Supporting Information

**HfO$_2$/HfS$_2$ hybrid heterostructure fabricated via controllable chemical conversion of two-dimensional HfS$_2$**

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References
**Table S1.** Summary of mobility values for HfS$_2$ channel FETs. Note that HfS$_2$ flakes in all below works are all prepared with same approach (mechanical exfoliation) to make fair comparison.

<table>
<thead>
<tr>
<th>References</th>
<th>Contact materials</th>
<th>Mobility (cm$^2$/Vs)</th>
<th>On/Off ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>Graphene</td>
<td>1-10</td>
<td>$10^7$</td>
</tr>
<tr>
<td>Ref S1</td>
<td>Ti or Pt</td>
<td>0.03 (Ti), 0.0015 (Pt)</td>
<td>$10^5$</td>
</tr>
<tr>
<td>Ref S2</td>
<td>Au or Cr</td>
<td>0.05-2.4 (Au), 0.001-1 (Cr)</td>
<td>$10^3$-$10^8$</td>
</tr>
<tr>
<td>Ref S3</td>
<td>Au</td>
<td>0.2</td>
<td>$10^7$</td>
</tr>
<tr>
<td>Ref S4</td>
<td>Au</td>
<td>0.1</td>
<td>$10^5$</td>
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</table>

Obvious mobility improvement are observed in our work thanks to the high interface quality between HfS$_2$ channel and converted HfO$_2$ dielectric. When a FET is working, carrier transport proceeds at channel/dielectric interface, thus a high quality interface will lead to less carrier scattering and result in higher carrier mobility.$^{55}$

However, contact resistance also has strong influence on field effect mobility.$^{56}$ Considering there is no contact engineering in our device, our mobility value should be much further improved after a careful contact engineering. In fact, mobility improvement from 1 cm$^2$/Vs to 50 cm$^2$/Vs in 2D MoTe$_2$ was observed with contact engineering.$^{57}$ Assuming a similar improvement after contact engineering, mobility of our device will reach the theoretical limit value (around 100 cm$^2$/Vs at room temperature)$^{58}$.

**Table S2.** The device performances of top-gated FETs based on the converted HfO$_2$/HfS$_2$ hybrid structure and other 2D materials with conventional deposited or transferred dielectrics.

<table>
<thead>
<tr>
<th>References</th>
<th>Channel</th>
<th>Dielectric</th>
<th>Method</th>
<th>$D_i$ (cm$^{-2}$eV$^{-1}$)</th>
<th>SS (mV/dec)</th>
<th>On/Off ratio</th>
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<tbody>
<tr>
<td>This work</td>
<td>HfS$_2$</td>
<td>15 nm HfO$_2$</td>
<td>Conversion</td>
<td>$6\times10^{11}$</td>
<td>67</td>
<td>$10^7$</td>
</tr>
<tr>
<td>Ref S4</td>
<td>HfS$_2$</td>
<td>5 nm HfO$_2$</td>
<td>ALD</td>
<td>$7\times10^{13}$</td>
<td>197</td>
<td>$10^4$</td>
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<tr>
<td>Ref S9</td>
<td>MoS$_2$</td>
<td>9 nm HfO$_2$</td>
<td>ALD</td>
<td>$2.3\times10^{12}$</td>
<td>65</td>
<td>$10^8$</td>
</tr>
<tr>
<td>Ref S10</td>
<td>MoS$_2$</td>
<td>6 nm Al$_2$O$_3$</td>
<td>Transfer</td>
<td>$2.2\times10^{13}$</td>
<td>180</td>
<td>$10^6$</td>
</tr>
<tr>
<td>Ref S11</td>
<td>WSe$_2$</td>
<td>Al$_2$O$_3$/Fluoropolymer</td>
<td>ALD</td>
<td>$2\times10^{12}$</td>
<td>400</td>
<td>$10^7$</td>
</tr>
<tr>
<td>Ref S12</td>
<td>ReS$_2$</td>
<td>30 nm Al$_2$O$_3$</td>
<td>ALD</td>
<td>$&gt;10^{13}$</td>
<td>750</td>
<td>$10^6$</td>
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<tr>
<td>Ref S25</td>
<td>MoS$_2$</td>
<td>15 nm Al$_2$O$_3$</td>
<td>ALD</td>
<td>$5.7\times10^{11}$</td>
<td>69</td>
<td>$10^6$</td>
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<td>Ref S26</td>
<td>MoS$_2$</td>
<td>16 nm Al$_2$O$_3$</td>
<td>ALD</td>
<td>$2.4\times10^{12}$</td>
<td>140</td>
<td>$10^5$</td>
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Samples shown in Figure S1a, b and c are corresponding to the schematic diagrams in Figure 1a, b and c in main manuscript, respectively. Partially converted HfO$_2$/HfS$_2$ hybrid structure (Figure S1b) possesses a lower contrast than as-exfoliated HfS$_2$ flakes (Figure S1a) because the remaining unconverted HfS$_2$ layers are thinner. The fully converted HfO$_2$ flakes (Figure S1c) are almost transparent. The above observations are consistent with the optical properties of HfO$_2$ thin films.$^{513}$

The thickness of the converted HfO$_2$ layer in the converted HfO$_2$/HfS$_2$ hybrid structure cannot be directly determined with AFM because the measured thickness includes both converted HfO$_2$ and unconverted HfS$_2$. We developed an indirect approach to extract this information as presented below.

We first define several relevant parameters as indicated by the blue arrows in the above schematic.
diagram.

Thickness of as-exfoliated HfS$_2$: $t_0$
Thickness of converted HfO$_2$: $t_1$
Thickness of original HfS$_2$ converted to HfO$_2$: $t_2$
Thickness of the converted HfO$_2$/HfS$_2$ hybrid structure: $t_3$

Then the quantitative relations between these parameters are as follows.

The unconverted HfS$_2$ in the converted HfO$_2$/HfS$_2$ hybrid structure remains intact as as-exfoliated HfS$_2$, so the difference between the thickness of the as-exfoliated HfS$_2$ ($t_0$) and that of the converted HfO$_2$/HfS$_2$ hybrid structure ($t_3$) is equal to the difference between the thickness of the original HfS$_2$ converted to HfO$_2$ ($t_2$) and that of the converted HfO$_2$ ($t_1$): $t_0 - t_3 = t_2 - t_1$.

Further, as shown in Figure 1 in the main manuscript, the thickness of original HfS$_2$ converted to HfO$_2$ ($t_2$) is 1.8 times the thickness of converted HfO$_2$ ($t_1$): $t_2 = 1.8 t_1$.

Considering the above two equations ($t_0 - t_3 = t_2 - t_1$ and $t_2 = 1.8 t_1$), we obtain the equation: $t_0 - t_3 = 1.8t_1 - t_1 = 0.8 t_1$.

As $t_0$ (the thickness of the as-exfoliated HfS$_2$) and $t_3$ (the thickness of the converted HfO$_2$/HfS$_2$ hybrid structure) can be directly measured with AFM, $t_1$ (the thickness of converted HfO$_2$) can be extracted by using the above quantitative relation, and thus the thickness of the converted HfO$_2$ layer in the converted HfO$_2$/HfS$_2$ hybrid structure can be determined.

We further performed plasma oxidation on a thick HfS$_2$ flake (around 50 nm) and extracted the thickness of converted HfO$_2$ for a wide range (2-15 nm) within which the oxidation rate still maintains constant (1.7 nm min$^{-1}$). This result confirms the high controllability of our plasma oxidation process.
Figure S3. Wide range Raman analysis of converted HfO$_2$.

The Raman spectra were recorded of all samples on SiO$_2$/Si substrates, and the Raman spectrum of the substrate was also recorded as a reference (green curve).
The evolution of the Raman modes in these wide range (70–1100 cm$^{-1}$) Raman spectra through the representative stages from the original HfS$_2$ (black curve) to the converted HfO$_2$/HfS$_2$ hybrid structure (red curve), then to fully converted HfO$_2$ (blue curve), is consistent with Figure 1k.
The representative Raman modes of crystalline HfO$_2$ are in the range 300–700 cm$^{-1}$. However, the Raman spectrum of fully converted HfO$_2$ (blue curve) matches that of the SiO$_2$/Si substrate (green curve), and there are no additional peaks due to crystalline HfO$_2$ in the range 300–700 cm$^{-1}$, which indicates that the converted HfO$_2$ is amorphous.

Figure S4. EDS mapping of a large-area converted HfO$_2$/HfS$_2$ hybrid structure.
To determine the cross-sectional element distribution of a converted HfO$_2$/HfS$_2$ hybrid structure, we performed EDS measurements on cross-sectional TEM samples (Figure S4a). Figures S4b-d show EDS element mapping images of the area enclosed by the white dashed lines in Figure S4a. The distributions of oxygen (Figure S4c) and sulfur (Figure S4d) are distinct in the corresponding regions of HfO$_2$ and HfS$_2$, whereas hafnium (Figure S4b) is present throughout the whole region. These distributions are consistent with the cross-sectional lattice structure in the TEM image in Figure 2 in main manuscript. Some oxygen is present in the HfS$_2$ region (Figure S4c) because of the ambient oxidation of HfS$_2$ during transfer of the sample from the FIB processing chamber to the TEM measurement chamber. Few sulfur is present in HfO$_2$ region due to the resolution error in EDS measurement. High resolution XPS measurements in Figure 3a in main manuscript clearly indicates a fully converted HfO$_2$ region without sulfur residue.

Figure S5. (a) TEM image, (b) HRTEM image, and (c) SAED pattern of a HfS$_2$ flake.

Figure S5a shows a low resolution TEM image of an exfoliated HfS$_2$ flake deposited onto carbon grids inside a Cu TEM grid. HfS$_2$ possesses a clear hexagonal lattice structure in the HRTEM image as shown in Figure S5b, and matches well with previous reports.$^{3}$ The selected area electron diffraction (SAED) pattern in Figure S5c indicates that the as-exfoliated HfS$_2$ flake is single crystalline, which is consistent with the single crystallinity of unconverted HfS$_2$ layers in the partially converted HfO$_2$/HfS$_2$ hybrid structure (Figure 2 in main manuscript).
In order to prepare a computational model for the HfO$_2$/amorphous HfS$_2$ interface, we adopted a modeling procedure similar to that used for the Si/amorphous SiO$_2$ interface.\textsuperscript{14, 15} First, we adopted the monoclinic-HfO$_2$ (m-HfO$_2$) crystal structure, and by using the m-HfO$_2$ (001) surface, which is the prominent surface during HfO$_2$ growth,\textsuperscript{17} we evaluated the lattice mismatches between the m-HfO$_2$ slab and the HfS$_2$ monolayer for various multiples of their unit cells. Based on the calculated lattice parameters of monolayer HfS$_2$ (a = b = 3.607 Å) and m-HfO$_2$ (a = 5.142 Å, b = 5.195 Å, c = 5.326 Å), which are in agreement with previously reported values,\textsuperscript{16, 18, 19} we prepared a HfO$_2$/HfS$_2$ heterostructure composed of a stretched (3 × 2) O-terminated m-HfO$_2$ (001) cell placed on top of (3 × 3 $\sqrt{3}$) monolayer HfS$_2$. Here, we attempted to model the experimental situation in which the deep HfS$_2$ layers are converted into amorphous HfO$_2$, so the lattice constants of the m-HfO$_2$ (001) slab model were scaled to those of monolayer HfS$_2$. For a three-layer thickness, the m-HfO$_2$ model consists of 72 oxygen and 36 hafnium atoms. The interlayer spacing for the optimized pristine HfS$_2$/HfO$_2$ interface model was 2.45 Å and the binding energy was $-1.76$ eV per S atom. A (3 × 3 $\sqrt{3}$) monolayer HfS$_2$ surface model was straightforwardly prepared from the interface model, and consists of 36 sulfur and 18 hafnium atoms. In both the HfS$_2$ surface and HfO$_2$/HfS$_2$ interface models, a vacuum space of approximately 15 Å along the surface-normal direction was included to prevent artificial interactions with periodic images.

\textbf{Figure S6. HfS$_2$ surface and HfO$_2$/HfS$_2$ interface models.} (a) Side and (b) top views.
The initial oxidation of the HfS₂ basal planes can proceed easily as follows: (a) an oxygen atom penetrates into the HfS₂ surface and bonds with two hafnium atoms. Due to the penetration of the O atom, the original bonding between the S and Hf atoms will be weakened and the S atom is accordingly pushed out of the HfS₂ plane. (b) Upon the supply of an additional O atom, it will attach to the nudged-out S atom, making its bonding with the Hf atom even weaker and pulling it out further (Step II). (c) When a further O atom approaches, the S atom finally becomes disconnected from the HfS₂ region and is extracted in the form SO₂, which completes the replacement of a S atom by an O atom. In (a), the green, purple, gray, and black circles indicate the bottom-S, Hf, top-S, and top-S-Hf bridge sites, respectively, which we considered as the initial O adsorption site. Blue, yellow, and red spheres correspond to Hf, S, and O atoms, respectively.
Figure S8. The mechanism of HfS$_2$ surface oxidation on sites next to an O atom.

We additionally confirmed that, even when an O atom is already present at a nearby site, oxidation will still proceed efficiently, with the difference that the replaced S atom is emitted as SO$_3$. Once an O atom has penetrated into the Hf-S bond along the armchair (zigzag) direction (Step I), another O atom can penetrate into the Hf-S bond along the neighboring zigzag (armchair) direction (Step I'), and the detachment process can occur with the continued supply of O atoms (Step I' → Step II' → Step III').
Figure S9. Formation energies of vacancy defects near the HfO$_2$/HfS$_2$ interface.

The energy cost for the formation of oxygen and sulfur vacancies in the HfO$_2$/HfS$_2$ interface model is shown as a function of the distance from the mid-point of the HfO$_2$/HfS$_2$ interfacial region ($z = 0$). The vacancy formation energy is defined as $E_{\text{vac-form}} = E_{\text{vac}} - E_{\text{pristine}} + n\mu_O + m\mu_S$, where $E_{\text{vac}}$, $E_{\text{pristine}}$, $\mu_O$, $\mu_S$, n, and m are the total energies of the vacancy and the pristine model for the HfO$_2$/HfS$_2$ interface structure, the chemical potentials of O and S, and the numbers of oxygen and sulfur vacancies, respectively. Comparing the energies of formation of an oxygen vacancy on the HfO$_2$ side (red triangles) and a sulfur vacancy on the HfS$_2$ side (the black circle), we conclude that the former is more favorable than the latter. In particular, we find that the oxygen vacancy at the HfO$_2$/HfS$_2$ interface region has the lowest formation energy of 0.48 eV, which is much lower than that for the deeper region of HfO$_2$ (3.28 eV). This indicates that the HfO$_2$/HfS$_2$ interface region will be dominated by oxygen vacancies.
Appropriate graphene flakes were exfoliated onto SiO$_2$ substrates as bottom source/drain electrodes and characterized with optical microscopy (Figure S10a). An HfS$_2$ flake (approximately 30 nm thick) was exfoliated onto a PDMS substrate and characterized with optical microscopy (Figure S10b). The HfS$_2$ flake was placed into contact with the graphene source/drain electrodes with a mechanical stacking process (Figure S10c).$^{20}$ After stacking process, the HfS$_2$/graphene contacts were annealed in vacuum (\(<10^{-6}\) Torr) at 200$^\circ$C for two hours. This annealing process would enhance the contact quality, removing possible bubbles and impurities induced during the stacking process. Then the contact pads were patterned with e-beam lithography (EBL), as shown in Figure S10d. After deposition of 10 nm Cr and 50 nm Pd with e-beam evaporation, a lift-off process was conducted. The resulting HfS$_2$ device (Figure S10e) was treated with O$_2$ plasma under fixed conditions (a power of 20 W, a flow rate of 5 sccm, a pressure of 470 mTorr) for 9 min to produce a 15 nm HfO$_2$ layer on top of the HfS$_2$ channel. The exposed section of graphene was removed by the O$_2$ plasma, leaving the part covered by the HfS$_2$ flake unaffected (Figure S10f). A top gate electrode was then patterned with EBL so as to overlap the bottom graphene source/drain electrodes (Figure S10g) in order to minimize parasitic resistance. Finally, 50 nm Pd was deposited with e-beam evaporation followed by a lift-off process (Figure S10h).
Figure S11 shows a schematic diagram of a metal/converted HfO$_2$/metal (MIM) capacitor. The bottom electrode (Au) was fabricated by using photolithography, e-beam deposition, and a lift-off process. The base pressure of the deposition reactor was $\sim$10$^{-6}$ Torr. The deposition rate was $\sim$0.1 nm/s. HfS$_2$ films with various thicknesses were transferred onto substrates prepared with a bottom electrode and then fully oxidized with O$_2$ plasma, as confirmed with Raman measurements. The same electrode (Au) preparation process was applied to prepare the top electrode.

The dielectric constants ($\varepsilon_r$) of the converted HfO$_2$ layers with various thicknesses are shown in Figure S11b. The $\varepsilon_r$ values were extracted by using the expression $C_{ox} = \varepsilon_0 \varepsilon_r / d$, where $\varepsilon_0$ is 8.85 $\times$ 10$^{-14}$ F cm$^{-1}$, $C_{ox}$ is the measured MIM capacitance, and $d$ is the physical thickness of fully converted HfO$_2$, as determined with AFM. When the thicknesses of converted HfO$_2$ are higher than 10 nm, the dielectric constant is almost constant (15–16). When the thickness is lower than 10 nm, the dielectric constant decreases. The low dielectric constants of ultrathin HfO$_2$ are consistent with previous reports.$^{52}$

The variations with voltage of the leakage current densities at the two metal electrodes and through the converted HfO$_2$ layers with various thicknesses were determined and are plotted in Figure S11c. Figure S11d plots the breakdown voltage and field at which a catastrophic increase in current through the MIM capacitor was observed, as a function of the converted HfO$_2$ thickness. A significant increase in the breakdown voltage is evident as the converted HfO$_2$ thickness increases. In contrast, the breakdown electric field decreases as the converted HfO$_2$ thickness increases. These results are
consistent with previously reported dielectric properties of HfO\textsubscript{2} thin films.\textsuperscript{52}

Figure S12. The variations with temperature and HfS\textsubscript{2} channel thickness in the SS value of a FET based on the converted HfO\textsubscript{2}/HfS\textsubscript{2} hybrid structure.

Figure S12a shows the SS values of an FET with a HfS\textsubscript{2} channel thickness of 3 nm at various temperatures. These results show that the behavior is nearly ideal for all temperatures with a linear relationship between SS and temperature, as is consistent with the equation SS = (k\textsubscript{B}T/q) ln10 (1+C\textsubscript{it}/C\textsubscript{ox}), which confirms a high interface quality.

The effects of varying the HfS\textsubscript{2} channel thickness on the device performance are shown in Figure S12b. The electrostatic control of the top gate on the HfS\textsubscript{2} channel decreases with the distance from the converted HfO\textsubscript{2}/HfS\textsubscript{2} interface. Thus, as the HfS\textsubscript{2} flake thickness increases, the channel cannot be completely depleted by applying a negative V\textsubscript{g}. Due to this effect, the SS values for devices with thicker channels are larger than those for the thinner channel device, as is evident in Figure S12b. Similar behavior has also been previously observed in MoS\textsubscript{2} devices.\textsuperscript{521}
Figure S13. Deconvolution of XPS Hf 4f spectra in converted HfO$_2$/HfS$_2$ hybrid structure before argon ion sputtering treatment (P1 in Fig. 3).

FWHM of Hf 4f$_{5/2}$ and Hf 4f$_{7/2}$ peaks were fixed to be equal and the intensity ratio of Hf 4f$_{5/2}$ peak to Hf 4f$_{7/2}$ peak was found to be 74%. Other than Hf 4f$_{5/2}$ at 17.9 eV (red line) and Hf 4f$_{7/2}$ at 16.3 eV (blue line) of HfO$_2$, the Hf 4f spectra contain two peaks at 15.3 eV (orange line) and 17.3 eV (green line), which may indicate the formation of Hf-suboxide with complex chemical states that might be created during the plasma oxidation process. Although origins of these two additional peaks are not clearly understood at this moment, they should not be related to HfS$_2$ because no sulphur was detected in P1. For Hf 4f spectra in P2 to P5, the argon ion sputtering treatment makes it very difficult to deconvolute the spectra, as such sputtering can be sufficiently energetic which may cause further reactions. A more meticulous study and analyses would be required to identify detailed chemical states of this hybrid structure.
References


