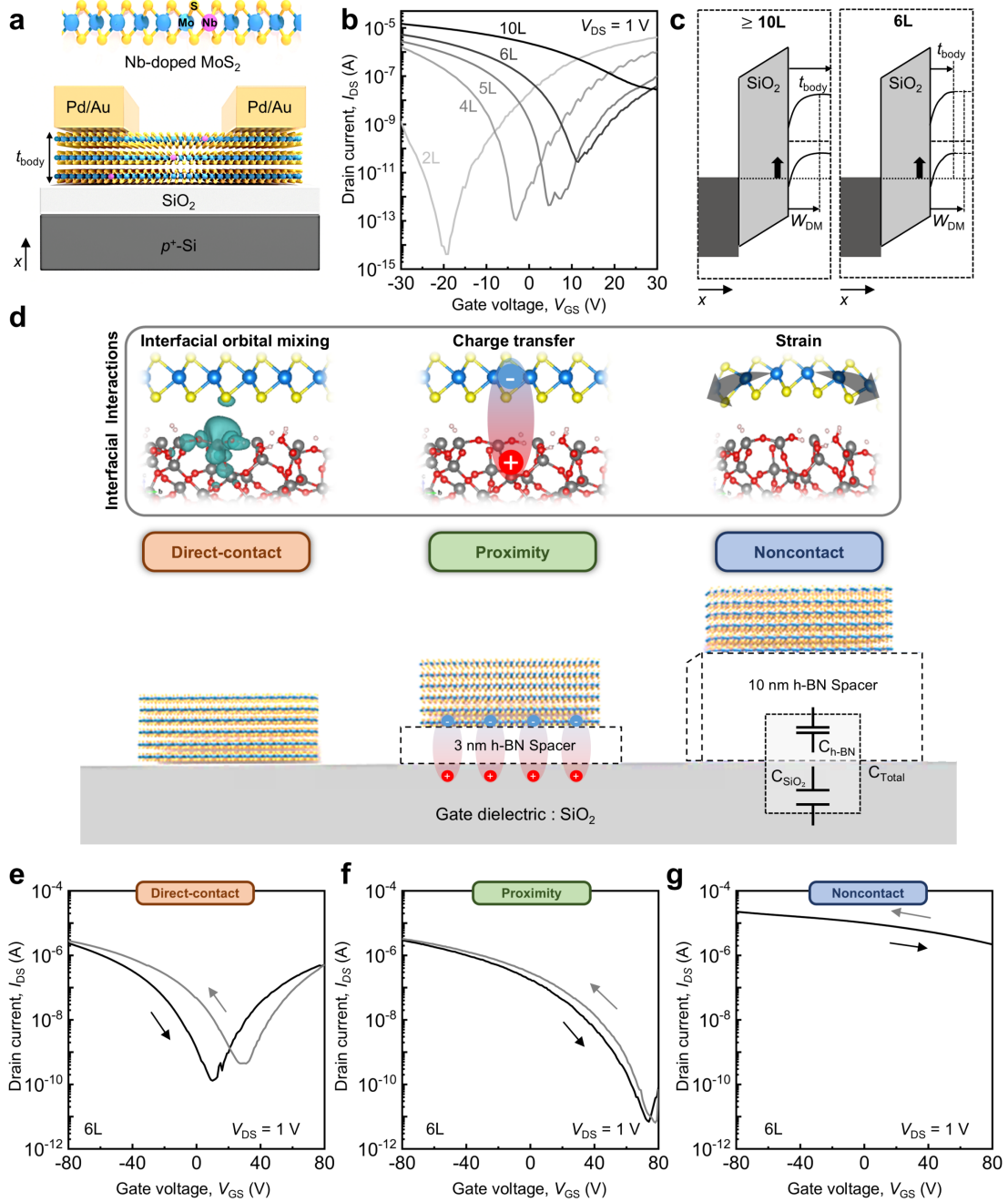


Figure 1. Transfer characteristics of Nb-doped MoS₂ FETs with varying channel thickness and the influence of the h-BN spacer on electrical transport in Nb-doped MoS₂ FETs. (a) Schematic representation of the investigated FET device based on Nb-doped MoS₂ channel, depicting the top-contact and back-gate configuration. (b) Transfer curves measured from FET devices with varying channel thicknesses (from 10L to 2L) at room temperature, presented in a semilogarithmic scale. (c) Energy band diagrams display depicting shunt ($t_{\text{body}} - W_{\text{DM}}$) and field effect region ($t_{\text{body}} \leq W_{\text{DM}}$) in the steady state of the back gate configuration along the x-axis, corresponding to FET operation modes: depletion. (d) Schematic illustration depicting interactions, including interfacial orbital mixing, charge transfer, and strain, along with the fabrication setup

where h-BN is inserted between the channel and gate dielectric to reduce the electronic influence from the dielectric. The configuration of the total oxide capacitor (C_{Total}) is illustrated. (e) Transfer curves measured on SiO₂. (f) Transfer curves measured with a 3 nm h-BN spacer. (g) Transfer curves measured on devices with a 10 nm h-BN spacer. Transfer curves comparing dielectric-contacted and spacer-added regions at room temperature are presented on a semilogarithmic scale.

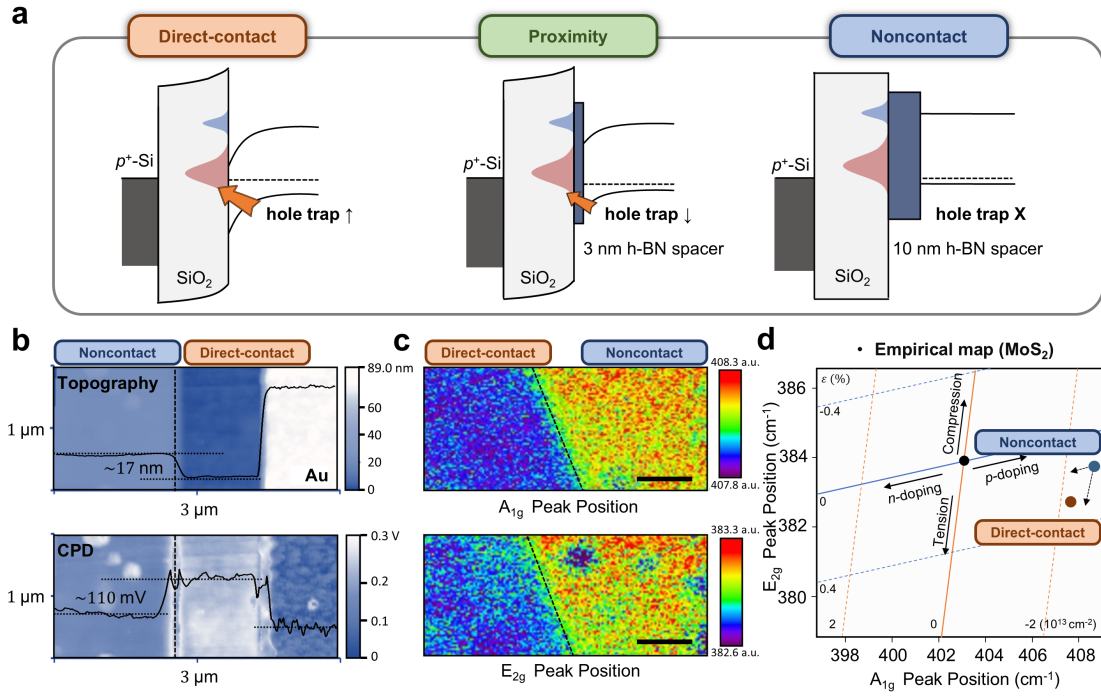


Figure 2. Influence of gate dielectric. (a) Energy diagram representation of the “Direct-contact,” “Proximity,” and “Noncontact” configuration with two defect bands of SiO₂. (b) Topography measurements illustrating thickness and KPFM measurements illustrating the contact potential difference across the Nb-doped MoS₂ channel, showing an upward shift of the Fermi level (E_F) by more than 100 meV in regions in direct-contact regions compared to noncontact regions. (c) Mapping of Raman data illustrating shifts in A_{1g} and E_{2g} peak positions transitioning from noncontact to direct-contact channel configurations. The scale bar is 900 nm. (d) Mapping of Raman data illustrating shifts in peak positions from noncontact to direct-contact channel configurations based on a map derived from previous studies representing doping and strain effects (constructed ϵ (strain%) vs. n (carrier concentration) space within the Peak Position (A_{1g}) vs. Peak Position (E_{2g}) plot). The data demonstrate shifts owing to the n -doping effect ($\Delta 0.5$ cm⁻¹) and global tensile strain effect ($\Delta 0.7$ cm⁻¹) in Nb-doped MoS₂.

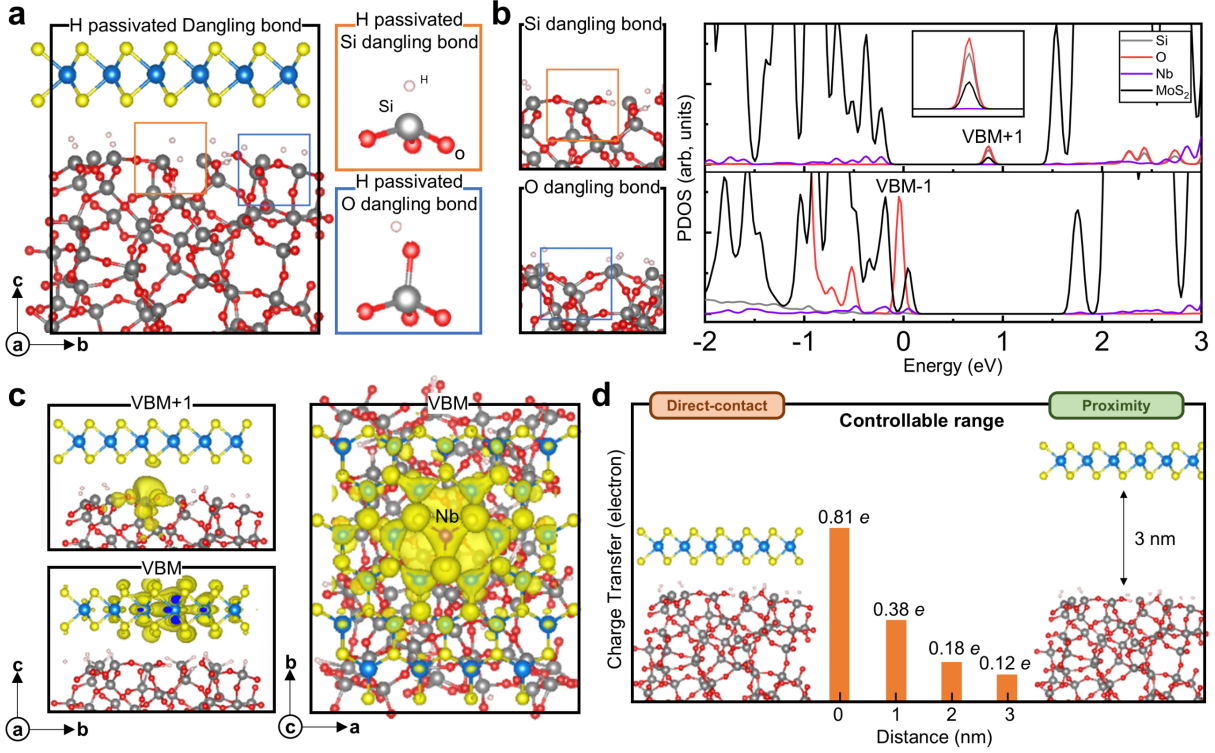


Figure 3. DFT analysis of SiO_2 and Nb-doped MoS_2 interactions. (a) Schematic illustration of $\text{SiO}_2/\text{MoS}_2$ systems with oxygen (O) and silicon (Si) dangling bonds. (b) Schematic illustrations and projected density of states for $\text{SiO}_2/\text{MoS}_2$ systems with different dangling bonds of Si (upper) and O (bottom). The inset shows the overlap of electron orbitals formed by O, Si, and MoS_2 , contributing to the VBM + 1 in the Si dangling bond configuration. (c) Isosurface plots of the Si dangling bond at VBM + 1 and VBM, showing a positively charged distribution. (d) Schematic representation of charge transfer per vacuum distance from direct-contact to proximity configurations.

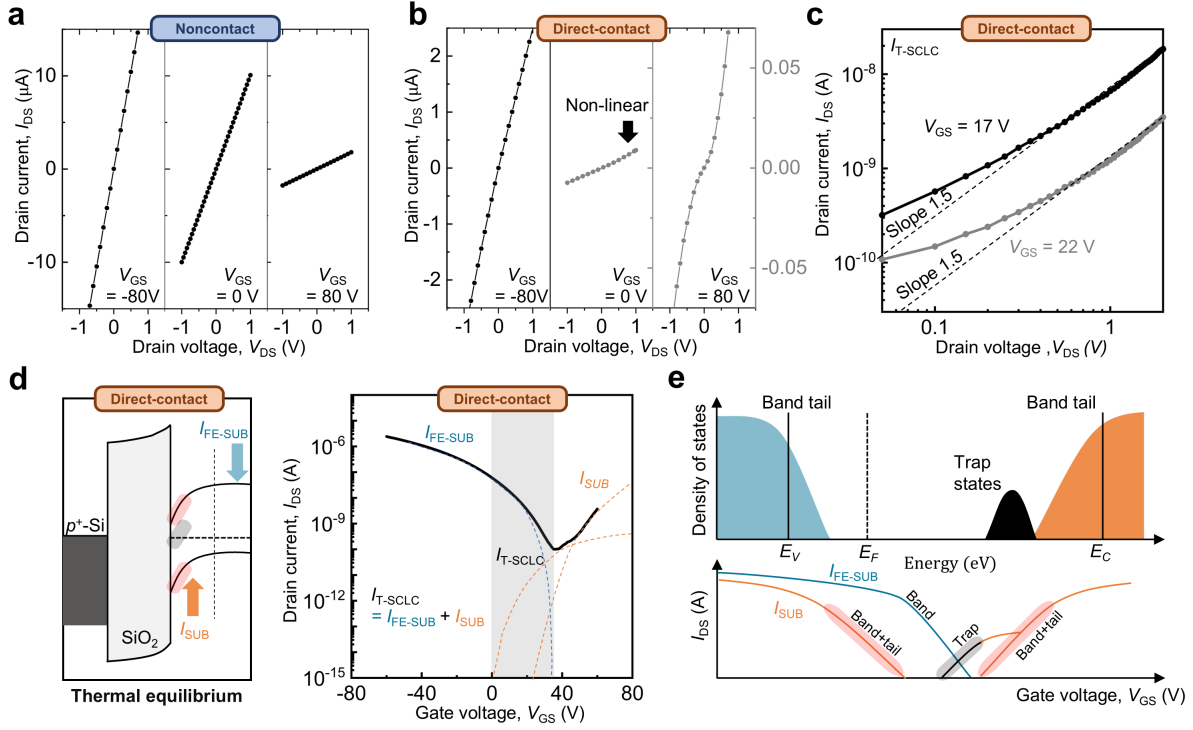


Figure 4. Analysis of electrical transport and conduction mechanisms in Nb-doped MoS₂ FETs. (a) Output characteristics of FETs in both noncontact and (b) direct-contact modes over a voltage range of -1 to 1 V at selected gate voltages ($V_{GS} = -80$, 0 , and 80 V). Linear Ohmic behavior is observed in most cases, except for a nonlinear I vs. V curve observed in the direct-contact device at the depletion and inversion regions. (c) Output curve data with gate voltages ($V_{GS} = 17$ and 22 V) fixed in the nonlinear region, depicting T-SCLC behavior with linear fitting in a double-logarithmic scale. (d) Representation of the currents flowing through the channel on the side closer to the gate dielectric (I_{SUB}) and the side farther from the gate dielectric (I_{FE-SUB}), corresponding to the MoS₂ density of state and energy graph. (e) Representation of the energy diagram of the channel on the side closer to the dielectric matter (I_{SUB}) and the side farther from the gate dielectric (I_{FE-SUB}), along with the trap-related current expression (I_{T-SCLC}), combining currents from both sides of the channel with ambipolar behavior. This includes decomposing I_{SUB} and I_{FE-SUB} (current flowing through the channel on the side farther from the gate dielectric) in the transfer curve.

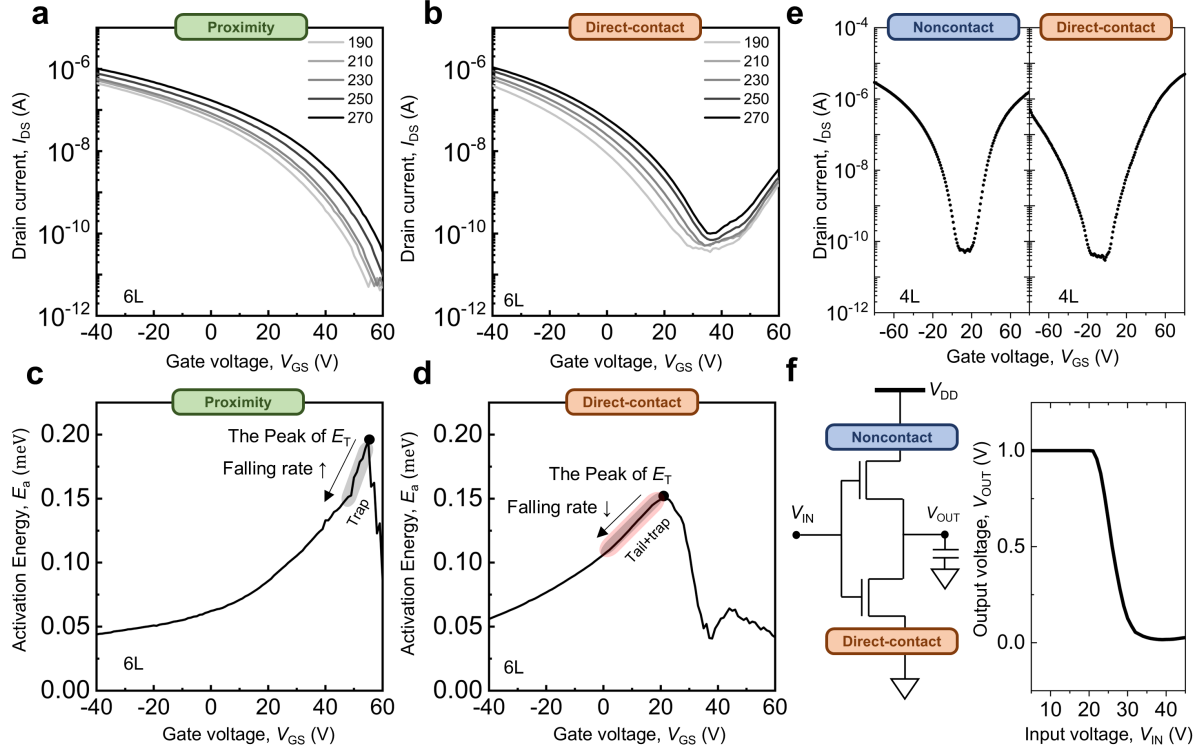


Figure 5. Trap energy analysis and inverter design. Transfer curves within the temperature range of near-complete ionization of Nb (190–300 K) in (a) proximity and (b) direct-contact modes. Quantitative analysis of trap energy (E_T) extraction and falling rate from transfer curves. The plot illustrates changes in trap energy as a function of gate voltage in (c) the proximity mode and (d) the direct-contact mode. (e) Transfer curves measured on SiO₂ with 4L Nb-doped MoS₂ and on the h-BN spacer with 4L Nb-doped MoS₂. (f) Schematic representation of an inverter circuit using 4L devices in both non-contact and direct-contact configurations, with its corresponding output voltage (V_{OUT}) measured as a function of input voltage (V_{IN}).

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