Supplementary Information: Topological-Insulator Heterophase Gate Stacks for Transistor Electrostatics

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Supplementary Note 1. Screening-Boundary Relocation as an Electrostatic Design Variable

A gate stack is commonly described by the capacitance of its bulk dielectric, but the gate electric field is ultimately screened at finite electronic and interfacial boundaries. For the two-dimensional (2D) semiconductor transistors considered here, a conventional stack can be represented as

$$\frac{1}{C_{\mathrm{g,conv}}} = \frac{1}{C_{\mathrm{d,g}}} + \frac{1}{C_{\mathrm{ins}}} + \frac{1}{C_{\mathrm{d,ch}}} + \frac{1}{C_{\mathrm{vdW}}},$$

where $C_{\mathrm{d,g}}$ denotes the effective gate-side interfacial response of the electrode/dielectric boundary, $C_{\mathrm{d,ch}}$ denotes the corresponding dielectric/channel interfacial response, and C_{vdW} denotes the geometric van der Waals (vdW)-gap contribution. In particular, $C_{\mathrm{d,g}}$ can incorporate finite electrode screening together with interface-specific bonding, polarization, chemical reconstruction and structural disorder. These gate-side contributions need not scale proportionally with the physical dielectric thickness and can therefore become increasingly important as the bulk-insulator capacitance increases during equivalent oxide thickness (EOT) scaling [1–5]. The bias-dependent semiconductor-body response is treated separately from the gate-stack contribution defined above. Thus, even for an intrinsically high-κ dielectric, the complete gate response depends on the electronic character and spatial position of the boundaries at which screening charge is established.

The topological-insulator heterophase gate stack (TIHGS) changes this gate-side boundary condition by separating dielectric isolation from the location of electronic screening. BiF_3 provides the insulating barrier facing the semiconductor channel, whereas residual conducting Bi_2Se_3 remains electrically coupled to the gate electrode. Position-resolved calculations further show that the structural a-BiF_3/c-Bi_2Se_3 interface is gap-opened while an electronically active gap-closed state is reconstructed in the adjacent c-Bi_2Se_3 subinterface layer. We therefore use the term "buried screening boundary" for this heterophase-associated electronic boundary region rather than for an ideal atomically sharp chemical interface. For the 2D devices studied here, the corresponding stack contribution is

$$\frac{1}{C_{\mathrm{g,TIHGS}}} = \frac{1}{C_Q} + \frac{1}{C_{\mathrm{BiF_3}}} + \frac{1}{C_{\mathrm{d,ch}}} + \frac{1}{C_{\mathrm{vdW}}},$$

where C_Q represents the effective electronic-compressibility response associated with the buried electronic boundary. At the level of this reduced electrostatic model, the defining change is therefore $C_{\mathrm{d,g}} \rightarrow C_Q$. This notation describes a change in the physical origin, location and electronic character of the gate-side series response; it does not imply that the series contribution is eliminated or that C_Q necessarily exceeds $C_{\mathrm{d,g}}$.

Finite C_Q does not enhance the nominal TIHGS capacitance; it lowers it by remaining in series with $C_{\mathrm{BiF_3}}$. The experimentally observed advantage must therefore be distinguished from conventional capacitance or EOT scaling. In the transistor comparison, the TIHGS- and BiF_3-gated devices retain a common BiF_3/MoS_2 channel-side material interface and closely matched insulating-layer thicknesses, while the TIHGS has the lower nominal stack capacitance. Nevertheless, the TIHGS-gated device exhibits lower subthreshold swing (SS), smaller hysteresis and markedly reduced drain-induced barrier lowering ($DIBL$). The functional significance of screening-boundary relocation is therefore not a larger nominal capacitance, but the ability of a deliberately redefined gate-side boundary condition to improve transistor electrostatics despite that capacitance penalty.

Screening-boundary engineering is complementary to, rather than a substitute for, semiconductor-side interface engineering. Channel-side trapping, fixed charge, dielectric disorder and remote-polar-phonon coupling remain relevant to transistor performance [6–8]. The present device comparison retains the same BiF_3/MoS_2 channel-side material interface while changing the gate-side boundary condition, thereby allowing the functional consequence of screening-boundary identity and location to be tested separately from a simple change in dielectric thickness or nominal capacitance.

Supplementary Note 2. Fluorine Penetration and Self-Limited Surface Conversion

SF_6-based processing of Bi_2Se_3 is known to produce a fluorinated, BiF_3-rich insulating surface layer [9]. To examine whether fluorine penetration can provide a characteristic length scale for the experimentally observed self-limited surface conversion, we performed stopping and range of ions in matter (SRIM) simulations [10]. SRIM treats energetic-ion transport through binary-collision physics, including nuclear and electronic stopping, and provides the depth distribution, projected range, and range straggling of implanted ions. Although SRIM does not reproduce the chemical conversion of Bi_2Se_3 into BiF_3, it provides a useful kinematic estimate of the depth over which energetic fluorine can be delivered into Bi_2Se_3. Comparison of this ballistic penetration scale with the experimentally observed conversion depth therefore provides a qualitative test of whether fluorine delivery can contribute to defining the spatial extent of the reaction front.

The ion-energy distribution incident on a surface in a radio-frequency (RF)-driven capacitively coupled plasma (CCP) is generally not represented by a single energy. RF sheath modulation, electrode asymmetry and self-bias, collisional transport through the sheath, and charge-exchange processes can broaden and reshape the ion-energy distribution at the sample surface [11–13]. In electronegative SF_6-containing plasmas, negative-ion formation can additionally modify the plasma potential and sheath structure [14, 15]. Furthermore, as the electrically insulating fluoride layer develops during conversion, surface charging and evolution of the reacted layer can modify the local sheath and subsequent ion-bombardment conditions. Because the ion-energy distribution was not measured directly in our plasma system, we do not assign individual SRIM energies to specific experimental ion populations.

We therefore calculated F^+ depth distributions at incident energies of 0.5, 1, 2.5, and 5 keV to examine how the accessible ballistic penetration length scale evolves with increasing ion energy. The 5-keV calculation represents a deliberately high-energy upper-bound case rather than an assertion that 5-keV F^+ ions constitute the dominant ion population under the experimental plasma conditions. Although the experiments employed an SF_6/Ar plasma containing multiple ionic and neutral reactive species, the simulations were simplified to F^+ projectiles to isolate the ballistic contribution associated specifically with fluorine delivery. Neutral fluorine radicals, chemical transport, and subsequent solid-state diffusion are not represented by this calculation.

The calculated fluorine depth distributions broaden systematically with increasing incident energy (Extended Data Fig. 1). At lower energies, implanted F remains concentrated in the near-surface region, whereas the 5-keV distribution develops an extended tail approaching the ∼40-nm depth scale of the experimentally observed saturated converted layer (Extended Data Fig. 1). The correspondence between the high-energy ballistic penetration envelope and the independently measured saturation thickness provides an important qualitative clue to the origin of the self-limited conversion depth. Specifically, it shows that a tens-of-nanometres reaction depth is physically accessible to energetic fluorine while suggesting that finite fluorine penetration can help define the maximum spatial extent of the conversion front.

This interpretation is also consistent with the experimentally observed evolution of the converted layer. During the initial stages of SF_6 exposure, fluorine can access and react with the near-surface Bi_2Se_3, rapidly increasing the converted-layer thickness. As an insulating BiF_3 layer progressively develops, fluorine delivery to the underlying unconverted Bi_2Se_3 is expected to become increasingly restricted, while the remaining accessible ballistic and chemically assisted fluorine flux decreases with depth. The combination of a finite fluorine-penetration window and progressive transport limitation through the reacted layer therefore provides a physically plausible explanation for the rapid initial conversion followed by saturation at a characteristic thickness of approximately 40–43 nm.

SRIM itself does not provide a quantitative model of this coupled process. It does not include chemical reactions or BiF_3 phase formation, transport of neutral reactive species, fluorine diffusion, sputter erosion, dynamic changes in target composition and density, plasma-sheath evolution, surface charging, or charge-exchange processes. These mechanisms can modify both fluorine delivery and movement of the reaction front. Nevertheless, the overlap between the calculated high-energy ballistic penetration envelope and the experimentally observed saturation scale is consistent with fluorine penetration contributing to the characteristic conversion depth, while not establishing penetration as the sole or rate-limiting mechanism of the self-limited fluorination process.

Supplementary Note 3. Electronic Structure of the Buried Heterophase Boundary

In the pristine Bi_2Se_3 slab comprising six quintuple layers (QLs), the position-resolved electronic-structure calculations in Fig. 3 were used to establish the reference electronic boundary before surface conversion. Bi_2Se_3 is a prototypical three-dimensional topological insulator whose bulk topology gives rise to a Dirac-like surface state within the bulk band gap [16–18]. Consistent with this established picture, the pristine slab exhibits a Dirac-like surface state within the calculated 0.31-eV bulk gap, with its Dirac point (E_D) approximately 0.043 eV below the Fermi level (E_F) (Fig. 3a,b). Hereafter, amorphous BiF_3 and crystalline Bi_2Se_3 are denoted a-BiF_3 and c-Bi_2Se_3, respectively.

Formation of the a-BiF_3/c-Bi_2Se_3 heterophase boundary produces a strongly position-dependent electronic reconstruction. The electronic states projected onto the immediate heterophase interface are gap-opened by approximately 0.72 eV, whereas the adjacent c-Bi_2Se_3 subinterface QL develops a reconstructed gap-closed Bi_2Se_3-derived Dirac-like feature centred approximately 0.146 eV below E_F, together with finite spectral weight extending to the Fermi level (Fig. 3c,d). The surface QL at the opposite side of the slab retains a pristine-like Dirac dispersion. Thus, the $\sim$ 0.146-eV value specifies the energetic position of the reconstructed subinterface feature relative to E_F and is not an interfacial band gap. More importantly, the calculations show that the chemical heterophase interface and the electronically active boundary are spatially distinct: surface conversion opens the immediate interface while relocating a gap-closed Bi_2Se_3-derived electronic response into the adjacent subinterface layer.

The calculated dipole-moment profile across the a-BiF_3/c-Bi_2Se_3 structure is sharply localized near the heterophase boundary (Fig. 3e). This localization is consistent with interfacial charge redistribution and with a local electrostatic contribution to the energetic reconstruction of the Bi_2Se_3-derived state. We do not assign the shift of the Dirac-like feature from $\sim$ 0.043 to $\sim$ 0.146 eV uniquely to the interface dipole, because local bonding, chemical reconstruction and band bending are not separately decomposed. Rather, the interface-localized dipole and the position-resolved band reconstruction provide complementary microscopic evidence that the electronic boundary is reorganized by formation of a-BiF_3. This physical picture is consistent with previous reports that surface modification or etching of Bi_2Se_3 can displace or reconstruct its surface-state distribution [9, 19].

A finite electronic density of states at the Fermi level provides a microscopic basis for finite electronic compressibility and quantum capacitance,

$$C_Q = e^2 D(E_F)$$

in the zero-temperature limit. The calculated near-E_F spectral weight of the subinterface boundary is therefore consistent with the finite C_Q extracted independently from the TIHGS capacitance measurements. The relevance of this response is not that C_Q increases the total gate capacitance—it does not. Rather, finite electronic compressibility allows the heterophase-induced buried boundary to support screening charge while the underlying c-Bi_2Se_3 remains electrically coupled to the external gate electrode. In this sense, C_Q is treated as an electrostatic signature of the relocated electronically active boundary rather than as an intrinsic dielectric contribution of BiF_3 or a capacitance-enhancement mechanism.

The calculations do not constitute an independent determination of the topological invariant of the chemically reconstructed interface. We do not extract an interface-specific Z_2 invariant or explicitly calculate the spin texture of the reconstructed subinterface state. We therefore interpret the calculations conservatively as evidence for a reconstructed Bi_2Se_3-derived Dirac-like electronic boundary whose relation to topological-insulator bulk–boundary physics is motivated by the established bulk topology of Bi_2Se_3. Additional chemically induced, band-bending-related or reconstructed states may coexist and contribute to the experimentally extracted electronic compressibility.

Supplementary Note 4. Effective Quantum-Capacitance Extraction and Model Assumptions

The effective quantum-capacitance contribution of the buried BiF_3/Bi_2Se_3 boundary was estimated by comparing the measured TIHGS capacitance with the dielectric capacitance expected for BiF_3. Throughout this analysis, all capacitances are expressed per unit area. The TIHGS response was represented as

$$\frac{1}{C_{\mathrm{TIHGS}}} = \frac{1}{C_{\mathrm{BiF_3}}} + \frac{1}{C_Q},$$

where

$$C_{\mathrm{BiF_3}} = \frac{\varepsilon_0 \varepsilon_{\mathrm{BiF_3}}}{t_{\mathrm{BiF_3}}}.$$

Here C_Q denotes an effective electronic-compressibility contribution associated with the buried electronically active boundary. It is a finite series response and should not be interpreted as an intrinsic dielectric property of BiF_3, a universal material constant, or a capacitance-enhancement term.

The BiF_3 dielectric response used for this analysis was obtained from the fully converted BiF_3-only (p20) reference. This structure was formed from a nominally 20-nm-thick polycrystalline Bi_2Se_3 film and exhibited an independently measured post-conversion BiF_3 thickness of ∼23 nm. Using this physical thickness, the measured capacitor statistics yield a mean relative permittivity $\varepsilon_{\mathrm{BiF_3}} = 28.65$ and a median value of 30.16. The mean value was used as the reference BiF_3 dielectric response for the primary C_Q extraction below. This extraction assumes that the converted BiF_3 region within the TIHGS has the same dielectric response as the fully converted BiF_3-only reference. Any systematic difference in the local structure, density, composition, or dielectric response of BiF_3 between the partially and fully converted configurations would renormalize the extracted C_Q. Accordingly, the reported C_Q values should be regarded as effective interfacial quantum-capacitance responses within this reference-based series-capacitance model rather than as model-independent microscopic constants.

For the TIHGS-13 (p20) structure,

$$C_{\mathrm{TIHGS}} = 1.10\ \mu\mathrm{F\,cm^{-2}}$$

and, using $t_{\mathrm{BiF_3}} \approx 13$ nm,

$$C_{\mathrm{BiF_3}} = 1.95\ \mu\mathrm{F\,cm^{-2}},$$

yielding

$$C_Q = \left(\frac{1}{C_{\mathrm{TIHGS}}} - \frac{1}{C_{\mathrm{BiF_3}}}\right)^{-1} \approx 2.52\ \mu\mathrm{F\,cm^{-2}}.$$

For the TIHGS-43 (p50) structure,

$$C_{\mathrm{TIHGS}} = 0.305\ \mu\mathrm{F\,cm^{-2}}$$

and, using $t_{\mathrm{BiF_3}} \approx 43$ nm,

$$C_{\mathrm{BiF_3}} = 0.590\ \mu\mathrm{F\,cm^{-2}},$$

giving

$$C_Q \approx 0.631\ \mu\mathrm{F\,cm^{-2}}.$$

As a sensitivity check, using the median BiF_3 relative permittivity of 30.16 instead of the mean value gives $C_Q \approx 2.37\ \mu\mathrm{F\,cm^{-2}}$ for TIHGS-13 (p20) and $C_Q \approx 0.599\ \mu\mathrm{F\,cm^{-2}}$ for TIHGS-43 (p50). Thus, the inference of a finite interfacial electronic-compressibility contribution is not sensitive to whether the mean or median BiF_3 reference permittivity is used.

The finite C_Q explains why the measured TIHGS capacitance is lower than that expected from BiF_3 alone. Accordingly, the present MIM measurements do not demonstrate a net capacitance or *EOT* advantage of the TIHGS structure over the BiF_3-only reference. Nor do they independently determine the magnitude of the conventional metal/BiF_3 gate-side interfacial capacitance, $C_{\mathrm{d,g}}$, and therefore they do not establish that $C_Q > C_{\mathrm{d,g}}$. Within this reference-based series-capacitance model, the capacitance measurements instead require a finite additional series response associated with the buried heterophase boundary.

The distinction between C_Q and a conventional gate-side interfacial or dead-layer capacitance is therefore primarily one of physical origin and boundary identity rather than the existence versus absence of a

finite series term. Finite gate-electrode/dielectric interfacial responses are well established as non-scaling contributions to deeply scaled gate-stack electrostatics [1, 5]. Conventional gate-side contributions can arise from finite electrode screening, altered interfacial polarizability, bonding, chemical reconstruction, or structural disorder. In the TIHGS architecture, the metal electrode is electrically coupled to residual Bi_2Se_3, so the conventional metal/BiF_3 interface no longer defines the active gate-side screening boundary. The remaining C_Q instead characterizes the effective electronic compressibility of the deliberately formed BiF_3/Bi_2Se_3 boundary. Thus, "boundary relocation" rather than "elimination of all interfacial capacitance" is the appropriate electrostatic description. The transistor comparison in Fig. 4 separately evaluates whether changing this boundary condition has a functional consequence for gate control.

The differing C_Q values obtained for the two conversion geometries indicate that the extracted quantity depends on the microscopic electronic structure and electrostatic environment of the reconstructed boundary rather than representing a universal material parameter. This interpretation is consistent with the position-resolved electronic-structure calculation in Fig. 3d, which predicts finite Bi_2Se_3-derived spectral weight at the Fermi level near the buried heterophase boundary.

An independent constraint on the spatial origin of this additional series-capacitance response is provided by the crystalline TIHGS-43 (cN) structures. When the nominal starting crystalline Bi_2Se_3 thickness is varied from ∼49 to ∼179 nm while maintaining approximately the same converted BiF_3 thickness, $\varepsilon_{\mathrm{eff,TIHGS}}$ remains within ∼15.9–17.4 without a systematic thickness dependence (Extended Data Fig. 5f). This weak dependence argues against a dominant electrostatic contribution from the Bi_2Se_3 bulk and is instead consistent with a contribution localized near the BiF_3/Bi_2Se_3 boundary.

Capacitance measurements alone cannot uniquely distinguish the reconstructed Bi_2Se_3-derived boundary state from additional electronic states that may coexist at a band-bent or chemically reconstructed interface. We therefore interpret C_Q conservatively as an effective electronic-compressibility response associated with the buried electronically active boundary. Its finite magnitude, together with the calculated near-Fermi spectral weight, provides mutually consistent electrostatic and microscopic evidence for an electronically compressible buried boundary.

Supplementary Note 5. Field-Assisted Leakage, Band Alignment and Effective Tunnelling Barrier

To examine the field dependence of gate-stack leakage in the TIHGS MIM capacitors, we analysed the current-density–voltage characteristics using field-assisted emission and tunnelling representations, including Simmons-modified Schottky emission, Poole–Frenkel emission, and Fowler–Nordheim tunnelling (Extended Data Fig. 6a–c) [20–22]. The electric field was calculated as

$$E = \frac{|V|}{t_{\mathrm{BiF_3}}},$$

where $t_{\mathrm{BiF_3}}$ is the physical thickness of the insulating BiF_3 layer. The electrically conducting Bi_2Se_3 region was not included in the dielectric thickness used for this field conversion. This treatment assumes that the applied voltage drop relevant to high-field transport occurs predominantly across the insulating BiF_3 layer; any additional voltage drop associated with the interfaces is not independently resolved and is therefore incorporated into the effective transport parameters extracted below.

At intermediate electric fields, the data in Extended Data Fig. 6b exhibit approximately linear behaviour when represented as $\ln(J/E)$ versus $E^{1/2}$, consistent with Simmons-modified Schottky and Poole–Frenkel descriptions [20, 22]. The corresponding field-lowering coefficients are

$$\beta_{\mathrm{S}} = \left[\frac{q^3}{4\pi\varepsilon_0\varepsilon_{\mathrm{r}}(\infty)}\right]^{1/2}$$

for Schottky-type barrier lowering and

$$\beta_{\mathrm{PF}} = \left[\frac{q^3}{\pi\varepsilon_0\varepsilon_{\mathrm{r}}(\infty)}\right]^{1/2} = 2\beta_{\mathrm{S}}$$

for Poole–Frenkel emission, where q is the elementary charge, ε_0 is the vacuum permittivity, and $\varepsilon_{\mathrm{r}}(\infty)$ is the ion-clamped high-frequency relative permittivity of the dielectric.

The Simmons-modified Schottky and Poole–Frenkel representations yield $\varepsilon_{\mathrm{r}}(\infty) \approx 4.99$ and ≈ 4.89, respectively, corresponding to refractive indices $n = \sqrt{\varepsilon_{\mathrm{r}}(\infty)}$ of $\sim$2.23 and $\sim$2.21. These values are reasonably close to the first-principles values calculated for amorphous BiF_3, $\varepsilon_{\mathrm{r}}(\infty) = 4.056$ and $n = 2.014$, providing a consistency check between the field-dependent transport response and the calculated electronic polarizability.

At higher electric fields, the Fowler–Nordheim (F–N) representation becomes dominant [21, 22]. Within the conventional triangular-barrier approximation, the F–N current density can be expressed in the form

$$J_{\mathrm{FN}} \propto E^2 \exp\left[-\frac{4\sqrt{2m_{\mathrm{t}}^*}\,\Phi_{\mathrm{B,FN}}^{3/2}}{3q\hbar E}\right],$$

where m_{t}^* is the tunnelling effective mass and $\Phi_{\mathrm{B,FN}}$ is the effective electron-injection barrier height. In this expression, $\Phi_{\mathrm{B,FN}}$ is expressed in joules. The corresponding linearized form is

$$\ln\left(\frac{J}{E^2}\right) = A_{\mathrm{FN}} - \frac{4\sqrt{2m_{\mathrm{t}}^*}\,\Phi_{\mathrm{B,FN}}^{3/2}}{3q\hbar}\frac{1}{E},$$

where A_{FN} contains the field-independent prefactor.

Because the device area and BiF_3 thickness are fixed for a given MIM capacitor and $E = |V|/t_{\mathrm{BiF_3}}$, the equivalent voltage-domain representation used in Extended Data Fig. 6c is

$$\ln\left(\frac{I}{V^2}\right) = A'_{\mathrm{FN}} - \frac{4t_{\mathrm{BiF_3}}\sqrt{2m_{\mathrm{t}}^*}\,\Phi_{\mathrm{B,FN}}^{3/2}}{3q\hbar}\frac{1}{|V|}.$$

Accordingly, if S_{FN} denotes the slope of the linear high-field region in a plot of $\ln(I/V^2)$ versus $1/|V|$, the effective F–N barrier height is obtained from

$$\Phi_{\mathrm{B,FN}} = \left[\frac{3q\hbar|S_{\mathrm{FN}}|}{4t_{\mathrm{BiF_3}}\sqrt{2m_{\mathrm{t}}^*}}\right]^{2/3}.$$

The quantity obtained from this equation is an energy in joules and was divided by q to report it in electronvolts.

For the Au/BiF_3/Bi_2Se_3/Au/Ti TIHGS MIM capacitor analysed in Extended Data Fig. 6a–c, $t_{\mathrm{BiF_3}} \approx 43$ nm. We adopted $m_{\mathrm{t}}^* = 0.25m_0$ as a representative tunnelling mass within the range reported for high-κ dielectrics, where m_0 is the free-electron mass [23]. Using the slope of the high-field linear regime gives an effective F–N barrier height of

$$\Phi_{\mathrm{B,FN}} \approx 0.27 \text{ eV}.$$

The high-field transport analysis must be distinguished from the equilibrium microscopic electronic structure of the heterophase boundary. Figure 3c–e shows that the immediate a-BiF_3/c-Bi_2Se_3 interface is gap-opened, whereas a reconstructed gap-closed Bi_2Se_3-derived state resides in the adjacent c-Bi_2Se_3 subinterface QL and the calculated dipole-moment profile is strongly localized near the heterophase boundary. The localized dipole establishes interfacial charge redistribution but does not by itself determine the magnitude of the reconstructed-state energy shift. The band alignment of the heterophase therefore cannot, in general, be represented solely by rigid alignment of isolated-material electron affinity and work function.

Extended Data Fig. 6d shows a vacuum-referenced constituent alignment before Au contact. Using the calculated Bi_2Se_3 work function $\phi_{\mathrm{Bi_2Se_3}} = 5.15$ eV and amorphous-BiF_3 electron affinity $\chi_{\mathrm{BiF_3}} = 4.3$ eV gives a nominal separation of approximately 0.85 eV between the Bi_2Se_3 Fermi level and the BiF_3 conduction-band reference. This value is a vacuum-level reference construction rather than an exact equilibrium conduction-band offset, because the interface dipole, chemical reconstruction and associated band bending can modify the local electrostatic potential. The reconstructed Bi_2Se_3-derived subinterface feature identified in Fig. 3d is therefore shown separately at approximately 0.146 eV below E_{F}.

After Au contact, the electrochemical potentials equilibrate across the contacted stack (Extended Data Fig. 6e). The Au work function, $\phi_{\mathrm{Au}} = 5.1$ eV, differs from the calculated Bi_2Se_3 work function by only approximately 0.05 eV, whereas the corresponding vacuum-referenced Au/BiF_3 separation is approximately 0.8 eV. These quantities provide a reference energetic sequence for the contacted capacitor but do not imply that the local heterophase or metal/dielectric band offsets are independently determined with this precision. The interface-localized dipole identified in Fig. 3e and any residual band bending remain incorporated implicitly in the contacted-state alignment.

Under the positive high-field condition used for the Fowler–Nordheim analysis, the potential drop across BiF_3 tilts the insulating barrier and enables tunnelling from the electrically connected residual Bi_2Se_3 towards accessible BiF_3 conduction-band states (Extended Data Fig. 6f). The experimentally extracted $\Phi_{\mathrm{B,FN}} \approx 0.27$ eV is therefore assigned to an effective high-field Bi_2Se_3-to-BiF_3 injection barrier. Its difference from the simple vacuum-referenced equilibrium separation is not interpreted as a direct measurement of the interface dipole or band bending; rather, it reflects a field-modified tunnelling barrier in a chemically and electronically reconstructed heterophase system. Because $\Phi_{\mathrm{B,FN}} \propto (m_{\mathrm{t}}^*)^{-1/3}$ and the BiF_3-specific tunnelling mass was not independently measured, the extracted value remains a model-dependent effective barrier rather than an exact equilibrium band offset.

Finally, the Fowler–Nordheim regime occurs well outside the gate-voltage window used for the MoS_2 transistor measurements and therefore does not represent the dominant transport process during normal transistor operation. Linearized Schottky, Poole–Frenkel and Fowler–Nordheim representations are also not unique microscopic fingerprints of individual leakage mechanisms [22]. We therefore use these analyses as mutually consistent descriptions of field-dependent transport and as a means to estimate the effective high-field injection barrier, rather than as independent determinations of the equilibrium interface band structure.

Supplementary Note 6. Flat-Band Extraction and Semiconductor Screening

The flat-band response and semiconductor-side screening parameters were analysed using the frequency-dependent capacitance–voltage (C–V) characteristics of the Au/Ag/Pt/WSe_2/BiF_3/Bi_2Se_3/Au/Ti metal–insulator–semiconductor capacitor (MISCAP). Throughout this analysis, all capacitances are expressed per unit area.

The flat-band voltage, V_{FB}, was determined from the accumulation-to-depletion transition using the capacitance–voltage inflection-point method identified from the second derivative of the measured C–V characteristic [24]. The 10-kHz C–V characteristic was used because the corresponding transition remained within the experimentally accessible low-leakage bias window. At higher frequencies, the transition shifted toward gate voltages above the measurement range, where increasing dielectric leakage prevented reliable determination of the flat-band condition. The physically relevant flat-band voltage was identified from the principal accumulation-to-depletion inflection in the 10-kHz characteristic, corresponding to

$$\left.\frac{\mathrm{d}^2 C_\mathrm{m}}{\mathrm{d}V_\mathrm{G}^2}\right|_{V_\mathrm{G}=V_\mathrm{FB}} = 0, \tag{S1}$$

with a corresponding change in the sign of $\mathrm{d}^2C_\mathrm{m}/\mathrm{d}V_\mathrm{G}^2$. This analysis gives

$$V_\mathrm{FB} \approx 0.58\ \mathrm{V}, \tag{S2}$$

as shown in Extended Data Fig. 7c. The measured 10-kHz capacitance at the flat-band condition is

$$C_\mathrm{FB} = C_\mathrm{m}(V_\mathrm{FB}) = 2.34 \times 10^{-7}\ \mathrm{F\,cm^{-2}}. \tag{S3}$$

We used an independent graphical consistency analysis to determine the effective capacitance of the TIHGS. At the independently determined V_{FB}, the two dimensionless functions

$$f_1 = \frac{1}{\sqrt{\dfrac{3k_\mathrm{B}T}{q}\dfrac{1}{C_\mathrm{m}}\dfrac{\mathrm{d}C_\mathrm{m}}{\mathrm{d}V_\mathrm{G}}}} - 1 \tag{S4}$$

and

$$f_2 = \frac{C_\mathrm{m}}{C_\mathrm{g} - C_\mathrm{m}} \tag{S5}$$

were evaluated, where k_B is the Boltzmann constant, T is the absolute temperature, q is the elementary charge, and C_g is the effective capacitance of the complete TIHGS. Trial values of C_g were varied until $f_1 = f_2$ at the independently determined V_{FB} (Extended Data Fig. 7d). The resulting gate-stack response corresponds to

$$\varepsilon_\mathrm{eff,TIHGS} \approx 16. \tag{S6}$$

For the approximately 43-nm-thick converted BiF_3 layer in the MISCAP, this effective relative permittivity gives

$$C_\mathrm{g} = \frac{\varepsilon_0 \varepsilon_\mathrm{eff,TIHGS}}{t_{\mathrm{BiF_3}}} = 3.29 \times 10^{-7}\ \mathrm{F\,cm^{-2}}, \tag{S7}$$

where ε_0 is the vacuum permittivity. As in the TIHGS MIM analysis, $\varepsilon_\mathrm{eff,TIHGS}$ is a BiF_3-thickness-normalized stack-level electrostatic quantity and should not be interpreted as the intrinsic dielectric constant of BiF_3. The value $\varepsilon_\mathrm{eff,TIHGS} \approx 16$ is consistent with the finite boundary response independently observed in the TIHGS MIM capacitors and is therefore not interpreted as evidence for a capacitance or *EOT* enhancement. Its purpose here is to parameterize the effective TIHGS capacitance required to de-embed the semiconductor-side response.

The measured flat-band capacitance contains the TIHGS capacitance in series with the semiconductor-side response. The effective semiconductor-side flat-band capacitance was therefore obtained from

$$\frac{1}{C_\mathrm{FB}} = \frac{1}{C_\mathrm{g}} + \frac{1}{C^*_\mathrm{s,FB}}, \tag{S8}$$

giving

$$C^*_{\mathrm{s,FB}} = \left(\frac{1}{C_{\mathrm{FB}}} - \frac{1}{C_{\mathrm{g}}} \right)^{-1} = 8.08 \times 10^{-7}\ \mathrm{F\,cm^{-2}}. \tag{S9}$$

The corresponding effective screening length was estimated as

$$L_{\mathrm{D,eff}} = \frac{\varepsilon_0 \varepsilon_{\perp,\mathrm{WSe_2}}}{C^*_{\mathrm{s,FB}}}, \tag{S10}$$

where $\varepsilon_{\perp,\mathrm{WSe_2}}$ is the out-of-plane relative permittivity of WSe_2. Using $T = 300$ K and a representative value $\varepsilon_{\perp,\mathrm{WSe_2}} = 4.2$, as adopted in continuum electrostatic modelling of bulk-like WSe_2 flakes [25], gives

$$L_{\mathrm{D,eff}} \approx 4.60\ \mathrm{nm}. \tag{S11}$$

The corresponding apparent volumetric majority-carrier concentration was estimated from

$$N_{\mathrm{app}} = \frac{k_{\mathrm{B}} T \varepsilon_0 \varepsilon_{\perp,\mathrm{WSe_2}}}{q^2 L^2_{\mathrm{D,eff}}}, \tag{S12}$$

yielding

$$N_{\mathrm{app}} \approx 2.83 \times 10^{17}\ \mathrm{cm^{-3}}. \tag{S13}$$

Because the flat-band response is evaluated at 10 kHz, traps that remain electrically responsive at this frequency can contribute to $C^*_{\mathrm{s,FB}}$. Accordingly, $L_{\mathrm{D,eff}}$ and N_{app} are interpreted as effective low-frequency screening parameters rather than intrinsic bulk-semiconductor quantities. The measured WSe_2 thickness, $t_{\mathrm{WSe_2}} = 37.37$ nm, nevertheless substantially exceeds $2L_{\mathrm{D,eff}} \approx 9.20$ nm, indicating that electrostatic perturbations originating from the two opposing WSe_2 surfaces do not strongly overlap across the full semiconductor thickness.

Supplementary Note 7. Effective Interface-Trap Extraction and Limitations

The effective electrically active trap density, $D_{\mathrm{it,eff}}$, was estimated from the frequency-dependent capacitance–voltage characteristics using the high–low-frequency Castagné–Vapaille approach [26, 27]. The method exploits the different frequency response of electrically active interface and near-interfacial traps and has been widely used to estimate trap densities from metal–insulator–semiconductor capacitance measurements, although the extracted values can depend on the assumed semiconductor response, measurement frequency window, and gate-stack electrostatics [27]. In this analysis, we denote the measured capacitances at 10 kHz and 1 MHz as C_{LF} and C_{HF}, respectively, so traps that respond differently over this frequency range contribute to the measured capacitance dispersion.

Throughout this analysis, all capacitances are expressed per unit area. The measured MISCAP capacitance contains the TIHGS electrostatic element in series with the semiconductor-side response. We use $C_{\mathrm{TIHGS}} = 3.29 \times 10^{-7}$ F cm^{-2}, obtained from the 10-kHz flat-band consistency analysis in Supplementary Note 6. Because an independently resolved frequency-dependent C_{TIHGS} is unavailable, this value is used for both the 10-kHz and 1-MHz de-embedding; any residual TIHGS dispersion is therefore included in the effective quantity $D_{\mathrm{it,eff}}$. The effective semiconductor-side capacitances were calculated as

$$C^{*}_{\mathrm{s,LF}} = \left(\frac{1}{C_{\mathrm{LF}}} - \frac{1}{C_{\mathrm{g}}} \right)^{-1}, \tag{S14}$$

and

$$C^{*}_{\mathrm{s,HF}} = \left(\frac{1}{C_{\mathrm{HF}}} - \frac{1}{C_{\mathrm{g}}} \right)^{-1}, \tag{S15}$$

where C_{LF} and C_{HF} are the measured capacitances at 10 kHz and 1 MHz, respectively.

Within the conventional high–low-frequency approximation, the low-frequency semiconductor-side response includes semiconductor charge modulation and trap contributions that remain responsive at lower frequencies, whereas the corresponding trap response is reduced at higher frequencies. The frequency-dependent excess capacitance was therefore defined as

$$C_{\mathrm{it,eff}} = C^{*}_{\mathrm{s,LF}} - C^{*}_{\mathrm{s,HF}}, \tag{S16}$$

and the corresponding effective electrically active trap density as

$$D_{\mathrm{it,eff}} = \frac{C_{\mathrm{it,eff}}}{q} = \frac{1}{q} \left[\left(\frac{1}{C_{\mathrm{LF}}} - \frac{1}{C_{\mathrm{g}}} \right)^{-1} - \left(\frac{1}{C_{\mathrm{HF}}} - \frac{1}{C_{\mathrm{g}}} \right)^{-1} \right]. \tag{S17}$$

The quantitative interpretation focused on the bias-dependent depletion-to-accumulation transition. The nearly gate-voltage-independent depletion floor was excluded because the semiconductor charge response is constrained by the finite WSe_2 thickness. Strong-accumulation values were likewise excluded because C_{LF} approaches C_{g}, making the semiconductor-side capacitance increasingly sensitive to small experimental uncertainties. Within the range (Extended Data Fig. 7e), the minimum extracted value is

$$D^{\mathrm{min}}_{\mathrm{it,eff}} \approx 7.48 \times 10^{11}\ \mathrm{cm}^{-2}\,\mathrm{eV}^{-1}. \tag{S18}$$

The parallel-conductance response, G_{p}/ω, was also examined over the same gate-voltage and frequency ranges (Extended Data Fig. 7b). No well-resolved G_{p}/ω maximum suitable for conventional conductance-method extraction of trap density or characteristic time constant was observed within the accessible gate-bias range, while higher positive gate voltages were precluded by increasing dielectric leakage (Extended Data Fig. 6a). We therefore do not extract a conductance-method D_{it} or trap time constant.

The high–low-frequency method attributes the low–high capacitance difference to electrically active trap-related dispersion within the selected frequency window. In the WSe_2/TIHGS MISCAP, this response may include contributions from the WSe_2/BiF_3 interface, near-interfacial or border traps, residual TIHGS dispersion, distributed WSe_2 resistance, contact resistance, dielectric leakage, and measurement parasitics. Moreover, because 10 kHz is not a true quasi-static limit, substantially slower traps are not sampled. Accordingly, the extracted $D_{\mathrm{it,eff}}$ should be interpreted as an effective electrically active trap response within the experimental frequency window rather than as a unique microscopic density of states exclusively at the WSe_2/BiF_3 interface, consistent with the known model and frequency dependence of high–low-frequency interface-trap extraction [27].

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